ELEMENTARY
PHYSICAL CHEMISTRY

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"It is also true that man sees more of the things themselves when he sees more of their origin; for their origin is a part of them and indeed the most important part of them. Thus they become more extraordinary by being explained. He has more wonder at them but less fear of them; for a thing is really wonderful when it is significant and not when it is insignificant."

G. K. CHESTERTON—"St. Francis of Assisi."

PREFACE TO THIRD EDITION

The preparation of the third edition of Elementary Physical Chemistry is the result of a desire to supplement the classical aspects of the subject, now so significantly the concern of general chemistry courses, with those newer phases of the subject which have caused physical chemistry to increase in relative importance in the whole domain of chemistry. The material which was added in the previous edition has been tested in a number of universities and colleges and found to be practicable teaching matter for such a course, and markedly to expand the horizons of the student of the science. The advances of the last five years appear to warrant a still further expansion of the content of the elementary course in physical chemistry.

The progress that has been made in the field of nuclear chemistry, especially in the production of radioactive isotopes and the achievement of nuclear fission, indicates quite definitely that the era of atomic energy is at hand. We shall need not only to teach that the second law of thermodynamics denies the possibility of continuously utilizing the thermal energy of the environment to move ships across the seven seas, but that these may soon be moved by the energies available from nuclear disintegration. The background of this development is presented in a greatly extended chapter on the atomic concept of matter.

The student of general chemistry is now thoroughly familiar with the concept of equilibria in simple systems and the elementary development of the law of mass action. The expanding science is facing the problem of equilibrium in systems where a complex of reactions simultaneously obtains. To explore such systems it is becoming increasingly necessary to make use of the statistical method of approach. As a consequence of this condition, there is added to the treatment of the second law of thermodynamics a quite elementary discussion of the statistical basis of the second law of thermodynamics which will give the student a first exposure to this increasingly important subject and will permit him to see its applicability to a few typical examples, the ideal gas law, the ortho-para hydrogen equilibrium and a simple chemical reaction. These should serve as a stimulus to further study and at the same time permit the student to recognize how the statistical theory is basically reorganizing the approach to problems of rate not only in chemical reactions but also in physical processes. These additions have, however, been so placed in the several chapters that they can, without interruption of the sequence, be omitted in a briefer treatment of the whole subject of physical chemistry. To achieve this end, it has been necessary to defer the treatment of chemical kinetics to a more usual position in the later chapters of the book.

Several other chapters have undergone re-organization. These include the chapter on the solid state, that on phase equilibria which has been somewhat abbreviated and the chapters dealing with ionic equilibria where the classical aspects have been given the briefer exposition that accords with the present status of this section. Many of the details of such reconstruction stem from the more intimate experience of my brother in the conduct of introductory courses in physical chemistry. Once more, also, he has shouldered more than his share of the preparation of the volume in its final form. Many of the errors of omission and commission that marked our earlier effort, and which we have attempted to correct in the present edition, we have learned through the kindly criticisms and suggestions of our colleagues here and abroad. In particular, we acknowledge the many comments and corrections placed at our disposal by Professor K. Fajans and his colleagues in the University of Michigan. We renew our request that shortcomings of the present effort be brought to our attention so that an ever-improving technique in the teaching of our science may be achieved.

HUGH S. TAYLOR.

PRINCETON, N. J.
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PREFACE TO FIRST EDITION

THE present volume attempts the presentation of material suitable for an introductory course in modern physical chemistry. It is adapted from the two-volume "Treatise on Physical Chemistry" which appeared under the author's editorship some three years ago. A need has been felt in several quarters for a single volume of a more elementary nature which should follow the general lines of development in the larger treatise, without, however, its detail. This book is offered in response to such a demand.

Anyone who has examined the scope of modern general chemistry cannot but be struck with the very considerable amount of physical chemistry which finds its place in such a course, often to the detriment of the purely inorganic chemistry. The physical chemistry is of course largely descriptive but it is substantially similar in form of presentation to that given in introductory physical chemistry courses a decade or so ago. Physical chemistry ought to reap the advantages of that development and is therefore offered the possibility of substituting for the descriptive, qualitative course a more rigorous and, therefore, more mathematical discipline. In the present case it has been decided to take advantage of this state of affairs and to presume in this outline of physical chemistry a knowledge of mathematics which can be obtained in a course covering the elements of the differential and integral calculus. Another and more compelling reason for this decision, however, is the modern trend in physical chemistry. Any teacher who would advise his students that he can attain to an understanding of the science as now developing without the mathematical knowledge required in the present volume is, in the opinion of the author, doing an ill service to his pupils. If one needs conviction on this point let him turn to the current issue of the Journal of the American Chemical Society and find how many of the articles in the section of General and Physical Chemistry, for example, in the March issue, can be read intelligently without such mathematical ability.

There are several differences in the order of presentation of subject material in the present volume from that in the *Treatise* and from that customary in physical chemistry texts. One object in the rearrangement has been to present the material more simply than in the larger text. Another reason is again concerned with the scope of the modern course in general chemistry. For pedagogical reasons as well as others the author has decided to follow the discussion of the atomic concept of matter with a discussion of the law of conservation of energy and its application in the science of thermochemistry. This introduces the student early in the course to one phase of theoretical chemistry which is still dismissed in a few paragraphs in general chemistry courses. In the discussion of the gaseous states of aggregation, the concepts of collision frequency and of varying velocity of gas molecules are introduced and emphasised. This has been done because, in *chemical* reactions, as opposed to physical properties, it is these factors which are of prime importance. This achieved, the student can venture, in Chapter VI, upon the study of velocity in gas reactions, the concept of activation by collision and of gas reactions occurring at surfaces. These are ideas which are fundamental in applied physical chemistry of the present day to an extent far greater than are the concepts of dilute solution and ionization. They permit also, after a discussion of the second law of energetics (Chap. VII), a more rational approach to the problem of equilibrium (Chaps. IX and X). The classical field of physical chemistry, the field of electrolytes, has been assigned to the later chapters; it has also been divided into two chapters in one of which weak electrolytes are treated, the other chapter being devoted to the modern approach to the problem of strong electrolytes. The author feels that no apology is needed for this rearrangement. Again also, by reason of the grounding received in general chemistry courses in problems of ionization, the author has no hesitation in attempting to introduce the thermodynamic treatment of solutions into an elementary course.

The indebtedness incurred in compiling the book cannot be discharged by acknowledgment. By arrangements between the publishers and the separate authors of chapters in the *Treatise* I have been able to use diagrams, tables and suitable sections of their contributions, oftentimes as written by them. There is much of Professor Maass' chapters on gases and liquids in Chapters III and IV. The present Chapter V is simply an abbreviation of the corresponding chapter in the *Treatise* by Professor R. N. Pease. The same is true of the chapter on dilute solutions, where I have retained most of Professor J. W. C. Frazer's article, and of the chapter on Heterogeneous Equilibrium by Professor A. E. Hill. Dr. Graham Edgar's chapter on Homogeneous Equilibrium is the basis of the present Chapter IX. Portions of the work of Dr. A. L. Marshall, Professor Patrick and Professor F. O. Rice are also incorporated in the book. Into the chapters on electrolytic phenomena the work of Professors J. R. Partington and H. S. Harned in the *Treatise* has been moulded. To all these authors, and to the publishers who facilitated this arrangement, I am indebted. Without this help I could not have undertaken the preparation of this text.

HUGH S. TAYLOR.

PRINCETON, N. J.,
April, 1927.

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CHAPTER 1

THE ATOMIC CONCEPT OF MATTER

THE inception of the modern era in chemical science may be attributed to the proposal of the atomic theory of chemical action by John Dalton in the first volume of his *New System of Chemical Philosophy*, 1808. The scientific era in which the Daltonian concept was formulated was especially favorable to its development. The theory of atomic constitution was no new theory. The Greek theory of atoms, due to Leucippus and handed down to us in the writings of Democritus, is the first of which we have record. Boyle included in his conception of elementary substances some notions of atomic constituents. Dalton himself was led to the atomic theory by reason of his admiration of the Newtonian doctrine of the atomic constitution of matter. Lavoisier's concept of elements and of compound substances and the quantitative era which he developed provided the circumstances favorable to the growth of Dalton's theory, which simplified and correlated much that the quantitative spirit had disclosed and had not yet explained. It provided the framework upon which was built the chemical philosophy and the chemical research of the nineteenth century. Towards the close of the century it seemed as though the theory might give way to an interpretation of the science based upon energetics. But, in the new century, it emerged once more, broadened and amplified by the discoveries of sub-atomic phenomena.

The atomic theory of Dalton postulated the existence of minute indivisible particles or atoms, each of equal weight for the same element, atoms of different elements, however, having different weights. Compounds were the result of union of dissimilar atoms the ratio of whose weights was proportional to their combining weights. This fundamental idea of atoms having characteristic weights and combining to form chemical compounds at once illuminated the quantitative facts of chemical combination then known. They may be thus briefly summarized:

1. **The Law of Definite Proportions,** established experimentally by Proust in 1799. *The elements which form a chemical compound are united in it in an invariable ratio by weight, which is characteristic of that compound.* Proust's analyses were made with carbonate of copper, artificial and natural, the two oxides of tin and the two sulfides of iron. Proust showed, in contradiction of claims put forward by Berthollet on behalf of variable composition due to mass action, that when a metal combines

with oxygen in more than one proportion there is no gradual increment of one element but a sudden, *per saltum*, increment. His analytical work was not sufficiently accurate to establish the law of multiple proportions.

2. **The Law of Multiple Proportions,** deduced from experimental work by Dalton and formulated by him in conformity with his preconceived atomic theory. *When an element combines with another to form more than one compound the masses of the second element combining with a fixed mass of the first element bear a simple ratio to one another.* The accurate analyses of Berzelius provided abundant evidence of the truth of this law which the less accurate efforts of Dalton produced.

3. **The Law of Reciprocal Proportions,** established by the experimental work of Richter (1792–1794). *When two or more elements combine with a third in certain proportions they combine with each other in the same proportions or in multiples of these proportions.* In his book *Stoichiometry of the Chemical Elements* published in the above years this law of reciprocal proportions is illustrated.

4. **The Law of Conservation of Mass,** formulated by Lavoisier in 1774 upon the basis of experimental measurement, states that *the total mass of the reactants in a chemical reaction is equal to the total mass of the products of reaction.* All these laws, quantitatively exact and experimentally verifiable, fitted admirably into the framework of chemical principles established by Dalton's Atomic Theory. Further support was quickly forthcoming. Gay-Lussac put forward in 1808 his **Law of Combining Volumes.** *When gases combine they do so in simple ratios by volumes, the volume of the gaseous product bearing a simple ratio to the volumes of the reactants when measured under the same conditions of temperature and pressure.* An attempt by Berzelius to interpret this law in terms of the atomic theory failed owing to a lack of understanding of the differences between atoms and molecules. Knowing, as a result of the earlier investigations of Gay-Lussac, that many gases vary similarly when subjected to temperature, and, from the investigations of Boyle, to pressure changes, Berzelius suggested that equal volumes of different gases under like conditions of temperature and pressure contain the same number of atoms.

5. **Avogadro's Hypothesis:** The correct correlation of the atomic theory with the characteristics of ideal gases is due to Avogadro, who propounded, in 1811, the Avogadro hypothesis. Though not accepted by the early proponents of the atomic theory and only commanding general adherence after the exposition of the hypothesis some 47 years later by his fellow countryman, the Italian scientist Cannizzaro, the hypothesis of Avogadro was a true exposition of the facts concerning gases. The hypothesis may be stated in the following terms: *Equal volumes of different gases under the same conditions of temperature and pressure contain*

the same number of molecules. The limitations of this hypothesis as regards actual gases and the many experimental methods which have now been developed actually to determine the number of molecules in a given volume of gas will be dealt with in appropriate portions of the following chapters. At this stage it will suffice to indicate the actual change introduced by the Avogadro hypothesis into the Daltonian concept of atoms and atomic combinations. On the Avogadro principle, the atom became the smallest particle which can enter into chemical combination. The molecule became the smallest particle of matter which was capable of independent existence. This distinction clarified the known experimental facts. It explained, for example, how one molecule of hydrogen and one molecule of chlorine combined to form two molecules of hydrogen chloride. Each molecule of hydrogen and chlorine contained two atoms whereas the molecules of hydrogen chloride contained an atom each of hydrogen and chlorine. It is perhaps advisable to point out, now that the difficulties associated with the terms atom and molecule no longer exist, that the definition of the molecule given above lacks somewhat in rigor. For, we now know that, under proper conditions, not only molecules of diatomic gases such as hydrogen, chlorine and iodine may exist in the free state but that atoms may also so exist provided the conditions of temperature and pressure be suitably chosen. Under such conditions the molecule and the atom become identical.

With the atomic theory as guide, Berzelius proceeded to the determination of atomic weights of a wide variety of elementary substances. The determination involves two steps, (1) the measurement of the combining weight and (2) the finding of the ratio of combining weight to atomic weight. The former is an experimental operation generally involving some kind of quantitative analytical procedure as, for example, the determination of the quantities of potassium and chlorine in unit quantity of potassium chloride, of hydrogen and oxygen in water or of hydrogen and chlorine in hydrogen chloride. From such determinations the combining weights of oxygen, chlorine and potassium in terms of hydrogen as unity may be determined. The second step, however, involves a knowledge of the number of atoms which are combined in a compound with the reference element. Thus, to take an example of historic interest, the atomic weight of oxygen relative to that of hydrogen as unity would be approximately 8 or 16 according as one or two hydrogen atoms combine with one atom of oxygen, the combining weight being 8. It is in the solution of this problem that the Avogadro hypothesis performed a most useful function, delayed, however, by the non-recognition of the importance of the hypothesis until Cannizzaro's demonstration of its utility in such connection. Until that demonstration was given, no general agreement as to atomic weights was possible, different observers using different values which, however, were simple multiples of other values for the same element, according to the preconceived idea of the experimenter as to the atomic ratios prevailing in the compound analyzed.

6. **Dulong and Petit's Law:** Two principles of great utility in deciding doubtful cases of atomic weight values were discovered and employed in the early years of the atomic theory. The one, the law of Dulong and Petit, was applicable to solid elementary substances. The law, formulated in 1819, states that *the product of the atomic weight and the specific heat is approximately 6 calories.* It will be shown that this law is a limiting law applicable to all solid elements under specified conditions. Known exceptions, such as boron and carbon, which show low atomic heats at ordinary temperatures, manifest at those temperatures a phenomenon common to all solid elements if the temperature chosen for the determination be sufficiently low. At higher temperatures, even these elements have atomic heats approximating those demanded by the law. Nevertheless, a sufficiently large number of elements obey the Dulong and Petit relation at ordinary temperatures as to make this principle of important assistance in deciding cases of doubt in reference to atomic weights deduced by other methods.

7. **Isomorphism:** The second principle was of assistance in the study of the atomic weights of elements present in crystalline compounds. In 1820 Mitscherlich called attention to the practical identity of crystalline forms of the corresponding salts of phosphoric and arsenic acids. They crystallized with the same molecular quantities of water of crystallization and possessed the power of forming mixed crystals. As a result of such observations, Mitscherlich concluded that *analogous elements or groups of elements can replace one another in compounds without material alteration of crystalline form.* Two compounds so related were termed isomorphous and the phenomenon was given the name Isomorphism. The identity of form is not absolute. The distance between atoms varies slightly in one compound from that in the compound of the next analogue. These differences persist even in the mixed crystal and result in distortion of the crystal angles. The variation of inter-atomic distances and the distortion of the crystal angles become greater the more widely divergent are the analogous elements. As a consequence, with the more widely divergent analogues, mixed crystals will not occur even though there is identity of crystal form between the compounds. Substances may crystallize in two distinct crystallographic systems having, nevertheless, constant chemical composition. Such behavior is termed dimorphism. If isomorphism occur between the two forms severally of two such dimorphous bodies the bodies are said to be isodimorphous, the phenomenon being, correspondingly, isodimorphism. Similarly, trimorphous substances are known.

From the standpoint of the atomic theory, isomorphism assisted greatly since it gave a ready indication of chemical composition in the case of substances crystallizing in the same form and isomorphously with substances of known composition. Berzelius made great use of the principle in fixing atomic weights and in checking the results of his analytical investigations.

8. **Prout's Hypothesis:** Side by side with the many achievements of theoretical chemistry in the 19th century, based fundamentally upon the atomic theory, there has persisted the essentially opposite viewpoint, namely that of continuity or unity of matter as opposed to the discontinuous view of material substances which the atomic theory postulates. This contrary viewpoint has been developed both consciously and unconsciously. Prout's hypothesis put forward in 1815 is the earliest illustration of conscious development. Prout, reasoning from the approximation to whole numbers of the atomic weights of several of the elements, suggested that the elements might be, in reality, polymers of hydrogen. This was a revival of the protyle theory of matter with quantitative investigations as its support. But further quantitative study tended to withdraw support from the hypothesis of Prout. The hypothesis gave an added stimulus to exact atomic weight determinations and these but served to demonstrate effectively that many of the atomic weights were markedly divergent from whole numbers. Stas's determinations of atomic weights, and notably that of chlorine, were classical researches, with this divergence from the whole number rule as the decisive result.

9. **Döbereiner's Triads:** Attempts at classification of the elements on the basis of similarity of properties are less conscious methods of establishing the essential unity of matter. Thus, Döbereiner's observation, in 1817, that groups of three elements, chemically similar, with atomic weights in arithmetic progression, could be compiled, while essentially an attempt at convenient classification, involves, in its fundamentals, an appreciation of a unifying principle. The chemical similarity of, for example, lithium, sodium and potassium, chlorine, bromine and iodine, calcium, strontium and barium, sulfur, selenium and tellurium with the very definite arithmetical relationships of their atomic weights, $\mathrm{Na} - \mathrm{Li} = 16.06$, $\mathrm{K} - \mathrm{Na} = 16.1$, suggests immediately a fundamental factor common to each group of three and so some unity underlying each group.

10. **Faraday's Laws of Electrolysis:** The electrochemical researches of Nicholson and Carlisle, 1800, on the decomposition of water, of Davy on the preparation of potassium, sodium, and other metals 1807–1808, and of Berzelius and Hisinger in Sweden 1803–1807, on the decomposition of neutral salts by the electric current, definitely brought electrochemistry to the fore as an auxiliary to other methods of chemical investigation. Davy's Electrochemical theory of affinity and Berzelius' theory of atomic polarization brought electrochemistry into the domain of theoretical chemistry. Faraday's researches in experimental electricity established quantitatively the relationship between electricity and the atomic

weights of the elements. Faraday observed that (Experimental Researches, 505): "*For a constant quantity of electricity, whatever the decomposing conductor may be, whether water, saline solutions, acids, fused bodies or the like, the amount of electrochemical action is also a constant quantity.*" Furthermore, "*with different solutions, the amounts of elementary constituents produced by unit quantity of electricity are proportional to their chemical equivalents.*" In these two laws the atoms and electricity are for the first time intimately associated. Faraday's ions, transferred through solutions by the agency of the current, were carried in definite amounts, one gram ion for every 96,500 coulombs of electricity.

11. The Periodic System of Classification: Mendeleeff, in 1869, developed a broad and comprehensive system of classification of the elements which, more decisively than hitherto, suggested a fundamental unity of elementary structure, though designed primarily to emphasize the periodic nature of chemical and physical properties. An effort of de Chancourtois (Vis Tellurique, Classement naturel des Corps Simples, 1862) excited little attention among chemists, though substantially a statement of periodicity of properties with increase of atomic weight. Newland's Law of Octaves, 1864, an arrangement of the elements in groups of eight bringing with each eighth element a repetition of properties like the eighth note of an octave in music, aroused much ridicule and little respect, though essentially the correct formulation of periodicity. It is noteworthy to record that, had Ramsay's discovery of the rare gases of the atmosphere preceded this formulation, the analogy with the musical octave would have been lost; the scoffers would have lacked one of their principal weapons of ridicule. Mendeleeff established periodicity of properties by arranging the elements in the order of increasing atomic weights. He employed the periodic law, so discovered, as a powerful instrument of chemical classification and a weapon for prosecuting chemical research.

Simultaneously, Lothar Meyer in Germany announced the same generalization. Meyer was more concerned with the periodic variation in the *physical* properties of the elements as a periodic function of the atomic weights of the elements, his graph of atomic volume plotted against atomic weight demonstrating the same broad periodic relationship that Mendeleeff found.

The periodic table, substantially in the form devised by Mendeleeff, is shown in Table 1.1. The table has been amplified by the insertion of the atomic numbers as well as the atomic weights. It includes the additional elements subsequently found, especially those of Group O, the rare gases of the atmosphere. The arrangement brings together, in one group, elements which have general family properties, physical and chemical, which vary gradually from first to last and which resemble one another more closely than do any of the other elements.

TABLE 1.1

THE PERIODIC TABLE

Periods		Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Formula of highest oxide...		—	R_2O	RO	R_2O_3	RO_2	R_2O_5	R_2O_6	R_2O_7	RO_4
Formula of hydride......		—	RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH	—
First short period.........		He *2* 4.003	H *1* 1.008 Li *3* 6.940	Be *4* 9.02	B *5* 10.82	C *6* 12.010	N *7* 14.008	O *8* 16.000	F *9* 19.00	
Second short period.......		Ne *10* 20.183	Na *11* 22.997	Mg *12* 24.32	Al *13* 26.97	Si *14* 28.06	P *15* 30.98	S *16* 32.06	Cl *17* 35.457	
First long period	Even Series..	A *18* 39.944	K *19* 39.096	Ca *20* 40.08	Sc *21* 45.10	Ti *22* 47.90	V *23* 50.95	Cr *24* 52.01	Mn *25* 54.93	Fe *26* Co *27* Ni *28* 55.85 58.94 58.69
	Odd Series...		Cu *29* 63.57	Zn *30* 65.38	Ga *31* 69.72	Ge *32* 72.60	As *33* 74.91	Se *34* 78.96	Br *35* 79.916	
Second long period	Even Series..	Kr *36* 83.7	Rb *37* 85.43	Sr *38* 87.63	Y *39* 88.92	Zr *40* 91.22	Cb *41* 92.91	Mo *42* 95.95	Ma *43*	Ru *44* Rh *45* Pd *46* 101.7 102.91 106.7
	Odd Series...		Ag *47* 107.880	Cd *48* 112.41	In *49* 114.76	Sn *50* 118.70	Sb *51* 121.76	Te *52* 127.61	I *53* 126.92	
Third long period	Even Series..	Xe *54* 131.3	Cs *55* 132.91	Ba *56* 137.36	La *57* 138.92	Ce *58* 140.13				
	Odd Series...			The Rare Earth Elements Pr *59* to Yb *71*						
Fourth long period	Even Series..					Hf *72* 178.6	Ta *73* 180.88	W *74* 183.92	Re *75* 186.31	Os *76* Ir *77* Pt *78* 190.2 193.1 195.23
	Odd Series...		Au *79* 197.2	Hg *80* 200.61	Tl *81* 204.39	Pb *82* 207.21	Bi *83* 209.00	Po *84*	—*85*	
Fifth long period		Rn An *86* Tn 222	—*87*	Ra *88* 226.05	Ac *89*	Th *90* 232.12	Pa *91*	U *92* 238.07		

The Applications of the Periodic Law: As pointed out by Mendeleeff the periodic law could be employed in: (1) The classification of the elements; (2) The estimation of atomic weights; (3) The prediction of properties of unknown elements; (4) The correction of atomic weights.

(1) In the classification of the elements the periodic arrangement has never been surpassed nor superseded. It is still a most useful and convenient method of classifying the data of inorganic chemistry whether of elements or of compounds.

(2) Mendeleeff assigned to indium an atomic weight of 113.4 on the basis of Winkler's value of 37.8 for the equivalent weight; this makes indium tervalent, gives it place in Group III of the table between cadmium and tin, below gallium, where it fits very well. Specific heat measurements of indium metal confirmed the correctness of this assignment.

(3) Mendeleeff used the table to predict the properties of missing elements in Group III and Group IV akin to boron, aluminum and titanium. The predictions concerning eka-boron, eka-aluminum and eka-silicon were abundantly justified and confirmed in the subsequent discoveries of scandium, gallium and germanium respectively.

(4) Mendeleeff predicted corrections in the atomic weights of osmium, iridium and platinum which gave to them this order rather than that given by the order of atomic weights accepted in 1870 which would have given platinum, iridium, osmium. The periodic law has not, however, always been the successful guide in corrections to accepted atomic weights as will now be discussed.

The Defects of the Periodic Law: On placing elements in the order of atomic weights two outstanding anomalies presented themselves to Mendeleeff. Tellurium, being assigned an atomic weight greater than that of iodine, would have passed into the halogen group, while iodine would have been placed in the oxygen, sulfur, selenium group. This would have been an obvious inversion of the periodicity of properties. Since the atomic weight of iodine had been many times checked and rechecked, so that considerable certainty could be attached to its value, Mendeleeff suggested that the atomic weight of tellurium must be wrong, that the correct value would be between 123 and 126 instead of the then accepted value of 128. Hence ensued a vigorous study of tellurium, its purity, purification and atomic weight determination. Efforts were made in abundance to separate therefrom some constituent of higher atomic weight which would have a position below tellurium in the 6th group. All these efforts were fruitless. A multiplicity of methods of purification all failed to yield a tellurium of atomic weight lower than that of iodine. The exception did not nullify the periodic law. The wonderful truth and value of the periodic relation were abundantly evident. As a consequence, and until the reason for the anomaly should reveal itself, tellurium and iodine were assigned to those group positions to which their properties, chemical and physical, indicated that they belonged, order of atomic weights notwithstanding.

Cobalt (58.94) and nickel (58.69) were similarly misplaced on the basis of order of atomic weights. The sequence from the standpoint of properties of the first three transitional elements is most certainly iron, cobalt, nickel, whereas the order of atomic weights is iron, nickel, cobalt.

One other pair of misfits arose with the discovery of the rare gases by Ramsay. Argon of atomic weight 39.944, an obvious member of Group O, was found to have an atomic weight greater than that of potassium, 39.096, again obviously a member of Group I. In view of these anomalies in the face of such overwhelming evidences of the approximate truth of the law in the majority of its details it is little wonder that Ramsay asked "Why this incomplete concordance?" The answer has emerged, and in the unfolding of the mystery the student of chemical philosophy has much to learn. He will find an answer to the query of Ramsay. The incomplete concordance is evidence of the limitations to which many laws are subject, is evidence that the laws in question are but *approximations* to the fundamental law. The incomplete concordance is evidence of incomplete truth. The realization of this will be valuable, for it will give to authentic exceptions to general laws a vital importance in the search for truth. Science is full of illustrations of this fact. The exceptions to the Law of Dulong and Petit were an index of the approximate truth only of the law. It will be shown later that they constituted a sign post to a more fundamental law of the specific heats of elements of which Dulong and Petit's Law is but a limiting case. Ramsay himself found in the anomalous density of nitrogen from air and from nitrogen compounds as determined by Lord Rayleigh the sign post to a whole group of chemical elements at that time unknown. The anomalies in the periodic law were the arrows pointing to the necessity of obtaining yet more fundamental truths concerning the nature, the architecture and the periodic relationships of elementary matter.

12. **Atomic Structure:** The atomic theory of Dalton provides, as has been shown, a satisfactory basis for the laws of chemical combination and the atomic weight provides a useful, if not completely satisfactory, basis for the classification of the elements. The concept of definite and indivisible atoms, of different weights, could not, however, be the ultimate solution of the problem of material structure. It provides no answers to a variety of problems. The difference in chemical properties between two atoms, say hydrogen and oxygen, can never be satisfyingly relegated to a simple difference in weight. Wherein does the difference in weight lie? What factors determine the weight difference? Furthermore, a number of physical and chemical properties of elementary substances cannot be explained upon any basis of weight variation of ultimate indivisible particles. The varying valence of the different elements and also the varying valences of a single element remain entirely unexplained on the basis of the simple atomic theory. The spectral differences among

the elements are likewise unexplainable. As has already been emphasized, *the similarity and periodicity* of properties, both physical and chemical, are the strongest possible evidence that like elements must possess similarities of architecture not envisaged by a theory of indivisible atoms. The inadequacies of the periodic system of classification are further sign posts indicating the need for further exploration of the composition of the individual atoms. Dalton had a glimpse whence progress might come, for in his address to the Royal Society, upon receiving the Royal Medal, he stated:

> "The causes of chemical change are as yet unknown, and the laws by which they are governed; but, in their connexion with electrical and magnetic phenomena there is a gleam of light pointing to a new dawn in science."

13. **The Electron:** It is of interest to note that the development of the concept of atomic structure commenced when the concept of atomic electricity received its first quantitative study. Faraday's experiments on the conduction of salt solutions are the first experiments indicative of discrete units of electricity. G. Johnstone Stoney, in an address before the British Association in 1874, published in 1881,[1] definitely emphasizes this fact:

> "Nature presents us with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear, I shall express Faraday's Law in the following terms, which, as I shall show, will give it precision, viz.: For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases."

Helmholtz in the Faraday lecture at the Royal Institution in 1881 emphasized the same point of view:

> "Now the most startling result of Faraday's Law is perhaps this, if we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

G. Johnstone Stoney, 1891, gave to the 'natural unit of electricity,' thus defined in reference to Faraday's Law, the name 'electron.' Faraday's Law, however, was not sufficient to establish the atomistic concept of electricity. It applied only to solutions of electrolytes. Metallic conduction was still discussed in terms of 'ether strains' and 'continuous homogeneous fluids.' The proof of atomic electricity did not come until the mechanism of gaseous conduction had been studied and the properties of gases acted upon by X-radiation and radioactive materials had become familiar.

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[1] *Phil. Mag.*, (5) 11, 384 (1881).

The experiments of J. J. Thomson and his collaborators at the Cavendish Laboratory, Cambridge, England, supplied the necessary information in this field. Gases treated with X-rays were found to be conducting. The conductivity thus induced in a gas was caused by an agency which could be removed by filtration through glass wool, by passage of the gas through metal tubes or between plates maintained at a sufficiently large potential difference. The conductivity was therefore due to electrically charged particles. More detailed knowledge of the nature of the charged particles was obtained by a study of the conduction of electricity through gases at low partial pressures. When currents at high potentials are discharged through gases at pressures of about 0.01 mm. or lower, charged particles or corpuscles are shot off from the cathode. These particles, first investigated by Sir Wm. Crookes, and called by him the 'fourth state of matter,' have properties the study of which led eventually to an appreciation of their importance in atomic structure. The cathode particles were shown to have the following properties:

(1) They travel in straight lines normal to the cathode and cast shadows of opaque objects placed in their path.

(2) They are capable of producing mechanical motion.

(3) They produce phosphorescence in many objects exposed to their action, e.g., blue phosphorescence in lead glasses.

(4) They produce a rise in temperature in objects which they strike.

(5) They may be deflected, by electromagnetic and electrostatic fields, from their normal rectilinear paths.

(6) The charge carried by the particles is negative since they electrify negatively, insulated metallic electrodes upon which they fall.

(7) They may penetrate thin sheets of metal, the stopping power of the metal varying directly with the thickness of the metal and with its density.

(8) They act as nuclei for the condensation of supersaturated vapors. The fogs thus formed are useful as a means of rendering the particles visible.

(9) The particles were identical in nature and in the ratio of charge carried to mass of the particles, *irrespective of the nature of the residual gas in the discharge tube* or of the metals used in the electrodes.

14. **The Velocity of the Cathode Particle:** The velocity of the particle can be determined by measuring the displacement effected by known electrostatic and electromagnetic fields on a fine pencil of cathode particles. Such a pencil of particles impinging on a phosphorescent screen may be located by the phosphorescent spot produced. If a strong magnetic field H be applied to such a pencil of rays they will be deflected from their rectilinear path. The force exerted by the field H on a particle carrying a charge e, moving with a velocity v, will be Hev. At equilibrium, this force will be equal to the centrifugal force of the moving particle acting outwards along its radius of curvature, r. Therefore, if

the mass of the particle be m, the following relation holds

$$\mathrm{H}ev = \frac{mv^2}{r}. \tag{1.1}$$

Since H and r are both measurable it follows that the ratio $mv/e = \mathrm{H}r$ can be determined. Now, by superposing on the pencil of cathode particles thus magnetically deflected a suitable electrostatic field X, the pencil may be restored to its original rectilinear path. In such case, by equating the electrostatic and electromagnetic forces involved, there follows

$$Xe = \mathrm{H}ev \tag{1.2}$$

whence v may be determined from the known values of X and H. Hence also the ratio e/m may be obtained.

Thomson was able to show that the ratio e/m was constant for all cathode rays, irrespective of the nature of the electrodes or the nature of the residual gas in the discharge tube for all velocities of travel not approaching the velocity of light. The average value of v was found to be 2.8×10^9 cm. per second. The value of e/m in such discharge tubes was approximately 1.79×10^7 electromagnetic units (e.m.u.). This may be compared with the ratio of e/m for a hydrogen ion. It was known that the charge carried by such an ion is about 4.8×10^{-10} electrostatic unit (e.s.u.). The mass of a hydrogen ion is 1.64×10^{-24} gram. Hence in electromagnetic units, the charge e/m for a hydrogen ion is

$$\frac{4.8 \times 10^{-10}}{1.64 \times 10^{-24} \times 3 \times 10^{10}} = 0.97 \times 10^4 \text{ electromagnetic units.}$$

For the cathode particle therefore the ratio e/m is approximately

$$\frac{1.79 \times 10^7}{0.97 \times 10^4} = 1845 \text{ times}$$

greater than that for the hydrogen ion. It is apparent that one of several factors may account for this: (1) either the charge on the particle is some 1845 times greater than that on the hydrogen ion, the masses being identical, or (2) the mass of the particle may be 1/1845 of the mass of the hydrogen ion and the charges identical or (3) the cathode particle may differ in both charge and mass from that of the hydrogen ion. It will now be shown that the charge of the cathode particle is identical with that of the hydrogen ion and that, therefore, the mass of the cathode particle is approximately 1/1845 of the hydrogen ion.

15. **The Charge Carried by a Cathode Particle:** The earliest efforts to determine e were made by Townsend, J. J. Thomson and H. A. Wilson. Townsend produced his charged particles by electrolysis of

solutions at high current densities. The gases thus evolved contain a small fraction of the molecules in the charged condition. When these charged gases were bubbled through water they formed a cloud or fog. Townsend assumed that the number of ions was the same as the number of fog particles. He determined the total electric charge per cubic centimeter carried by the gas. He determined the total weight of the cloud by absorbing the water in sulfuric acid. He found the average weight of the water droplets by observing their rate of fall under gravity, computing their mean radius by the application of Stokes's law,

$$v = 2gr^2d/9\eta, \tag{1.3}$$

where v is the velocity of fall of a drop of water of radius r and density d, falling through a gas of viscosity η, under the acceleration of gravity g. Such determinations gave $e = 3 \times 10^{-10}$ electrostatic unit.

Thomson's method was similar to Townsend's but utilized the observation of C. T. R. Wilson that the sudden expansion and consequent cooling of the air in the ionization vessel gave a convenient method of producing the cloud formation. The ionization was produced by means of X-rays. Thomson obtained his measurement of total charge by determination of the current carried by the cloud under the influence of a weak electromotive force. He weighed the cloud produced and utilized Stokes's Law as in Townsend's work.

Thomson's mode of experimentation was modified by H. A. Wilson who studied the rate of fall of the cloud under gravity alone and also under the combined action of gravity and an electrostatic field. The ratio of the velocities, v_1 and v_2, under gravity alone and with the combined action of gravity and an electrostatic field X is given by the equation

$$\frac{v_1}{v_2} = \frac{mg}{mg + Xe}, \tag{1.4}$$

Combining this with Stokes's Law (1.3) for v_1 and eliminating m by the expression $m = \frac{4}{3}\pi r^3 d$, Wilson obtained the expression

$$e = \left\{ \frac{4}{3}\pi \left(\frac{9\eta}{2g} \right)^{3/2} \right\} \frac{g}{X} \frac{(v_2 - v_1)}{d^{1/2}} v_1^{1/2}. \tag{1.5}$$

This yielded for e a mean value of 3.1×10^{-10} e.s.u.

Millikan's 'Balanced Drop' Method: This represents a distinct advance on the H. A. Wilson method. Millikan succeeded in studying the behavior of individual droplets which could be held suspended in the field from 30 to 60 seconds and carried charges varying from 1e to 6e. The charges were all exact multiples and revealed positively the unitary nature of electricity. The ionized cloud after formation between parallel plate electrodes was subjected to a potential gradient which eliminated all particles except those with the right ratio of charge to mass to be held in suspension in the field. The rate of fall of such particles under gravity was observed with a telescope in the eye-piece of which three equally spaced cross hairs were placed. Any error due to evaporation could be checked firstly by its stationary condition in the field and also by the times taken to fall through the two equal distances between the cross hairs. From such determinations a value of $e = 4.65 \times 10^{-10}$ e.s.u. resulted.

Millikan's Oil Drop Method:[1] A diagram of the apparatus used is shown in Fig. 1.1. The droplets investigated were introduced into the chamber *D* by means of the atomizer *A* in the form of a finely divided spray. Eventually one of these droplets finds its way through the aperture, *p*, into the space between the condenser plates, *M* and *N*. The hole *p* is then closed and the air between the plates ionized by a source of X-rays, *X*. Illumination is secured from the arc lamp, *a*, the heat rays being removed in filters *w* and *d*. The motion of the illuminated droplet is observed through a microscope fitted with an engraved scale. By collision with ions of the air the droplet acquires an electric charge, and then moves between plates *M* and *N* in a direction governed by the sign of the acquired charge and with a speed indicative of the size of the charge carried. By reversal of the sign of the charge on *M* and *N* the direction of motion of the droplet can be reversed. In this way the droplet could be kept travelling back and forth between the plates. As a mean of 17 determinations of the times which the droplet required to fall between two

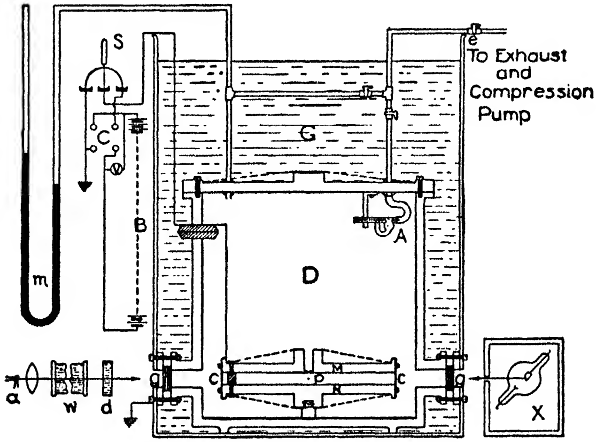

FIG. 1.1. Millikan's Oil Drop Apparatus

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[1] *Phys. Rev.*, 2, 143 (1913).

fixed cross hairs in the observing telescope, whose distance apart corresponded to a distance of fall of 0.5222 cm., a value of 13.595 seconds with a maximum deviation of ± 0.2 sec. was obtained. When rising under the influence of an electric field produced by applying a potential difference of 5051 volts, the successive times required varied in the following way: 12.5, 12.4, 21.8, 34.8, 84.5, 84.5, 85.5, 34.6, 34.8, 16.0, 34.8, 34.6, 21.9 seconds. It will be seen that, after the second trip up, the time changed from 12.4 to 21.8, indicating, since in this case the drop was positive, that a negative ion had been caught from the air. On the next trip another negative ion had been caught. The next time, 84.5, indicates the capture of still another negative ion. From the equation

$$\frac{v_1}{v_2} = \frac{m_d g}{Xe - m_d g} \quad \text{or} \quad e = \frac{m_d g}{X v_1}(v_1 + v_2), \tag{1.6}$$

where m_d is the mass of the droplet, it follows that the change in velocity produced by the acquiring of an extra charge can be given by eliminating m_d and solving the equations thus:

$$(a)\ t = 34.8 \text{ secs. against gravity } v_1 + v_2 = \left(\frac{0.5222}{13.595} + \frac{0.5222}{34.8}\right);$$

$$(b)\ t = 84.5 \text{ secs. against gravity } v_1 + v_2 = \left(\frac{0.5222}{13.595} + \frac{0.5222}{84.5}\right).$$

The velocity difference between (*a*) and (*b*) is

$$0.5222[(1/34.8) - (1/84.5)] = 0.00891 \text{ cm. per second.}$$

In this manner it was shown that successive captures of an ion effected changes in the velocity of rise against gravity respectively equal to 0.008912, 0.008911, 0.008903, 0.008883 and 0.008931 cm. per second, all of which are within 1/5th of 1 per cent of the mean value of 0.00891 cm. per second. This therefore represents the change in the sum of the speeds v_1 and v_2 caused by the capture of one ion. Relationships of this sort were found to hold absolutely without exception, no matter in what gas the droplets had been suspended or what sort of droplets were used upon which to catch the ions. Experiments were conducted over five or six hours, hundreds of ions per droplet were caught and recorded by the change of speed. Here then is direct proof that the electrical charges found on ions all have exactly the same value or else small exact multiples of that value. This is the most conclusive proof of the 'atomic' nature of electricity.

From the preceding equation, with the data obtained in this study of the behavior of the oil droplets, accurate values for the ratio e/m_d could be deduced. To obtain the magnitude of the unit charge e it was necessary however to determine the mass of the droplet. For this purpose

Stokes's Law could be employed to determine the radius and therefore the volume and mass of the droplet. To attain in these calculations the same high degree of precision which was obtained in the velocity determinations just recorded, Millikan found it necessary to make an investigation into the limitations of Stokes's Law with variation in the medium and with variation in the droplet size. On completion of this study, which revealed the necessity of correcting Stokes's Law for inhomogeneities in the medium—a correction which was finally made as an empirical function of the ratio of the mean free path of the gas molecules of the medium l to the radius of the droplet r—Millikan derived a corrected form of the Stokes's equation from which the radius of the droplet was determined,

$$v_1 = \frac{2}{9}\frac{gr^2}{\eta}(d_d - d_m)\left(1 + A\frac{l}{r}\right) \tag{1.7}$$

in which d_d is the density of the drop, d_m that of the medium, A an empirical constant, the other terms having the same significance as given previously. In this manner, the magnitude of e was finally obtained with a degree of precision embodied in the following expression:

$$e = (4.774 \pm 0.005) \times 10^{-10} \text{ e.s.u.}$$

Subsequent research has revealed that this determination of e does not possess the accuracy indicated. The principal source of error was in the value assumed for the viscosity of the air in which the droplets moved. Millikan employed a value of $(1822.6 \pm 1.3) \times 10^{-7}$ c.g.s. unit. More recent viscosity determinations give a weighted mean value of $(1832.5 \pm 1.5) \times 10^{-7}$ c.g.s. unit and a weighted mean value from oil-drop determinations of

$$e = (4.8036 \pm 0.0048) \times 10^{-10} \text{ e.s.u.}$$

16. **Electron Charge from Other Measurements:** It is now believed that the elementary charge e on the electron is more accurately determined by other measurements than by the oil-drop method. A number of different methods have been employed to give values for three fundamental constants, the electron charge, e, the specific charge, e/m, and the ratio of Planck's constant, h (see Chap. 4) to the electron charge, e. These interlocking determinations have revealed small discrepancies between the three constants that have, thus far, not been resolved. The methods enjoying a high degree of confidence include a determination of e from measurements with X-radiation and a ruled grating to determine wave length (Chap. 7), from spectroscopic determinations, and from the minimum voltage V at which electrons are able to produce X-rays (Chap. 4). Birge[1] has recently examined all the available data and

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[1] *Rev. Mod. Phys.*, **13**, 233 (1941).

concludes that, at the present time, the following represent the best 'consistent' set of values for these several quantities

$$\begin{aligned} e &= (4.8025 \pm 0.0010) \times 10^{-10} \text{ abs. e.s.u.} \\ e/m &= (1.7592 \pm 0.0005) \times 10^{7} \text{ abs. e.m.u.g}^{-1}. \\ h/e &= (1.37929 \pm 0.00023) \times 10^{-17} \text{ erg sec. e.s.u}^{-1}. \\ h &= (6.624_2 \pm 0.002_4) \times 10^{-27} \text{ erg sec.} \end{aligned}$$

17. **The Avogadro Constant:** This constant is secured by combining the value of e with that obtained in electrochemical work for the value of the faraday, the quantity of electricity necessary to liberate one gram ion of a univalent element in electrolysis. From the data of Birge just cited this amounts to 9648.7 ± 1 e.m.u. or in electrostatic units to $9648.7 \times 2.99776 \times 10^{10}$ e.s.u. This quantity is equal to the elementary charge, e, multiplied by the number of atoms in one gram atom, i.e. the Avogadro number, N: thus,

$$\begin{aligned} N &= \frac{9648.7 \times 2.99776 \times 10^{10}}{4.8025 \times 10^{-10}} \\ &= (6.0228 \pm 0.0011) \times 10^{23} \text{ mole}^{-1}. \end{aligned}$$

18. **The Mass of the Hydrogen Atom:** Given N, the Avogadro number, the mass of the hydrogen atom is obtained from the atomic weight of hydrogen by simple division. On the chemical scale the atomic weight is $(1.00785_6 \pm 0.00001_8)$ according to data subsequently to be discussed, derived from observations of nuclear change. The mass of the individual atom becomes

$$1.00785_6/6.0228 \times 10^{23} = (1.67339 \pm 0.00031) \times 10^{-24} \text{ g.}$$

19. **The Mass of the Electron and Derived Quantities:** The mass of the electron is most readily derived from the accepted values for e and e/m. Expressing both in electrostatic units one obtains

$$\begin{aligned} m_0 &= 4.8025 \times 10^{-10}/(1.7592 \times 10^{7} \times 2.99776 \times 10^{10}) \\ &= (9.1066 \pm 0.0032) \times 10^{-28} \text{ g.} \end{aligned}$$

It should be observed that m_0 is the so-called rest-mass of the electron, the mass of an electron which is moving slowly relative to the velocity of light. This is true of electrons produced in discharges through gases. Electrons produced in some processes of radioactive decay have velocities more than 90 per cent that of light. The mass, m, of such particles, on the basis of the theory of relativity is $m = m_0/(1 - (v/c)^2)^{1/2}$ where v is the velocity of the electron and c that of light.

The ratio of the mass of the hydrogen atom to that of the electron becomes $1.67339 \times 10^{-24}/9.1066 \times 10^{-28} = 1837.5 \pm 0.5$. By deducting the mass of the electron from that of the hydrogen atom the mass of the proton becomes $(1.67248 \pm 0.00031) \times 10^{-24}$ g. The ratio of the mass of the proton to that of the electron becomes 1836.5 ± 0.5. Also, on the chemical scale, the atomic weight of the electron becomes $1.00785_6/1837.5 = (5.4847 \pm 0.0017) \times 10^{-4}$.

20. **The Size of the Electron:** The radius, r, of the electron is given, at least as to order of magnitude, by the expression $r = c^2/mc^2$ which, with the data of the preceding sections, is approximately 2.8×10^{-13} cm. It is of importance to note that this is an entirely lower order of magnitude than the atomic radius which approximates to 10^{-8} cm. (See Chapters 3 and 7.)

21. **The Inter-relation of Mass and Energy:** The relativity expression for the mass of a particle in terms of its velocity $m = m_0/(1 - (v/c)^2)^{1/2}$ involves as a consequence a direct relation between mass and energy. The increase in kinetic energy dE resulting when a force F acting on a body moves through a distance dx is equal to Fdx. If, for the force F, the rate of change of momentum be substituted then

$$dE = d(mv)/dt \cdot dx. \tag{1.8}$$

Since the velocity v of the particle is dx/dt the expression takes the form

$$dE = vd(mv) = v^2dm + mvdv. \tag{1.9}$$

The relativity expression for velocity in the form $m^2(c^2 - v^2) = m_0^2c^2$ gives on differentiation

$$(c^2 - v^2)dm - mvdv = 0. \tag{1.10}$$

From this expression it follows, by combination with (1.9), that

$$dE = c^2dm. \tag{1.11}$$

This relation may be extended to all forms of energy such that, quite generally,

$$E = mc^2, \tag{1.12}$$

where c is the velocity of light in cm./sec., energy being expressed in ergs and mass in grams. This is the generalized law which governs all mass-energy relations.

The law of conservation of mass was formulated by Lavoisier upon the basis of his own experimental measurements. It received its most critical experimental test when applied to ordinary chemical processes in the closing decade of the 19th century and the first decade of the present century at the hands of Landolt. He determined the masses of various reacting systems before and after reaction in closed glass vessels. The masses of reagent approximated 300 g. and could be weighed to an accuracy of several thousandths of a milligram. The greatest precautions were necessary to eliminate errors due to changes in adsorbed moisture, in the volume and temperature of the reaction system. The reactions were double decompositions, for example, $HIO_3 + 5\,HI = 3\,I_2 + 3\,H_2O$, the majority in aqueous solutions. Of approximately fifty different experiments approximately one half showed a slight gain, the others a slight loss, all the differences lying, however, within the limits of error of $\pm$ 0.03 mg. This signifies that, in such chemical processes, the law of conservation of mass holds to within an error of 1 part in 10^7.

According to the mass-energy relationship just established, $E = mc^2$, for a reaction involving the evolution of 10^4 calories per mole, the system should suffer a loss in mass of $10^4 \times 4.2 \times 10^7/9 \times 10^{20}$ = ca. 0.5×10^{-9} g. per mole. It is thus evident that, for a system of mean molecular weight of 100 g., the occurrence of a chemical reaction involving 10 kcal. per mole is constant in weight to within 1 part in 2×10^{11}. The Landolt experiments attained a precision some 1000 times less than would have been necessary to detect such changes in mass. It is further evident, however, that, in the nuclear reactions now attainable and involving energy changes corresponding to millions of electron-volts (M.e.v.), changes in mass, readily detectable by modern precision measurements, will occur. These changes are related to the energy changes by the Einstein relation which becomes therefore the basis for a comprehensive principle of conservation, that of energy and mass, regarded as equivalent one to another, and related by the expression $E = mc^2$.

22. **The Investigation of Atomic Architecture:** The methods employed for exploring the architecture of the atom consist in determining the influence of the atomic constituents on various impinging radiations. Lenard and his co-workers examined the scattering of beams of electrons by atoms. It was found that swift electrons (cathode particles) encountered little resistance in their passage through atoms which behaved as though they were largely transparent to such impinging particles. Massive atoms with a radius of $\sim 10^{-8}$ cm. would be practically impenetrable to electrons. It was these experiments which suggested to Lenard a concept of an atom with a small impenetrable center surrounded by a cloud of electrons, this latter offering but little resistance to the passage of swiftly moving electrons.

The quantitative development of the concept of the nuclear atom is due to Rutherford who in 1911 initiated experiments on the scattering of α-particles by atoms. Owing to their great mass relative to the electrons, α-particles are uninfluenced by the electrons with which they come in contact. They are, however, stopped or deflected by the more massive positive nuclei of the atoms through which they pass.

Proof of the minuteness of the atomic nuclei is obtained by a study of the tracks of the α-particles and β-particles or electrons through gases. Photographs of such tracks are obtainable since the gas through which the particles pass is ionized and the ions may be rendered visible by the condensation of water vapor upon them. This is the technique of the Wilson cloud chamber. Study of photographs so obtained shows that a β-particle may pass through as many as 10,000 atoms before it comes near to an electronic constituent of any of the atoms to detach it from its system and form an ion, a circumstance indicative of the relative freedom of the atomic space from such electronic constituents. The cloud photographs reveal, on the other hand, that, on the average, an α-particle passes through 200,000 atoms without approaching near enough to the nucleus to suffer appreciable deflection. This leads to the conclusion that the positive nucleus is but a minute fraction of the total atomic volume.

23. **The Nuclear Charge:** The number of free positive charges on the nuclei of atoms was defined by studies of Rutherford and his co-workers on the scattering of α-particles in passing through various metal foils. The effective deflecting force causing the scattering of an α-particle of charge $2e$ by a massive atom of charge Ze is the coulomb force $2Ze^2/r^2$ where r is the distance separating the nuclei. The orbit of the α-particle is, therefore, a hyperbola with the nucleus, of charge Ze, as the focus. The distribution of the scattered α-particles is determined by projecting a stream of α-particles normally to a thin metal foil and counting scintillations produced on a fluorescent screen located at various positions on a circular arc centered at the scattering foil.

TABLE 1.2

NUCLEAR CHARGES FROM SCATTERING EXPERIMENTS

Element	Atomic Number	Z	Investigator
Pt	78	77.4 ± 1	Chadwick
Ag	47	46.3 ± 0.7	"
Cu	29	29.3 ± 0.5	"
Au	79	79 ± 2	Chadwick and Rutherford
A	18	19	Auger and Perrin
Air	6,7	6.5	C. T. R. Wilson

The conclusion initially reached in the scattering experiments was that the nuclear charge was approximately equal to one-half the atomic weight. This conclusion agreed with earlier work by Barkla on the scattering of X-rays. As is now well known, the charge Z on the nucleus and the number of extra-nuclear electrons are equal and the number is known as the atomic number. In Table 1.2 the results of scattering experiments are compared with known data for the atomic numbers.

24. **The Atomic Number:** The actual count, with precision, of the extranuclear electrons in elementary substances was accomplished by Moseley, 1914. The suggestion of Laue, 1912, that the regular spacing of atoms in a crystal could be utilized, on the principle of a grating, for the analysis of short wave-length ether waves, had been translated into actual practice by the Braggs, an X-ray spectrometer devised and the wave lengths of various X-rays determined. Moseley, in 1914, utilizing a wide variety of elements as targets in the X-ray bulb, found that, in additon to general X-radiation which all emitted, each element emitted X-radiations characteristic of the given element. As the voltage over an X-ray tube is raised above a certain definite value, the anti-cathode is observed to emit an X-radiation which is characteristic of the material of the target and which is much more intense than the continuous radiation. For each element it is thus possible to obtain a series of monochromatic X-radiations. These rays as shown in Fig. 1.2 (which is a typical spectrum) are classified according to their wave lengths into *K*, *L*, *M*, etc. Moseley carried out an investigation in which he measured the wave lengths of the lines in the *K* and *L* series for most of the elements. He found that the spectra of the different elements, beginning with that of aluminum and ending with that of gold, could be arranged in the same order as in the periodic table, and that under these conditions the wave length of any one characteristic line of the *K* or *L* series decreased regularly with increase in the ordinal number of the element in the table. Furthermore, Moseley found that if he assigned to each element a number, Z, corresponding to its place in the periodic table (Al = 13, Si = 14, etc., as far as Au = 79), there exists for each type of radiation a simple relation of the form

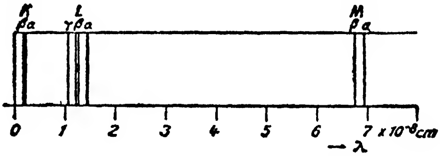

FIG. 1.2. *K*, *L*, *M*, etc., Series

$$\sqrt{\nu} = a(Z - N_0), \tag{1.13}$$

where ν is the frequency, and a and N_0 are constants.

These measurements have been repeated and extended by de Broglie, A. W. Hull, and M. Siegbahn.[1] Fig. 1.3 shows the *K* series for some of the elements between As and Rh as photographed by the latter. The dark line on the extreme left hand corresponds to a wave length zero. The first line in each spectrum is found on closer examination to consist of two lines very close together. These are known as the α_2 and α_1 lines of the *K* series. The darker lines to the left may also be separated into

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[1] M. Siegbahn has reviewed the observations on X-ray spectra and their relation to Moseley's law in *Jahrb. d. Rad. u. Elektronik*, **13**, 296 (1916).

two lines, known as the β_1 and β_2 lines of the K series. Now the significance of Moseley's law is this: If we plot the square roots of the frequency, or (what amounts to the same thing) the values of $\sqrt{1/\lambda}$ for any

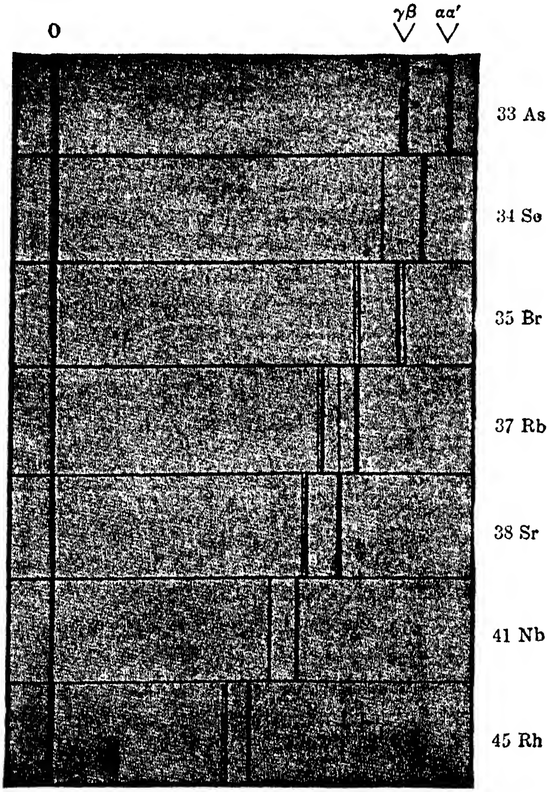

FIG. 1.3. K Series for Elements As-Rh

one of these lines, as ordinates against the ordinal number Z, we obtain a straight line for each of these characteristic radiations, as shown in Fig. 1.4. The value of Z thus determined is known as the *atomic number*.

The order of increasing frequency was that of the elements arranged in the order of their atomic weights with conspicuous and significant exceptions. A missing element in the periodic order gave a missing step in the increment of the square root of the frequency. In the whole series of elements ranging from hydrogen = 1 to uranium = 92, six such gaps were found indicating that six elements were still unknown in this interval. In 1923, Hevesy and Coster discovered Hafnium, $Z = 72$. In 1925, Noddack announced the discovery of Masurium (43) and Rhenium (75). In 1926, Hopkins indicated the possible presence of Illinium (61) in association with rare-earth elements. Element No. 87 has been found by Mlle Perey as a rare branching product in the natural radioactive actinium family (Sect. 27). Perrier and Segré found No. 43, the masurium of Noddack among the products of bombardment of molybdenum nuclei. Element No. 61 has probably been produced by nuclear bombardment of neodymium. In 1940 the final missing element, No. 85, was prepared by α-particle bombardment of bismuth. It is more metallic than iodine but accumulates, like iodine in the thyroid gland. It is radioactive emitting 2 α-particles. Element No. 93 arises from neutron bombardment of uranium.

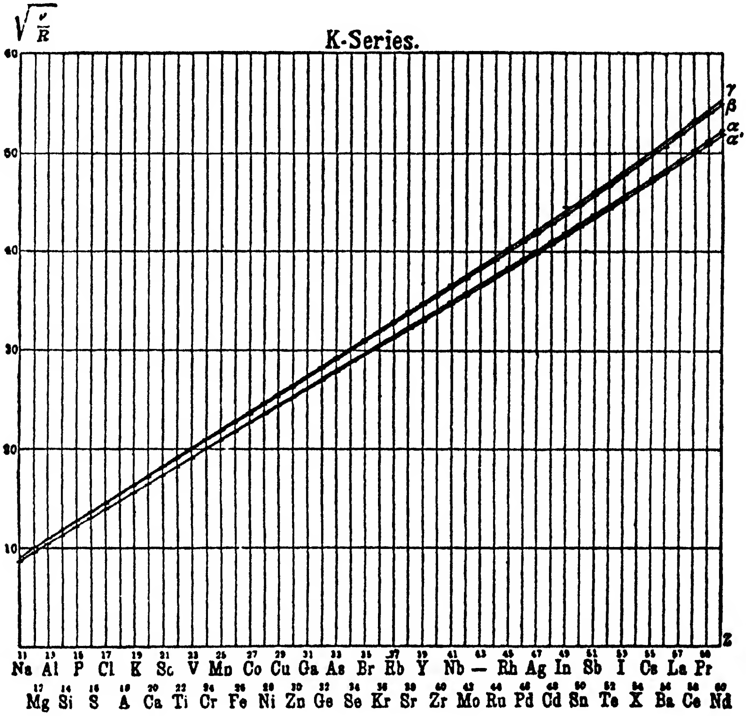

FIG. 1.4. Relation between Atomic Number and Frequency

25. **Nuclear Constitution:** The mass of the atom, save for the minor amount associated with the extra-nuclear electrons, is concentrated in the nucleus. If this nuclear mass were ascribed to constituent protons the number of these would be given by the atomic weight *A*. Since the

atomic weight is greater than the net nuclear charge Z it was suggested that the nucleus might also contain electrons, $A-Z$ in number. The stability of such systems was regarded as doubtful.

Rutherford in 1920 had suggested the existence of particles of unit mass and no charge. To these possible particles he gave the name neutrons. Experimental proof of the existence of such neutral primary particles was furnished in 1932, by J. Chadwick, as products of bombardment of light nuclei by α-particles. With such particles, the characteristics of the nucleus as to charge and mass can be accounted for on the assumption that the nucleus contains Z protons and $A-Z$ neutrons.

26. **Radioactive Disintegration:** The phenomenon of spontaneous disintegration in the radioactive substances discovered by Becquerel, Pierre and Marie Curie (1896–1898) is to be attributed to an instability of their nuclei. Three types of radiations were recognized by their behavior under the influence of a magnetic field, α-particles carrying a positive charge, β-particles a negative charge and γ-rays uninfluenced by the field.

The α-particle was shown by Rutherford to be a helium atom, of mass 4, with a double positive charge, He^{++}. This is now known as the helium nucleus. The α-particles are emitted with a velocity 1/15 to 1/20 that of light and, in their progress through their environment, both capture electrons and lose them again. As their velocity diminishes, they tend more and more to retain captured electrons yielding, finally, neutral helium atoms. At high velocities they travel in straight lines *through* the electronic fields of the atoms, removing electrons and thus producing ionization. As their velocity approaches zero, they suffer deflections from their straight line of flight, a phenomenon termed scattering. Very rarely, a large deflection or reversal of direction occurs. The great rarity of this phenomenon led Rutherford to the conception of the nuclear atom, a minute nucleus surrounded by planetary electrons.

The β-particles emitted by radioactive matter are swift electrons which also originate in the nucleus. Some β-particles have a velocity which is 99.8 per cent of the velocity of light. Owing to their small mass, they are more easily deflected by electrostatic and electromagnetic fields than are α-particles; they have a much smaller ionizing power, are more easily scattered and therefore pursue a more tortuous path in a gas.

The γ-rays are extremely short wave-length X-rays, are, therefore, electromagnetic disturbances of the same nature as light. They have extremely great penetrating power, in excess even of the hardest X-rays produced in discharge tubes. They are not deflected by magnetic or electrical fields.

27. **The Radioactive Series:** The spontaneously radioactive elements, some forty in number, with atomic weights lying, with the exception of the feebly radioactive elements K, Rb and Sm, between the atomic weight

limits of 206 and 238, belong to three radioactive series. These are designated by the parent elements of each series, respectively uranium, thorium and actinium. Radium belongs to the uranium series; the parent in the actinium series is probably a uranium isotope present in constant amount in the uranium minerals. Each series, in addition to the normal sequence of disintegration products, shows a branching of the series occurs. Thus the change from uranium X_1 to uranium-II occurs in two branches, 99.65 per cent over uranium X_2 and the residue by uranium Z; also the change from uranium C to D occurs 99.97 per cent via RaC′ and 0.03 per cent via RaC″. A similar branching occurs in the thorium series from ThC to ThD, 65 per cent over ThC′ and 35 per cent over ThC″. For the actinium series a branching from AcC to AcD occurs 0.16 per cent over AcC′ and 99.84 per cent over AcC″. This branching is shown graphically for the RaC–RaD transition in Fig. 1.5. The UZ transition

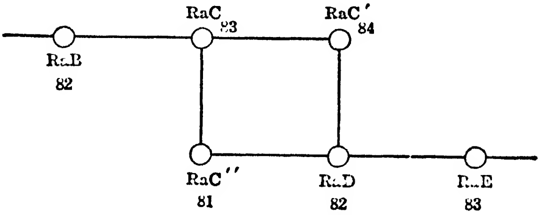

FIG. 1.5. RaC–RaD Branched Transition

to U-II is not shown on this diagram. The individual radioactive elements, their atomic weights and atomic numbers together with their important constants are summarized in the three tables which follow (Tables 1.3, 1.4 and 1.5).

28. **Radioactive Disintegration and the Periodic Table:** As knowledge of the properties of the elements formed in the successive stages of radioactive decay became more complete, it emerged that the loss of α-particles and β-particles by a radioactive element corresponded to a definite shift of the group classification of the elements produced in the process of decay. The loss of an α-particle in *every* case produced a shift, two groups to the left in the periodic table. Thus Radium (Group II) loses an α-particle to give Radon (Ra. Emanation) Group 0. Similarly loss of a β-particle gives rise to a shift of one group to the right in the periodic table. The change of Radium B, Group IV to Radium C, Group V is one illustration of such change of which, however, there are many. This important generalization is shared by several investigators: notably Soddy, Fleck, Russell and Fajans. Now, since the α-particle is a helium nucleus carrying a double positive charge and since the β-particle is none other than an electron, and since, moreover, these particles are certainly ejected

TABLE 1.3

THE URANIUM SERIES

Element	Symbol	At. Wt.	At. No.	Rays	Half-life Period
Uranium-I	UI	238.2	92	α	4.4×10^9 yr.
Uranium-X_1	UX_1	(234)	90	β	24.5 days
Uranium-X_2	UX_2	(234)	91	β	1.14 min.
Uranium-II	UII	(234)	92	α	3.4×10^5 yr.
Ionium	Io	(230)	90	α	8.3×10^4 yr.
Radium	Ra	226.05	88	α	1590 yr.
Radon (Emanation)	Rn	222	86	α	3.82 days
Radium-A	RaA	(218)	84	α	3.05 min.
Radium-B	RaB	(214)	82	β	26.8 min.
Radium-C 99.97% | 0.03%	RaC	(214)	83	β and α	19.7 min.
Radium-C′	RaC′	(214)	84	α	10^{-6} sec.
Radium-C″	RaC″	(210)	81	β	1.32 min.
Radium-D	RaD	(210)	82	β	22 yr.
Radium-E	RaE	(210)	83	β	5.0 days
Radium-F (Polonium)	RaF	(210)	84	α	140 days
Radium-G (Uranium lead)	RaG	206	82	—	—

from the nucleus, it follows that the difference between the nuclei of successive atoms in neighboring groups of the periodic table consists in the extra unit of positive charge which the heavier nucleus possesses. The atom itself being electrically neutral, it therefore follows that the extra-nuclear electrons must increase by one as the atomic table is ascended. The progressive variation in the square root of the frequency of the characteristic X-radiation as discovered by Moseley is therefore paralleled by a progressive increase of net positive nuclear charge and of extra-nuclear electrons.

29. The Atomic Number and Defects in the Periodic Table: It was shown that, on the basis of weight classification, certain definite transpositions of the elements would occur which would not be in harmony with

TABLE 1.4

THE ACTINIUM SERIES

Element	Symbol	At. Wt.	At. No.	Rays	Half-life Period
Protoactinium	Pa	(231)	91	α	3.2×10^4 yr.
Actinium	Ac	(227)	89	β	13 yr.
Radioactinium	RaAc	(227)	90	α	18.9 days
Actinium-X	AcX	(223)	88	α	11.2 days
Actinon (Emanation)	An	(219)	86	α	3.92 sec.
Actinium-A	AcA	(215)	84	α	2×10^{-3} sec.
Actinium-B	AcB	(211)	82	β	36 min.
Actinium-C 99.84% 0.16%	AcC	(211)	83	α and β	2.16 min.
Actin.-C′	AcC′	(211)	84	α	5×10^{-3} sec.
Actin.-C″	AcC″	(207)	81	β	4.76 min.
Actinium-D	AcD	(207)	82	—	—

the periodicity of properties shown by the bulk of the elements when arranged on a weight basis. The transposition of argon and potassium, of tellurium and iodine and of cobalt and nickel was noted. When studied by the Moseley method, the order of the square root of the characteristic frequencies of these elements was such as would be anticipated on the basis of properties and not that obtained on the basis of atomic weight. Argon therefore has an atomic number of 18, potassium 19, cobalt 27, nickel 28, tellurium 52, iodine 53. The answer to the query of Ramsay as to the lack of complete concordance in the periodic classification was evident and revolutionary. The atomic weight is not the fundamental factor in atomic behavior. The properties of the elements are a function of their atomic architecture. Atomic weight is a secondary factor useful as a guide in the great majority of cases but at fault in the cases just mentioned and certain others now to be discussed.

30. Isotopes: The existence of elements differing in mass yet identical in chemical properties was made familiar by the study of radioactive decay. It gradually emerged that the end product in the decay of radium was Radium G, radio-lead, identical in chemical properties with that of ordinary lead. Moreover, as the change in group classification brought about by loss of α- and β-particles became understood, it was further

TABLE 1.5

THORIUM SERIES

Element	Symbol	At. Wt.	At. No.	Rays	Half-life Period
Thorium	Th	232.12	90	α	1.34×10^{10} yr.
Mesothorium 1	$MsTh_1$	(228)	88	β	6.7 yr.
Mesothorium 2	$MsTh_2$	(228)	89	β	6.13 hr.
Radiothorium	RaTh	(228)	90	α	1.90 yr.
Thorium-X	ThX	(224)	88	α	3.64 days
Thoron (Emanation)	Tn	(220)	86	α	54.5 sec.
Thorium-A	ThA	(216)	84	α	0.14 sec.
Thorium-B	ThB	(212)	82	β	10.6 hr.
Thorium-C 65% ∣ 35%	ThC	(212)	83	β and α	60.5 min.
Thorium-C′	ThC′	(212)	84	α	c. 10^{-11} sec.
Thorium-C″	ThC″	(208)	81	β	3.1 min.
Thorium-D	ThD	208	82	—	—

evident that Radium B, Radium D and Radium G were all members of Group IV in the periodic classification. This is evident from the accompanying chart, Fig. 1.6. Furthermore, since loss of an α-particle (helium nucleus) results in a diminution in the atomic weight by four units, while the β-particle change is without influence on the weight, it is evident that, by calculation of the α-particles lost in the successive changes, the atomic weights of successive products could be deduced from that of radium. Assuming an atomic weight of 226 for radium, that of Ra B becomes 214 (3 α-particles lost), that of Ra D becomes 210 (4 α-particles lost), and Ra G becomes 206 (5 α-particles lost). All these elements have properties identical with those of ordinary lead, whose atomic weight is 207.2, in all properties except those dependent upon mass. The masses differ as can be seen from the above examples by so much as eight units (206–214). The end-product of the thorium series of radioactive elements is likewise a member of Group IV analogous to lead with an atomic weight of 208.1. To such elements, identical in properties other than those dependent upon mass, the term ***isotopes*** was applied. The conclusions reached upon the basis of calculation from the atomic weight of lead and the α-particle loss have been abundantly confirmed by actual atomic weight determinations.

The wide variety of elements produced in radioactive decay, their similarity of properties, in spite of wide differences in atomic weight, would have presented a problem of considerable complexity for periodic classification had not the Moseley discovery elucidated the true basis of classification and demonstrated the secondary importance of the weight

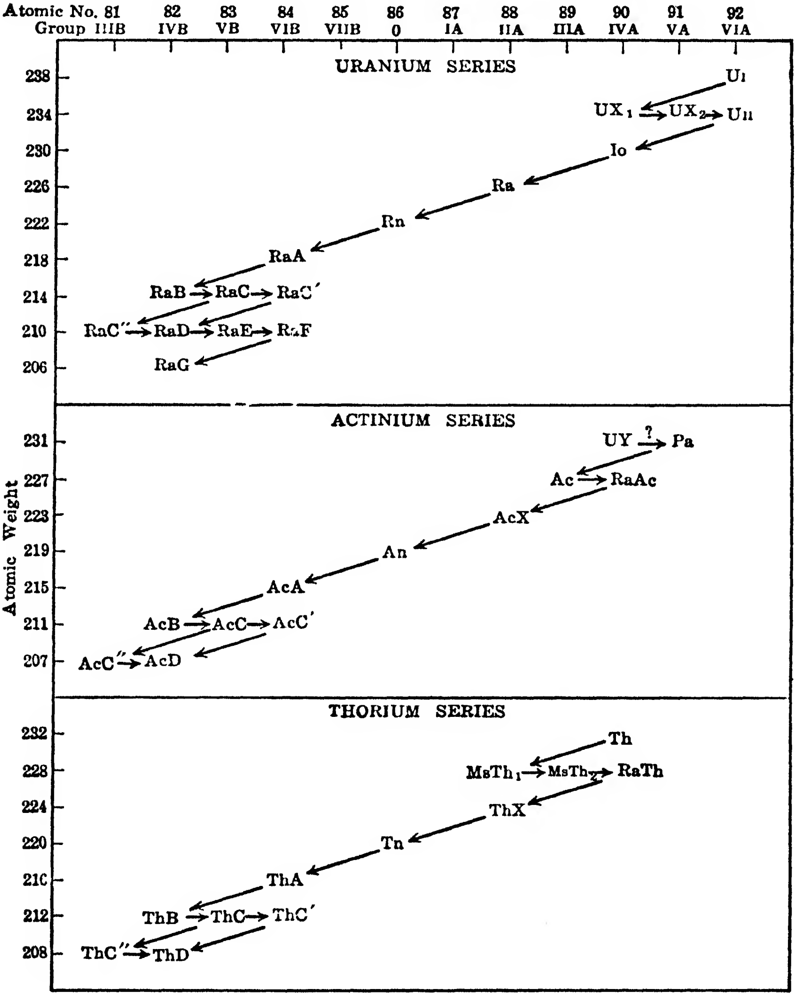

FIG. 1.6. Radioactive Disintegration Series

relationship. All such isotopes while differing greatly in mass are identical in atomic number. Their net nuclear charges are identical. They have a common extra-nuclear electronic configuration. They differ only in the mass of the nucleus.

31. Non-Radioactive Isotopes: The existence of atoms of identical nuclear charge but differing masses, outside the range of radioactive materials, was demonstrated by the investigations of J. J. Thomson and of Aston on the properties of the positive rays from a discharge tube. In the earlier sections, a considerable discussion has been given of the electrons liberated from atoms by the action of various forms of energy. Little has been stated concerning the residues from such changes. Positive rays were discovered by Goldstein in 1886 in the discharge of electricity through gases at low pressure. Using a perforated cathode he showed that streamers of light were present behind the cathode perforations, and assumed that the light indicated the presence of rays travelling in the opposite direction from the cathode rays. From the manner of their production he termed them 'kanal strahlen.' Wien showed that they could be deflected by a magnetic field. The detailed investigation of their properties was undertaken by J. J. Thomson, who gave to them the term Positive Rays since they were shown to carry a positive charge. The rays are produced by ionization of gases at low pressure by a strong electric field of the order of 30,000-50,000 volts. They are the residues from such ionization processes.

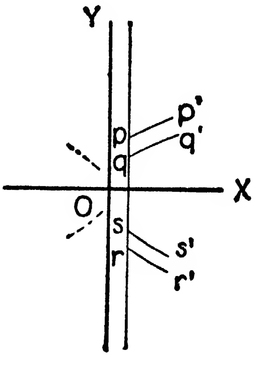

FIG. 1.7. J. J. Thomson's Parabola Method

The method of measurement employed by Thomson to investigate the charge and mass of such rays is known as the 'Parabola' method. It consisted essentially in allowing the rays to pass through a very narrow tube and then in analyzing the fine beam so produced by electric and magnetic field. Under the combined influence of an electrostatic and an electromagnetic field a ray will be deflected from its normal path and will strike a receiving screen at a point x, y, where y/x is a measure of its velocity and y^2/x is the measure of e/m, the ratio of charge to mass. This follows from the application of simple dynamics to the separate actions of the electrostatic field X and the electromagnetic field H since

$$x = k(Xe/mv^2) \tag{1.14}$$

and

$$y = k'(\mathrm{H}e/mv) \tag{1.15}$$

in the manner previously demonstrated for the electron. The velocity

v of the rays may vary however over a considerable range. Hence, for constant m but variable v, the locus of impact of the rays with the screen will be a parabola, pp' (Fig. 1.7). Rays of larger mass m' yield a similar parabola of smaller magnetic displacement qq'. The displacement of the parabolas along the magnetic axis OY at a given value along the electric field gives a measure of the relative masses since

$$m'/m = (pn)^2/(qn)^2 \tag{1.16}$$

With one known parabola, the mass of all other rays can be identified.

The sharpness of the parabolas, obtained photographically in this way by using a photographic plate as receiving screen for the rays, established experimentally for the first time the fundamental assumption of the Daltonian atomic theory, that the atoms (in these experiments the positive rays) of the same element had the same mass.

32. **Mass Spectrographs:** Aston improved the technique of positive ray analysis by the use of the mass-spectrograph illustrated in Fig. 1.8.

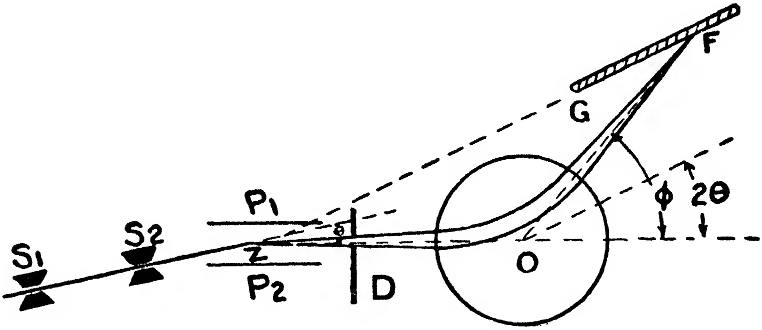

Fig. 1.8. Aston's Positive Ray Spectrograph

Positive rays are sorted out into a thin ribbon by means of two parallel slits, S_1 and S_2, and are then spread into an electric spectrum by means of the charged plates, P_1 and P_2. A portion of this spectrum deflected through an angle θ is selected by the diaphragm D and passed through the circular poles of a powerful electromagnet O, the field of which is such as to bend the rays back again through an angle ϕ, more than twice as great as θ. The result of this is that rays having a constant ratio m/e will converge to a focus F. If a photographic plate is placed at GF as indicated, a spectrum dependent on mass alone is obtained.

Aston, by successive improvements, has increased the accuracy of his measurements to 1 part in 10,000. His earliest results showed that the light elements as well as the radio-elements exist as isotopes and that the large deviations in atomic weights from whole numbers are due to the presence of several isotopes of such masses and in such proportions as will yield the observed atomic weight. Chlorine ($A = 35.457$) contains 75.4 per cent of the isotope of mass 35 and 24.6 per cent of mass 37. The individual isotopes show small deviations, expressible in parts per 10,000, from whole numbers. Aston termed such deviations the 'packing fraction'; they are important in the problem of nuclear structure and stability.

The discovery of isotopes explained the inverted orders in the periodic classification. Thus, argon ($A = 39.944$) has isotopes of masses 40, 38 and 36, the first present to the extent of 99.6 per cent. Potassium isotopes have masses 39 and 41, the former amounting to 93.3 per cent.

Other instruments aiming at high precision have been developed by Dempster,[1] Bainbridge,[2] Bleakney,[3] Mattauch [4] and Nier.[5] Nier has also developed an effective instrument for abundance ratio determinations, readily constructed at only moderate expense and very suitable for physico-chemical investigations. The apparatus is shown in essential outline in Fig. 1.9. Ions of controlled voltage are accelerated through a slit system and emerge as a beam at S_4. The ion beam enters perpendicularly the homogeneous magnetic field between the V-shaped poles of the magnet; it is bent through such an angle as will cause the beam to leave the field boundary perpendicularly to reach the collector through slit S_5. The radius of curvature of an ion in the field is given by the formula $m/e = 4.82 \times 10^{-5} r^2 H^2/V$ where m/e is the mass-charge ratio of the ion, r the radius in cm., H the field in gauss and V the energy of the ion in electron volts. The various masses are focussed by keeping H constant with varying V. Suitable amplification and measurement of the ions collected permits a determination of relative ion peaks and hence the abundance ratios.

33. **Precision Masses of the Ions:** Masses determined from traces on a photographic plate are compared with that of the oxygen isotope, ^{16}O. Such a scale of masses is known as the 'physical scale'; the 'chemical scale' is based on $O = 16$, where the oxygen is known to contain isotopes of masses 16, 17 and 18. The present accepted relation between the two scales taking account of the isotope content of molecular oxygen ($^{16}O : {}^{18}O : {}^{17}O = 510 \pm 40 : 1 : 0.2$) is:

$$\text{Ratio of physical to chemical scale, } r = 1.0002$$

Errors in mass spectrographic determinations of mass have been considerably minimized by simultaneous measurement of 'ion doublets,' with

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[1] Dempster, *Phys. Rev.*, 20, 631 (1922); *Proc. Am. Phil. Soc.*, **75**, 755 (1935).

[2] Bainbridge and Jordan, *Phys. Rev.*, **50**, 282 (1936).

[3] Bleakney and Hipple, *Phys. Rev.*, **53**, 521 (1938).

[4] Mattauch, *Phys. Rev.*, **50**, 617 (1936).

[5] Nier, *Rev. Sci. Inst.*, **11**, 212 (1940).

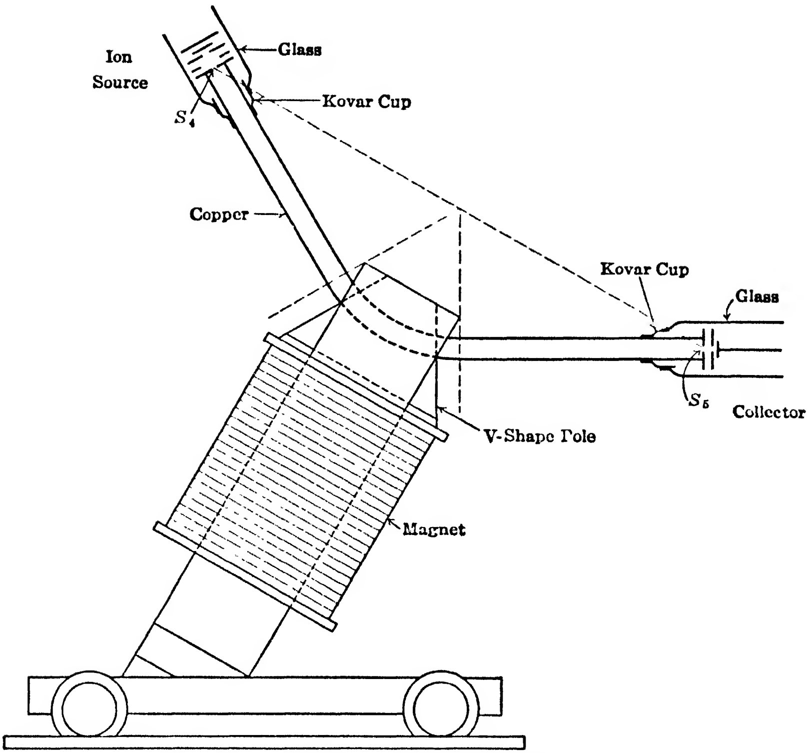

FIG. 1.9. General View, Nier Mass Spectrograph

nearly the same m/e but different in nature. Two closely-spaced traces can be obtained whose spacing represents the mass-difference of the ions. Errors in the calibration of the mass scale are simultaneously re-

TABLE 1.6

NUCLEAR MASSES FROM MASS SPECTROGRAPH (LIVINGSTON AND BETHE)
PHYSICAL SCALE

Nucleus	Mass	Nucleus	Mass
^{1}H	$1.00813 \pm 0.0_417$	^{11}Be	$11.01292 \pm 0.0_316$
^{2}D	$2.01473 \pm 0.0_42$	^{12}C	$12.00398 \pm 0.0_49$
^{4}He	$4.00389 \pm 0.0_47$	^{13}C	$13.00761 \pm 0.0_315$
^{7}Li	$7.01818 \pm 0.0_312$	^{14}N	$14.00750 \pm 0.0_48$
^{9}Be	$9.01516 \pm 0.0_32$	^{15}N	$15.00489 \pm 0.0_32$
^{10}Be	$10.01631 \pm 0.0_32$	^{16}O	16.00000

duced. Typical doublets studied are: $^{12}CH_4$-^{16}O; H_2-D; D_3^+-C^{++}; D_2-He; $^7Li^+$-$^{14}N^{++}$; CO-N_2; CH_4-NH_2; OH-NH_3; O-NH_2. Complete cycles of interlocking doublets give accurate masses for most of the light elements and their isotopes with errors indicated by the data in the attached Table 1.6.

34. **Isotope Discovery from Light Spectra:** In 1929 the discovery of isotopes by examination of spectra produced by absorption or emission of light was successful in the case of oxygen, an element which had hitherto been thought to contain only the atoms of mass 16. Giauque and Johnston [1] examined the absorption spectra of the atmosphere and found absorption bands which were interpreted as belonging to compounds containing two new oxygen isotopes, one of mass 18 and the other a much rarer one of mass 17. Oxygen, of mass 16, had been used as the standard of mass reference for historical reasons and because of its assumed simplicity. Its established complexity at once raised doubts as to the simplicity of carbon and hydrogen, hitherto also thought to contain only atoms of single masses. Birge and King,[2] from a study of band spectra of gaseous compounds including carbon monoxide, cyanogen and the spectra of C_2, reported the existence of an isotope of carbon of mass 13. This discovery led Birge and Menzel [3] to a calculation that the discrepancies between the chemical atomic weight and the mass spectrograph value for hydrogen would be resolved if hydrogen contained about one part in 4500 of an isotope of mass 2. The experimental search for such an isotope by Urey, Brickwedde and Murphy,[4] was successful in 1932, fractional distillation of liquid hydrogen concentrating the heavy isotope in the residue. The presence of the isotope was demonstrated by the presence of a faint spectral line in the emission spectrum of the enriched hydrogen near the H_α line of hydrogen and spaced from it at the correct theoretically calculable distance. The discovery by Washburn and Urey [5] of the method of concentration by electrolysis of water, led to the separation of the pure isotope of mass 2, now known as deuterium.

35. **The Separation of Isotopes:** The development of the mass spectrograph revealed that, at least in principle, the isotopes were separable and that the separation was dependent on the differences in masses accompanying the identity of nuclear charge. Any property dependent on mass can be utilized, the attainable efficiency being characteristic of the isotopic elements and the method in question. The efficiency is normally expressed in terms of a separation or fractionation factor. If n_1 and n_2 are the numbers (or moles) of light and heavy isotopic species in a mixture

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[1] Giauque and Johnston, *Nature*, **123**, 318, 831 (1929).

[2] Birge and King, *Astrophys. J.*, **72**, 251 (1930).

[3] Birge and Menzel, *Phys. Rev.*, **37**, 1669 (1931).

[4] Urey, Brickwedde and Murphy, *Phys. Rev.*, **39**, 164, 864 (1931); **40**, 1 (1932).

[5] Washburn and Urey, *Proc. Nat. Acad. Sci.*, **18**, 496 (1932).

before, and N_1 and N_2 are the corresponding quantities after, a given separation process which has enriched the lighter isotope then the separation factor α for the lighter isotopic substance is

$$\alpha = (N_1/N_2)/(n_1/n_2). \tag{1.17}$$

If the total process be composite of a series of x single separation processes then the total or overall enrichment factor A is given by the expression

$$A = \alpha^x. \tag{1.18}$$

The methods of separation employed are generally chosen for their suitability for the isotope in question and the use to which the product is to be put. The more important methods employed are:

(*a*) *Separation by the Mass Spectrograph:* The separation is as efficient as the focusing equipment but the quantity separable is small since the ion beam is small ($\sim 10^{-8}$ amp.). In this way, ^{6}Li has been separated from ^{7}Li, in quantities of $\sim 10^{-8}$ g., for disintegration studies. The ^{41}K constituent of potassium and ^{87}Rb of rubidium were thus separated and shown to be radioactive.

(*b*) *Separation by Diffusion Processes:* Aston used this method originally on neon but Hertz in 1932 enormously increased its efficiency by a continuous and automatic system employing a series of mercury diffusion pumps first with a porous tube and later with a column of mercury vapor as the diffusion membrane. Hertz used this to separate pure ^{20}Ne, and hydrogen and deuterium. It has also been used to concentrate $^{15}N_2$ and heavy carbon in methane, yielding over 50 per cent $^{13}CH_4$. The method is convenient but the yields per unit of time are low.

(*c*) *Separation by Gravitational or Centrifugal Diffusion:* The well known separation of gases occurring in the atmosphere under the influence of the gravitational field (Chap. 3) can be adapted to separation by centrifugal diffusion with the enormous centrifugal fields now available in modern high speed centrifuges. Since the separation factor is

$$\alpha = e^{-(M_2-M_1)v^2/2RT}, \tag{1.19}$$

where M_2 and M_1 are the masses and v the linear velocity of motion in the centrifuge, the advantage of centrifugal action is obvious. Also, the method is important in that the separation depends on the mass difference, not the absolute masses, an especially favorable condition for separation of heavy elements. Thus, the chlorine isotopes in carbon tetrachloride have been partially separated and the bromine isotopes in ethyl bromide, the latter in a centrifugal field equal to 388,000 g at a peripheral speed of 400 metres per second. An 11 per cent enrichment of ^{79}Br was obtained.

(*d*) *Separation by Thermal Diffusion and Convection:* This separation was developed as an effective method by Clusius and Dickel in 1938.

The separation produced by thermal diffusion under a temperature gradient is multiplied by thermal convection whereby the hot gas is carried upwards and the cold gas downwards in a vertical tube with an electrically heated wire, axially disposed, as the hot surface. Hydrogen chloride was separated into the two constituents, $H^{35}Cl$ and $H^{37}Cl$, with more than 99.4 per cent purity of each. The neon isotopes and isotopic methanes have been partially separated by this method. The separation factor is of the form

$$\alpha = e^{kl}, \tag{1.20}$$

where l is the length of the column and the constant k involves the masses of the species and the temperature gradient

$$k = \text{const.}\ (M_2 - M_1)(\ln\ (T'/T))/l_i(M_2 + M_1), \tag{1.21}$$

l_i being the length of an ideal unit, that is the column length which gives a vertical concentration gradient equal to that produced by thermal diffusion alone.

(*e*) *Separation by Electrolysis:* This method yielded a successful fractionation of the hydrogen isotopes to Lewis and his collaborators. The procedure involves electrolysis, generally of 0.5 molar sodium hydroxide, between nickel anodes and iron cathodes. Separation factors $\alpha = [H/D]_{gas} \div [H/D]_{liq.}$ of approximately 5 are obtainable, values as low as 3 and as high as 8 having been reported. The separation factor decreases with increasing temperature and may be influenced by the nature of the electrode material, because of a competitive exchange equilibrium $H_2O_{(l)} + HD = HDO_{(l)} + H_2$, for which the equilibrium constant is approximately 4 at room temperature and 2 at 100° C.

With other elements the fractionation factor is much smaller. For oxygen it is 1.008 only. For lithium isotopes $\alpha = 1.055$.

(*f*) *Separation by Fractional Distillation:* Separations by this method are positive but small. Small concentrations of heavy hydrogen, neon, oxygen and nitrogen have thus been obtained. The fractional distillation of water to yield $H_2{}^{18}O$ has been the most successful method of concentrating ^{18}O but $\alpha = 1.089$ at 11° C., 1.062 at 46° and 1.025 at 100° C.

A molecular still was early used by Brönsted and Hevesy for minute separations of mercury isotopes. It has also been applied to zinc and potassium.

(*g*) *Separation by Chemical Exchange:* This important technique was developed by Urey. It depends indirectly on the isotopic masses since these influence the zero-point energies of the isotopic compounds (Chap. 5) and the zero point energies in turn determine, in part, velocity of reaction (Chap. 15). Urey has applied this method to the separation of the isotopes of carbon, nitrogen and sulfur. Thus, for example, in the reaction,

$$^{15}NH_3 + {}^{14}NH_4{}^+(aq) = {}^{14}NH_3 + {}^{15}NH_4{}^+(aq),$$

the calculated equilibrium constant at 25° C. is 1.033. This separation factor is multiplied by the following device. Ammonium nitrate solution is flowed down a column past an ascending stream of ammonia, produced at the base of the column by interaction of the descending ammonium salt with sodium hydroxide. The heavy nitrogen accumulates in the ammonium salt solution. In a three-stage cascade unit operating on this principle the ^{15}N concentration was increased progressively to 2.6, 18.9 and 72.8 per cent in the three units, the initial abundance of ^{15}N being 0.38 per cent. Similarly the ^{13}C abundance in sodium cyanide solutions was raised from 1.1 to 22 per cent. The separations by chemical exchange appear to be the best suited for large scale isotope separation when suitable reactions are available.

36. **Nuclear Transformations by α-Particles:** Rutherford achieved the transformation of stable nuclei in 1919 using swift α-particles from RaC′ as the bombarding source. These α-particles have a range of 6.97 cm. in air. With an apparatus filled with hydrogen, scintillations were observed at distances equivalent to 29 cm. in air, arising from elastic collisions between hydrogen and helium nuclei.

With nitrogen, particles with a range equivalent to 40 cm. in air were observed. Since such ranges could not arise from elastic impacts with helium it was assumed that they must be due to protons ejected from the nitrogen nucleus. We may formulate such a nuclear reaction by the equation

$$^{4}_{2}\mathrm{He} + {}^{14}_{7}\mathrm{N} = {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H},$$

where the mass is indicated at the upper left and the atomic number at the lower left. If protons are the only ejected product the conservation principle demands that the nuclear residue shall be of mass 17 and atomic number 8, i.e. an oxygen isotope. Chadwick and Rutherford found hydrogen nuclei from collisions of α-particles with boron, nitrogen, fluorine, neon, sodium, aluminum, silicon, phosphorus, sulfur, chlorine, argon and potassium.

37. **Further Nuclear Bombarding Agents:** In 1932, Chadwick identified *the neutron,* a particle of unit mass and no charge, arising from the α-particle bombardment of beryllium. The possibility of employing such a particle in nuclear reactions, due to the absence of charge, was immediately obvious. In the same year Cockcroft and Walton imparted high velocities to protons and showed them to be effective agents for bombarding the lithium nucleus, to yield helium nuclei with a range of 8.4 cm.

$$^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H} = 2\,{}^{4}_{2}\mathrm{He}.$$

Simultaneously, in California, Lawrence and his co-workers employed deuterons in the newly-developing cyclotron. Thus,

$$^{6}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{D} = 2\,{}^{4}_{2}\mathrm{He}$$

and

$$^{7}_{3}\mathrm{Li} + ^{2}_{1}\mathrm{D} = 2\,^{4}_{2}\mathrm{He} + ^{1}_{0}n,$$

where the symbol $^{1}_{0}n$ designates a neutron. In addition to these material particles short wave photons, or γ-rays, have also been employed for nuclear reactions

$$^{2}_{1}\mathrm{D} + h\nu(\gamma) = ^{1}_{1}\mathrm{H} + ^{1}_{0}n.$$

38. **The Neutron:** The principal neutron-producing processes are

(*a*) Deuteron-Deuteron interaction,	$^{2}\mathrm{D} + ^{2}\mathrm{D} = ^{3}\mathrm{He} + ^{1}n,$
(*b*) Lithium-Deuteron interaction,	$^{7}\mathrm{Li} + ^{2}\mathrm{D} = ^{8}\mathrm{Be} + ^{1}n,$
(*c*) Beryllium-Helium interaction,	$^{9}\mathrm{Be} + ^{4}\mathrm{He} = ^{12}\mathrm{C} + ^{1}n,$
(*d*) Deuterium-γ-ray interaction,	$^{2}\mathrm{D} + h\nu(\gamma) = ^{1}\mathrm{H} + ^{1}n.$

Neutrons are uncharged particles of approximately unit mass with a unique penetrating power. Because of their lack of charge they are uninfluenced by the outer electrons of atomic systems and suffer collisions with nuclei, the approach being unhampered by the repulsive forces operative between positively charged particles and other nuclei. Again, because of lack of charge, their range is large, equivalent to several kilometers in air. In collision with light nuclei they give up energy, especially to hydrogen-rich materials such as water and paraffin. In this way Fermi reduced the speed of neutrons finally to values comparable with those due to thermal motion. With decrease in neutron-energy the cross-section of the nucleus for capture of a neutron is markedly increased. For fast neutrons this cross-sectional area is about 10^{-24} cm^2. but with slow neutrons, areas 10^2–10^4 times this value have been observed. Neutrons thus become valuable bombarding agents for nuclear transformations.

The interaction between a deuteron and a γ-ray is the basis for determining the neutron mass. From the Einstein mass-energy relation, if the energy E ergs is employed to disintegrate a mass m_1 into masses m_2 and m_3, it follows that $m_1 + E/c^2 = m_2 + m_3$ where c is the velocity of light. Such observations with deuterons and γ-rays yield a value for the mass of the neutron of 1.00893.

Similar calculations from nuclear processes may be used to give exact nuclear masses of the lighter elements and these, in general, confirm those from mass spectrographic data.

39. **The Production of High Velocity Ions as Projectiles:** Five different techniques have been employed to produce nuclear projectiles: (*a*) the voltage multiplier, (*b*) the cascade transformer, (*c*) the electrostatic generator, (*d*) the high intensity discharge tube, and (*e*) the cyclotron.

Cockcroft and Walton developed the voltage multiplier. Condensers are charged in parallel and discharged in series. Alternating current at 250 kv. can thus be multiplied to give potentials of 800 kv. at currents as large as 100 μa. (microamperes). The cascade transformer was developed for deep-therapy X-ray tubes. Recently currents of 250 μa. at 10^6 volts (1 million volts = 1 M.v.) have been focused on a target of 1.2 cm. diameter. The Van de Graaff electrostatic generator carries, on an endless belt of insulating material, an electric charge from a high voltage rectifier to a large hollow collecting sphere, which accumulates the potential steadily. Ion currents of a few milliamperes at potentials up to 5 M.v. have thus been obtained. Smaller generators built inside pressure tanks at 6–7 atm. yield ions up to 2.2 M.e.v. High intensity discharge tubes yielding 200 μa. at 200 kv. intensity have been employed by Oliphant.

The most popular technique for the attainment of high energy ions is that developed by E. O. Lawrence, known as the magnetic resonance accelerator or, more generally, the cyclotron. Lawrence's method makes use of the principle of repeated acceleration of the ions by a sort of resonance with an oscillating field. The ions circulate back and forth from the interior of one electrode to the interior of another, as may be seen from the diagrammatic outline in Fig. 1.10. Two electrodes, A, B, in the form of semi-circular hollow plates are mounted in a vacuum tube in coplanar fashion with their diametral edges adjacent. By placing the system between the poles of a magnet, a magnetic field, H, is introduced normal to the plane of the plates. High frequency electric oscillations are applied to the plates so that there results an oscillating electric field in the diametral region between them.

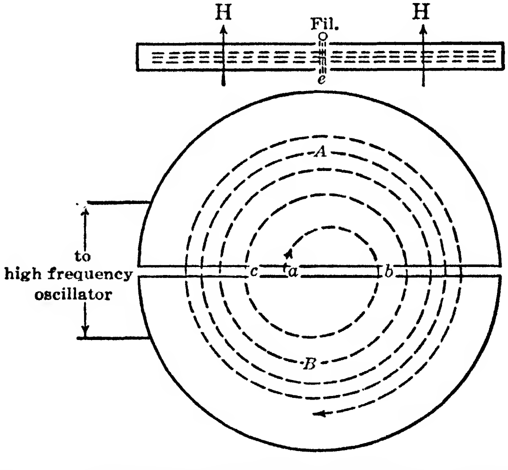

FIG. 1.10. Schematic Diagram of the Lawrence Cyclotron

With this arrangement it is evident that, if at one moment there is a positive ion at *a* between the electrodes and electrode A is negative with respect to B, the ion will be accelerated to the interior of the former. Within the electrode the ion traverses a circular path because of the magnetic field, and ultimately emerges again between the electrodes; this is indicated in the diagram by the arc (*a* . . . *b*). If the time consumed by the ion in making the semi-circular path is equal to the half-period of the electric oscillations the electric field will have reversed and the ion will receive a second acceleration, passing into the interior of B with a higher velocity. Again it travels on a semi-circular path (*b* . . . *c*) but this time the radius of curvature is greater because of the greater velocity. For all velocities (neglecting variation of mass with velocity) the radius of the path is proportional to the velocity, so that the time required to traverse a semi-circular path is independent of ion velocity. Therefore, if the ion travels its first half circle in a half cycle of the oscillations it will do so on all succeeding paths. Hence, it will circulate on ever widening semi-circles from the interior of one electrode to the interior of the other, gaining an increment of energy on each crossing of the diametral region corresponding to the momentary potential difference between the electrodes. Thus if, as in the early experiments of Lawrence and Livingston, high frequency oscillations having peak values of 4000 volts are applied to the electrodes and protons are caused to spiral around in the electrodes 150 times they will receive 300 increments of energy acquiring thereby a speed corresponding to 1.2 M.v. Lawrence has built a sequence of cyclotrons varying in beam energy from 80 kv. to 16 M.e.v. The beam from this latter extends 60 inches through air after leaving the chamber. A new giant cyclotron whose beam, it is expected, will range in voltage from 100 to 300 M.v. is under construction in Berkeley. This beam may be expected to penetrate 140 feet of air.

40. **Type-Reactions of Nuclear Disintegration:** The number of nuclear reactions has become so large that they are now subdivided into type-reactions with a shorthand notation descriptive of each. There are used as projectiles, and appear as disintegration products, α-particles, protons, deuterons, neutrons and γ-rays. To these are assigned respectively the symbols α, p, d, n and γ. The reactions are designated by the symbols of the projectile and product. Thus, α-particle disintegrations yielding protons are of the α–p type. A neutron bombardment which yields an α-particle would be symbolized as n–α. If such a designation is preceded by the chemical symbol of the substance bombarded, the reaction is completely specified. Thus, ^{6}Li, n—α designates the reaction ${}^6_3\mathrm{Li} + {}^1_0n = {}^3_1\mathrm{H} + {}^4_2\mathrm{He}$, since from the required balance of charge and mass, the other disintegration product must be a hydrogen isotope ($Z = 1$) and of mass 3. Quite generally for a nuclear charge Z of atomic weight A, an α–p type reaction can be written:

$$^{A}Z + {}^4\mathrm{He} = {}^{A+4}(Z + 2) = {}^{A+3}(Z + 1) + {}^1\mathrm{H}.$$

Eighteen such types of nuclear disintegration are known and are summarized in Table 1.7.

TABLE 1.7

TYPE-REACTIONS IN NUCLEAR TRANSFORMATIONS

Number	Shorthand Notation	Nuclear Reaction
1	α–p	${}^AZ+{}^4\text{He}={}^{A+4}(Z+2)={}^{A+3}(Z+1)+{}^1\text{H}$
2	α–n	${}^AZ+{}^4\text{He}={}^{A+4}(Z+2)={}^{A+3}(Z+2)+{}^1n$
3	α–$2n$	${}^AZ+{}^4\text{He}={}^{A+4}(Z+2)={}^{A+2}(Z+2)+2{}^1n$
4	p–α	${}^AZ+{}^1\text{H}={}^{A+1}(Z+1)={}^{A-3}(Z-1)+{}^4\text{He}$
5	p–d	${}^AZ+{}^1\text{H}={}^{A+1}(Z+1)={}^{A-1}Z+{}^2\text{D}$
6	p–γ	${}^AZ+{}^1\text{H}={}^{A+1}(Z+1)={}^{A+1}(Z+1)+\gamma$
7	p–n	${}^AZ+{}^1\text{H}={}^{A+1}(Z+1)={}^A(Z+1)+{}^1n$
8	d–α	${}^AZ+{}^2\text{D}={}^{A+2}(Z+1)={}^{A-2}(Z-1)+{}^4\text{He}$
9	d–p	${}^AZ+{}^2\text{D}={}^{A+2}(Z+1)={}^{A+1}Z+{}^1\text{H}$
10	d–p, α	${}^AZ+{}^2\text{D}={}^{A+2}(Z+1)={}^{A-3}(Z-2)+{}^1\text{H}+{}^4\text{He}$
11	d–n	${}^AZ+{}^2\text{D}={}^{A+2}(Z+1)={}^{A+1}(Z+1)+{}^1n$
12	d–n, α	${}^AZ+{}^2\text{D}={}^{A+2}(Z+1)={}^{A-3}(Z-1)+{}^1n+{}^4\text{He}$
13	d–$2n$	${}^AZ+{}^2\text{D}={}^{A+2}(Z+1)={}^A(Z+1)+2{}^1n$
14	n–α	${}^AZ+{}^1n={}^{A+1}Z={}^{A-3}(Z-2)+{}^4\text{He}$
15	n–p	${}^AZ+{}^1n={}^{A+1}Z={}^A(Z-1)+{}^1\text{H}$
16	n–γ	${}^AZ+{}^1n={}^{A+1}Z={}^{A+1}Z+\gamma$
17	n–$2n$	${}^AZ+{}^1n={}^{A+1}Z={}^{A-1}Z+2{}^1n$
18	γ–n	${}^AZ+\gamma={}^AZ={}^{A-1}Z+{}^1n$

The product in the final column of this table can be generalized by the symbol ${}^{A+x}(Z \pm y)$ where x varies from $+3$ to -3 and y varies from $+2$ to -2, depending on the nature of the emitted particle or radiation. If the product corresponds with one of the stable isotopes the nuclear transformation is complete. There are 277 stable isotopes of the elements already known.

The products of these nuclear transformations are not always stable nuclei. In some 350 cases already known the product is not stable but undergoes further radioactive change as was first pointed out by Joliot-Curie and Joliot early in 1934. The phenomenon is termed artificial or induced radioactivity.

41. **Products of Induced Radioactivity:** The principal types of radiation from induced radioactive elements are negative β-particles or electrons (β^-), positive β-particles or *positrons* (β^+) and γ-rays. The positrons were observed by Curie and Joliot in their earliest experiments on induced radioactivity which resulted from α-particle bombardment of boron, magnesium or aluminum. Thus,

$$ {}^{27}_{13}\text{Al} + {}^4_2\text{He} = {}^1_0n + {}^{30}_{15}\text{P}. $$

The phosphorus is radioactive disintegrating to a silicon isotope with positron emission

$$^{30}_{15}\mathrm{P} = {}^{30}_{14}\mathrm{Si} + \beta^{+}.$$

This sequence of reactions constitutes about 5 per cent of the total nuclear reaction, the direct reaction being

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} = {}^{30}_{14}\mathrm{Si} + {}^{1}_{1}\mathrm{H}.$$

Bombarding agents other than α-particles yield radioactive products as illustrated in the reactions:

$$^{12}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} = {}^{13}_{7}\mathrm{N} + \gamma,$$

$$^{12}_{6}\mathrm{C} + {}^{2}_{1}\mathrm{D} = {}^{13}_{7}\mathrm{N} + {}^{1}_{0}n.$$

In each case the ^{13}N has a half-life of 9.93 minutes, and emits positrons and gamma rays. Longer half-lives with positron emission are illustrated by ^{34}Cl (from P, α-*n*) with a half-life of 33 minutes and ^{42}Sc (from K, α-*n*) with a positron activity of 13.5 days half-life.

Positron-production also results from the interaction of hard γ-rays with metals (Anderson). The rays from ThC′, with energies of 2.6 M.e.v., absorbed by a lead target produce positron-electron pairs, whose tracks are visible in the cloud chamber, the maximum energy of the positron of 1.55 M.e.v. The positron has the same e/m as the electron but in contrast to this latter has a very short life. Within a period of the order of 5×10^{-10} sec. it loses the greater part of its kinetic energy and is then annihilated by interaction with an electron, with the simultaneous production, to conserve momentum, of two γ-ray photons $\beta^{+} + \beta^{-} = 2\gamma(2 \times 0.5$ M.e.v.).

42. **Nuclear Fission:** Early in 1939 Hahn and Strassmann announced a new type of nuclear process involving neutron interaction with uranium and thorium. The work derived from earlier experiments, begun by Fermi in 1934, on neutron capture by uranium to yield the so-called 'transuranium' elements. Fermi showed that the uranium nucleus captures a neutron and, reverting to stability by expulsion of a β-particle, produces a nucleus of atomic number 93. The process was, however, more complex and several β-ray activities were observed.

Hahn and Strassmann finally produced the evidence for nuclear fission, the breakdown of the uranium-neutron complex into two groups of radioactive fission products with masses distributed around the mean masses of 96 and 143. In the light weight group, radioactive nuclei of atomic numbers 34–48, including Se, Br, Kr, Rb, Sr, Y, Zr, Cb, Mo, Ma, Pd, Ag and Cd, have been identified. In the heavier group are Sb, Te, I, Xe, Cs, Ba and La with atomic numbers from 51 to 57.

The fission process and its nature are dependent both on the energy of the neutron and on the isotope of uranium (or thorium) which is bombarded. With neutron energies up to ~ 10 M.e.v. no fission products with atomic numbers between 43 and 51 have been reported. They are produced with energies of ~ 17 M.e.v. Both fast neutrons (> 0.5 M.e.v.) and very slow thermal neutrons (~ 0.025 M.e.v.) are effective in producing uranium fission.

By experiments on the bombardment of uranium isotopes separated in the mass-spectrograph it is now certain that it is the uranium isotope ^{235}U which undergoes the major portion, if not the whole, of the fission with slow neutrons. This isotope is present in uranium to the extent of about 1 part in 140.

The energy of the fission fragments is about 175 M.e.v. ± 10 per cent. Two maxima are observed at 65 and 98 M.e.v. inversely proportional to the mass ratio of the fission fragments. Fission is accompanied by the emission of neutrons since the proton-neutron ratio in the fragments is such that they may be regarded either as too feebly charged for their mass (i.e. electron emitters) or too massive for their charge and therefore neutron emitters. There is evidence that 3 to 4 neutrons may be emitted per fission.

The emission of more than one neutron, on the average, as a result of the fission process evidently suggests the possibility of the whole fission reaction as a self-perpetuating or chain process capable of yielding, from an initial neutron-uranium nuclear interaction, a multiplying chain of similar processes. In view of the extremely high energy yield of each unit fission (~ 175 M.e.v.) the possibility of energy production by these nuclear processes is obviously a matter of first importance.

Photo-fission, by γ-rays from proton bombardment of calcium fluoride and aluminum fluoride targets, has been observed with an efficiency of one fission per 3×10^{13} protons hitting calcium fluoride, the protons being estimated to yield 10^8 γ-quanta. Deuterons and α-particles also have been shown to yield fissions.

43. **Thermo-nuclear Processes:** To produce by thermal means the reactions attained by high speed projectiles such as α-particles, protons, deuterons and neutrons, temperatures of one or more million degrees would be necessary for any reasonable rate of change. Actually such temperatures, quite impracticable in the laboratory, occur in the interior of the sun and many stars. The central solar temperature of 20×10^6 degrees makes the occurrence of such nuclear reactions rapid processes in the sun's interior. Indeed, it is now believed that such nuclear reactions are responsible for the enormous energy resources of the sun, which previously had never been satisfactorily explained. Independently, Bethe and Weizsacker found a sequence of nuclear changes which is in satisfactory accord with the best data on the energy output of the sun. The sequence of reactions forms a closed circular chain in which the participants are nuclei of carbon, nitrogen and the thermal protons with

which they collide. The sequence may be summarized thus:

$$\begin{aligned}
&(1) & {}^{12}C + {}^{1}H &= {}^{13}N + h\nu,\\
&(2) & {}^{13}N &= {}^{13}C + \beta^{+},\\
&(3) & {}^{13}C + {}^{1}H &= {}^{14}N + h\nu,\\
&(4) & {}^{14}N + {}^{1}H &= {}^{15}O + h\nu,\\
&(5) & {}^{15}O &= {}^{15}N + \beta^{+},\\
&(6) & {}^{15}N + {}^{1}H &= {}^{12}C + {}^{4}He.
\end{aligned}$$

It will be noted that the ^{12}C consumed in the first reaction is regenerated in the final reaction to permit the repetition of the cycle. The carbon and nitrogen nuclei, ^{12}C and ^{14}N, are catalysts for the net overall change which may be represented as the summation of the sequence in the equation

$$4{}^{1}H = {}^{4}He + 2\beta^{+} + 3h\nu.$$

Hydrogen, which is present in the sun's atmosphere in abundance (sufficient for 10^9 years yet!), is converted into helium, two positrons and the energy of three γ-rays given in reactions 1, 3 and 4 of the sequence, and of magnitude determined by the mass-energy relation applied to these processes.

44. **The Arrangement of the Extra-Nuclear Electrons.** The Rutherford atom consists, as we have seen, of a nucleus of atomic number Z having a net positive charge equal to Ze together with Z extra-nuclear electrons making the atom electrically neutral. From the studies of the characteristic X-radiation of the elements, initiated by Moseley, together with considerations based upon the optical spectra of the elements, Bohr introduced the concept of shells of extra-nuclear electrons, built around the nucleus at increasing distances from it. Thus, in the first two elements, hydrogen and helium, the electrons are presumed to occupy positions relative to the nucleus which would give rise to those X-radiations already discussed as the K-series. In the elements, 3 to 10, a shell of electrons further removed from the nucleus and giving rise to characteristic X-radiations, known as the L-series, is built up, so that these elements may show both the K-series of the inner shell and the L-series of the second shell. From elements, 11 to 18, another grouping is formed giving the M-series as well as the K and L-series from the inner shells. As we pass thence to the heavier elements, X-radiations of the N and O series are to be expected. With a given element, the K-series are the radiations of shortest wave length, and this latter increases from series to series as they change from K to O. (See Fig. 1.2.)

As with the K-series already discussed, there is a relationship between the atomic number and the square root of the frequency or reciprocal wave length of the series. The relation, however, is no longer linear. The accompanying diagram (Fig. 1.11) shows a plot of a function which is proportional to the square root of the frequency against the atomic number for the *K*, *L*, *M*, *N* and *O*-series. It will be noted that beyond the *K*-series, the increments are no longer equal but vary, giving the wavy lines of the diagram.

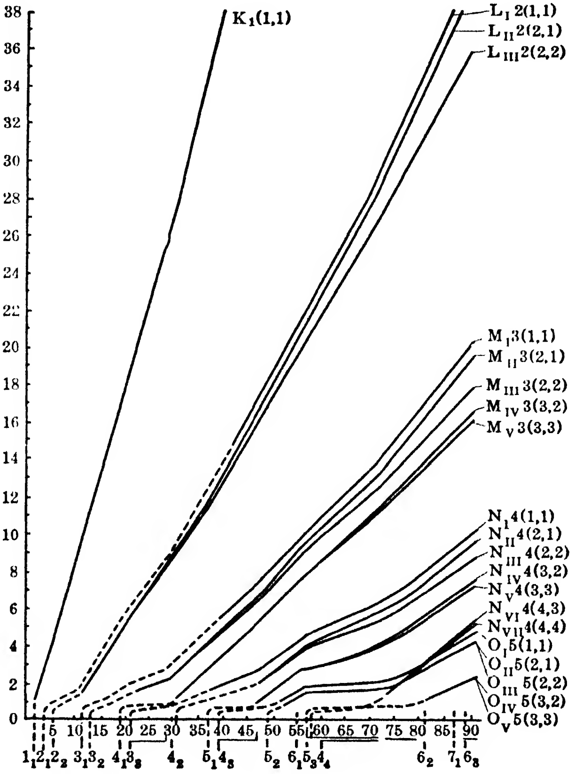

FIG. 1.11.

This is interpreted to mean that, in the first 20 elements, the extra electron entering the atomic architecture, to neutralize the extra positive charge in the nucleus of the new atom, takes up a position in the outer portion of the atom. In the elements, 21 to 28, and also in elements, 39 to 46, the electron penetrates into an interior shell of the atom. This reveals itself in the diagram by a more nearly horizontal portion of the curve over these ranges. In the case of the rare earth elements, 58 to 72, this penetration of the entering electron into the interior is particularly deep. The outer electron systems of these elements remain therefore sensibly unchanged while this deep penetration of entering electrons occurs. It is in this way that the similarity of the chemical properties of the rare earth elements is formulated. Indeed, it may be pointed out as a general principle, that similarity of chemical properties as exhibited, for example, by elements in the same group of the periodic table is to be associated with a similarity of the architecture of the outermost electrons of the atoms.

The following Table 1.8 illustrates this similarity of arrangement of the outer electrons of the atoms of the rare gases.

TABLE 1.8

Electron Shells of the Rare Gases

Atom	Shell					
	K	L	M	N	O	P
He	2					
Ne	2	8				
A	2	8	8			
Kr	2	8	18	8		
Xe	2	8	18	18	8	
Rn	2	8	18	32	18	8

Beyond helium the outer shell of the rare gases contains, in each case, eight electrons. The case of xenon illustrates the ability of an atom to start a new shell, in this case the O shell before the preceding shell, N, contains its maximum number of electrons. The case of radon shows that as many as 32 electrons can be built into the N shell.

The subdivision of the respective shells, L, M, N, etc., is based upon the so-called quantum numbers of the atom and upon a principle formulated by Pauli, and known as the *exclusion principle.*

It has been found that, to classify the electronic states of atoms as they are revealed by optical spectra, a set of quantum numbers must be given to each extra-nuclear electron and another set is given to the atom as a whole. Four quantum numbers, n, l, m and m_s, are employed to specify a given electron. The *principal or total quantum number*, n, designates the shell in which the electron is situated. Thus $n = 1$ in the K shell, 2 in the L shell, 3 in the M shell and so on. Each electron has an angular momentum, $\sqrt{l(l+1)}\cdot h/2\pi$, specified by the *azimuthal quantum number*, l, which may have the values $l = 0, 1, 2, 3 \ldots n - 1$. The value of the azimuthal quantum number is specified by the letters, s, p, d, f, according as $l = 0, 1, 2, 3$. In addition if, with Pauli, we imagine the atom to be subjected to an applied magnetic field so strong that there is no coupling between the electronic motions, two additional quantum numbers serve to specify an electron. One is the *magnetic quantum number*, m, which may have the values $m = -l, -l+1, \ldots -1, 0, 1, \ldots l$, in all, $2l+1$. The other quantum number, m_s, arising from the *spin* of the electron, takes either of two values, $-\frac{1}{2}$ or $+\frac{1}{2}$, the component of the angular momentum of the electron about any prescribed axis being either $-\frac{1}{2}\cdot h/2\pi$ or $+\frac{1}{2}\cdot h/2\pi$. These four quantum numbers n, l, m and m_s are necessary and adequate to account for the complexities of the one-electron system which we recognize as the hydrogen atom. Each electron in any atom requires similar specification.

We can specify the shells and the sub-shells or groups in terms of the quantum numbers n and l. Thus, all the electrons with a common value of n form a shell. A complete shell contains n groups each of which contains electrons with a common value of l. A complete l group contains $4l+2$ electrons and a complete n shell contains a summation of all such groups of $4l+2$ electrons. Since l can have the values $0, 1, 2 \ldots n-1$ it follows that this summation, $\Sigma(4l+2) = 2n^2$ electrons, as seen from the following classification:

n	=1	2		3			4			
l	=0	0	1	0	1	2	0	1	2	3
Electrons in complete l groups	=2	2	6	2	6	10	2	6	10	14
Electrons in complete n shells	=2	8		18			32			
Notation	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$3d^{10}$	$4s^2$	$4p^6$	$4d^{10}$	$4f^{14}$

Pauli's exclusion principle demands that *no two electrons in an atom have one and the same set of values for the four quantum numbers n, l, m and m_s* if a very strong field were applied. We see that our subdivision into shells and groups obeys this principle since in any of the completed l groups, there are $4l+2$ electrons. For these electrons we have $2l+1$ different values of m and each of the electrons with specification m may have either $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$.

These principles together with the data obtained from examination of the characteristic X-radiations of the atoms as indicated by the curves in Fig. 1.11 lead to the extra-nuclear electron configurations detailed in Table 1.9.

The table expresses the underlying principle connecting electron configuration and chemical properties, that these latter are determined by the electrons in the outer shells, furthest removed from the nucleus. The

TABLE 1.9

Extra-Nuclear Electron Configurations of the Elements

Element	Z	K	L		M			N	
		1s	2s	2p	3s	3p	3d	4s	4p
H	1	1							
He	2	2							
Li	3	2	1						
Be	4	2	2						
B	5	2	2	1					
C	6	2	2	2					
N	7	2	2	3					
O	8	2	2	4					
F	9	2	2	5					
Ne	10	2	2	6					
Na	11	Neon "Shell"			1				
Mg	12				2				
Al	13				2	1			
Si	14				2	2			
P	15				2	3			
S	16				2	4			
Cl	17				2	5			
A	18				2	6			
K	19	Argon "Shell"						1	
Ca	20							2	
Sc	21						1	2	
Ti	22						2	2	
V	23						3	2	
Cr	24						5	1	
Mn	25						5	2	
Fe	26						6	2	
Co	27						7	2	
Ni	28						8	2	
Cu	29	Argon "Shell"					10	1	
Zn	30						10	2	
Ga	31						10	2	1
Ge	32						10	2	2
As	33						10	2	3
Se	34						10	2	4
Br	35						10	2	5
Kr	36						10	2	6

TABLE 1.9—*Continued*

EXTRA-NUCLEAR ELECTRON CONFIGURATIONS OF THE ELEMENTS

Element	Z	Number in Inner Shells	N		O			P
			4d	4f	5s	5p	5d	6s
Rb	37	Krypton Shell			1			
Sr	38				2			
Y	39		1		2			
Zr	40		2		2			
Cb	41		4		1			
Mo	42		5		1			
Ma	43		6		1			
Ru	44		7		1			
Rh	45		8		1			
Pd	46		10					
Ag	47	Palladium Shell			1			
Cd	48				2			
In	49				2	1		
Sn	50				2	2		
Sb	51				2	3		
Te	52				2	4		
I	53				2	5		
Xe	54				2	6		
Cs	55	(1s–4d=46)			(5s–5p=8)			1
Ba	56							2
La	57						1	2
Ce	58			1			1	2
Pr	59			2			1	2
Nd	60			3			1	2
Il	61			4			1	2
Sa	62			5			1	2
Eu	63			6			1	2
Gd	64			7			1	2
Tb	65			8			1	2
Dy	66			9			1	2
Ho	67			10			1	2
Er	68			11			1	2
Tu	69			12			1	2
Yb	70			13			1	2
Lu	71			14			1	2

TABLE 1.9—*Continued*

EXTRA-NUCLEAR ELECTRON CONFIGURATIONS OF THE ELEMENTS

Element	Z	Number in Inner Shells	O		P			Q
			5d	5f	6s	6p	6d	7s
Hf	72	(1s–5p = 68)	2		2			
Ta	73		3		2			
W	74		4		2			
Re	75		5		2			
Os	76		6		2			
Ir	77		9					
Pt	78		9		1			
Au	79	(1s–5d = 78)			1			
Hg	80				2			
Tl	81				2	1		
Pb	82				2	2		
Bi	83				2	3		
Po	84				2	4		
	85				2	5		
Rn	86				2	6		
	87	(1s–5d = 78)			(6s–6p = 8)			1
Ra	88							2
Ac	89						1	2
Th	90						2	2
Pa	91						3	2
U	92			3			4	2

whole of classical chemistry, outside of the recently developed chemistry of the nucleus considered in previous sections, is concerned with the interactions of the outermost electrons of these atoms with the corresponding electrons of like or unlike atoms, or with variations in the properties of these atoms due to changes in the location of the extra-nuclear electrons and hence to changes in their total energy. In contrast to nuclear chemistry also, classical chemistry is the chemistry of systems whose mass remains sensibly constant as embodied in the Law of Conservation of Mass (section 1.4). Our science, therefore, must largely be concerned with energy changes in material systems of constant mass. For this reason we now turn our attention to certain general principles which underlie such energy changes.

EXERCISES (1)

1. Three oxides of rhenium contain respectively 85.25, 76.90 and 74.42 per cent of rhenium. Calculate the combining weights of rhenium and show that the oxides obey the law of multiple proportions.

2. The chlorine in 2.44580 g. RbCl is equivalent to 2.18166 g. silver. Taking the atomic weights of Ag and Cl as 107.880 and 35.457 respectively, calculate the atomic weight of rubidium.

3. A certain metallic oxide showed on analysis 19.689 per cent of oxygen. The specific heat of the metal is 0.092. Find the atomic weight of the metal.

4. Write the graphic structures for all the deutero-derivatives of: (a) CH_4 (b) C_2H_6 (c) C_2H_4 (d) C_6H_6.

5. In Millikan's oil drop experiment the time taken for a drop to fall under gravity alone was 13.595 sec. The times for various upward trips under the combined electric field and gravity were: 12.5, 21.8, 34.8 and 84.5 sec. Calculate the number of charges carried in each case.

6. Calculate the pressure in a liter vessel which contains (a) 10^6 (b) 10^{12} molecules at 0° C.

7. Assuming the abundance ratio for oxygen to be $^{16}O : {}^{17}O : {}^{18}O = 510 : 0.2 : 1$, calculate the chemical atomic weight of ^{16}O.

8. Assuming a heat of combustion of coal of 7 kcal./g. and an energy yield of 175 M.e.v. from the interaction of a neutron and ^{235}U, calculate the tons of coal equivalent to 1 g. ^{235}U.

9. The average energy received by the earth from the sun is 8×10^{13} kcal./sec. The earth intercepts about 5×10^{-10} of the total solar output. Calculate the rate of loss of mass of the sun in tons/sec.

CHAPTER 2

ENERGY IN CHEMICAL SYSTEMS

The physical and chemical properties of any system are determined not only by the atomic or molecular constituents of the system but also by the variations in temperature, pressure, heat content, motion, electrical potential, illumination and the like. Hot copper differs from cold copper, a metal at high potential from one uncharged. Motion gives definite properties to an α-particle. Even at constant temperature the form of matter may vary. Thus, gaseous, liquid and solid mercury may exist separately or together at certain temperatures. Compression may also determine the changes which a system may undergo. Systems stable in the dark may change on illumination. These variables, to which all forms of matter are subject and from which they cannot entirely be dissociated, are all energy variables of material things.

Every variation in the properties of a given species of matter is to be associated with a variation of one or more of several energy variables. These energy variables are convertible one into another, matter being the medium whereby such conversion is effected. Thus, heat energy is converted into molecular motion when gas molecules, the medium, receive heat. Motion may be converted into heat by friction. The boring of steel is one example cited by Count Rumford. Electrical energy produces heat, light and chemical energy. The chemical energy of coal and oxygen is the source of much of our electrical energy. It is evident therefore that the forms of energy are interchangeable. The quantitative aspects of such energy interchange are an important branch of physicochemical study.

1. **The Definition of Energy:** Every change in the condition of matter is to be ascribed to the operation of one or another form of energy. The energy is composed of two factors, an intensity factor and a capacity factor, and is, indeed, the product of these two factors. The intensity factor is the measure of the resistance offered to the change of condition resulting from the operation of the energy. The energy can only operate when this resistance is either withdrawn or overcome. Such an intensity factor tending to produce a change is known as a force.

2. **A force** overcoming a resistance to an extent which we may designate as the capacity factor, performs work, expends *energy.*

With a given force, the energy expended or the work performed varies directly as the capacity factor. In the production of motion the energy expended depends, therefore, on the force required to produce motion against the resistance and on the distance through which the object acted upon is moved. In the raising of an object of mass, m, against gravity, g, through a height, h, the force exerted in opposition to gravity is mg and the capacity factor is the height h. The energy expended becomes, therefore, the product mgh. In the production of a volume change, Δv, in any body against an external pressure, p, the intensity factor or force per unit area, p, acts through a volume Δv which is the capacity factor; the work done or volume energy expended is the product of the two factors, $p\Delta v$. All energy changes of whatever form may be similarly resolved into two such factors.

3. **The unit of energy** in the c.g.s. system of units is the *erg*. It is the energy expended, when a force of one *dyne* acts through one centimeter.

4. **A dyne** is the force which, acting for one second on one gram, produces a velocity of one cm. per second in the body upon which the force is impressed.

5. **Gravity** produces an acceleration of 980.6 cm. per sec.^{2} when acting upon a mass at sea-level and 45° latitude. The weight of one gram is, under these circumstances, equivalent to 980.6 dynes.

6. **The unit of pressure** in c.g.s. units is the *bar*, equal to a force of one dyne acting on an area of one square cm. **One atmosphere pressure** (1 atm.) is equivalent to the pressure of 76 cm. of mercury at 0° C., sea-level and 45° latitude. Expressed in dynes per cm.^{2}, since the specific gravity of mercury is 13.595

$$\begin{aligned} 1 \text{ atm.} &= 76 \times 13.595 = 1033.3 \text{ g. cm.}^{-2} \\ &= 1033.3 \times 980.6 = 1.0133 \times 10^6 \text{ dynes cm.}^{-2}. \end{aligned}$$

It is evident that 10^6 bars = 1 megabar is approximately one atmosphere.

A pressure of 1 atm. acting through a unit volume change of 1 cm.^{3} is, thus, an energy unit, termed the *cubic centimeter-atmosphere*.

7. **Dimensions:** A physical quantity may be expressed in terms of the fundamental units of mass, m, length, l, and time, t, out of which it may be built. Thus, a force has the dimensions, g. cm. sec.$^{-2}$ or mlt^{-2} and energy, the dimensions, dyne × cm. or g. cm.^{2} sec.$^{-2}$ or ml^2t^{-2}.

Heat energy, electrical energy and all other forms of energy have the same dimensions, ml^2t^{-2}. Their energy units may be related to those already given and to each other by the aid of a law of energy convertibility now to be discussed.

The First Law of Thermodynamics

8. **The Law of Conservation of Energy:** Human experience has led to the conclusion that: *In systems of constant mass, energy can neither be created nor destroyed.* One form of energy may disappear but another

takes its place. Energy is convertible but cannot be annihilated. Helmholtz enunciated this principle in 1847 in the following form: "*In all processes occurring in an isolated system, the energy of the system remains constant.*"

A variety of experience has led to the acceptance of this generalization concerning energy. It is the century-old experience of investigators that it is impossible to produce a perpetual motion machine which, without expenditure of energy, shall produce energy. Definite proof of the impossibility of constructing such a machine cannot be achieved. It is necessary to rely upon the cumulative experience of investigators that the search for such a machine is fruitless. Furthermore, by assuming the impossibility of perpetual motion of this type, conclusions may be drawn which may be verified and, in their turn, be employed for the discovery of further facts or laws. Thus, the definite and general belief as to the truth of the fundamental law is attained.

The discoveries in the chemistry of nuclear transmutations have, as we have already seen, placed a limitation on the applicability of the law, namely, to systems in which mass varies negligibly. Such limitations, arising from practical experience, do not in any way impair the usefulness of the law within the sphere in which it is applicable. Indeed, science grows by a more definite prescription of the applicability of its generalizations.

9. **The Mechanical Equivalent of Heat:** The statement of equivalence between mechanical energy expended and heat energy thereby produced is one special case of the general law of conservation of energy. This equivalence was assumed by Mayer in 1842 in attempts he made to calculate the proportionality factor connecting them. The experimental demonstration of the equivalence of heat energy and mechanical energy was made by Joule in the years 1843–1880. He measured the heat, q, produced by most divergent mechanical processes and showed that in every case the proportionality factor, J, was approximately constant,

$$w = Jq. \tag{2.1}$$

Joule's experiments included the following:

(1) The heat produced when various liquids, water, oil and mercury, were stirred was compared with the work involved in producing the stirring by falling weights.

(2) The heat produced in a coil of wire by induction currents set up by rotation of the wire between the poles of an electromagnet was compared with the work done by falling weights in rotating the coil. The heat produced was measured by the rise in temperature of water in which the coil was rotated.

(3) The heat produced by compression of water through narrow openings or capillaries was compared with the work required to drive the water through the openings or capillaries.

(4) The heat produced by compressing air to 22 atmospheres was compared with the work of compression.

(5) The heat produced by the passage of an electric current through a coil of wire immersed in a calorimetric fluid was compared with the energy of the current consumed.

Joule concluded that "772 lbs. falling one foot would heat a pound of water one degree." Transformed into modern units Joule's measurements gave approximately

$$J = 4.17 \times 10^7 \text{ ergs per } 15° \text{ cal.}$$

The fact that independent methods of producing heat gave closely concordant values for J constituted the desired proof of the law of equivalence of heat energy and mechanical energy.

The necessity for defining a unit of energy in terms of the heat capacity of water disappeared about thirty years ago when it became possible to measure quantities of energy more accurately by electrical methods. These energy measurements are based upon the second as the unit of time and upon working standards of electromotive force and resistance maintained at various national standardizing laboratories. The working standards are manganin wire resistance coils and saturated cadmium sulfate (Weston) cells which are calibrated in terms of the international ohm and the international volt.

10. **Electrical Units:** The electrical method involves a definition of electrical potential, the intensity factor, and quantity of current, the capacity factor. The measurement of electrical energy is based on the law, known as **Ohm's Law,** discovered by Ohm in 1827. Ohm's law states that the current C is directly proportional to the voltage E and inversely proportional to the resistance R.

$$C = E/R. \qquad (2.2)$$

The unit of resistance, the **ohm,** is defined as the resistance at 0° C., of a column of mercury uniform in cross section 106.30 cm. in length and weighing 14.4521 grams. Under such conditions the column of mercury is one square mm. in cross section.

The unit of electricity is the **coulomb,** the quantity of electricity which will deposit 0.0011180 gram of silver from solutions of silver nitrate in a standard coulometer. 96,494 coulombs of electricity is known as one **faraday** and is the quantity which will deposit one gram atomic weight of silver or its chemical equivalent.

The unit of current is the **ampere** and is the current of one coulomb per second.

The unit of potential is the **volt.** It may be defined as the potential which, applied to a conductor of unit resistance, will cause a current of one ampere to flow. It is defined practically in terms of the electromotive force (e.m.f.) of a cell which yields electrical energy equivalent to 1 joule (10^7 ergs) when the quantity of electricity produced is one coulomb. Herein lies the relation of electrical to mechanical energy.

$$1 \text{ volt coulomb} = 1 \text{ volt ampere-second} = 1 \text{ absolute joule} = 10^7 \text{ ergs.}$$

The Weston cell is the standard cell chosen for its reproducibility to serve as the standard of electromotive force. The cell consists of: 12.5 per cent cadmium amalgam | $CdSO_4 . 8/3H_2O$ + Saturated Solution | Hg_2SO_4 | Hg, and by international agreement, in 1908, was stated to have an electromotive force of 1.0183 volts at 20° C. In terms of this definition of voltage it is known, by reason of subsequent more accurate measurements of the standards involved, that the associated international joule is actually greater than the absolute joule defined above. The U. S. Bureau of Standards, in 1930, while continuing to report all thermochemical data in terms of the international joule concluded that, on the basis of available measurements, 1 int. joule = 1.0004 absolute joules = 1.0004×10^7 ergs. At the same time it was decided to define the calorie arbitrarily by the relation

$$4.1850 \text{ absolute joules} \equiv 1 \text{ calorie.}$$

In terms of international joules, therefore, the relation is

$$4.1833 \text{ int. joules} = 4.1850 \text{ abs. joules} \equiv 1 \text{ calorie.}$$

The absolute unit of quantity of electricity, the so-called electrostatic unit, is that quantity which exerts a force of one dyne upon a quantity of equal magnitude at a distance of one centimeter. This follows immediately from the equation for the electrostatic force F between two charges e_1 and e_2 at a distance r, namely $F = e_1e_2/Kr^2$ where K is set equal to unity in a vacuum. Since the dimensions of force are mlt^{-2}, it follows that the quantity e must have the dimensions $(ml^3t^{-2})^{1/2}$ or $m^{1/2}l^{3/2}t^{-1}$. It follows also that the dimensions of current or quantity per sec. must be $m^{1/2}l^{3/2}t^{-2}$.

Similarly the electromagnetic force between two poles of strength m_1 and m_2 is given by $F = m_1m_2/\mu r^2$, where μ is set equal to unity in a vacuum. Again the dimensions of the pole strength will be $m^{1/2}l^{3/2}t^{-1}$. The product of pole strength and current has the dimensions of work, i.e., ml^2t^{-2}. Hence the dimensions of current in this case are $ml^2t^{-2}/m^{1/2}l^{3/2}t^{-1} = m^{1/2}l^{1/2}t^{-1}$. It will be noted therefore that the electromagnetic unit is related dimensionally to the electrostatic unit as $m^{1/2}l^{1/2}t^{-1} : m^{1/2}l^{3/2}t^{-2}$ or as $1 : lt^{-1}$, which latter term has the dimensions of a velocity, actually, the velocity of light $c = 2.998 \times 10^{10}$ cm. sec.$^{-1}$. Hence, 1 e.s.u. : 1 e.m.u. = $1 : c$. The practical unit of current, the ampere, is defined as one-tenth of the electromagnetic unit of current.

Since current and potential are reciprocally related by means of Ohm's law it follows that the electromagnetic unit of potential must be $1/(3 \times 10^{10}) = 0.33 \times 10^{-10}$ electrostatic units of potential. The practical unit of potential, the volt, is defined as 10^8 electromagnetic units of potential and therefore 1/300 electrostatic units of potential.

For an ideal gas, it will be shown (equation 3.12) that the fundamental equation connecting pressure, volume and temperature is, for one mole,

$$pv = RT,$$

where R is the gas constant connecting the three magnitudes. On the absolute scale 0° C. = 273.16° K. (K. = Kelvin or Absolute Scale of Temperature). For one mole of gas under standard conditions, the accepted value of V is 22,414 cc. (Chap. 3, Section 4). Hence,

$$R = \frac{22{,}414 \times 1}{273.16} = 82.055 \text{ cc. atm. per degree per mole.}$$

When this value is transformed into the other units of heat energy, we obtain

$$R = \frac{82.055 \times 1.0133 \times 10^6}{10^7} = 8.3145 \text{ absolute joules per degree per mole}$$

$$= 1.9869 \text{ cals. per degree per mole.}$$

11. The Energy of a Chemical System: The energy of a system is a function only of the state of the system at the given moment, irrespective entirely of its past history, the manner or method of its origin. It is especially to be emphasized that this independence of past history refers only to systems whose identity is complete in all except the element of time. It is not enough that the atomic or molecular make-up shall be the same, for this may be secured even though the energies of the systems differ widely. Thus, for example, stick lead and electrolytic lead might be identical as to atomic content, pressure, temperature, volume and the like, but be different in energy content by reason of state of division, size of crystal and the like. Only with complete identity in all factors except the element of time can it follow that the energy is a function of the momentary state of the system. The energy change accompanying a transformation is then a function only of the initial and final states of the system independent of the path between. For, if it were possible to effect a change in any system from state A to state B such that the energy change involved was dependent on the path by which the change was achieved, it would be possible to construct a perpetual motion machine. All that would be necessary would be that one such method of conducting the change could be reversed. Then, by a suitable coupling of two processes,

$$A \longrightarrow B \text{ by path I,}$$
$$B \longrightarrow A \text{ by path II,}$$

if the energy produced in path I were larger than that consumed in path II, the system would be, on completion of the reverse process, in its initial state and a surplus of energy would be available. By repetition of the process, energy could be continuously produced—a perpetual motion would be possible. This is denied by human experience as embodied in the first law of thermodynamics.

12. **Internal Energy:** If we heat a mole of hydrogen gas enclosed in a cylinder at constant volume the heat energy supplied is absorbed by the system. The atomic or molecular make-up of the system remains essentially unchanged but, by the process, the system gains an increment of energy which the gas molecules store. They have received a perfectly definite increment of internal energy, which we may designate by ΔU and define by the expression

$$\Delta U = U_B - U_A. \tag{2.3}$$

In such case, U_A represents the internal energy of the system initially, U_B the internal energy of the final state. These quantities U_B and U_A are energy quantities of unknown absolute magnitude. Their difference, ΔU, is in this case perfectly definite; it is the heat energy supplied to the system, and, as we have shown, is independent of the mode of procedure from A to B. But, the internal energies of the gas in the two states may include the energy resultant from such factors as motion and position of the molecules, molecular attraction, intra-molecular forces, intra-atomic vibrations, chemical and possibly other forces. We therefore note that the absolute magnitudes U_B and U_A are not ascertainable. The change of internal energy ΔU is, however, definite and measurable.

Any such change in the internal energy of a system can only be achieved with a simultaneous change in the energy of surrounding systems, since the law of conservation of energy *must* be obeyed. An increment in internal energy of the system is secured, therefore, at the expense of a decrement in the energy of its surroundings. A decrement in the internal energy results in an increase of the energy of its surroundings. If we consider any process of change from state A to state B, whereby an increment of internal energy $\Delta U = U_B - U_A$ occurs, which results in the abstraction of heat, q, from the surroundings and simultaneously the performance of external work, w, by the system on the surroundings; then, by application of the law of conservation of energy,

$$\Delta U = q - w. \tag{2.4}$$

It has been shown that ΔU is a perfectly definite quantity for any given process of change, dependent only on the initial and final states, independent of the path. This is not true of either q or w. According as the experimental conditions change q and w will both vary. This may be illustrated, for example, by a change of state involving both temperature and pressure. Thus, to transform one gram of ice at 0° C. and 1 atm. pressure to water vapor at 25° C. and 15 mm. pressure there are several possible paths each of which will involve values of q and w characteristic of the path, all of which involve a definite and unchangeable value of ΔU. One path involves fusion at 0° C. and 1 atm. requiring the absorption of the latent heat of fusion, then the raising of the temperature of the water from 0° to 25° C. at 1 atm. pressure, involving the heat capacity of the water, and finally the evaporation of the water at 25° C. by change in the pressure. This stage involves latent heat of vaporization and all three steps involve smaller or larger changes in the work terms, w. An alternative path involves a change in the pressure at 0° C. from 1 atm. to below the saturated vapor of ice with consequent vaporization. Subsequent steps involve raising the temperature of the water vapor to 25° C. and adjustment to the final pressure (15 mm.). This path has its own characteristic values of q and w, which will be different from those involved in the path first discussed. Quite generally, any particular path will have its own characteristic values of q and w, different from the values of these quantities for any other paths. Their algebraic sum, by the law of conservation of energy, will be equal to the change in internal energy by equation (2.4).

If a process be carried out at constant volume and no energy factors other than those of volume energy are involved in the external work performed then, since $w = 0$, it follows that $\Delta U = q$; the whole increment of internal energy is secured at the expense of the heat of the surroundings.

If a process be conducted, not at constant volume, but at constant pressure, it will ordinarily be accompanied by a volume change. The external work done by the system on the surroundings will be $p(v_B - v_A) = p\Delta v$, p being the prevailing pressure and Δv the increase in the volume of the system during the change from state A to state B. The heat q abstracted from the surroundings will then be given by the expression

$$q = \Delta U + w = \Delta U + p\Delta v. \qquad (2.5)$$

If a process be conducted so that heat is neither gained nor lost by the system to the surroundings the process is known as an *adiabatic* process. The quantity q is then zero. The work performed by the system on the surroundings is then done at the expense of the internal energy of the system, or

$$\Delta U = -w. \qquad (2.6)$$

In the preceding paragraph the quantity w has been limited to the case of changes in mechanical energy. It will later be shown that the quantity w may be composite of several forms of energy, of which electrical energy may be an important unit. The magnitude of the quantity w will be dependent on the mode of conduct of the process, on the extent to which the process is harnessed to produce the various forms of external work.

13. **The Heat Content of a System:** For a change involving an increase in internal energy, heat absorption from the surroundings and a

volume change v_A to v_B against a constant external pressure p, the first law of thermodynamics demands that

$$\Delta U = U_B - U_A = q - p(v_B - v_A). \tag{2.7}$$

This may be transformed thus:

$$(U_B + pv_B) - (U_A + pv_A) = q. \tag{2.8}$$

In this case the heat, q, absorbed by the system is evidently defined by the initial and final states of the system. If we define a quantity

$$H = U + pv \tag{2.9}$$

and term this quantity, H, the heat content of the system, the equation becomes

$$H_B - H_A = q = \Delta H. \tag{2.10}$$

It will be noted that the quantity ΔH, like ΔU, is dependent only on the initial and final states of the system.

14. The Heat Capacity of a System: The mean heat capacity, $\bar{c}$, of a system between two temperatures may be defined as the quantity of heat q necessary to raise the system from the lower to the higher temperature divided by the temperature difference,

$$c(T_2, T_1) = \frac{q}{T_2 - T_1}. \tag{2.11}$$

Since the heat capacity is known to vary with temperature, the true heat capacity at a given temperature is given by the differential expression

$$c = \frac{dq}{dT}. \tag{2.12}$$

The heat capacity may be determined either at constant volume or constant pressure, the magnitude of the heat capacity being dependent on the prevailing condition. In the determination of heat capacity at constant volume, none of the absorbed heat is employed in the performance of external work. Hence, the heat absorbed, q, is equal to the increase in internal energy. That is, $q = \Delta U$, and the mean heat capacity at constant volume per mole of substance becomes

$$\bar{c}_v = \Delta U/\Delta T, \tag{2.13}$$

and the true molal heat capacity at constant volume becomes

$$C_v = (\partial U/\partial T)_v. \tag{2.14}$$

At constant pressure, since by equation (2.5)

$$q = \Delta U + w,$$

the heat absorbed to produce a given rise of temperature will be greater by an amount equivalent to the external work performed by the system on the surroundings. Hence, the mean heat capacity at constant pressure becomes

$$\bar{c}_p = \left(\frac{q}{T_2 - T_1}\right)_p = \left(\frac{\Delta U + p\Delta v}{T_2 - T_1}\right)_p = \left(\frac{\Delta H}{T_2 - T_1}\right)_p \tag{2.15}$$

and the true molecular heat capacity at constant pressure is

$$C_p = (\partial H/\partial T)_p. \tag{2.16}$$

15. **Heat Content and Change of State:** At the melting point of any substance, the solid is converted into a liquid by absorption of heat without change of temperature. The heat absorbed is designated as the *latent heat of fusion.* The heat is consumed in producing the change of state and in performing the small amount of external work consequent on the relatively small volume change at pressure p accompanying the change of state. If the latent heat of fusion per mole of substance be λ_F it follows that, by the first law,

$$\lambda_F = \Delta U_F + p\Delta v = \Delta H_F \tag{2.17}$$

where $\Delta U_F = U_l - U_s$, the internal energy of the liquid, U_l, less that of the solid, U_s, $\Delta v = v_l - v_s$ and $\Delta H_F = H_l - H_s$.

In a similar manner, the vaporization of a liquid involving a *latent heat of vaporization* per mole at constant pressure p, λ_V, is by application of the first law,

$$\lambda_V = \Delta U_V + p\Delta v = \Delta H_V. \tag{2.18}$$

In this case $\Delta U_V = U_g - U_l$ and $\Delta H_V = H_g - H_l$ where the subscripts designate the gaseous and liquid states. In this case the quantity $p\Delta v$ is a much larger quantity than in the former case since Δv now represents $v_g - v_l$ in which v_g is a relatively large quantity compared with v_l.

In the case of sublimation of a solid, it follows also that the *latent heat of sublimation* per mole at constant pressure p is

$$\lambda_s = \Delta U_s + p\Delta v = \Delta H_s. \tag{2.19}$$

16. **The Heat of a Chemical Reaction:** Chemical reactions are in general accompanied by absorption of heat from or evolution of heat to the surroundings; they are either endothermic or exothermic. For a reaction occurring at constant volume the heat absorbed or evolved is equal to the change in internal energy, ΔU, of the system, since no external work is performed. In this particular case the change in internal energy, ΔU, is equal to the change in heat content, ΔH. Reactions are

ordinarily conducted at constant pressure, p, and are accompanied by a volume change, Δv. The heat absorbed, q, is equal to the increase in internal energy plus the external work performed, and, thus, is equal to the change in the heat content, ΔH. Calorimetric data are, therefore, normally expressed in terms of the change in heat content. Two examples may be cited which are basic data of the highest accuracy in the calorimetry of organic compounds, the heats of formation of water and carbon dioxide from their elementary constituents at 25° C. = 298.16° K.

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l);\ \Delta H^\circ_{298.16}$$
$$= -\ 285{,}795 \pm 40 \text{ int. j. per mole}$$
$$= -\ 68{,}318.1 \pm 9.6 \text{ cal. per mole,}$$
$$C(c, \text{graphite}) + O_2(g) = CO_2(g);\ \Delta H^\circ_{298.16}$$
$$= -\ 393{,}355 \pm 46 \text{ int. j. per mole}$$
$$= -\ 94{,}029.8 \pm 11.0 \text{ cal. per mole.}$$

The symbols in parentheses designate the physical state of the substance: c = crystal; l = liquid; g = gas. The values expressed in calories are carried to more figures than are significant, but are so given that one may recover the value in international joules on reconversion to that unit by means of the factor 4.1833.[1]

17. Heat of Reaction at Constant Pressure and Constant Volume: It will be noted that for chemical reactions at constant pressure in which there is no volume change the numerical values of ΔU and ΔH are identical. When a volume change occurs at constant pressure the definitions already given show that

$$\Delta H = \Delta U + p\Delta v \tag{2.20}$$

where Δv is the increase in volume which occurs during the process. For reactions involving only liquids and solids the volume change is generally negligible. With gaseous reactions on the other hand the appearance of 1 mole of gas involves, at standard temperature and pressure, an energy quantity equal as we have seen to 22,414 cc. atmospheres or

$$\frac{22{,}414 \times 1.0133 \times 10^6}{10^7 \times 4.185} = 543 \text{ calories}$$

or, approximately, 1.986 × 273 calories of energy per mole at 0° C. This may be expressed otherwise by pointing out that, in the case of ideal gases, for 1 mole, $pv = RT$.

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[1] The data are cited from F. D. Rossini, *Chem. Rev.*, **27**, 1 (1940). Actually, the data on hydrogen refer to hydrogen which contains its natural isotopic content of HD, amounting to 0.0004 mole fraction of HDO in the resultant water. The heat of formation of ^1H_2O from $^1H_2 + O_2$ would have the value, $\Delta H^\circ_{298.16} = -\ 285{,}793 \pm 40$ int. j./mole (Rossini, Knowlton and Johnson, *J. Res. Nat. Bur. Stand.*, **24**, 369 (1940)). The oxygen used was the normal mixture of oxygen isotopes.

18. **Hess's Law of Constant Heat Summation:** Hess found experimentally, in 1840, that *the heat evolved in any chemical reaction is constant, independent of the manner in which the reaction is achieved, whether in one or many steps.* This law is one special case of the first law of thermodynamics, the law of conservation of energy.

Hess's law forms the theoretical basis of the classical experimental work of Thomsen and Berthelot on the thermal magnitudes of a wide variety of chemical compounds. The law involves as corollaries a number of useful conclusions. The heat of formation of a compound must be independent of the manner of its formation; the heat of reaction must be independent of the time consumed in the process; the heat of reaction must be equal to the sum of the heats of formation of the products of the reaction minus the sum of the heats of formation of the initial reactants.

19. **Thermochemical Data:** Thermochemistry is concerned fundamentally with the determination of the heat changes accompanying two types of process (*a*) change of state, (*b*) chemical reaction. The important calorimetric quantities are therefore (1) heats of vaporization and sublimation, (2) heats of fusion, (3) heats of transition, (4) heats of formation together with, (5) specific heats. In multicomponent systems it is necessary also to know (1) heats of solution, (2) heats of dilution and (3) heats of interaction, for example, neutralization, in solution. A thermochemical investigation involves, in modern procedure, two types of measurement. In one there is measured the amount of chemical reaction or physical change the occurrence of which produces a specified change in a calorimeter, and in the other there is measured the quantity of electricity that produces the same change in the calorimeter. In formulating, thus, the fundamentals of thermochemical investigation Rossini[1] has pointed out that present day requirements place a heavy burden upon accuracy and precision of measurements which the great body of thermochemical data accumulated by Thomsen, Berthelot and others prior to 1900 falls far short of meeting. In the earlier work an accuracy of ± 1 kcal. would be regarded as satisfactory; to-day's thermodynamic requirements frequently demand a precision ten times as great.

The chemical reactions whose heats require measurement are grouped by Rossini in three classes:

1. Reactions substantially in the gaseous phase at constant pressure.
2. Reactions substantially in the liquid phase at constant pressure.
3. Reactions in a closed bomb at constant volume.

As examples of the first class, occurring in the calorimeter vessel, generally in a flame or at the surface of a catalyst, the following may

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[1] F. D. Rossini, *Chem. Rev.*, **18**, 233 (1936); **27**, 1 (1940).

be cited:

$$
\begin{array}{lrcl}
(a) & H_2(g) + \tfrac{1}{2}O_2(g) & = & H_2O(l), \\
(b) & \tfrac{1}{2}Cl_2(g) + \tfrac{1}{2}H_2(g) & = & HCl(g), \\
(c) & CH_4(g) + 2O_2(g) & = & CO_2(g) + 2H_2O(l), \\
(d) & C_2H_4(g) + H_2(g) & = & C_2H_6(g), \\
(e) & O_2(g) + S(c) & = & SO_2(g).
\end{array}
$$

They include heats of combustion (*a*), (*c*) and (*e*), of hydrogenation and of chlorination (*b*) and (*d*), with the last example (*e*) occurring in a flame with oxygen burning in an excess of sulfur vapor, sulfur being present initially and finally in the solid state. In general, one of the reactants is maintained in excess and the amount of reaction is best determined by measuring the mass of one of the products.

As examples of the second class the following are illustrative:

$$
\begin{array}{lrcl}
(a) & HCl.100H_2O(l) + NaOH.100H_2O(l) & = & NaCl.201H_2O(l), \\
(b) & HCl(g) + 100H_2O(l) & = & HCl.100H_2O(l), \\
(c) & NaCl(c) + 100H_2O(l) & = & NaCl.100H_2O(l), \\
(d) & NaCl.100H_2O(l) + 100H_2O(l) & = & NaCl.200H_2O(l), \\
(e) & NaCl(aq) + AgNO_3(aq) & = & AgCl(c) + NaNO_3(aq), \\
(f) & Na(c) + H_2O(l) & = & NaOH(aq) + \tfrac{1}{2}H_2(g).
\end{array}
$$

They include heats of neutralization (*a*), of solution both of gas (*b*) and solid (*c*), of dilution (*d*) and of chemical reaction between two solutions to form a solid precipitate (*e*) and a reaction between a solid and a liquid (*f*).

Reactions of the third class, involving bomb calorimetry in a closed bomb at constant volume and, normally, elevated pressures, are usually combustion reactions. Gases, liquids and solids may thus be treated. The method is particularly applicable to organic compounds, from the heats of combustion of which, much of our knowledge of the heats of formation of organic compounds is derived. The normal combustion products in such cases are carbon dioxide and water. In commenting on the precision of such bomb calorimetric measurements, Rossini makes the following pertinent observations.

The increasing accuracy and precision of thermochemical measurements has resulted in increasing the significance of information concerning the exact thermodynamic state of each substance participating in the chemical reaction. In former years, for example, the observed value of the heat evolved in the bomb calorimeter was taken as $-\Delta U$, the decrease in internal energy, for the pure reaction at 1 atmosphere. Several years ago, Washburn[1] investigated in considerable detail the reaction that actually occurs in the bomb calorimeter and showed that the value observed for the bomb reaction differs from $-\Delta U$ for the pure reaction

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[1] E. W. Washburn, *Bur. Standards J. Res.*, **8**, 729 (1932).

TABLE 2.1

HEATS OF FORMATION OF GASEOUS HYDROCARBONS FROM SOLID CARBON (GRAPHITE) AND GASEOUS HYDROGEN AT 25° C.

Substance	Formula and State	$\Delta H^\circ_{298.16}$	
		Int. j. per mole	Cal. per mole
Paraffins:			
Methane	$CH_4(g)$	−74,735±310	−17,865±74
Ethane	$C_2H_6(g)$	−84,465±450	−20,191±108
Propane	$C_3H_8(g)$	−103,535±520	−24,750±124
n-Butane	$C_4H_{10}(g)$	−124,305±640	−29,715±153
Isobutane	$C_4H_{10}(g)$	−131,145±550	−31,350±132
n-Pentane	$C_5H_{12}(g)$	−145,325±890	−34,739±213
2-Methylbutane	$C_5H_{12}(g)$	−153,405±640	−36,671±153
Tetramethylmethane	$C_5H_{12}(g)$	−164,865±950	−39,410±227
Monoölefins:			
Ethylene	$C_2H_4(g)$	52,526±280	12,556±67
Propylene	$C_3H_6(g)$	20,732±460	4,956±110
1-Butene	$C_4H_8(g)$	1,602±750	383±180
cis-2-Butene	$C_4H_8(g)$	−5,806±750	−1,388±180
trans-2-Butene	$C_4H_8(g)$	−9,781±750	−2,338±180
"Isobutene" (2-methylpropene)	$C_4H_8(g)$	−13,407±690	−3,205±165
1-Pentene	$C_5H_{10}(g)$	−19,427±1260	−4,644±300
cis-2-Pentene	$C_5H_{10}(g)$	−26,794±1260	−6,405±300
trans-2-Pentene	$C_5H_{10}(g)$	−30,756±1260	−7,352±300
2-Methyl-1-butene	$C_5H_{10}(g)$	−35,240±840	−8,424±200
3-Methyl-1-butene	$C_5H_{10}(g)$	−27,518±750	−6,578±180
2-Methyl-2-butene	$C_5H_{10}(g)$	−41,812±750	−9,995±180
Diolefins:			
Allene	$C_3H_4(g)$	192,624±1090	46,046±260
1,3-Butadiene	$C_4H_6(g)$	112,384±1000	26,865±240
1,3-Pentadiene	$C_5H_8(g)$	79,002±1260	18,885±300
1,4-Pentadiene	$C_5H_8(g)$	106,946±1260	25,565±300
Acetylenes:			
Acetylene	$C_2H_2(g)$	226,852±980	54,228±235
Methylacetylene	$C_3H_4(g)$	185,358±1000	44,309±240
Dimethylacetylene	$C_4H_6(g)$	147,340±1490	35,221±355

at 1 atmosphere by amounts ranging from several hundredths to nearly 1 per cent.

To obtain the required thermochemical value for the reaction at 1 atmosphere, the observed value for the bomb reaction must be corrected with regard to the changes in internal energy with pressure of the initial oxygen and of the mixture of oxygen and carbon dioxide of the final state, the heat of solution of oxygen and carbon dioxide in water, and the heat of vaporization of water.

In the case of the combustion of organic compounds containing sulfur or a halogen, the reaction is even more complicated than that described above. In each such combustion involving sulfur or a halogen, the investigator must determine, with an accuracy commensurable in significance with his calorimetric accuracy, just what the actual reaction is that occurs in the bomb. The observed heat effect must then be corrected by the appropriate amount necessary to give the heat of a reaction in which all the reactants and products are in definite known states.

The degree of precision which may be attained in modern calorimetric techniques is well illustrated by the data recently accumulated on the heats of formation of gaseous hydrocarbons from solid carbon and gaseous hydrogen at 25° C. The case in question represents a favorable condition for the attainment of precision because of the possibility of control using two techniques, one that of heats of combustion, used by Rossini and collaborators at the National Bureau of Standards, the other the heats of hydrogenation, from the work of Kistiakowsky and his collaborators at Harvard University. Data obtained from these sources during the last fifteen years on hydrocarbons containing five or less carbon atoms per molecule are presented in Table 2.1. The data for the paraffins depend on heats of combustion alone. The data for olefines and acetylenes are derived from a combination of data on the two techniques.

TABLE 2.2

HEATS OF ISOMERIZATION OF SATURATED AND UNSATURATED HYDROCARBONS

Isomerization	$\Delta H°$(298.16° K.) kcal. per mole
n-butane = isobutane	-1.64 ± 0.20
n-pentane = 2Me-butane	-1.93 ± 0.26
n-pentane = Tetramethylmethane	-4.67 ± 0.31
1-butene = 2-cis-butene	-1.67 ± 0.12
1-butene = 2-trans-butene	-2.72 ± 0.12
1-butene = 2Me-propene	-3.59 ± 0.25
1-pentene = 3Me-1-butene	-1.93 ± 0.30
1-pentene = 2Me-1-butene	-3.78 ± 0.30
1-pentene = 2Me-2-butene	-5.35 ± 0.30

Such data may be utilized by application of Hess's law, to obtain the heats of isomerization of saturated and unsaturated hydrocarbons. The data so obtained by Rossini collected in Table 2.2 exhibit excellently the reason for the precision of measurement required in modern thermochemistry.

Tables of 'best' self-consistent values for the heats of formation of chemical compounds, other than those of carbon compounds containing more than two carbon atoms, and including heats of transition, fusion, vaporization and ionization, at a standard temperature of 18° C. have been compiled by Bichowsky and Rossini.[1] In these tables, for the element carbon, diamond was chosen as the standard state. As a result of more recent researches,[2] it is concluded that the existence of more than one form of graphite is improbable and that there is every reason to use graphite as the reference state for carbon.

TABLE 2.3

Typical Thermochemical Data (Bichowsky and Rossini, 1936)

Reaction	$\Delta H(t = 18° \text{ C.})$ in kcal.
$H(g) + H(g) = H_2(g)$	−102.9
$\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) = HF(g)$	− 64.0
$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(g)$	− 22.06
$\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) = HBr(g)$	− 8.65
$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) = HI(g)$	− 5.91
$H_2(g) + S(\text{rhomb.}) = H_2S(g)$	− 5.3
$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g)$	− 11.00
$\frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + \frac{1}{2}H_2(g) = HNO_3(g)$	− 34.4
$HNO_3(g) = HNO_3(l)$	− 7.2
$HNO_3(l) + 300H_2O(l) = HNO_3(aq.)$	− 7.44
$Na(s) + \frac{1}{2}I_2(s) = NaI(s)$	− 69.28
$2Na(s) + C(s) + \frac{3}{2}O_2(g) = Na_2CO_3(s)$	−269.89
$K(s) + \frac{1}{2}I_2(s) = KI(s)$	− 78.87
$Ca(s) + I_2(s) = CaI_2(s)$	−128.48
$Ag(s) + \frac{1}{2}F_2(g) = AgF(s)$	− 48.7
$Ag(s) + \frac{1}{2}Cl_2(g) = AgCl(s)$	− 30.30
$Ag(s) + \frac{1}{2}Br_2(l) = AgBr(s)$	− 23.81
$Ag(s) + \frac{1}{2}I_2(s) = AgI(s)$	− 14.94
$Pb(s) + Cl_2(g) = PbCl_2(s)$	− 85.71
$Pb(s) + Br_2(l) = PbBr_2(s)$	− 66.27
$Pb(s) + I_2(s) = PbI_2(s)$	− 41.77
$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) = NO(g)$	21.6

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[1] F. R. Bichowsky and F. D. Rossini, 'The Thermochemistry of the Chemical Substances,' Reinhold Pub. Corp., New York, 1936.

[2] P. H. Dewey and D. R. Harper, *J. Res. Nat. Bur. Standards*, 21, 457 (1938); R. S. Jessup, *J. Res. Nat. Bur. Standards*, 21, 475 (1938); F. D. Rossini and R. S. Jessup, *J. Res. Nat. Bur. Standards*, 21, 491 (1938).

To familiarize himself thoroughly with the principles involved in thermochemical data the student may, with advantage, verify the following data relative to the formation of sulfuric acid from its elements, the data coming from Bichowsky and Rossini (1936).

$$SO_2(g) + 200\,H_2O = SO_2\,\text{aq}; \qquad \Delta H = -\ 7.45\ \text{kcal.} \tag{a}$$

$$H_2SO_4(l) + 200\,H_2O = H_2SO_4\,\text{aq}; \qquad \Delta H = -\ 17.75\ \text{kcal.} \tag{b}$$

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(g); \qquad \Delta H = -\ 22.06\ \text{kcal.} \tag{c}$$

$$HCl(g) + 200\,H_2O = HCl\,\text{aq}; \qquad \Delta H = -\ 17.405\ \text{kcal.} \tag{d}$$

$$S(s) + O_2(g) = SO_2(g); \qquad \Delta H = -\ 70.92\ \text{kcal.} \tag{e}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l); \qquad \Delta H = -\ 68.370\ \text{kcal.} \tag{f}$$

$$Cl_2(g) + SO_2\,\text{aq} + 2H_2O(l) = H_2SO_4\,\text{aq} + 2HCl\,\text{aq}; \quad \Delta H = -\ 74.32\ \text{kcal.} \tag{g}$$

$$\text{From } (c) \text{ and } (d),\ \Delta H_{HCl\,\text{aq}} = -\ 39.465\ \text{kcal.} \tag{h}$$

$$\text{From } (a) \text{ and } (e),\ \Delta H_{SO_2\,\text{aq}} = -\ 78.37\ \text{kcal.} \tag{i}$$

$$\text{From } (f),\ (g),\ (h) \text{ and } (i),\ \Delta H_{H_2SO_4(200H_2O)} = -\ 210.5\ \text{kcal.} \tag{k}$$

$$\text{From } (b) \text{ and } (k),\ \Delta H_{H_2SO_4(l)} = -\ 193.75\ \text{kcal.}$$

Thus, by the use of Hess's law, we have found the heat of formation of 98 g. sulfuric acid from 2 g. hydrogen, 32 g. sulfur and 64 g. oxygen to be $\Delta H = -\ 193.75$ kcal.

20. **Calorimeters:** *Electrical Calorimeter:* A very convenient form of calorimeter for many purposes used by U. Fischer[1] in his work on silver iodide is illustrated in Fig. 2.1. It consists of a large well-evacuated Dewar vessel (A) having an easily removable wooden cover (B) carrying a stirrer (C), Beckmann thermometer and electrical heating coil (D). The heat capacity of the calorimeter can be determined by supplying, electrically, the same amount of heat as that generated by the reaction and over a similar period of time as that taken by the experiment, so that errors due to thermal leakage are similar to those occurring during the reaction. If a current of i amps. is passed for t seconds, and the resistance of the heater is r, and the rise in temperature produced is T_1; and, if the reaction studied causes a rise of T_2, then q, the heat in calories evolved by the reaction, is given by the expression

$$q : i^2\cdot r\cdot t \times 0.2389 = T_2 : T_1. \tag{2.21}$$

The second term represents the electrical energy consumed, converted to calories.

The Bomb Calorimeter: This apparatus was developed by Berthelot to measure heats of combustion of organic compounds. A modified form of such a bomb is shown in Fig. 2.2. The bomb itself is made of gun metal steel, the cover is heavily threaded and screws down on to a lead washer. The material is suspended in a platinum dish in the bomb and oxygen is admitted to a pressure of about 25 atmospheres. Ignition is brought about by means of a weighed piece of iron wire which is heated

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[1] *Z. anorg. Chem.*, 78, 57 (1912).

electrically. Before ignition of the substance under investigation, the bomb is placed in a calorimeter and the heat evolved is measured in the usual way.

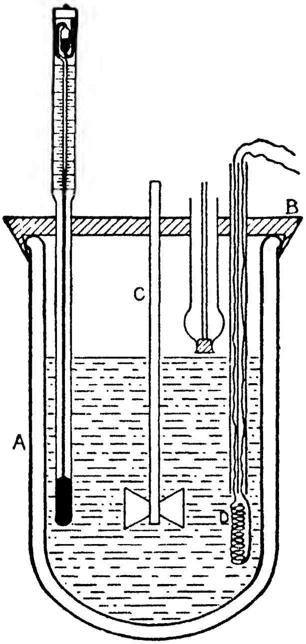

Fig. 2.1. Electrical Calorimeter

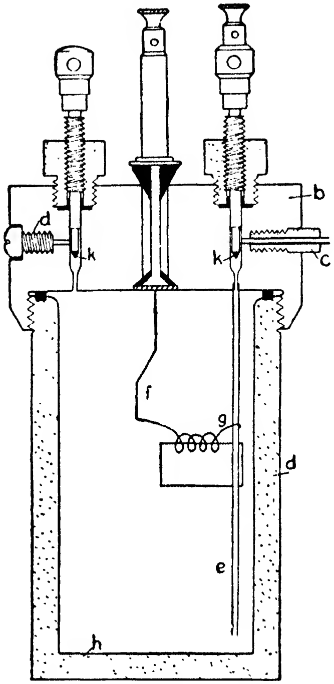

Fig. 2.2. Combustion Bomb

The heat capacity of the calorimeter can be determined by the combustion of known amounts of standard substances of high purity whose heats of combustion have been carefully determined. Such standards are

Substance	ΔH cals.
Naphthalene	−1,231,800 ± 250
Benzoic Acid	− 771,200 ± 125
Sucrose	−1,350,000 ± 700
Salicylic Acid	− 723,100 ± 250

21. **Variation of Heat of Reaction with Temperature:** Each heat of reaction is given for a definite temperature but this does not mean that the temperature has been constant throughout the reaction. In a combustion bomb the temperature may be very high at the moment of the combustion but the final temperature is only a few degrees different from

the initial temperature. All we are concerned with is the initial and final state. For the applications of Hess's law, it is necessary for all the heats of reaction concerned to be calculated for a single temperature. Most of the calorimetric data in the literature are for a temperature of about 18° C. It is frequently required to know the heat of some particular reaction at another temperature and this can be readily calculated from a knowledge of the heat capacities of the resultants and reactants of the reaction. Let ΔH_1 be the heat of reaction at temperature T_1 and ΔH_2 at T_2. Let us consider the following alternative reaction paths: the reaction is carried out at T_1 with an absorption of heat ΔH_1 and the resultants of the reaction are heated to T_2 whereby an amount of heat $(T_2 - T_1)C''$ is absorbed, where C'' is the mean molal heat capacity of the resultants between T_1 and T_2; again, let us heat the reactants from T_1 to T_2 with an absorption of heat $(T_2 - T_1)C'$, where C' is the mean molal heat capacity of the reactants, and then carry out the reaction at T_2 with an absorption of heat ΔH_2. Then, by the First Law of Thermodynamics,

$$\Delta H_2 + C'(T_2 - T_1) = \Delta H_1 + C''(T_2 - T_1), \tag{2.22}$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C'' - C'. \tag{2.23}$$

When the difference between T_2 and T_1 becomes infinitesimal, this reduces to

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p, \tag{2.24}$$

where ΔC_p is the sum of the heat capacities of the resultants less that for the reactants or the total increase in heat capacity from the reaction. This equation was first deduced by Kirchhoff. Over small temperature ranges, the heat capacity C_p may be regarded as constant as assumed in the following example:

For the reaction,

$$2H_2(g) + O_2(g) = 2H_2O(g), \qquad \Delta H_{373^\circ} = -116{,}115 \text{ cals.}$$

The molal heat capacities are as follows:

H_2; $C_p = 6.818$,
O_2; $C_p = 6.960$,
H_2O; $C_p = 9.000$.

Hence, $\Delta C_p = -2.596$. For the interval 100° C. to 130° C.,

$$\Delta H_{403^\circ} - \Delta H_{373^\circ} = -2.596 \times 30 = -77.88 \text{ cals.};$$

hence

$$\Delta H_{403^\circ} = -116{,}193 \text{ cals.}$$

For rapid variations in heat capacity or large temperature ranges, an empirical equation can be set up to express the variation of heat capacity with temperature.

$$C_p = a + bT + cT^2 + \ldots, \tag{2.25}$$

where the number of terms will depend on the temperature range and the accuracy of the data. In dealing with a chemical reaction for each of whose members a heat capacity equation has been determined over a range of temperature,

$$\Delta C_p = a_0 + b_0T + c_0T^2 + \ldots, \tag{2.26}$$

where a_0 is the algebraic sum of all the a's, b_0 of all the b's and so on. By the use of this equation we are now in a position to integrate the equation (2.24)

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p$$

$$\Delta H = \Delta H_0 + a_0T + \tfrac{1}{2}b_0T^2 + \tfrac{1}{3}c_0T^3 + \ldots, \tag{2.27}$$

where ΔH_0 is an integration constant and can be calculated from a single experimental value of ΔH.

Let us illustrate the usefulness of this method by calculating $\Delta H_{1273°}$ for the reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g)$$

from the following data:

$$\begin{array}{lrl} (a) & H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l); & \Delta H_{293} = -68{,}400 \text{ cals.} \\ (b) & H_2O(l) = H_2O(g); & \Delta H_{373} = 9{,}670 \text{ cals.} \end{array}$$

The molal heat capacities at constant pressure of the gases involved are given by the equations:

$$\begin{array}{ll} O_2(g); & C_p = 6.69 + 0.0007T, \\ H_2(g); & C_p = 6.54 + 0.0007T, \\ H_2O(g); & C_p = 8.81 - 0.0019T + 0.00000222T^2. \end{array}$$

For the liquid

$$H_2O(l); \qquad C_p = 18.0.$$

For the reaction, $H_2O(l) = H_2O(g)$,

$$\Delta C_p = -9.19 - 0.0019T + 0.00000222T^2$$

and

$$\Delta H = \Delta H_0 - 9.19T - 0.00095T^2 + 0.00000074T^3.$$

Whence, at 100° C., $9670 = \Delta H_0 - 3428 - 132 + 38$; hence

$$\begin{array}{ll} (c) & \Delta H = 13{,}192 - 9.19T - 0.000957T^2 + 0.00000074T^3. \\ (d) & \Delta H_{293} = 10{,}439. \end{array}$$

Now, summing (*a*) and (*d*),

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g), \qquad \Delta H_{293} = -57{,}961,$$

and

$$\Delta C_p = -1.08 - 0.0029T + 0.00000222T^2.$$

This gives a value for $\Delta H_0 = -57{,}339$ cals. Hence,

$$\Delta H = -57{,}539 - 1.08T - 0.00145T^2 + 0.00000074T^3;$$

and

$$\Delta H_{1273°} = -59{,}738 \text{ cals.}$$

EXERCISES (2)

1. Calculate the work done when one kilogram is raised one meter. Express the result in ergs, in joules and in calories.

2. Calculate the energy in joules necessary to heat a kilogram of lead from 20° to 100° C. The specific heat of lead is 0.0305.

3. A battery with an E.M.F. of 4 volts is short-circuited through a resistance. Evaluate in calories the energy consumed when one faraday of current has passed through the circuit.

4. A current of 1 ampere was passed for 10 minutes through a coil of wire immersed in a calorimeter, the resistance of the wire being 10 ohms. Calculate the energy liberated and also the temperature rise produced in the calorimeter, it being known that the heat capacity of the calorimeter was 1000 calories.

5. From the data in Section 2.16 calculate the heat of combustion of hydrogen at constant volume and at 298° K.

6. The heat of combustion of ethyl alcohol at 298° K. and one atmosphere pressure is − 328 kcal. Calculate its heat of formation.

7. From the data in Table 2.3 calculate ΔH for the reactions:

$$(a)\quad H_2S + Cl_2 \rightarrow 2HCl + S,$$
$$(b)\quad 2AgI + Cl_2 \rightarrow 2AgCl + I_2.$$

8. From the data in Table 2.1 calculate the heats of hydrogenation of the monoölefines to the corresponding paraffins. Calculate the energy difference between the formation of a primary and a secondary C − H bond and between a primary and tertiary C − H.

CHAPTER 3

THE GASEOUS STATE. I

THE ENERGY OF MOTION AND OF INTER-MOLECULAR ATTRACTION

Matter may exist in three homogeneous states known respectively as the solid, liquid and gaseous states of aggregation. The difference between the three states is essentially one of energy content. The solid state has the least energy of the three. The addition of heat energy to a solid causes it to pass, unless decomposition of the substance occurs, either through the liquid state to the gaseous state, or directly to the gaseous state. In the former case the energy received first raises the temperature of the solid, is then consumed, as *latent heat of fusion,* in the conversion of a solid to a liquid, next raises the temperature of the liquid until finally the liquid vaporizes with consumption of energy as *latent heat of vaporization.* These several changes may be illustrated by the change at one atmosphere from ice to water at 0° C., the rise in temperature of the water and its ebullition at 100° C. Above 100° C. water exists as a gas up to temperatures ($> 1000°$ C.) at which decomposition occurs. The direct passage from the solid to the gaseous state is known as *sublimation.* In accord with the law of conservation of energy, the heat energy consumed must reappear as some other form of energy. It is transformed into the potential energy of the attractive forces which molecules exert upon each other. In the solid state this potential energy is less than in the gaseous state; the constituent units of the solid maintain their relative positions one to another. The solid has shape, size and rigidity. In the liquid state the forces determining shape and rigidity have been overcome by the thermal energy but the volume is still relatively insensitive to alteration. The gaseous state is characterized by the condition that its shape and volume are determined entirely by the system which encloses it. Within such a system a gas distributes itself homogeneously unless acted upon by some external force.

1. **The Gas Laws:** The conditions of pressure and temperature which obtain when a gas distributes itself uniformly throughout a given volume were discovered experimentally by Boyle and by Gay-Lussac.

2. **Boyle's Law** states that the pressure of a gas varies inversely as the volume at constant temperature. This law may be stated mathematically in several forms. At constant temperature,

$$p \propto 1/v \qquad \text{i.e.} \qquad pv = \text{const.} \tag{3.1}$$

or

$$pv = p_0v_0. \tag{3.2}$$

Experiment shows that over a range of pressures the product pv for any gas is only approximately a constant. The variations from constancy will be discussed in detail later. At low pressures the deviations from constancy decrease and finally disappear as the pressure approaches zero. The average value of the constant obtained by extrapolation to zero pressure for a large number of gases is 22,414 cc. atm. per mole at 0° C.

3. **Gay-Lussac's Law** states that at constant volume the pressure of a gas varies uniformly with the temperature or that at constant pressure the volume varies uniformly with the temperature.

$$p = p_0(1 + \alpha t). \tag{3.3}$$

At constant pressure

$$v = v_0(1 + \beta t). \tag{3.4}$$

In these expressions p_0 and v_0 are the pressure and volume respectively of a given mass of gas at zero degrees Centigrade; p and v are the pressure and volume of the same mass of gas at the temperature t° C.

Careful measurements of the values of α and β have shown that they are slightly different for different gases and depend also on the volume or pressure respectively. At very low pressures α and β become equal for all gases and have the value 1/273.16, a quantity having the dimensions, degree^{-1}

$$p = \frac{p_0}{273.16}(273.16 + t) \tag{3.5}$$

or

$$v = \frac{v_0}{273.16}(273.16 + t). \tag{3.6}$$

If a temperature T be defined by the relation

$$T = 273.16 + t, \tag{3.7}$$

then

$$p = \frac{p_0}{273.16}T \qquad \text{or} \qquad p \propto T \tag{3.8}$$

and

$$v = \frac{v_0}{273.16}T \qquad \text{or} \qquad v \propto T. \tag{3.9}$$

The temperature T is termed the absolute temperature.

4. **The Ideal Gas Law:** Since Boyle's law and Gay-Lussac's law are only obeyed by actual gases at low pressures it has been found convenient to introduce the concept of an ideal gas, that is, a gas which under all conditions would obey both laws. The simultaneous variation of all

three variables, temperature, pressure and volume of an ideal gas may be derived by a combination of Boyle's and Gay-Lussac's laws. Consider a given mass of an ideal gas under the conditions p_1, v_1 and T_1 and let the pressure be changed at constant temperature to p_2. By Boyle's law the resulting volume v_1' is given by (3.2), $p_2v_1' = p_1v_1$. Maintaining the pressure constant at p_2 let the temperature now be changed to T_2. The resulting volume v_2 will be given by Gay-Lussac's law

$$v_2/T_2 = v_1'/T_1. \tag{3.9}$$

Substitution for v_1' gives

$$v_2/T_2 = p_1v_1/p_2T_1 \tag{3.10}$$

or

$$p_1v_1/T_1 = p_2v_2/T_2. \tag{3.11}$$

Thus pv/T is constant

or

$$pv = RT \tag{3.12}$$

where R is termed the gas constant and has a value $p_0v_0/T = 22{,}414/273.16 = 82.055$ cc. atm. per degree per mole.

We shall discuss in detail the extent to which gases approximate to this fundamental gas law after an enquiry into the theoretical significance of this law from the standpoint of the kinetic theory.

5. **The Kinetic Theory of Gases:** Among the first to suggest the explanation for the behavior of gases was Daniel Bernouilli (1738). The kinetic theory which has been built up since his time rests upon two postulates: The Daltonian concept of discrete particles (molecules) as the unit and the postulate that the particles are in continual and chaotic motion, which motion manifests itself by the phenomenon of temperature. In its simplest form, the kinetic theory further assumes that the particles are spherical in form and perfectly elastic in collision with themselves or with the walls of the containing vessel. The pressure on the walls of such vessel is due to the force of the impacts of these molecules. It is readily seen that such a concept is qualitatively in agreement with the known facts. When the gas is compressed, the number of molecules per unit volume increases and, hence, the number of impacts per unit time on the walls of the containing vessel, i.e., the pressure. Increase of temperature at constant volume increases the average velocity of the molecules and, hence, the force with which they strike the walls. The pressure is therefore increased.

The kinetic theory may also be applied quantitatively to the explanation of the properties of the gaseous state, the more completely the more rigorously true are the assumptions upon which the derivations are based. This close interpretation of gaseous behavior constitutes a triumphant attainment of a long succession of scientists, principally mathematical physicists, of whom the outstanding contributors are Clausius, Clerk

Maxwell, Boltzmann, van der Waals and Jeans. We shall illustrate such a quantitative application by the simplest form and show that, in this form, the laws of a perfect gas are indicated.

Consider a mass of gas enclosed in a cube of length, l. In order to calculate the pressure let it be assumed that the molecules, which are, in reality, moving with velocities varying from zero to infinity, are all moving with the same velocity, u, which is the square root of the mean square velocity. This velocity, which will be considered in more detail subsequently, is resolvable into components normal to the three directions, related to u in the following way:

$$u_x^2 + u_y^2 + u_z^2 = u^2. \tag{3.13}$$

Pressure is a force per unit area, and, from Newton's second law, is equal to the product of the mass, m, of a particle and its acceleration, a.

$$f = ma = m\frac{du}{dt} = \frac{d(mu)}{dt}. \tag{3.14}$$

A molecule with component of velocity, u_x, in the direction normal to the side upon which it impinges, approaches this side with momentum $+ mu_x$; after impact it rebounds with a momentum $- mu_x$, the change in momentum being $2mu_x$. The number of impacts on the two walls which are perpendicular to the x axis per unit of time is u_x/l, and the total change in momentum in one direction per unit of time is $2mu_x^2/l$; the total change in momentum per unit of time in all three directions is $2mu_x^2/l + 2mu_y^2/l + 2mu_z^2/l$, which expression, by equation (3.13), is equal to $2mu^2/l$. Since the total area upon which this force is exerted is $6l^2$, the force per unit area, that is, the pressure, is $mu^2/3l^3$, or $mu^2/3v$, where v is the volume of the cube.

If instead of one molecule in the cube, there is one mole of the gas, that is, N molecules, where N is the Avogadro number, the expression for the pressure becomes

$$p = Nmu^2/3v$$

or

$$pv = Nmu^2/3. \tag{3.15}$$

Since the total kinetic energy of the molecules is $Nmu^2/2$ it follows that

$$pv = 2E/3, \tag{3.16}$$

where E is the kinetic energy of translation of the molecules.

The relation between the energy and the temperature must now be examined. In general, when two bodies are placed in "thermal contact," energy flows from one to the other. This flow of energy from the hotter to the colder body will continue only so long as a difference in temperature exists between the bodies. When no further energy flow occurs the bodies are said to be at the same temperature. Such is the fundamental concept of temperature. On the other hand the units whereby numerical values may be assigned to different temperatures are purely arbitrary. The mechanism by which this energy exchange occurs between gases at two different temperatures depends, according to the kinetic theory, on the exchange of energy between individual molecules on collision. If the molecules have on the average equal energies, then no exchange can occur and, by definition, the gases are at the same temperature. It may be rigorously proven by kinetic theory that for all gases, regardless of their nature, the temperature is determined by the average kinetic energy of the molecules alone; thus $mu^2/2 \propto T$. The choice of the proportionality factor is again arbitrary. It is so chosen that the volume of an ideal gas in a constant pressure gas thermometer is directly proportional to the absolute temperature. This gives $mu^2/2 = 3RT/2N$, or

$$pv = RT, \tag{3.12}$$

which is the ideal equation.

6. **Kinetic Theory and Avogadro's Hypothesis:** Equation (3.12) is valid for a given mass of a particular gas. If the mass of gas taken as a standard is the molecular weight expressed in grams, the constant R assumes a definite value, and the general equation for any mass of an ideal gas is

$$pv = wRT/M, \tag{3.17}$$

where w is the mass of the gas considered and M its molecular weight. The experiments which led to the above generalization are also the experiments that led to Avogadro's hypothesis; in fact, this hypothesis is embodied in the above equation.

It has been shown that two gases are at the same temperature when their mean kinetic energies are equal, that is to say when $m_1u_1^2/2 = m_2u_2^2/2$. Equal volumes of the two gases will exert the same pressure when $n_1m_1u_1^2/3 = n_2m_2u_2^2/3$ since, as has been shown, each of these terms is equal to the pressure-volume product, n_1 and n_2 being the numbers of molecules of the two gases in equal volumes. When the two equations hold simultaneously

$$n_1 = n_2$$

that is, equal volumes of any two gases under the same conditions of temperature and pressure contain the same number of molecules. This is the important generalization of Avogadro.

The facts embodied in the above equations are in agreement with the observations of Gay-Lussac and Humboldt that the reacting volumes of gaseous substances at the same temperature and pressure are in the ratio of small whole numbers. According to one of Dalton's fundamental assumptions, chemical reactions take place only between whole numbers of atoms, from which the following expression is obtained,

$$m_1 : m_2 = k_1Q_1 : k_2Q_2, \tag{3.18}$$

where k_1 and k_2 are integers and Q_1 and Q_2 are stoichiometrical weights of the two gases. Since the gases are at the same temperature and pressure, $m_1u_1^2/2 = m_2u_2^2/2$ and $n_1m_1u_1^2/3 = n_2m_2u_2^2/3$, where n_1 and n_2 are now the numbers of molecules per unit volume of the two gases and are equal. The densities of the gases ρ_1 and ρ_2 are therefore n_1m_1 and n_2m_2. The densities are also equal to Q_1/v_1 and Q_2/v_2 where v_1 and v_2 are the reacting volumes. Hence

$$Q_1/v_1 : Q_2/v_2 = \rho_1 : \rho_2 = m_1 : m_2 = k_1Q_1 : k_2Q_2 \tag{3.19}$$

or

$$v_1 : v_2 = k_2 : k_1. \tag{3.20}$$

This equation expresses mathematically the observation of Gay-Lussac in connection with volume relationships of gaseous reactants.

7. Diffusion Through Capillary Tubes: The phenomenon of gaseous diffusion can be strikingly visualized with the aid of the kinetic theory. Let A (Fig. 3.1) be a vessel containing an equimolecular mixture of oxygen and hydrogen, connected by capillary tubes to the vessel B in which a vacuum is maintained. Provided the diameters of the capillary tubes are much smaller than the average distance between molecules, it is found that four times as much hydrogen diffuses through the tubes as oxygen. Only those molecules which strike the openings of the tube will be in a position to diffuse. Although there is the same number of each kind of molecule, the hydrogen molecules are moving with much greater velocities, and therefore more of them will strike the openings per unit of time than oxygen molecules. The velocities of the two types of molecules are given by

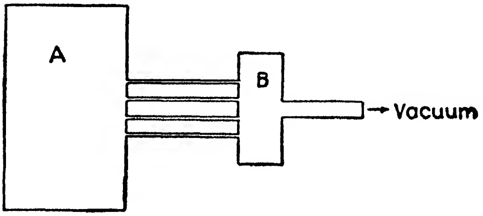

FIG. 3.1

$$u_{O_2} = \sqrt{3pv/m_{O_2}n} = \sqrt{3RT/m_{O_2}n}$$

and

$$u_{H_2} = \sqrt{3pv/m_{H_2}n} = \sqrt{3RT/m_{H_2}n}.$$

Since n is the same in the two cases, $u_{H_2}/u_{O_2} = \sqrt{32/2} = 4$. This means that hydrogen has four times the chance of diffusion that oxygen has, and therefore its accumulation in the evacuated vessel should be four times that of the oxygen. Evidence confirming this deduction was presented by Graham from his experiments dealing with the diffusion of gases through porous plates.

Graham's Law of Diffusion may therefore be expressed in the form: *Gases diffuse at rates which are inversely proportional to the square roots of their densities.*

8. **Thermal Diffusion:** Gases may also be separated by differences in the rate of diffusion under a temperature gradient. The apparatus used by Reynolds in his study of thermal diffusion is shown in Fig. 3.2. The two chambers, *A* and *B*, were connected by capillary tubes *E*, made of meerschaum, and also by a tube of comparatively large diameter, containing the tap *F*. *M* was a manometer. The chamber *B* was surrounded by ice and *A* by steam. A gas was introduced into the chambers, and, with the tap *F* open, equilibrium was obtained. When tap *F* was closed, the pressure in the hot chamber increased, as indicated by the manometer. The difference in pressure in the two vessels reached a definite amount, which was a maximum when the original pressure was of the order of one or two centimeters of mercury; at one atmosphere pressure, the difference was not perceptible. The lower the original pressure, the greater was the percentage difference in pressure registered.

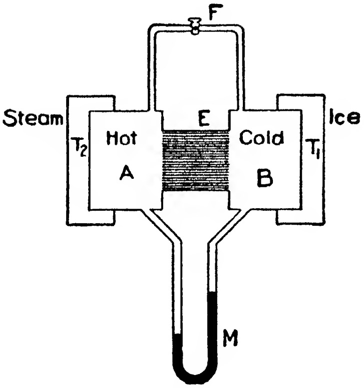

Fig. 3.2

If T_2 and T_1 were the temperatures of the hot and cold chambers respectively, then, when tap *F* was open and there was therefore no pressure difference, the number of molecules in *A* was inversely proportional to T_2; the number in *B* was inversely proportional to T_1. When tap *F* was closed the number of molecules leaving *A* was proportional to the number present and also to their average velocity, i.e., proportional to $1/T_2$ and also to $\sqrt{T_2}$, or proportional to their product $1/\sqrt{T_2}$. Likewise, the number leaving *B* was proportional to $1/\sqrt{T_1}$. Since $1/\sqrt{T_1} > 1/\sqrt{T_2}$, more left *B* than left *A*, and the pressure in *A* increased.

The problem of thermal diffusion acquired importance by reason of the possibility of its use in the separation of gaseous isotopes. It has been shown theoretically[1] and experimentally[2] that if a gaseous mixture

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[1] Enskog, *Physik. Z.*, **12**, 538 (1911); *Ann. Physik*, **38**, 750 (1912). Chapman, *Phil. Trans.*, **217A**, 115 (1916); *Phil. Mag.*, **34**, 146 (1917).

[2] Chapman and Dootson, *Phil. Mag.*, **33**, 248 (1917).

is present in a container one portion of which is kept hot, and another cold, an equilibrium is attained in which there is an increased concentration of the larger or heavier molecules at the cold end and vice versa. This method of separation grew in practical importance with the discovery by Clusius and Dickel[1] of a simple way of cascading the effects. This involves the use of a horizontal temperature gradient between two vertical walls. Convection which might normally be expected to obliterate separation is actually responsible for an accumulative effect. In this manner a multiplication of the effect by a factor up to 50 per meter of length of the vertical walls has been found.

9. **Gas Mixtures: Dalton's Law** states that the pressure of a gas mixture is equal to the sum of the partial pressures of the gases composing the mixture. For gases to which the fundamental gas law in its kinetic derivation applies, this follows at once. For, according to the theory,

$$\begin{aligned} p_1v &= \tfrac{1}{3}m_1n_1u_1^2, \qquad (3.15)\\ p_2v &= \tfrac{1}{3}m_2n_2u_2^2,\\ Pv &= \tfrac{1}{3}m_1n_1u_1^2 + \tfrac{1}{3}m_2n_2u_2^2, \end{aligned}$$

and, hence,

$$P = p_1 + p_2, \tag{3.21}$$

where m_1, m_2 are the weights, n_1, n_2 are the numbers and u_1, u_2 are the velocities of the two gases; p_1 and p_2 are the pressures exerted when each of the gases separately occupy the volume v, and P is the pressure exerted when both occupy the volume at the same time.

10. **Barometric Formula:** It is a practical observation that the atmospheric pressure diminishes with increasing height above the earth. This may be accounted for in terms of the gravitational attraction on the molecules of the atmosphere. Consider a column of gas of unit cross section and height h. The pressure at the top of the column will be less than that at the bottom by an amount which is the weight of the gas, since the weight is the force which the column of gas exerts and the force per unit area is the pressure. The volume of gas being considered is h cc. Hence if ρ is the average density, its mass is ρh and its weight ρhg where g is the acceleration due to gravity.

Consider a thin section of this column of height dh. Let the pressure at the height h be p and at $h + dh$ be $p - dp$. Hence as before

$$dp = -\rho g dh. \tag{3.22}$$

By the gas law (3.17), $pv = wRT/M$. Since $\rho = w/v$,

$$\rho = Mp/RT \tag{3.23}$$

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[1] *Naturwiss.*, 26, 546 (1938); 27, 148 (1939). See Gillespie, *J. Chem. Phys.*, 7, 530 (1939).

and

$$dp/p = -Mgdh/RT$$

or

$$d \ln p = -Mgdh/RT. \tag{3.24}$$

Integrating from p_0 the pressure at sea level to p the pressure at the height h, gives

$$\ln (p/p_0) = -Mgh/RT, \tag{3.25}$$

or

$$p = p_0 e^{-\frac{Mgh}{RT}}, \tag{3.26}$$

from which equation the pressure at any height may be calculated.

A useful application of this principle was first made by Perrin in the calculation of the Avogadro constant by the so-called "sedimentation equilibrium." On the assumption that suspended particles would behave like molecules of a gas, a suspension of gamboge particles in water was examined under a microscope and the number of particles in the field of view at different heights determined. The mass of a single particle was obtained from the density of the bulk material and a direct measurement, microscopically, of the volume of the particle. The Avogadro constant could then be calculated in the following manner. Since the pressure of a gas is directly proportional to its density, the relation between pressure and height given above may be written:

$$d \ln n = -Mgdh/RT = -Nmgdh/RT, \tag{3.27}$$

where n is the number of particles per cc., N is the Avogadro number and m is the mass of a particle. Integrating between the two heights h_1 and h_2, for densities n_1 and n_2:

$$\frac{n_2}{n_1} = e^{\frac{Nmg}{RT}(h_1 - h_2)}. \tag{3.28}$$

The quantities involved in this equation were all determined by Perrin and hence N could be calculated. The value found was $6{\cdot}8 \times 10^{23}$. Later work by Svedberg, Westgren and others using gold and selenium colloids gave a mean value of 6.05×10^{23} in good agreement with values determined by other methods.

11. The Distribution of Velocities Among Molecules: In the preceding paragraphs the deductions have been made with an assumed constant velocity, u, the root mean square velocity. As we have seen, it leads to conclusions in agreement with the fundamental gas law and other laws of gaseous behavior. The velocities of the individual gas molecules are, however, constantly changing as a result of collisions among themselves. The molecules will possess velocities varying between a momentary state of rest and velocities much higher than the mean velocity; these high velocities would be acquired by several successive and favorable collisions.

Now, this varying velocity of gas molecules in a volume of gas maintained at constant temperature and therefore at a constant mean kinetic energy is, as we shall later see, of very great importance in determining whether chemical reaction results from such collisions. The law which governs the distribution of velocities in such a gaseous volume was deduced by Maxwell on the basis of probability considerations. His law may be expressed thus: The number of molecules, dN, out of a total number, N, whose velocities lie between c and $c + dc$ is given by the equation:

$$dN = \frac{4N}{\sqrt{\pi a^3}} \cdot c^2 \cdot e^{-(c^2/a^2)} dc. \tag{3.29}$$

The derivation of this equation is complex. One method of derivation is given in Appendix I at the end of this book. It is sufficient for our purpose here to illustrate the results that are obtained from the use of this equation. In the following table we summarize the results of applying such an equation to the distribution of velocities in numbers per 1000 molecules of oxygen at 0° C. According to Meyer,[1] on the average, the number of molecules within the given velocity limits are:

TABLE 3.1

DISTRIBUTION OF VELOCITIES IN OXYGEN AT 0° C.

From	13 to 14	per thousand have velocities	less than	100 meters per second
	81 to 82		between	100 and 200 meters per second
	166 to 167		"	200 and 300 " " "
	214 to 215		"	300 and 400 " " "
	202 to 203		"	400 and 500 " " "
	151 to 152		"	500 and 600 " " "
	91 to 92		"	600 and 700 " " "
and	76 to 77		above	700 meters per second

It is evident that if such data be plotted in the form of a diagram (Fig. 3.3), with the percentage numbers within given velocity limits as ordinates against the velocities as abscissas the curve obtained shows a maximum value at a given velocity. We may term this velocity *the most probable velocity*; in the Maxwell equation given above, the quantity a is this most probable velocity. Since it corresponds to the maximum of the curve in Fig. 3.3 its value can be found by placing $d\left(\frac{dN/N}{dc}\right)\Big/dc = 0$. At a given temperature T, it has the value

$$a = \sqrt{2kT/m} = 12{,}900\sqrt{T/M} \text{ cm. per sec.,} \tag{3.30}$$

where m is the mass of the molecule and k is the gas constant per molecule,

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[1] Kinetic Theory of Gases, Longmans, Green and Co., 1899.

equal therefore to R/N_A where R is the gas constant per mole and N_A is the Avogadro number. In the alternative form M is the molecular weight of the gas. For a given gas, therefore, the most probable velocity increases as the square root of the absolute temperature. That is to say, as the temperature increases the maximum occurs at increasingly large velocities as shown in the diagram.

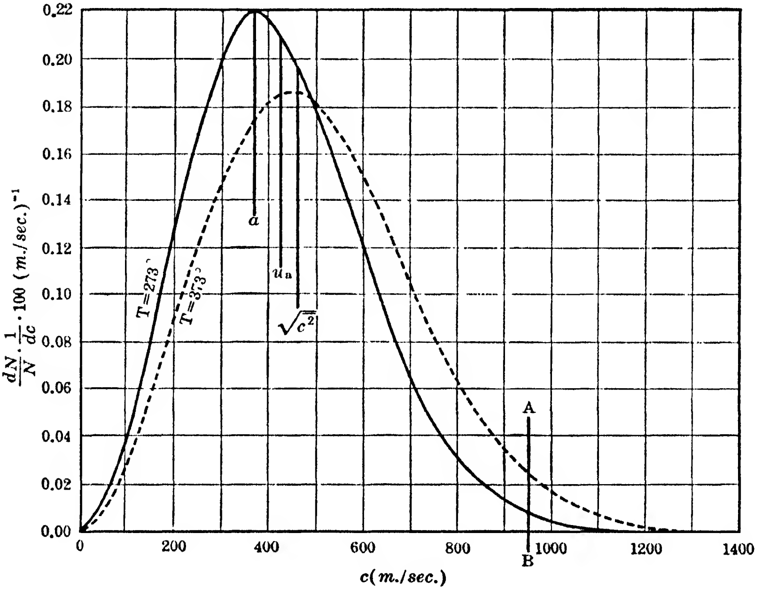

Fig. 3.3 Distribution of velocities among molecules at two temperatures (*a*) most probable velocity; (u_a) average velocity; $\sqrt{\overline{c^2}}$ root mean square velocity

The average velocity of the molecules at any given temperature, u_a, is the sum of all the velocities represented, divided by the total number of molecules. The value of this average velocity is:

$$u_a = \frac{1}{N}\int_0^\infty c\,dN_c = \left(\frac{8kT}{\pi m}\right)^{1/2} = 14{,}500\left(\frac{T}{M}\right)^{1/2} \text{ cm. per sec.} \quad (3.31)$$

The *root mean square velocity* is obtained by a similar process of summation and has the value

$$\sqrt{\overline{c^2}} = \left[\frac{1}{N}\int_0^\infty c^2 \cdot dN_c\right]^{1/2} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$

$$= 15{,}800\sqrt{T/M} \text{ cm. per sec.} \quad (3.32)$$

It was shown in section (5) of this chapter that, for one mole of gas, $pv = RT = \frac{1}{3}nmu^2 = Mu^2/3$ since nm for one mole is equal to M, the molecular weight. It is therefore evident that u, of the derivation in section (5), is equal to $(3RT/M)^{1/2}$ and is therefore identical with the quantity which we have here named $\sqrt{\overline{c^2}}$, the root mean square velocity. Since this is the velocity which represents the mean kinetic energy of the gas molecules it is sometimes called the *mean energy velocity*. The three ordinates on the diagram, Fig. 3.3, represent the most probable, the average and the root mean square velocities.

An approximate form of the distribution law, which is sufficiently exact for many applications to chemical processes, may be obtained by considering distribution of velocities in two dimensions instead of three. The advantages of this approximation are its simplicity and the ease with which it may be applied. For the distribution of velocities in two dimensions only,

$$dN = (2N/a^2)e^{-(c^2/a^2)}cdc. \tag{3.33}$$

In this equation the constant, a, is once more the most probable velocity $= (2RT/M)^{1/2}$. If E, the kinetic energy of the molecules, be set equal to $\frac{1}{2}Nmc^2$, the equation becomes

$$dN = (N/RT)e^{-E/RT}dE. \tag{3.34}$$

This expression may be used to determine the number of molecules N_E which have a velocity in excess of that which corresponds to the mean kinetic energy E of the molecules.

$$\frac{N_E}{N} = \frac{1}{RT}\int_E^\infty e^{-E/RT}dE = e^{-E/RT}. \tag{3.35}$$

The general effect of temperature on the distribution of velocities may be seen from the distribution curves plotted for two temperatures. Increase of temperature decreases the fraction at low velocities. It increases the fraction at high velocities. It should also be noted that the higher the temperature the lower is the fraction having the most probable velocity at the given temperature.

The Maxwell equation (3.35) shows a close similarity to that derived for the distribution of molecules at different heights under gravitational attraction (Equation 3.26) when it is remembered that the number of molecules per unit volume can replace the pressures. Quite generally, for distribution in a non-homogeneous field, Boltzmann deduced that the number of molecules, n, per cc. with a potential energy E_p per mole was related to the number, n_0, per cc. where the potential energy was zero by the expression $n = n_0e^{-E_p/RT}$. Also, for quantized energy, whether electronic, vibrational or rotational (Chapter 4) the fraction of the molecules possessing a quantum of energy per molecule is given by the expression $e^{-\epsilon/kT}$, or $e^{-E/RT}$ where $N\epsilon = E$, $Nk = R$, and N is Avogadro's number.

12. **Frequency of Collisions:** It is desirable to know not only the energy of colliding molecules but also the frequency with which they collide. Let us understand by a collision the approach of two molecules to within a distance, σ, of each other, where σ is the diameter of a molecule effective in such collisions. To facilitate the calculation let us imagine one molecule moving in a mass of stationary molecules. It will possess a motion equal to the mean relative velocity, r.

Imagine a system of molecules, each moving with the average velocity u_a. Consider one of the molecules represented by the point A in Fig. 3.4 moving in the direction AB. If at the point B it collides with another molecule its direction of motion will in general be changed, depending upon the direction of motion of the molecule struck. Thus, if the second molecule were travelling in the direction CB, resulting in a head-on collision, the first molecule would have its direction completely reversed and would return from B towards A. If, on the other hand, the collision of the molecule at B was a grazing collision in which it only just touched a second molecule, its direction of motion would be unaltered and it would continue its motion after the collision from B towards C. Between these two extremes, of head-on or grazing collision, any intermediate type is possible which would result in the molecule moving towards any point on the circle circumscribing point B. Since all these directions are equally probable the average direction, when a large number of molecules are so considered, will be BD or BE, that is, a direction making an angle of 90° with the original direction of motion of the molecule. This is equivalent to the statement that the angle between the directions of motion of two molecules in collision is on the average 90°. Their relative velocity by the law of Pythagoras is therefore $\sqrt{2}u_a$. This is therefore the mean relative velocity, r. If the moving molecule be imagined to have a radius equal to σ instead of a diameter equal to this amount, the stationary molecules may be thought of as points. In one second, such a moving molecule will sweep out a volume element

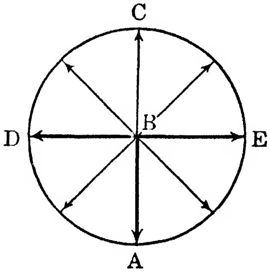

FIG. 3.4

$$\sqrt{2}u_a \times \pi\sigma^2.$$

If the concentration of stationary molecules be n per cubic centimeter, the number of encounters between the moving molecule and the stationary points will be $\sqrt{2}u_a\pi\sigma^2 n$. But each molecule can be regarded as undergoing this same procedure. Hence the total number entering into collision per cubic centimeter per second among n molecules is

$$\sqrt{2}u_a\pi\sigma^2n^2.$$

The actual number of collisions will be one half this number since two molecules entering upon a collision with each other only give rise to one collision. This would give a value

$$\tfrac{1}{2}(\sqrt{2}u_a\pi\sigma^2n^2).$$

Now the average velocity is given by the relation (3.31): $u_a = \sqrt{8kT/\pi m}$. Hence the number of collisions is:

$$2n^2\sigma^2\sqrt{\pi kT/m}.$$

13. **Mean Free Path:** If the velocity of a particle be u_a and the particle makes $\sqrt{2}\pi u_a\sigma^2n$ collisions per second it is apparent that the particle will traverse a path,

$$l = u_a/\sqrt{2}\pi u_a\sigma^2n = 1/\sqrt{2}\pi\sigma^2n \tag{3.36}$$

without encounter with other molecules. This distance is known as the mean free path.

14. **Viscosity of a Gas:** The mean free path is related to the viscosity of a gas by the expression

$$\eta = \tfrac{1}{3}\rho ul, \tag{3.37}$$

where η is the viscosity and ρ is the gas density. In agreement with this equation it is found that the viscosity of a gas is independent of the pressure over short ranges of pressure. Doubling the pressure doubles the density, but, at the same time, the mean free path is halved. The velocity of the gas molecules is proportional to the square root of the absolute temperature. It follows, therefore, from the above relationship, that the viscosity should also vary as the square root of the absolute temperature. Actually it increases more rapidly, so that we must conclude that temperature exercises some influence on the mean free path, increasing it with increasing temperature. Sutherland has attempted an explanation of this on the basis of the existence of attractive forces between real gas molecules. If two molecules of an ideal gas were moving in such a manner that they just escaped colliding with each other, two such molecules in a real gas would be pulled into collision by their mutual attractions. Hence the frequency of collision in real gases will be higher than that calculated by the previous expression. The relative effect of the attractive forces will diminish, however, as the temperature rises, since the kinetic energy of the molecules will be higher. At extremely high temperatures the attractive forces will be completely negligible; the frequency of collision and the mean free path will have their ideal values. Now an increased frequency of collision means a decreased mean free path. Hence at lower temperatures a real gas will have a free path which is less than the ideal but it will increase as the temperature increases up to the ideal value. Sutherland shows this effect to be given by the equation:

$$l_\infty/l = 1 + (C/T), \tag{3.38}$$

where l_∞ is the limiting mean free path at high temperatures (the ideal value); l is its value at the temperature T and C is a constant whose value ranges from 50 to 300 for different gases. Rankine has utilized determinations of gaseous viscosity to determine the dimensions of gas molecules. Some of his data, compared with magnitudes deduced from crystallographic analysis by the X-ray method, are reproduced in the following table.

TABLE 3.2

MOLECULAR RADII FROM CRYSTAL MEASUREMENTS AND GASEOUS VISCOSITIES

Gas	Radius (Bragg)	Radius (Rankine)	Gas	Radius (Bragg)	Radius (Rankine)
Helium		0.94×10^{-8} cm.	Hydrogen fluoride	0.65	1.17
Neon	0.65×10^{-8} cm	1.17	Hydrogen chloride	1.02	1.43
Argon	1.02	1.43	Hydrogen bromide	1.17	1.58
Krypton	1.17	1.59	Hydrogen iodide	1.35	1.75
Xenon	1.35	1.75			

It will be noted that the examples cited yield values for the molecular radii of the order of 10^{-8} cm. The utility of these data in calculating the number of collisions among gas molecules is apparent from the preceding paragraphs.

15. **Mass of Gas Striking Unit Area:** This quantity is of importance in calculations of reaction between gases and solid surfaces. Consider a unit cube of 1 cm. side containing n molecules. The number approaching one side of the cube at any instant will be approximately $n/6$, since there are six sides to the cube. However, when full account is taken of the direction of approach of the molecules to the wall, the correct number is $n/4$. If u_a is the average velocity of the molecules, all of those molecules that are within a distance u_a of a wall will strike it in one second. The number of molecules striking one side of the cube, that is, an area of 1 cm.^{2} in each second will be $nu_a/4$. If m is the mass of each molecule, the mass of gas striking the unit area will be $nmu_a/4$.

Now n being the number of molecules in 1 cc. is related to the prevailing pressure and temperature by the gas law: $n = p/kT$. Furthermore, the average velocity (equation 3.31) is also a function of the temperature: $u_a = \sqrt{8kT/\pi m}$. Making these substitutions, the mass of gas, W, striking unit area in unit time has the value:

$$W = nmu_a/4 = p \cdot m \cdot \sqrt{8kT/\pi m}/4kT = p\sqrt{m/2\pi kT}$$

or in terms of the molecular weight M and R the gas constant per mole, 8.32×10^7 ergs:

$$W = p\sqrt{M/2\pi RT}. \tag{3.39}$$

16. Heat Capacity of Monatomic Gases: The mean kinetic energy of a gas at temperature T is given by the equation (3.16) of the kinetic theory,

$$E = \tfrac{3}{2}pV = \tfrac{3}{2}RT.$$

If, under the given experimental conditions, the heat supplied to a gas is employed solely to increase the kinetic motion of the molecules, the increase in the mean kinetic energy ΔE is exactly equal to the increase in internal energy ΔU, the volume being kept constant. As shown in Section 14, Chap. 2, the true heat capacity at constant volume is:

$$C_v = dU/dT$$

and hence, for the present case,

$$C_v = dE/dT = \tfrac{3}{2}R = 2.979 \text{ cals. per mole.} \tag{3.40}$$

The heat capacity of such gases at constant volume should thus be independent both of the temperature and the nature of the gas. This is true for all monatomic gases, including helium and the other rare gases and mercury vapor. Experiments have been made with helium at the temperature of liquid hydrogen ($\sim$ 15° K.), and also at very high temperatures by determining the rise in temperature produced by the explosion of gas mixtures. The heat of the explosion increases the gas temperature to an extent depending on the heat capacity of the gases present after reaction. By studying the effect of additions of monatomic gases to explosive mixtures the heat capacity could be determined over the temperature range in question. Over this whole temperature range, 255–2000° C., the molar heat capacity at constant volume was found to be $\tfrac{3}{2}R$, for monatomic gases, within the experimental error.

The mean kinetic energy, $\tfrac{3}{2}RT$, is associated with the three components of the motion of the gas molecules. According to Maxwell, the molecule possesses three degrees of freedom of translatory motion, all equivalent, and such that, along the three component axes, x, y and z, the energy may be resolved

$$\tfrac{1}{2}mu_x^2 = \tfrac{1}{2}mu_y^2 = \tfrac{1}{2}mu_z^2 = \tfrac{1}{3}(\tfrac{3}{2}pv) = \tfrac{1}{2}RT. \tag{3.41}$$

Every gas possesses these three degrees of freedom of translatory motion and to the heat capacity of every gas at constant volume there will be the contribution of $\frac{3}{2}R$ per mole from such translatory motion. Inspection of Table 3.3, however, indicates that the value of C_v for the gases other than the monatomic gases exceeds the value $\frac{3}{2}R = 2.989$ cals. per mole. It will be noted that the value of C_v increases with increasing complexity of the molecule, the molecule ether, $(C_2H_5)_2O$, showing values as high as 30–40 cals. per mole. In a later chapter we shall return to a discussion of the heat capacities of diatomic and polyatomic molecules to show that intra-molecular motions, the rotation of the molecule as a whole, and the vibrations of the constituent atoms with respect to one another, are responsible for heat capacities in excess of those ascribable to translatory motion.

TABLE 3.3

C_v FOR VARIOUS GASES

Gas	Temp. in ° C.					
	0°	100°	200°	500°	1200°	2000°
Argon	2.98	2.98	2.98	2.98	3.0	3.0
N_2, O_2, HCl, CO	4.90	4.93	5.17	5.35	5.75	6.22
H_2	4.85	4.93	5.00	5.21	5.70	6.26
Cl_2	5.97	6.32	6.53	6.78	6.9	7.0
CO_2, SO_2	6.80	7.43	8.53	9.43	11.1	11.5
$(C_2H_5)_2O$	32	32.6	41.6			

17. **Heat Capacity of Monatomic Gases at Constant Pressure:** If a gas be heated at constant pressure, more heat is required to raise the temperature one degree than is required at constant volume. For, at constant pressure, increase in temperature results in a volume expansion. The heat added at constant pressure is spent partly in increasing the internal energy and partly as work done $p\Delta v$ against the external pressure. The relation between C_p and C_v is therefore given, in accord with the first law of thermodynamics, by the equation

$$\begin{aligned} C_p(T_2 - T_1) &= C_v(T_2 - T_1) + p\cdot\Delta v \\ &= C_v(T_2 - T_1) + p(v_2 - v_1), \end{aligned} \tag{3.42}$$

where v_1 and v_2 are the initial and final gas volumes. If the gas laws are obeyed, it is evident that

$$C_p(T_2 - T_1) = C_v(T_2 - T_1) + R(T_2 - T_1), \tag{3.43}$$

for one mole of the gas in question. Hence the relationship,

$$C_p = C_v + R$$

or

$$C_p - C_v = R$$

or

$$C_p/C_v = 1 + (R/C_v). \tag{3.44}$$

Since, for monatomic gases, $C_v = \frac{3}{2}R$ it follows that the ratio of C_p/C_v for such gases is $1 + (\frac{2}{3}) = 1.667$. The above will be true only if the internal energy of the gas is independent of the volume, that is, for an ideal gas. It may be shown for the general case, namely, for any gas, liquid or solid, that

$$C_p - C_v = \left[p + \left(\frac{\partial U}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial T}\right)_p = \frac{\alpha^2 vT}{\beta}, \tag{3.45}$$

where α is the coefficient of thermal expansion and β is the compressibility. Since for an ideal gas $pv = RT$ this equation reduces to $C_p - C_v = R$. Hence $C_p/C_v = 1.667$. This ratio is found for all monatomic gases. For polyatomic gases, as C_v increases the ratio C_p/C_v falls. Thus, for nitrogen it is 1.414, for carbon dioxide 1.303, for ammonia 1.317, for benzol 1.13 and for ether vapor 1.08.[1]

18. **Thermal Conductivity of Gases:** Specific thermal conductivity, K, is defined as the number of calories required to enter unit area of plane A in order that the temperature of planes A and B may remain constant at $T + 1°$ and $T°$ respectively, when the planes are unit distance apart. It is apparent that the carriage of heat from one plane to another will be a function of the number, n, and velocity, u, of the gas molecules, the mean free path, l, and also the heat capacity, which in its turn is dependent on the number of degrees of freedom, f, of the gas molecule. This is expressed by the relation

$$K = k \cdot l \cdot u \cdot f \cdot n \tag{3.46}$$

or, since u varies inversely as $\sqrt{M}$, where M is the molecular weight,

$$K = k'lf/\sqrt{M}. \tag{3.47}$$

This relationship is shown by the following table.

It will be noted that with an almost ten-fold variation in thermal conductivity shown by helium and argon the quantity, k', remains sensibly constant (8.6, 8.8), the number of degrees of freedom, f, being the three degrees of freedom of translatory motion. With the diatomic gases, more than three degrees of freedom are required. With $f = 5$ a

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[1] For experimental methods of measuring this ratio see Mack: Laboratory Manual of Physical Chemistry, D. Van Nostrand Co., New York, 1934.

TABLE 3.4

THERMAL CONDUCTIVITIES

Gas	$K \times 10^6$	f	$\sqrt{M}$	k'
He	336.0	3	2.00	8.6
H_2	397.0	5	1.41	6.8
CO	54.2	5	5.29	6.7
N_2	56.6	5	5.29	6.8
O_2	57.0	5	5.66	6.8
Ar	39.0	3	6.32	8.8
CO_2	33.7	6	6.63	6.5

reasonable constancy of k' is obtained with wide variations in thermal conductivity. With the triatomic molecule, CO_2, six degrees of freedom are indicated. Again, with the diatomic and polyatomic molecules we must look for additional degrees of freedom in the intra-molecular motions.

19. **Expansion of Gases:** In discussing the heat capacity at constant volume of a monatomic gas we assumed that all the heat energy absorbed was converted into kinetic energy of the gas molecules. At constant pressure, we considered also the energy involved in the expansion of the gas. There is, in addition, one other mode of energy consumption which must be considered. If the gas molecules possess an attraction for one another, energy must be expended to overcome such attraction when the gas is expanded, that is to say, when the distance between the individual molecules is increased. Gay-Lussac first attempted to ascertain whether such an effect existed by allowing the gas from one vessel, I, to stream into an evacuated vessel, II, until pressure equilibrium was established in the complete system, I + II. By having the system immersed in water in a calorimeter he hoped to be able to notice any temperature variation. In his experiments, Gay-Lussac noted no such change in temperature and concluded that the effect of attraction among the molecules was negligible. More exact experiments show that a very small decrease in temperature always occurs. If the temperature is to be maintained constant, heat must be absorbed, that is, $q > 0$. But since, in this experiment, there is no communication between the gas and the surroundings, the expansion of the gas does no work on the surroundings and $w = 0$. Hence by the first law $\Delta U = q > 0$ or for real gases $(\partial U/\partial v)_T > 0$. It is further found that the lower the pressure in vessel I the smaller is the temperature change, that is, the smaller is the change in internal energy necessary to maintain constant temperature during the expansion and, on extrapolation to zero pressure, $\Delta U = 0$. Hence for an ideal gas $(\partial U/\partial v)_T = 0$.

20. **Joule-Thomson Effect:** Experiments by Joule and Thomson (later

Lord Kelvin) gave further evidence concerning the conclusions drawn above from Gay-Lussac's work. The difference between the two experiments is that in Gay-Lussac's system no external work is involved and for real gases the decrease in temperature on expansion is due to the internal work against the forces of attraction. In the Joule-Thomson experiments external work may be involved since the gas communicates with the surroundings.

The experimental method employed by Joule and Thomson was to cause the change from a high pressure p_1 to a lower pressure p_2 to occur slowly by interposing a resistance to the gas flow in the form of a porous plug. As the gas passed through the plug under compression on the high pressure side, the volume on the low pressure side was increased. Diagrammatically this is illustrated in Fig. 3.5. For a volume decrease

FIG. 3.5

v_1 on the high pressure side and a volume increase v_2 on the low pressure side, the external work w done by the gas on the surroundings is

$$w = p_2v_2 - p_1v_1. \tag{3.48}$$

The apparatus being insulated, the process is adiabatic. Hence if U_1 and U_2 are the corresponding energies it follows from the first law, since $q = 0$, that

$$U_2 - U_1 = -w = p_1v_1 - p_2v_2$$

or

$$U_2 + p_2v_2 = U_1 + p_1v_1$$

or

$$H_2 = H_1, \tag{3.49}$$

that is, the heat content remains constant.

The change in temperature which occurs may be expressed by the Joule-Thomson coefficient $(\partial T/\partial p)_H$. Since H is a function of p and T

$$dH = (\partial H/\partial T)_p dT + (\partial H/\partial p)_T dp \tag{3.50}$$

or, since $dH = 0$

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{C_p}$$

$$= -\frac{\left(\frac{\partial U}{\partial p}\right)_T + \left(\frac{\partial (pv)}{\partial p}\right)_T}{C_p} \tag{3.51}$$

and the magnitude of the Joule-Thomson coefficient is dependent on the isothermal variation of U and of pv with pressure since C_p is a definite numerical quantity. Now

$$(\partial U/\partial p)_T = (\partial U/\partial v)_T(\partial v/\partial p)_T. \tag{3.52}$$

It has been shown that for real gases $(\partial U/\partial v)_T$ is always positive. On the other hand $(\partial v/\partial p)_T$ is negative. $(\partial U/\partial p)_T$ is therefore negative. The variation of pv with p will be discussed in detail later where it will be seen that at ordinary temperatures and moderate pressures $(\partial(pv)/\partial p)_T$ is negative for most gases with hydrogen and helium as conspicuous exceptions. Hence under these conditions the Joule-Thomson coefficient will normally be positive, but negative for hydrogen and helium. At sufficiently high pressures $(\partial(pv)/\partial p)_T$ becomes positive for all gases. The two factors $(\partial U/\partial p)_T$ and $(\partial(pv)/\partial p)_T$ may thus enhance or oppose each other. It may be stated that there exists for every gas a characteristic temperature at which $(\partial T/\partial p)_H$ is zero; below this temperature the coefficient is negative and above it, positive. Table 3.5 gives the value of the coefficient for several gases.

21. **Approximate Molecular Weights:** The fundamental gas law can be utilized to determine the approximate molecular weights of gases and vapors. If we write equation (3.12) in the form

$$pv = nRT,$$

where n is the number of gram molecules of gas or vapor, we can substitute for n the quantity w/M where w is the mass and M the molecular weight of the gas. The equation becomes $pv = wRT/M$ and by determining the four quantities p, v, w, and T, the molecular weight may be calculated. The equation is the basis for the Dumas, Victor Meyer, and Lumsden methods of molecular weight determination.[1]

22. **Apparent Deviations from the Ideal Gas Law:** The vapors of such substances as sulfur, iodine, phosphorus pentachloride and ammonium chloride, investigated by Dumas, do not conform to the equation $pv = nRT$. Thus, ammonium chloride, in the vapor state, gives pressures greatly exceeding those calculated from the above equation. The abnormally high pressure can be accounted for by the dissociation of the molecules in the vapor state into ammonia and hydrogen chloride according to the equilibrium

$$\underset{1-\alpha}{NH_4Cl} \rightleftharpoons \underset{\alpha}{NH_3} + \underset{\alpha}{HCl}.$$

If this chemical equilibrium exists and α is the fraction of ammonium

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[1] For the experimental methods involved in such determinations, see Mack: Laboratory Manual of Physical Chemistry, D. Van Nostrand Co., 1934.

TABLE 3.5

JOULE-THOMSON COEFFICIENTS

Gas	t° C.	$k = \Delta T/\Delta p$ at Pressure:				
		0–6	2	10	15	40 atm.
Hydrogen........	6.8	−0.030[a]				
	90.1	−0.044[a]				
Carbon Dioxide...	0	1.35[a]				1.46[c]
	20	1.14[a]	1.21[b]	1.31[b]	1.37[b]	1.20[c]
	40	0.96[a]				1.04[c]
	100	0.62[a]				
		$p = 0$	25	50	100	150 Kg./cm.²
Air[d]............	−55	0.44	0.40	0.3	0.28	0.18
	0.6	0.27	0.25	0.24	0.19	0.16
	49	0.20	0.18	0.17	0.15	0.12
	150	0.09	0.09	0.07	0.06	0.05
	250	0.02	0.02	0.02	0.01	0.01
		$p = 1$	4.5	6.4 m. Hg.		
Air[e]............	0	0.399	0.378	0.359		
	50	0.298	0.278	0.270		
	100	0.224	0.210	0.213		

[a] Joule-Thomson.

[b] Natanson, *Wied. Ann.*, **31**, 502 (1887).

[c] Kester, *Phys. Rev.*, **21**, 260 (1905).

[d] Noell, Forsch. Arbeiten No. 184 (1916).

[e] Hoxton, *Phys. Rev.*, **13**, 438 (1919).

chloride dissociated, the total number of gram molecules present will be $n(1 + \alpha)$, so that

$$pv = n(1 + \alpha)RT \qquad (3.53)$$

and the gas law is found to hold when the chemical dissociation is taken into account. That this chemical dissociation actually occurs is proven by diffusion experiments carried out with the apparatus represented in Fig. 3.1. It was found that the gas which diffused through the capillary tube contained an excess of ammonia. This can only be the case if the ammonium chloride is split up into hydrogen chloride and ammonia molecules, in which case the lighter ammonia molecules would diffuse more rapidly. Similar phenomena of chemical association and dissociation were found to occur in the gases investigated by Dumas.

23. **Real Deviations from the Ideal Gas Law:** With increased refinement in experimental technique it was found that the gas laws of Boyle and Gay-Lussac did not hold exactly. For any given gas, the magnitude of the discrepancy increased with increase in pressure and lowering of temperature, with every indication that the gas law would hold exactly only at infinite dilution of the gas. As an example of the magnitude of the variation, a number of values for M for methyl ether, determined at various temperatures and pressures, and calculated on the basis of the ideal gas law $pv = wRT/M$, are given in Table 3.6, and represented in the accompanying diagram, Fig. 3.6.

TABLE 3.6

Temp.	Pres.	M	Temp.	Pres.	M	Temp.	Pres.	M
−19.1	76.00	47.695	0.0	76.00	47.22	98.0	76.00	46.49
	62.22	47.42		73.80	47.19		74.37	46.48
	33.83	46.84		35.63	46.59		34.31	46.30
	19.54	46.47		18.55	46.38			
	9.76	46.365	21.5	76.00	46.94			
−14.5	76.00	47.53		35.28	46.475			
	74.12	47.495		19.49	46.255			
	37.73	46.83		18.98	46.25			

The figure shows that the isothermal M curves converge to the same value for M at $p = 0$, the value there being exactly that demanded by the theory. At all other values of the pressure p, deviations exist and, for equal values of p, they are greater the lower the temperature.

These discrepancies, which are illustrated by the above example, but which are found to exist to a greater or less extent for all gases, cannot be explained on the basis of the chemical association or dissociation of the molecules. Diffusion experiments do not reveal any such influences at work as were found with ammonium chloride. Some other effect, or effects, must be the cause of these departures from the ideal gas law.

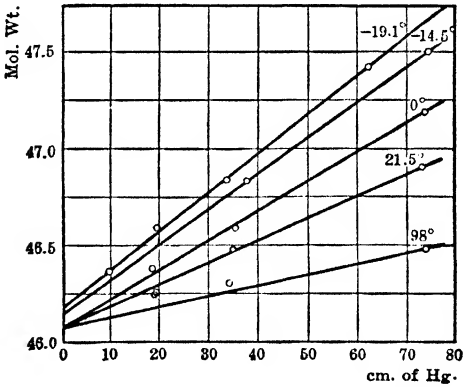

Fig. 3.6. Isothermal Molecular Weight Curves for Methyl Ether

24. Van der Waals's Equation: A careful study of Fig. 3.7, which shows how the product *pv* varies with pressure for a number of gases, reveals at once that the deviations of real gases from ideality must be at least twofold. The *pv* curve for an ideal gas would be a horizontal straight line showing constant *pv* for varying pressure. Against this, hydrogen and helium show *pv* increasing with increasing pressure, whilst for all other gases *pv* first decreases to a minimum, then increases again. Two factors, one causing an increase in *pv* and one causing a decrease, are to be sought.

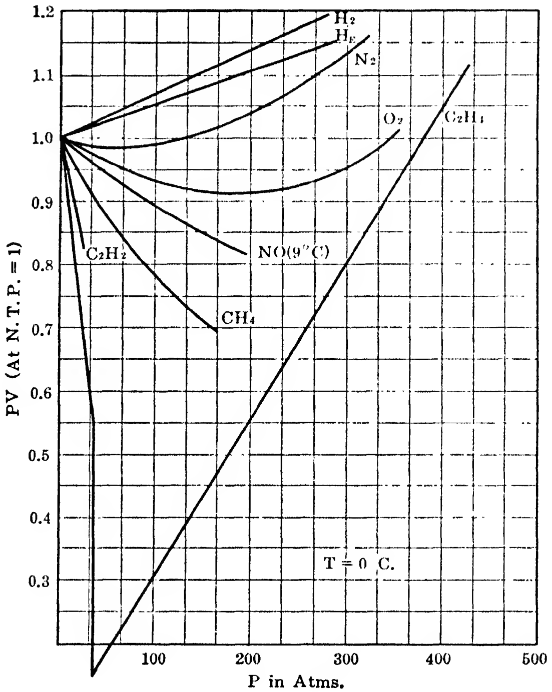

FIG. 3.7

The simplest method of accounting for these deviations was put forward by van der Waals in 1873. The two factors suggested were (1) the volume of the molecules themselves and (2) the existence of attractive forces between molecules.

Since the molecules are not points but possess finite dimensions, the actual free space in a volume, v, in which the molecules can move will be $(v - b)$ where b is related to the volume of the molecules themselves, since that space already occupied by one molecule is not at the same instant available to another.

The Joule-Thomson effect and the variation of the viscosity of a gas with temperature, as already discussed, indicate the existence of attractive forces between molecules. These attractions, pulling the molecules together, actually assist the external pressure which pushes them together and may be considered to correspond to an internal pressure. The range of action of these intermolecular forces is very small and thus they are effective only when molecules approach each other closely, that is to say, virtually collide. It has been shown that the probability of a collision between two molecules is proportional to the square of the number of molecules per unit volume. Assuming that the less probable collision of more than two molecules does not contribute appreciably to the attractive force, the force should vary directly as the square of the gas concentration or, in other words, be inversely proportional to the square of the molar volume. Now a molecule in the interior of the gas is surrounded uniformly in all directions by other molecules whose attractions for it will therefore neutralize each other. A molecule in the surface of the gas, however, will be drawn towards the body of the gas. Hence the pressure actually exerted by attracting molecules is less than would be expected for non-attracting ideal molecules. The deficit is the internal pressure which is proportional to the attractive force or equal to a/v^2 where a is a constant characteristic of the gas. Making this correction together with the volume correction factor, the ideal equation becomes

$$(p + a/v^2)(v - b) = RT, \tag{3.54}$$

which is the van der Waals equation.

The equation may be expanded as follows

$$pv = RT + bp - a/v + ab/v^2. \tag{3.55}$$

For moderate pressures where v is large, the last term ab/v^2 may be neglected since a and b are small. Hence the equation may be written

$$pv = RT + p(b - a/pv) \tag{3.56}$$

which, taking pv in the last term as approximately RT, becomes

$$pv = RT + p(b - a/RT). \tag{3.57}$$

This form of the equation explains the initial slopes of the $pv - p$ curves in Fig. 3.7, for when $b > a/RT$, pv will increase with p and when $b < a/RT$, pv will decrease as p increases. The value of the constant a is relatively small for hydrogen and helium, hence pv increases with p. For other gases a is much larger and pv decreases. It can be seen, however, that temperature plays an important role in this connection for, whatever the values of a and b, if T is large enough a/RT will always be less than b while for low temperatures the reverse will be the case. In Fig. 3.8 $pv - p$ curves for nitrogen at a series of temperatures are given to illustrate what occurs with all gases in the lower pressure range, namely, pv increasing at high temperatures and decreasing at low temperatures. It is apparent that there exists a temperature for every gas such that $b = a/RT$. In this case $pv = RT$; the gas at small pressures behaves ideally. This is called the Boyle temperature or simply the Boyle point. For nitrogen, the value is about 55° C.

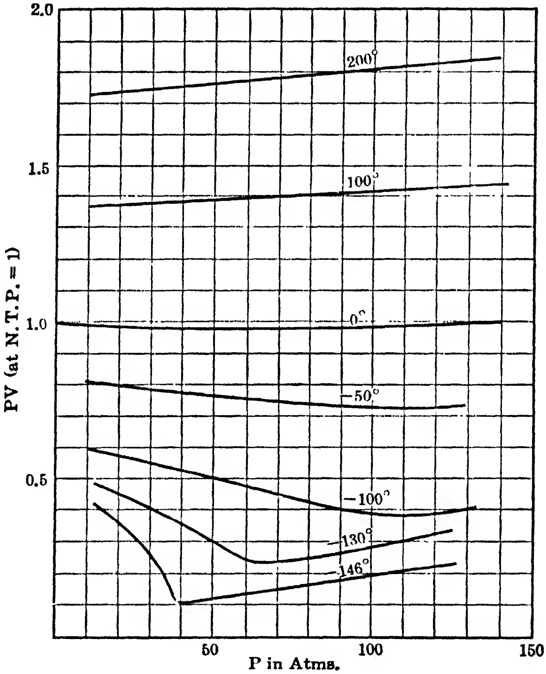

Fig. 3.8

In the higher pressure range, where the molar volume is small, the term ab/v^2 is no longer negligible and at lower temperatures pv passes through a minimum and increases again. Thus when $bp - a/v + ab/v^2 = 0$, pv again has the ideal value RT. It would, however, be incorrect to say that the gas is ideal simply because $pv = RT$, since the slope of the curve at this point does not correspond to pv being independent of p. Similarly at the minimum point of the curve although pv is here independent of p since the tangent to the curve is horizontal, the value of pv is less than RT; the gas is not ideal.

(*b*) *Adiabatic expansion:* In this case, $q = 0$. Hence

$$\Delta U = -w = -p\Delta v.$$

Since, in the expansion, work is done by the system on the surroundings, the temperature of the gas must fall. The magnitude of the decrease in temperature may be calculated when it is recalled that $\Delta U = C_v \cdot \Delta T$. Hence, $C_v \cdot \Delta T = -p \cdot \Delta v$. For an infinitesimal change,

$$C_v dT = -pdv \tag{3.65}$$

and, on integration,

$$C_v(T_1 - T_2) = \int_{v_1}^{v_2} pdv. \tag{3.66}$$

This assumes that C_v is a constant and is exact only for monatomic gases. Alternatively, since $pv = RT$,

$$C_v dT/T = -Rdv/v \tag{3.67}$$

that is

$$C_v d \ln T = -Rd \ln v$$

or

$$C_v \ln \frac{T_2}{T_1} = R \ln \frac{v_1}{v_2} \cdot \tag{3.68}$$

Since $C_p - C_v = R$ and putting $C_p/C_v = \gamma$

$$\ln (T_2/T_1) = (\gamma - 1) \ln (v_1/v_2)$$

or

$$T_1 v_1^{\gamma - 1} = T_2 v_2^{\gamma - 1}. \tag{3.69}$$

Whence

$$p_1 v_1^{\gamma} = p_2 v_2^{\gamma}. \tag{3.70}$$

In an adiabatic compression the gas temperature will rise to an extent corresponding to the equations already given for adiabatic expansions.

EXERCISES (3)

1. The volume of one mole of a perfect gas is 22,414 ccs. at 0° C. and 760 mms. Calculate its volume at 25° C. and 755 mm.

2. Calculate the volume of 10 g. of helium (assumed ideal) at 25° C. and 760 mm.

3. Calculate (*a*) the average velocity, (*b*) the root mean square velocity, and (*c*) the most probable velocity of a hydrogen molecule at 25° C., in meters per second.

4. Calculate the barometric pressure at a height of 1 kilometer above sea level assuming uniform temperature of 25° C. in the atmosphere.

5. Calculate the number of collisions made by one hydrogen molecule per second at (*a*) 0° C. and 760 mm., (*b*) 0° C. and 0.01 mm. What is the mean free

path in each case? The diameter of the hydrogen molecule may be taken as 2×10^{-8} cm.

6. Calculate the total number of collisions occurring under the conditions indicated in problem 5.

7. What fraction of the molecules of a gas at 300° K. has an energy greater than 30,000 calories per mole?

8. What is the weight of hydrogen striking one square centimeter of a nickel surface at 200° C. and 200 mm. pressure?

9. When 377 ccs. of electrolytic gas ($2H_2 + O_2$) were adiabatically compressed to 30.2 ccs. the mixture exploded. The initial temperature was 18° C. and the pressure, one atmosphere. The mean value of $C_p/C_v = \gamma = 1.4$. Calculate the temperature and pressure at the moment of the explosion.

10. Expressing pressure in atmospheres and taking the volume of the gas at 0° C. and one atmosphere as unity the van der Waals constants a and b for methane are 0.00449 and 0.001910 respectively. Calculate the pv product for methane at 0° C. and 100 atmospheres and compare your results with Fig. 3.7.

CHAPTER 4

THE ATOMIC CONCEPT OF ENERGY—ENERGY QUANTA

1. **Principle of Equipartition of Energy:** The average kinetic or translatory energy of a gas is representable in terms of its motion along three co-ordinates of that motion and is equal to $\frac{1}{2}kT$ per molecule for each of the three directions in which it can move. This conclusion is a special application of a general principle, due to the theoretical work of Maxwell and Boltzmann, known as the principle of Equipartition of Energy. It was extended by Boltzmann not only to kinetic energies but also to potential energies when these latter are representable as the sum of quadratic terms analogous to the $\frac{1}{2}mu^2$ terms which we have used for kinetic energies. For the total energy of a system we assign a quantity $\frac{1}{2}kT$ per molecule for each degree of freedom of kinetic energy and also for each term in the expression for potential energy which can be represented in the form $\frac{1}{2}aq^2$.

It has been shown that the three degrees of freedom of kinetic energy are insufficient to describe the energies of diatomic or polyatomic molecules, as the data on heat capacity and thermal conductivity have already indicated. In the case of diatomic gases, Boltzmann pointed out that the molecules may be regarded as dumb-bell structures and that collisions may cause them to rotate about the center of gravity of the structure. Such rotation may occur with two degrees of freedom of rotation. Together with the translatory motion this represents five degrees of freedom in all and, hence, by the principle of Equipartition of Energy, the total energy should be $\frac{5}{2}RT$ per mole and the heat capacity at constant volume ought to be $\frac{5}{2}R$. Tables 3.3 and 3.4 have already given experimental evidence in support of this deduction.

Certain diatomic gases, however, show heat capacities at constant volume in excess of $\frac{5}{2}R$, notably chlorine, Table 3.3, and, in one case discovered much more recently, namely hydrogen, at low temperatures ($<273°$ K.) the heat capacity falls steadily from $\frac{5}{2}R$ to the $\frac{3}{2}R$ characteristic of a monatomic gas. Values in excess of $\frac{5}{2}R$ suggest at once another type of energy with other degrees of freedom, for example, vibrational energy, due to the vibrations of the atoms about their mean positions at a given distance from one another in the molecule. Such vibrational energy would involve not only kinetic but also potential energy. All these observations suggest, however, two problems. Why do diatomic molecules at room temperature indicate, by their heat capacities, that vibrational energy is in some cases present and in other cases absent? Secondly, why do most diatomic gases show rotational energy while hydrogen at low temperatures appears to lose its rotational energy? The answers to such questions require the development of an atomic concept of energy, the concept of energy quanta.

2. Origin of the Quantum Concept. Radiation: The concept of quanta originated with Planck in 1901 in an effort to interpret experimental observations on the distribution of energy in black-body radiation. A black-body, or full radiator, has the property that, for monochromatic radiation of any wave length, λ, the energy emitted per unit area at any temperature is equal to that absorbed. The black-body is an ideal radiator but certain materials, such as lamp black, approach the ideal surface very closely. Experiments to determine the laws of distribution of black-body radiation were carried out with great precision by Lummer and Pringsheim in the years 1897–1901. Their results are shown diagrammatically in Fig. 4.1 where the ordinates represent the absolute values of the energy emitted, E_λ, that is, the energy emitted per square centimeter of the black-body per second in the wave length interval between λ and $\lambda + d\lambda$. The abscissas are wave lengths of radiation expressed in $\mu = 10^{-4}$ cm. These curves show maxima of emission at wave lengths dependent on the temperature. At 723° K. the maximum is about 4μ and the radiator shows a red color. At 1646° K. the maximum emission is at wave length 1.78μ and the radiation has changed to a bright white color.

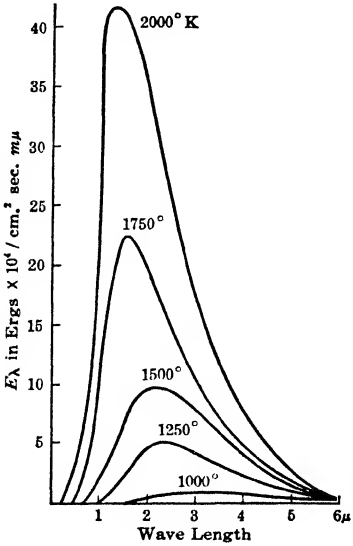

FIG. 4.1. The Lummer-Pringsheim Data on Radiation Distribution for a Black Body

3. Stefan-Boltzmann Law: The area under any given curve in Fig. 4.1 represents the total energy emitted per square centimeter of the black-body per second at a given temperature. The energy emitted obviously increases rapidly with temperature. The actual relation was pointed out empirically by Stefan and interpreted by Boltzmann. The Stefan-Boltzmann Law states that the total energy flux, E_T, from a black-body is proportional to the fourth power of the absolute temperature. Thus

$$E_T = \int_0^\infty E_\lambda d\lambda = \sigma T^4. \tag{4.1}$$

If E_T be expressed in ergs per sq. cm. per sec. the value of the proportionality factor σ is 5.709×10^{-5}. Since radiant energy is propagated in space with finite velocity there must be, in any given volume, a definite amount of energy, that is, there exists a certain density of radiation.

This is represented by u_λ or u_ν as the density of radiation emitted in the wave length interval between λ and $\lambda + d\lambda$ or the frequency interval between ν and $\nu + d\nu$. The value of the energy will depend on the size of the interval $d\lambda$ or $d\nu$. Thus the energy density of the total radiation, u_T, at a given temperature is given by

$$u_T = \int_0^\infty u_\nu d\nu = \alpha T^4 \tag{4.2}$$

and follows the Stefan-Boltzmann Law. The constant α is related to σ by the relation $\alpha = 4\sigma/c$ where c is the velocity of light.

4. **The Distribution of Radiation:** Numerous efforts were made to express the density of radiation of a particular wave length as a function of the temperature. An attempt by Lord Rayleigh in 1900, refined by Jeans in 1909, *based upon the principle of equipartition of energy* led to the Rayleigh-Jeans Distribution Equation:

$$u_\lambda d\lambda = (8\pi kT/\lambda^4)d\lambda \tag{4.3}$$

or

$$E_\lambda d\lambda = (2\pi ckT/\lambda^4)d\lambda. \tag{4.4}$$

The principle of equipartition leads to the conclusion that the intensity of radiation must increase continuously with decreasing wave length and must become infinitely great for very small wave lengths. The Lummer-Pringsheim data of Fig. 4.1 do not confirm this. Actually the Rayleigh-Jeans formula only applies to the data at any given temperature in the region of longer wave lengths such as the infra-red and heat radiations.

5. **Planck's Distribution Law:** In view of this and other failures to account for the experimental data of black-body radiation, Planck abandoned in 1901 the classical method of approach to the problem of radiation. Instead he assumed (*a*) that in a black-body enclosure there existed linear oscillators or vibrators of molecular dimensions, (*b*) that a vibrator cannot take up energy continuously but discontinuously in multiples of a unit quantum ϵ which is in its turn proportional to the frequency, ν, the proportionality factor being a universal constant, h. Hence the fundamental equation for the quantum,

$$\epsilon = h\nu, \tag{4.5}$$

where $\nu = c/\lambda$, c being the velocity of light and λ the wave length.

Planck deduced (see Appendix 2) that the average energy, $\bar{\epsilon}$, of a vibrator of frequency ν is given by the equation,

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} = \frac{\epsilon}{e^{\epsilon/kT} - 1}\,. \tag{4.6}$$

This expression is of interest because it displays the nature of the break, made by the Planck postulates, from the principle of equipartition of energy. If we let the quantity ϵ/kT approach zero, that is for low values of ϵ or high values of temperature, we obtain on expanding, according to the exponential theorem,

$$\bar{\epsilon} = \frac{\epsilon}{1 + \frac{\epsilon}{kT} + \cdots - 1} = kT, \tag{4.7}$$

which is the result required for a vibrator on classical equipartition theory for one degree of freedom of kinetic and one of potential energy. On the other hand, at sufficiently low temperatures the denominator tends towards infinity and the average value of the energy, $\bar{\epsilon}$, approaches zero. The principle of equipartition of energy thus becomes a limiting law valid for low frequencies or for long wave lengths or alternatively for high temperatures. This is precisely the region in which the Rayleigh-Jeans Law finds its approximate validity.

The Planck expression for the density of radiation of a given frequency becomes:

$$u_\nu d\nu = \frac{8\pi h\nu^3 d\nu}{c^3(e^{h\nu/kT} - 1)}\,. \tag{4.8}$$

Since $\nu = c/\lambda$, $d\nu = -\,cd\lambda/\lambda^2$ and

$$u_\nu d\nu = -\,u_\lambda d\lambda = -\,\frac{8\pi hcd\lambda}{\lambda^5(e^{hc/\lambda kT} - 1)}\,. \tag{4.9}$$

This equation was found to reproduce excellently the data of experiment on black-body radiation. The proportionality constant, Planck's constant, h, was found to have the value $h = 6.55 \times 10^{-27}$ erg. sec. It has the dimensions of energy × time, has, therefore, the dimensions of action. Since the frequency has the dimensions of reciprocal time, the product $h\nu = \epsilon$ is an energy quantity.

The concept of an energy quantum developed thus by Planck to account for radiation phenomena led immediately to striking developments in all branches of science dealing with the energy of atomic and molecular systems. The more important of these as they relate to physical chemistry will now be briefly sketched.

6. The Photo-Electric Effect: Lenard, in 1902, investigated the phenomenon known as the photo-electric effect, the liberation of electrons from metal surfaces by impinging ultra-violet light. The electrons were found to have velocities which were independent of the intensity of the light but which were dependent on the frequency of the light, increasing in velocity with increasing frequency. If the electronic velocities were measured by the voltage V required to prevent all the liberated electrons from leaving the metal it was found that V varied linearly with the frequency of the light, or

$$V = C\nu - V_0, \tag{4.10}$$

where C and V_0 are positive constants, V_0 characteristic of the metal employed, C independent of the metal and the same for all metals. If we multiply equation (4.10) by e, the electronic charge, and rearrange, we obtain

$$e(V + V_0) = Ce\nu. \tag{4.11}$$

Now eV is an energy quantity equal to the kinetic energy of the electrons leaving the metal with the highest velocity. It follows, therefore, that the product $Ce\nu$ must also have the dimensions of energy. Since the frequency ν has the dimensions of reciprocal time, Ce must then have the dimensions of action as does, also, Planck's constant, h. As C is a universal constant and e also, the product Ce must also be a universal constant. Measurements of the photo-electric effect showed that the constant Ce has the same magnitude as $h = 6.55 \times 10^{-27}$ erg. sec. We can therefore express the relationship between the electronic velocities v and the frequency of the impinging radiation by means of the equation

$$eV = \tfrac{1}{2}mv^2 = h\nu - h\nu_0. \tag{4.12}$$

The quantity $h\nu$ measures the energy absorbed by the electron from the radiation; $h\nu_0 = eV_0$ is the work necessary to get the electron through the surface of the metal. The potential, V_0, is known as the "*work function*" for electrons passing through the surface.

If X-radiation be used instead of ultra-violet light to liberate the electron, the frequency of the X-rays is so large that the quantum $h\nu$ is very large compared to the quantity, $h\nu_0$. Hence, to a close approximation, the velocity of the liberated electron is given by the expression

$$\tfrac{1}{2}mv^2 = h\nu. \tag{4.13}$$

The converse of this process also occurs. If we direct a stream of electrons against any solid, X-rays are produced, and it was early discovered that the "hardness" (frequency) of the rays increases with the voltage applied to the impinging electrons.

Measurements of the photo-electric effect constitute one important means for determining the precise value of Planck's constant, h.

7. Einstein's Concept of Light Quanta: In 1905 Einstein definitely proposed that light might be regarded as atomic or corpuscular, the energy of the individual light quanta being given by the product of Planck's constant, h, and the frequency of the light. In the photoelectric effect, one light quantum liberated one electron. This explained why the number of emitted electrons was proportional to the intensity of the light. In photo-chemistry one light quantum activated one atom or molecule of the photo-active constituent. For each elementary process involving simultaneously light energy, one quantum of the energy in question must be either produced or consumed. The Einstein proposal was therefore also fundamental in the theoretical treatment of fluorescence and luminescence produced by chemical action; it provided the setting in which the Bohr theory of spectra could be developed.

8. **Bohr Theory of Atomic Spectra and the Quantum Concept:** The emission of line spectra by atomic systems in states of excitation obtained a quantum interpretation in the postulate put forward by Bohr in 1913 that when an atom falls from one energy level, E_n, to a lower level, E_m, the frequency of the emitted radiation is expressible by the equation

$$E_n - E_m = h\nu. \tag{4.14}$$

A quantum of light energy, $h\nu$, is also involved when absorption raises an atom from a lower to a higher energy level. We shall illustrate the applicability of this postulate in a discussion of the spectrum of atomic hydrogen.

In 1885 Balmer pointed out that, in the case of the ordinary spectrum of hydrogen, consisting of a series of lines known as H_α, H_β, H_γ, H_δ, etc., extending from the red into the ultra-violet region, the wave length of each line of the series then known could be represented satisfactorily by a formula to which we shall give the form

$$\nu = \frac{c}{\lambda} = Rc\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \tag{4.15}$$

where n has the values 3, 4, 5 and 6 for H_α, H_β, H_γ, H_δ. In 1890 Rydberg showed that for a number of elements (alkalis and alkaline earths) the spectral lines of each could be arranged in series and expressed by a formula similar to that just considered and in which the quantity R was approximately constant. Rydberg and subsequently Ritz showed that two different series each described by a Balmer formula could be combined to give yet another series with emission lines of observed frequencies. Thus, we might have a whole group of series representable by a general formula

$$\nu = Rc\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{4.16}$$

Such series have actually been observed. Lyman found a series of hydrogen lines in the ultra-violet in which $m = 1$; Paschen found a series in the infra-red in which $m = 3$, Brackett one in the infra-red with $m = 4$, and Pfund one in which $m = 5$. In each series m is constant and n takes on successive values $m + 1$, $m + 2$, $m + 3$, etc. If we multiply each side of our general formula by Planck's constant, h, we obtain the expression

$$h\nu = Rch(1/m^2 - 1/n^2). \qquad (4.17)$$

Comparing this with the Bohr postulate (4.14), $h\nu = E_n - E_m$, where E_n and E_m correspond to the energy of the system before and after emission of the quantum $h\nu$, it follows also that, apart from an additive constant, we may write

$$E_n = - Rch/n^2, \qquad (4.18)$$

the negative sign indicating that the energy of the atom increases as n increases. We reproduce in Fig. 4.2 an energy diagram for hydrogen which indicates some of these transitions from a higher to a lower energy level. The Bohr postulate is really a two-fold postulate (*a*) that the atoms exist and can only exist in a set of discrete states corresponding to a discontinuous series of energy values and (*b*) that transitions from one state to another involve absorption or emission of light quanta of magnitude, $h\nu_{(m,\ n)}$. Furthermore, the development of the quantum postulate led to the identification of m and n as the quantum states of the atom, the orbits which the electron occupied after and before the transition. Orbits could be either circular or elliptical. In the nth quantum state, n different orbits were allowed, one circular and $n - 1$ elliptical orbits. All of the ellipses had their semi-major axis equal to the radius of the circular orbit of the nth state. Two quantum numbers are required to determine the major axis and the eccentricity. In more complex atoms than hydrogen the electrons are subject to magnetic and electric fields due to other electrons in the atom. To specify these effects an additional quantum number is necessary. Finally, to specify the spin ascribed to electrons a fourth quantum number is employed.

9. **Ionization by Light Absorption:** There is a practical limit to the quantized absorption of light energy by atomic systems which obtains when $n = \infty$ in the series relationship $h\nu = Rch(1/m^2 - 1/n^2)$. As we have seen, the absorption of light produces a change from a stationary state of lower energy to one of higher energy and these changes are revealed in the form of absorption line spectra. The line spectrum of absorption by atoms is much simpler than the emission spectrum, because, in an unilluminated atomic system, the great majority of the atoms are present in the stationary state of lowest energy, the normal state, and such atoms can only undergo a few transitions from that state to those of higher energy. Thus, in the case of sodium as an example, normal sodium atoms can absorb light of the two wave lengths 5891.8 and 5897.8 Å[1] respec-

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[1] Wave lengths are expressed in Ångstrom units = 10^{-8} cm.

tively, the first *resonance lines* of the sodium atom. The energy gained is, according to the quantum relation, $E_n - E_m = h\nu$ = approximately 2.09 electron-volts or 48.2 kcal. per gram atom. An electron-volt (e.v.) is the kinetic energy acquired by an electron when accelerated through a potential of one volt. For one faraday of electrons this energy will be 96,494 volt coulombs = 96,494 joules = 23.06 kcal. Sodium atoms in these excited states, so-called *excited atoms*, may re-emit their energies as fluorescent light of the frequencies absorbed, yielding therefore the same two lines in emission, the well-known D sodium lines. Normal sodium atoms can also absorb the second resonance lines (3306 – 3302 Å)

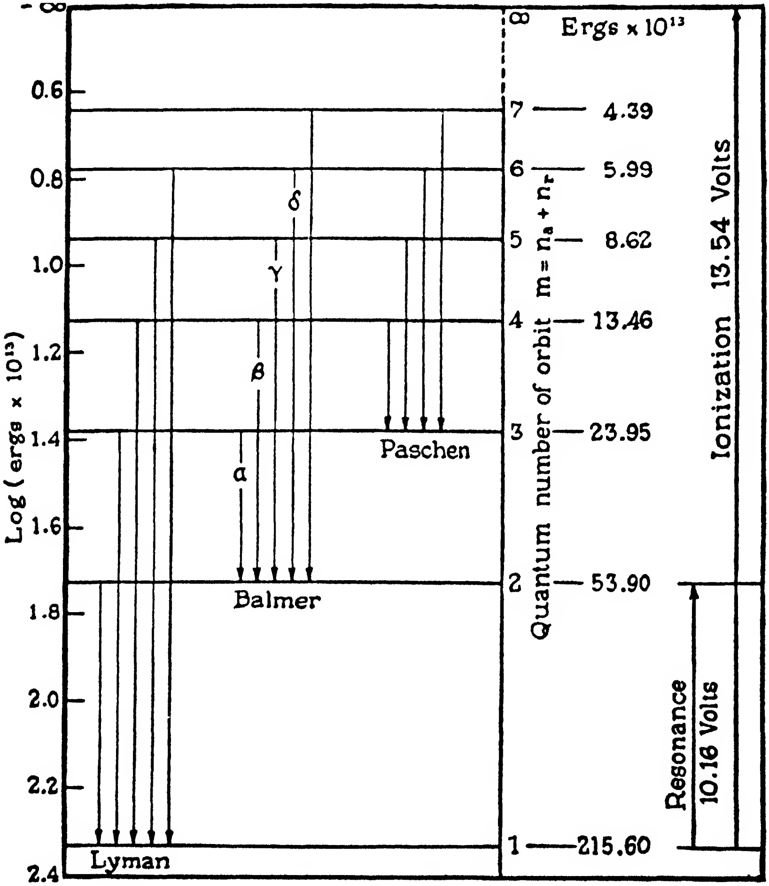

FIG. 4.2. Energy Diagram for Hydrogen Atom

corresponding to 86.0 kcal. of excitation energy. Still further in the ultra-violet the absorption of light of wave length 2412.8 Å frees the electron from the rest of the atom, and ionization of the atom is produced. The energy corresponding to this frequency of light is for one mole, $Nh\nu = Nhc/\lambda = 2.837 \times 10^{-3}/\lambda$ kcal. when λ is expressed in cm. Thus for $\lambda = 2412.8$ Å $= 2412.8 \times 10^{-8}$ cm., $Nh\nu = 117.6$ kcal. $= 5.10$ e.v., which is the ionization potential of sodium. At this point, the character of the spectrum changes. The absorption spectrum is no longer a line spectrum but a spectrum showing continuous absorption. The quantum restriction of Bohr is no longer operative. The explanation for this is that any light of higher frequency than this limiting frequency produces a dissociation of the atom into an ion and an electron

$$\mathrm{Na} + h\nu_c = \mathrm{Na}^+ + e^-.$$

All energy in excess of the critical energy, $h\nu_c = 5.10$ e.v., can be absorbed, the excess over that required for ionization being converted into the kinetic energy of the two separating fragments Na^+ and e^-. In atomic spectra, therefore, a continuous absorption spectrum is indicative of the absence of the quantum restriction due to ionization of the absorbing atom.

10. **Molecular Spectra:** The spectra of molecules are necessarily more complex than those of atoms. In the latter case, motion of the electrons about the nucleus only is involved. With molecules, in addition to the motion of the electrons, two new possibilities arise, a rotation of the nuclei about the center of gravity of the molecule and a vibration of the nuclei about their mean positions in the molecule. The molecular energy, therefore, apart entirely from any energy of motion which it may possess, can be regarded as consisting of these parts: (*a*) rotational, (*b*) vibrational and (*c*) electronic energy.

$$E = E_r + E_v + E_e. \tag{4.19}$$

Of these, the rotational energy, E_r, is frequently much smaller in magnitude than the vibrational, E_v, which in its turn is normally smaller than the electronic energy E_e.

As with atoms, it is found that the molecule can have only a set of discrete values corresponding to a set of energy levels, emission or absorption of light occurring in quanta governed by the frequency condition of Bohr $h\nu = E' - E''$. In spectroscopic practice today E' is the designation for the higher energy level so that the transition $E' \longrightarrow E''$ is an emission while $E'' \longrightarrow E'$ is an absorption. Associated with each electronic level which a molecule may possess, one for each discrete value of E_e, the magnitudes of the separations between these levels being comparable with those in an atom, there is a set of vibrational levels designated by $v = 0, 1, 2, 3$, etc., one for each value of E_v. The separation of the vibrational levels is in general much smaller than the separation of the electronic levels. These vibrational levels slowly decrease in spacing as the number of the level, v, increases. Each vibrational level, v, has associated with it a set of rotational levels, each corresponding to a discrete rotational state, J, of the molecule in the particular vibrational and electronic state. These rotational levels are always closely spaced relative to the vibrational levels. They crowd close together when J is small and become more widely spaced as J increases. The spacing varies from one vibrational level to another and also from one electronic level to another. In Fig. 4.3 we reproduce a schematic diagram indicating two electronic states A and B of a diatomic molecule, with vibrational levels $v = 0, 1, 2, 3$, etc., and rotational levels $J = 0, 1, 2, 3$, etc. The energy of the electronic state E_e depends only upon the state of electronic excitation; E_v depends both on the electronic state and the value of v; E_r depends upon the electronic state and the values of v and J. Transitions may occur between energy states in one electronic state and another or between vibrational-rotational states within one electronic state or between rotational states within a given vibrational state. There are certain restrictions on these transitions which have been learned from observation. With changes in vibrational-rotational states within a given electronic state, v usually changes by 1 or 2. Changes between rotational levels alone have only been recorded for the vibrational state $v = 0$ in the so-called pure rotational spectra; the rotational level J in such cases never changes by more than 1.

The observed spectra of molecules therefore correspond to these many possible changes in energy levels. Instead of a line spectrum as with atoms, we receive a band spectrum, each band resolvable under high resolution into lines which are determined by the changes in rotational levels which have occurred. Pure rotation bands, for $v = 0$, correspond to such small energy changes that they are to be found only in the far infra-red. Vibration-rotation bands are somewhat larger in energy change and are normally to be found in the near infra-red. Electronic bands occur in the visible and ultra-violet since the energy level changes are comparable with those in atoms.

11. Energies of Molecular Levels: It is outside the scope of this volume to develop the quantum theory of band spectra in its determination of the energies associated with the various energy levels of a molecule. It will suffice for our purposes to state the conclusions which have been reached during the past decade, from the standpoint of quantum mechanics, in respect to these magnitudes.

The energy of rotation, which is entirely kinetic, of a rigid diatomic molecule, pictured as a rigid dumb-bell (no vibration of the nuclei) rotating with one of a discrete set of angular velocities about an axis through its center of mass and perpendicular to the nuclear axis is given by the expression

$$E_r = hcBJ(J + 1), \tag{4.20}$$

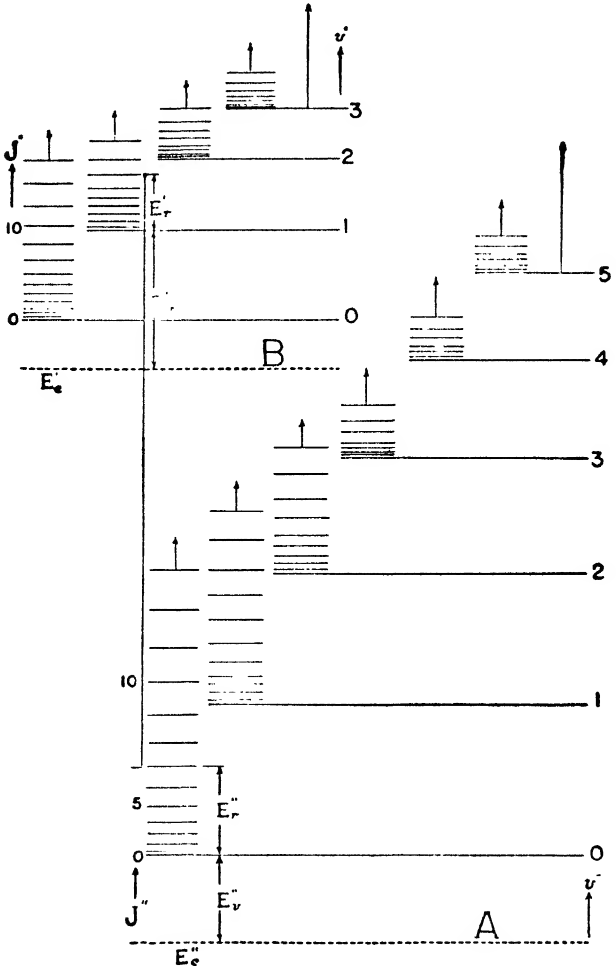

FIG. 4.3. The Energy Levels of Two Electronic States A and B of a Molecule

where J may have the values 0, 1, 2, 3, 4, etc., and the constant B has the value

$$B = h/8\pi^2cI. \tag{4.21}$$

In this expression I is the moment of inertia of the molecule and is expressed, in terms of the masses M_1 and M_2 of the constituent atoms and their distances r_1 and r_2 from the center of gravity of the molecule, by the equation

$$I = M_1r_1^2 + M_2r_2^2. \tag{4.22}$$

It will be noted that $M_1r_1 = M_2r_2$ by definition of the center of gravity and $r_1 + r_2 = r$, the distance of the atoms from one another in the rigid molecule. Consequently,

$$I = M_1r_1^2 + M_2r_2^2 = \frac{M_1M_2}{M_1 + M_2}(r_1 + r_2)^2 = \mu r^2 \tag{4.23}$$

where μ is the reduced mass equal to $M_1M_2/(M_1 + M_2)$ or alternatively

$$1/\mu = 1/M_1 + 1/M_2. \tag{4.24}$$

If the rotating, non-vibrating molecule is assumed to be no longer rigid but may expand under the influence of centrifugal force, the expression for the energy is extended to take account of this by means of correction terms thus:

$$E_r = hc(B_eJ(J + 1) + D_eJ^2(J + 1)^2 + \cdots). \tag{4.25}$$

In these expressions the term B_e refers to a quantity $h/8\pi^2cI_e$ where I_e is the moment of inertia of a supposedly rigid molecule with $r = r_e$. D_e is a small, negative correction constant also expressible in terms of I_e.

The vibrational energy term according to quantum mechanics is given by the expression

$$E_v = hc(\omega_e(v + \tfrac{1}{2}) - x_e\omega_e(v + \tfrac{1}{2})^2 + \cdots). \tag{4.26}$$

The vibrational quantum number may have values, $v = 0, 1, 2, 3$, etc., ω_e is the frequency expressed in cm.$^{-1}$ $(1/\lambda)$ and $c\omega_e = \nu$ is the frequency of vibrations in sec.$^{-1}$ of small amplitude about the equilibrium positions in the molecule; the second and higher terms are correction terms introduced because the vibrations of the nuclei are not strictly harmonic. The form of this equation is of interest in that it indicates that a molecule even in its lowest vibrational state possesses a definite amount of vibrational energy, $E_{v=0}$, which, neglecting higher terms, is given by,

$$E_{v=0} = \tfrac{1}{2}hc\omega_e = \tfrac{1}{2}h\nu. \tag{4.27}$$

This is the *zero-point energy* which molecules possess even in their lowest energy states. The existence of such zero-point energy had long been suspected. The quantum mechanics definitely established its existence when it demonstrated that the quantum number came into the energy expression in the form $(v + \frac{1}{2})$.

For vibrating molecules, the expression for rotational energy is similar to that given above (4.25) except that the coefficients B_e, D_e, etc., are changed to B_v, D_v, etc., corresponding to an effective moment of inertia, I_v, of the molecule in the vibrational state, v. The quantities B_v and D_v are often expressible by empirical relationships

$$B_v = B_e - \alpha(v + \tfrac{1}{2}) + \cdots \tag{4.28}$$

$$D_v = D_e - \beta(v + \tfrac{1}{2}) + \cdots \tag{4.29}$$

12. **Potential Energy Function of a Diatomic Molecule:** Consideration may now be given to the potential energy of a diatomic molecule in a given electronic state in virtue of the force which the constituent atoms exert on each other at varying distances apart. This force is the algebraic sum of an attractive and a repulsive force. At large distances of the atoms the attractive force may predominate and the potential energy, V, decrease. If the interatomic distance r continues to decrease, the potential energy must finally begin to increase since, at small values of r, the electrostatic repulsion of the two similarly charged nuclei will exceed all other effects. Consequently, at some distance, r_e, the potential energy curve will pass through a minimum. This type of interaction between two atoms is the type which gives rise to stable diatomic molecules, with an equilibrium nuclear distance of approximately r_e. There is, however, another type of interaction between two atoms corresponding to a net repulsion at all distances, in which therefore the potential energy, V, steadily increases with decreasing r. On the basis of the new wave mechanics this repulsive curve represents the approach, for example, of two hydrogen atoms in such a way that the electrons tend to take up positions on the outside of the approaching nuclei. In the approach leading to molecule formation the electrons tend to assume positions between the two nuclei thus forming a bond between them, a bond corresponding to the shared electron pair of Lewis's valence theory. The two curves in Fig. 4.4 illustrate both these possibilities, the full line curve indicating that potential function which leads to a stable molecule, in a particular electronic state, which may of course be either the lowest electronic state or any higher electronic state that

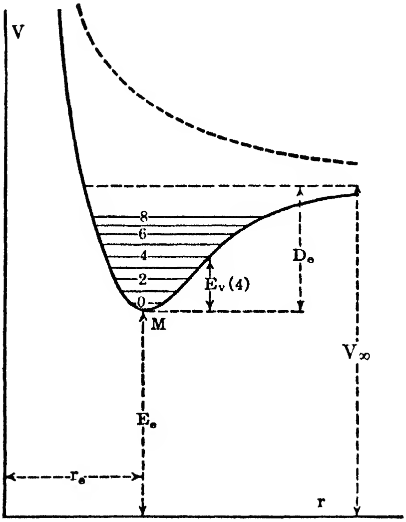

Fig. 4.4. Potential Energy Curves, Attractive and Repulsive Types

gives rise to a stable molecular form. The electronic state is specified by the ordinate, E_e, the electronic energy (which may be zero) on the potential energy axis of the diagram.

We can represent vibrational energy levels of such a stable electronic state by a series of horizontal lines. The ordinate for a particular vibrational level, say $v = 4$, is the total energy $E_e + E_v$, where E_v is the height of the fourth vibrational level above the potential energy minimum. The level $v = 0$ represents the lowest vibrational level, with its zero-point energy, $E_{v=0}$. The vibrations of the nuclei along the internuclear axis about their mean positions, is denoted by the horizontal lines, the extremities of each line, as measured on the r axis, representing the minimum and maximum values of r during one period of vibration. Consideration of the nature of a vibration will disclose that, at these extreme positions, where the direction of vibration changes, the nuclei are momentarily at rest. The kinetic energy of vibratory motion vanishes, the potential energy reaches its maximum value $E_e + E_v$. In the period between these extreme positions the kinetic energy increases at the expense of the potential energy, the kinetic energy at any intermediate distance in a particular vibrational level being given by the ordinate at that distance from the horizontal level to the full-line potential energy curve.

The energy which is necessary to separate the constituent atoms from the distances they occupy in the lowest vibrational state to an infinite distance apart, i.e., to produce free atoms, is of course the heat of dissociation of the molecule into atoms. Some of the best available data of such heats of dissociation, which are equal numerically to the heats of formation from the atoms (see Chapter 2, Section 19), have been obtained from the data on spectra of such molecules. In the diagram is shown the quantity, D_e, the energy difference between that of the two atoms at infinite separation and the minimum, M, in the potential energy curve. This energy quantity is greater than the ordinary heat of dissociation ΔH by the zero point energy of the molecule

$$\mathrm{D}_e = \Delta H + \tfrac{1}{2}hc\omega_e = \Delta H + \tfrac{1}{2}h\nu_0. \tag{4.30}$$

13. **An Empirical Potential Energy Function:** It is useful to have a formula which is capable of expressing the potential energy of a diatomic molecule as a function of the distance of nuclear separation, r. Several such functions are known, more or less significant theoretically. An *empirical* expression due to Morse is, however, a sufficiently good approximation in many cases and is capable of reproducing rapidly the potential energies of a two atom system in terms of the energy, D_e, the distances, r and r_e, and a constant a related to the frequency of vibration in the equilibrium position. The Morse expression takes the form

$$V = \mathrm{D}_e(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}). \tag{4.31}$$

The constant a has the value $a = 0.1227\omega_e \sqrt{\mu/D_e}$, where ω_e is the frequency of the equilibrium vibration expressed in cm.$^{-1}$, and μ is the reduced mass of the molecule. Since ω_e is expressed in wave numbers (cm.$^{-1}$) the value of D_e which is usually expressed in electron-volts or in calories must be brought to the same units; 352 wave numbers = 1 kilocalorie; 8100 wave numbers = 1 electron-volt. With ω_e and D_e in wave numbers the constant a is obtained from the equation in Ångström units (10^{-8} cm.) which is the usual unit in which r is expressed. The equation may therefore be written in the form

$$V = D_e(10^{-2x} - 2 \times 10^{-x}), \tag{4.32}$$

where $2.303x = a(r - r_e)$ or $(r - r_e) = 2.303x/a$. We shall see that such an empirical expression has considerable utility in expressing the potential energies not only of two atom systems, but also of systems containing three and four atoms. Also, we shall see that the potential energies of such systems are important in the problem of rate of chemical change.

14. **The Binding of Atoms in Molecules:** In our discussion of the potential energy of a diatomic molecule concerning curves of attraction leading to stable molecules and curves which are of a repulsive character throughout, we associated the attraction and repulsion with the location of the electronic charges with respect to the approaching nuclei. In the attractive curve, leading to a stable molecule, the electrons were between the approaching nuclei. This concept, which derives from the new quantum mechanics, regards the bond in the diatomic covalent molecule as due to the pairing of two electrons which were unpaired in the atoms from which the molecule was formed. On the basis of this concept London has developed a quantum mechanical interpretation of valence which is in essentials identical with the shared pair of electrons characteristic of the *Lewis theory of the covalent bond.* The valence of an atom is determined, according to London, by the number of its unpaired electrons. In the formation of a bond the spins of the two electrons forming the bond must be different, one positive, one negative, a pair of opposite spins constituting saturation. These conclusions correspond exactly with chemical experience in the matter of saturation valence of atoms and lead to the shared-electron pair formulas of a wide variety of chemical compounds which was characteristic of the Lewis theory of covalence and its later development by Langmuir and others. On the other hand, there exist compounds in which the binding is ascribable to the electrostatic attractions between oppositely charged ions which attain their charges by gain or loss of electrons from the neutral atoms from which the ions were formed. Such compounds are said to exhibit *electro-valence.* The alkali halides approach most nearly the ideal ionic binding. The diatomic molecules of some of the elements, as well as the

diamond crystal, are examples of the non-polar covalent binding. Fajans and his co-workers have shown, however, that the physical and chemical properties of many simple inorganic substances clearly indicate that they cannot be classified as belonging to one or other of these two extreme types. Intermediate types of linkage are frequent, involving varying degrees of polarization or of deformation of the anion in the field of the cation. The measurement of molar refraction of the ions has been especially useful in the demonstration of the intermediate types of binding with compounds derived from ions of noble gas character. The type of binding becomes less ionic and more covalent when (1) the polarizing field of the cation is greater, i.e. when its charge is higher and its size smaller, and (2) when the polarizability of the anion is greater. Crystal structure, ionic distances, lattice energies, solubilities and complex ion formation give additional information with ions of all types as to the character of the binding and its deviation from the ideal ionic type (see Chap. 7.12).

15. **Raman Effect:** An effect, which had previously been predicted by Smekal upon the basis of quantum theory, was discovered experimentally by Raman in 1928. He observed that when any medium, solid, liquid or gaseous, is exposed to light of a given frequency ν_i, the light scattered at right angles contains frequencies differing from ν_i which are characteristic of the scattering medium. If ν_s represents a scattered frequency, the difference $\nu_i - \nu_s$, called a Raman frequency, is usually found equal to a rotation or vibration frequency of the molecule. The mechanism of the Raman effect involves the elevation of the energy of the molecule to a higher level by absorption of the incident quantum followed by the emission of the Raman scattered radiation whereby the energy falls to a level usually between the initial and excited states. The Raman frequency corresponds to the energy difference between the initial and final states. In some cases the final level is lower than the initial so that ν_s is greater than ν_i.

Study of the Raman effect provides an alternative method of obtaining infra-red frequencies, since appropriate choice of the incident light will bring the scattered light into a spectral field more convenient for measurement than direct observation in the infra-red. The experimental technique has been especially developed by R. W. Wood[1] and since 1928 an enormous amount of information on the characteristic intra-molecular motions has been collected, which, as will be shown, is of especial value in determining not only the inter-nuclear dimensions of molecules but also their physical properties.

The Raman effect is not only advantageous as a confirmation of direct infra-red observation but is actually complementary. Thus any vibra-

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[1] R. W. Wood, *Phys. Rev.*, **36**, 1421 (1930).

tions which are symmetrical with respect to the center of symmetry of a molecule are not observed in the infra-red; only those vibrations which bring about a change in the electric moment will be active in absorption. On the other hand a vibration is active in the Raman spectrum when it is accompanied by a change in the polarizability of the molecule. For instance, the homonuclear molecules H_2, O_2, N_2 show no infra-red spectra but do have rotational Raman spectra. Again, the symmetrical stretching frequency in CO_2 wherein the two oxygen atoms move symmetrically towards and away from the carbon atom, is inactive in the infra-red since no change in the electric moment of the molecule is involved during the vibration; the polarizability, on the other hand, may be expected to be different for the expanded and contracted forms of the molecule and thus the vibration will be active in the Raman spectrum. The Raman effect thus confirms and also complements direct infra-red study.

16. **The Wave Theory of Matter:** Progress in the quantum theory of energy made familiar the concept of units of energy, light quanta, or photons,[1] with the discontinuous structure hitherto characteristic of matter. The reversal of this mode of thought, the concept of material particles with the wave nature of light, was proposed in 1924 by Louis de Broglie. It led to the wave mechanics of Schrödinger and to the quantum mechanics of Heisenberg, two aspects of the general problem of wave theory of matter intensively developed in the last years. The wave theory of matter assigns to each material particle a wave of a characteristic wave length bearing the same relation to its mass and velocity as was found in quantum theory for the photons. This relation is expressed in the equation

$$\lambda = h/mv \tag{4.33}$$

where λ is the wave length of the particle with mass m and velocity v, h being again Planck's constant.

It is of interest to point out the significance of this equation when applied to the electron, the smallest unit to which material properties have hitherto been assigned. The velocity of the electrons is determined by the applied potential V, i.e. $\frac{1}{2}mv^2 = eV$. Hence $\lambda = h/\sqrt{2meV}$ which yields, on insertion of the numerical values for h, m and e, the equation $\lambda = \sqrt{150/V}$ Ångström units, or wave lengths of the same order of magnitude as X-rays. Herein lay a possibility of experimental test, since the wave lengths of X-rays are determinable by well-known reflection and diffraction methods using crystals. (See Chapter 7.)

Such a test was applied by Davisson and Germer[2] successfully in 1927. They showed that a stream of electrons emitted from a hot fila-

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[1] G. N. Lewis, *Nature*, **118**, 874 (1926).

[2] Davisson and Germer, *Nature*, **119**, 558 (1927); *Phys. Rev.*, (2), **30**, 705 (1927).

ment was selectively reflected from a single crystal of nickel in a manner entirely analogous to the reflection of X-rays first studied by W. H. and W. L. Bragg. The intensity of the reflection in a given direction was governed, as with X-rays, by the lattice structure of the crystal. With this experiment, therefore, the fusion of the corpuscular and undulatory aspects of both matter and energy was achieved. It gave a marked impetus to the examination of matter from the standpoint of wave theory. Simultaneously, G. P. Thomson showed that electrons could be diffracted on passage through thin metal foils with the production of diffraction patterns entirely analogous to those produced by X-rays when the Laue technique is employed (Chap. 7).

Stern and his collaborators (1932) showed that molecular beams of hydrogen and helium showed the same type of behavior as electrons when reflected from crystal faces, a still more impressive demonstration of the wave aspects of material particles and of the necessity of substituting the new wave mechanics for classical mechanics when dealing with atomic phenomena generally.

17. **X-ray and Electron Diffraction of Vapors:** We shall illustrate this fusion of the particle and wave aspects of matter and energy by brief reference to the work of Debye on the scattering of X-rays by gases and vapors and its analogue in the work of Mark and Wierl substituting cathode rays or electrons for the X-rays. In each case the scattering produces interference patterns which can be recorded photographically. The mathematical analysis of the results is very complex but the method is steadily increasing in importance for the determination of molecular dimensions in gases, vapors and liquids in the way that X-ray studies of crystals have permitted the determination of the dimensions of crystal lattices (see Chapter 7).

Largely due to the work of Pauling and Brockway and their students, using the diffraction of electrons, a considerable body of data has now been accumulated concerning the inter-atomic distances and valence angles in a wide variety of gases, leading to a more precise knowledge of molecular structure than was hitherto possible. Data so accumulated supplement the conclusions from spectroscopic and other methods of measurement of such molecular magnitudes. The electron diffraction method is superior to that using X-rays since higher intensities can be employed, with the result that brief exposures suffice to give the desired interference photographs.

18. **The Electron Microscope:** The wave nature of the electron has also been utilized in the development of the electron microscope. The great utility of this new instrument arises from the limitations of the optical microscope and ultra-violet microscope which utilize visible and ultra-violet light respectively as the illuminating agent. Apart from the limitations due to the optical deficiencies in the lens systems, the limita-

tion in possible magnifying power arises from the wave length of the medium used. In visible light the wave length is of the order of 4–8 $\times$ 10^{-5} cm. Objects which are smaller than this wave length cannot easily be resolved. In the ultra-violet type of microscope, by decreasing the wave length of the medium the resolution can be doubled, magnifications of around 2500 are possible and objects separated by distances of the order of 1 $\times$ 10^{-5} cm. can be seen.

The electron microscope permits a large increase in resolution because, in agreement with the wave theory of matter, a beam of electrons under high potentials, of the order of 60 kilovolts, has an associated wave length of the same order as that of X-rays and many times smaller than that of ultra-violet light. As a result it has been found that magnifications up to approximately 100,000 may be employed without exhausting detail and separations of 2 $\times$ 10^{-7} cm. can be observed. Special focussing mechanisms are necessary. A magnetic field can be employed to act as a converging lens. Three such magnetic lenses serve in lieu of the condensing lens, the magnification lens and the image projector. The electron beam is produced by means of a heated filament; the whole microscope system obviously must be highly evacuated. After passing through the object examined, the emergent electrons strike a fluorescent screen, the image on which can be photographed. Alternatively, direct exposure of a photographic plate to the emerging electrons yields a photo-micrograph.

Exercises (4)

1. Calculate the density of radiation emitted from the surface of the sun, assuming it to be a black body at a temperature of 6000° K.

2. Calculate the average energy of vibration of a chlorine molecule at 0° C., given that the vibration frequency is 1.70×10^{13} sec.$^{-1}$.

3. Derive a numerical relation between the velocity, v, in cm. per sec. with which electrons are emitted in the photo-electric effect and the retarding potential, V, in volts necessary to inhibit the emission.

4. Taking 3×10^{-18} sec.$^{-1}$ as a mean value of the frequency of X-rays, calculate the number of quanta that are equivalent to one calorie.

5. Show that the ionization potential of the hydrogen atom given in Fig. 4.2 as 13.54 volts is consistent with the energy in the first level of 215.60×10^{-13} erg.

6. Calculate the zero-point energy for hydrogen molecules, given that $\omega_e = 4417.19$ cm.$^{-1}$ and the anharmonic constant $x_e = 0.02973$.

7. Calculate the theoretically possible wave lengths of Raman lines that could be obtained, using the mercury line 4358 Å. as the exciting source, for hydrogen chloride, whose fundamental frequency is 2989 cm^{-1}.

CHAPTER 5

THE GASEOUS STATE. II

1. Rotational Heat Capacity of Gas Molecules: The kinetic energy of rotation of a diatomic molecule has been expressed by means of the equation (4.20)

$$E_r = hcBJ(J + 1),$$

where J, the rotational quantum number, may have the values 0, 1, 2, 3, etc., and the constant $B = h/8\pi^2cI$ involves the moment of inertia, I. The size of the quantum is evidently determined by the magnitude of B which, in its turn, is inversely proportional to the moment of inertia. The larger the latter, the smaller the quantum. Furthermore, it has been shown that the quantum interpretation of energy quite generally approaches the classical interpretation based upon the principle of equipartition of energy the smaller the magnitude of the quantum, the more nearly, that is, the discrete discontinuous quantized energy approaches the concept of continuously varying energy. Since the moment of inertia is, in its turn, dependent on the masses of the constituent atoms we may expect small quanta of rotational energy with relatively large masses and conversely relatively large rotational quanta with small atomic masses. Our knowledge of the rotational energy of gas molecules as deduced from heat capacity measurements is in entire accord with these conclusions. For all molecules, save those of hydrogen and its isotopes, the moments of inertia are so large and the quanta so small that the rotational motion of the molecules is *effectively classical.* Hence, in most diatomic molecules, with two degrees of freedom of rotation, we expect, and find, a contribution from rotational energy of $2(\frac{1}{2}kT) = kT$ per molecule, or, correspondingly, a contribution of R calories per mole to the rotational heat capacity. For polyatomic, linear molecules also having two degrees of freedom of rotation, the same contribution obtains. For non-linear polyatomic molecules, where there are three degrees of freedom of rotation, we may expect, and find, a contribution of $\frac{3}{2}kT$ per molecule from rotational energy and a corresponding contribution of $\frac{3}{2}R$ calories per mole for the rotational heat capacity.

The case of hydrogen is exceptional by reason of the smallness of the moment of inertia. This is small for two reasons. Since $I = \mu r^2$ its value is small in the case of hydrogen because the reduced mass μ is the smallest possible, since M_1 and $M_2 = 1$ and also because the interatomic distance, $r = 0.75$ Å., is also the smallest known interatomic distance. The value of I is therefore 0.467×10^{-40} g. cm.^{2} as compared with normal moments of inertia such as 19.25×10^{-40} g. cm.^{2} for oxygen. The rotational motion of hydrogen molecules is effectively classical only above 0° C. Below this temperature the rotational energy is less than kT and approaches zero as the temperature approaches zero. The quantization of the rotational energy accounts therefore for the observed data on the heat capacity of hydrogen which show that, at 35° K., the total heat capacity is 2.98 cals., characteristic of a monatomic gas.

2. **Ortho- and Para-Hydrogen:** The case of hydrogen becomes more complex by reason of the existence of two *spin-isomers* of molecular hydrogen. On the basis of quantum mechanics it was predicted by D. M. Dennison and by Heisenberg and Hund that two kinds of hydrogen or, quite generally, two kinds of molecules with identical nuclei, should exist, on the assumption that the two nuclei of the molecule possess nuclear spins which may have either a parallel or an anti-parallel orientation. These different orientations would, combined with certain values of the rotational quantum numbers, distinguish the two modifications from each other. On this theory, para-hydrogen molecules possess *anti-parallel* nuclear spins and *even* rotational quantum numbers, $J = 0, 2, 4,$ etc. Ortho-hydrogen would possess *parallel* nuclear spins and *odd* rotational quantum numbers, $J = 1, 3, 5,$ etc. In ordinary hydrogen these two forms should be present in the ratio 1 para- to 3 ortho-, and this ratio would account for the alternating intensities in the molecular spectra observed by Mecke. Bonhoeffer and Harteck, in 1929, verified these predictions experimentally by isolating pure para-hydrogen, formed from the normal 1 : 3 mixture at liquid hydrogen temperatures in presence of catalysts such as charcoal. By measurements of thermal conductivity, which, as already shown, is related to heat capacity, they verified the assignment of even rotational quantum numbers to the para- variety.

In the neighborhood of the absolute zero the rotational energy of para-hydrogen is zero since all molecules occupy the rotational level, $J = 0$. Since ortho-hydrogen molecules would all be in the level $J = 1$, the equation for the rotational energy shows that such ortho-molecules would have a value of $E_r = 337$ cals. per mole. At such low temperatures the equilibrium mixture is practically 100 per cent para- so that the rotational energy of the equilibrium mixture would be zero. If, as is true in the absence of catalysts, the equilibrium mixture was not established, the rotational energy of normal hydrogen would be found from that of its components, $E_{rot.}^{n\text{-}H_2} = \frac{1}{4}E_{rot.}^{p\text{-}H_2} + \frac{3}{4}E_{rot.}^{o\text{-}H_2} = \frac{3}{4} \times 337 = 252.9$ cals. The attached table, calculated by Giauque, shows the rotational energies of para-, ortho-, equilibrium and normal hydrogen over the whole range from 0° to 298° K.

TABLE 5 1

ROTATIONAL ENERGIES OF HYDROGEN GAS IN CALORIES PER MOLE

Temp. ° K.	Para-Hydrogen	Ortho-Hydrogen	Equilibrium Mixture		Normal 1 : 3
			% p-H_2	$E_r^{e\text{-}H_2}$	
0	0.00	337.17	100	0	252.88
20	0.00	337.17	99.82	0.63	252.88
40	0.05	337.17	88.61	38.63	252.89
50	0.20	337.18	76.89	78.38	252.94
100	30.56	338.59	38.51	219.78	262.17
200	290.22	393.59	25.9	366.76	367.75
273.1	473.34	502.16	25.1	494.84	494.91
298.1	529.12	546.92	. . .	542.46	542.47

In these calculations the number of molecules N_j in the rotational state J is given by a special form of the Boltzmann distribution law, $N_j = N_0 p_j e^{-E_j/kT}$. The value of p_j is $2J + 1$ when J is even and $3(2J + 1)$ when J is odd. These values of p_j lead to the high temperature ratio of 3 ortho- : 1 para-. The rotational heat capacities deduced from these data are shown diagrammatically in Fig. 5.1.

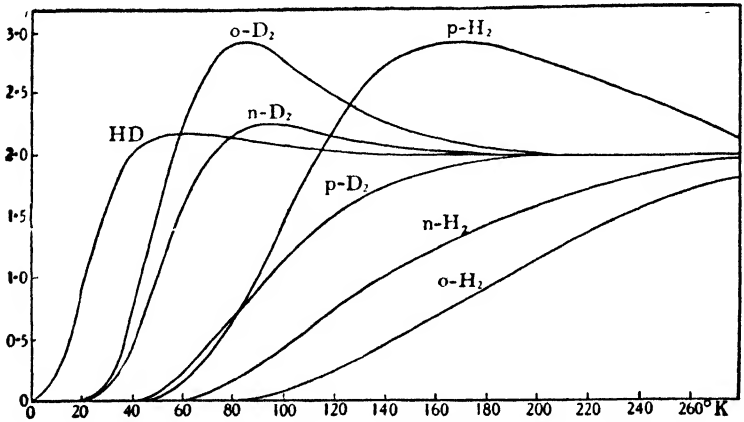

FIG. 5.1. Rotational Heat Capacities of H_2, D_2 and HD

3. Rotational Heat Capacity of Deuterium: Similar conditions obtain with the hydrogen isotope, D_2. The following divergences occur: the moment of inertia 9.31×10^{-41} g. cm.^{2} is twice as large, due to μ, the reduced mass; the ortho- states of the D_2 molecule have even rotational quantum numbers, the para- have the odd and the ratio at high temperatures is 2 ortho- : 1 para-. The rotational energies calculated by Johnston and Long are given in Table 5.2 and the derived heat capacities are shown along with those of ortho-, para- and normal hydrogen in Fig. 5.1.

TABLE 5.2

ROTATIONAL ENERGIES OF DEUTERIUM GAS IN CALORIES PER MOLE

Temp. ° K.	o-D_2	p-D_2	e-D_2	n-D_2	HD
0	0.00	170.22	0.00	56.74	0.00
20	0.01	170.22	3.46	56.74	1.27
25	0.09	170.22	8.10	56.80	4.50
50	14.62	170.61	46.74	66.62	49.31
100	143.54	197.20	160.81	161.43	154.15
150	265.38	274.32	268.35	268.36	232.99
200	369.41	370.54	369.79	369.79	355.39

The molecule hydrogen deuteride, HD, has a moment of inertia equal to 6.21×10^{-41} g. cm.[2] It exists in only one form since the two nuclei are not of equal mass. The rotational energy data are shown in Table 5.2 and the rotational heat capacities in Fig. 5.1. An inspection of Fig. 5.1 is very instructive as to the influence of moment of inertia and of odd and even quantum states on the rotational heat capacity. This assumes measurable values at the lower temperatures in the case of D_2 compared with H_2 because the moment of inertia is higher and hence the quantum of rotational energy is smaller. The heat capacity assumes measurable values at lower temperatures in the case of molecules with even quantum states, namely ortho-deuterium and para-hydrogen, as compared with molecules having odd quantum states, para-deuterium and ortho-hydrogen. The molecule HD assumes measurable values at lower temperatures than any of the other hydrogen molecules because the transition between levels with odd and even rotational quantum numbers is not forbidden in this hetero-nuclear molecule as contrasted with the homonuclear molecules, H_2 and D_2. One analytical method of determining concentrations of H_2, D_2, HD in mixtures, and for mixtures of ortho-para varieties, that of Farkas and Farkas, is based on the thermal conductivity method of determining heat capacities of the gas mixtures.

4. **Vibrational Heat Capacity of Gas Molecules:** The spectral evidence showed that the quanta of vibrational energy are often considerably larger than the quanta of rotational energy. It is therefore to be expected that vibrational energies of gas molecules cannot be treated classically. Actually, only in a few cases do the heat capacities of diatomic molecules indicate any contribution from vibrational energy at room temperatures.

The data on chlorine in Table 3.3 definitely show a small vibrational energy contribution.

In discussing Planck's Distribution Law (4, 5) we found that the average energy of a linear vibrator with frequency $\nu = c\omega$ is given by the expression

$$\bar{\epsilon} = \frac{\epsilon}{e^{\epsilon/kT} - 1} = \frac{h\nu}{e^{h\nu/kT} - 1} = \frac{hc\omega}{e^{hc\omega/kT} - 1}. \tag{4.6}$$

At high temperatures, neglecting higher terms in the expansion,

$$\bar{\epsilon} = \frac{h\nu}{1 + h\nu/kT + \cdots - 1} = kT. \tag{4.7}$$

For 1 mole of gas we must multiply the energy per molecule, $\bar{\epsilon}$, by Avogadro's number N and obtain:

$$\bar{E}_\nu = N\bar{\epsilon} = \frac{Nh\nu}{e^{h\nu/kT} - 1} = \frac{R\theta}{e^{\theta/T} - 1}, \tag{5.1}$$

where we have made the substitutions $Nk = R$ and $\theta = h\nu/k$ and note that θ has the dimensions of temperature, analogous to the characteristic temperatures of solids (Chap. 7). Differentiation of this expression with respect to T gives the vibrational heat capacity in terms of θ and T.

$$C_{(\mathrm{vib})} = \frac{d\bar{E}_\nu}{dT} = R\frac{\left(\frac{\theta}{T}\right)^2 e^{\theta/T}}{(e^{\theta/T} - 1)^2}. \tag{5.2}$$

Inspection of this formula shows that, at high temperatures, the value of $C_{(\mathrm{vib})}$ approaches the classical value of R cals. for one mode of vibration, the kinetic and potential energies contributing $R/2$ calories for each degree of freedom of vibration. At low temperatures, the value sinks to zero. We can illustrate the applicability of such an equation to the calculation of vibrational heat capacities by considering the case of chlorine, for which we shall use a value of $\theta = 810°$ derived from spectral data. Table 5.3 shows the experimental and calculated values at a series of temperatures.

TABLE 5.3

VIBRATIONAL HEAT CAPACITY OF CHLORINE $\theta = 810°$

$T°$ K............ =	243	270	318.5	391.4	451.7
$C_{(\mathrm{vib})}$ experimental =	0.840	0.977	1.148	1.459	1.553
$C_{(\mathrm{vib})}$ calculated.... =	0.848	0.985	1.188	1.407	1.530

The θ values for a number of other diatomic gases are: $I_2 = 306$; $Br_2 = 463$; $O_2 = 2250$; $NO = 2705$; $N_2 = 3370$; $HI = 3198$; $HBr = 3785$;

HCl = 4276; H_2 = 6100. The big increase in θ as we pass from the halogens to oxygen indicates why, at room temperatures, the vibrational heat capacity of oxygen is negligibly small.

In the case of polyatomic molecules there are more modes of vibration than one. In a molecule of n atoms the total number of degrees of freedom is $3n$. Of these, three are translational degrees of freedom. In diatomic and linear polyatomic molecules there are two degrees of freedom of rotational motion. Hence, there are $3n - 5$ vibrational degrees of freedom in a linear polyatomic molecule and $3n - 6$ in a non-linear molecule. As an example of a linear molecule we choose carbon dioxide, in which $n = 3$ and there are therefore $3n - 5 = 4$ modes of vibration. The vibrational heat capacity of carbon dioxide is well interpreted by calculated data, obtained by use of the same heat capacity formula that was adequate with chlorine, employing, however, *four* values of θ, 960, 960, 1920, 3360. The water vapor molecule is non-linear. For this molecule we have three values of θ = 2340, 5350 and 5500. The ammonia molecule has six modes of vibration, with four distinct fundamental frequencies of which two are double. In the case of methane the spectral analysis by Dennison indicates one single, one double and two triple frequencies, nine in all, of four independent frequencies.

5. **Isotopes and Vibrational Energy:** The effect of isotopic substitution on vibrational energy and heat capacity will be most pronounced in the case of the hydrogen isotopes. The three isotopic molecules H_2, HD and D_2 each possess the same value for the dissociation energy to the potential minimum, D_e, recently estimated by Beutler at 108.91 ± 0.02 kcal. The spectral data from which the energy of the various vibrational states of the three molecules can be computed are contained in Table 5.4 where the symbols have the significance applied to them in the preceding chapter (4.20).

TABLE 5.4

SPECTROSCOPIC CONSTANTS FOR HYDROGEN ISOTOPES IN WAVE NUMBERS (cm.$^{-1}$)

	H_2	HD	D_2
ω_e	4417.19	3826.6	3125.4
$x_e\omega_e$	131.315	98.52	65.72
B_e	60.872	45.668	30.645
α_e	3.0671	1.9931	1.0859
$-D_e$	0.04652	0.002618	0.001165
β_e	0.00101	0.000495	0.00018

It is evident from these data that hydrogen will possess the largest θ value, deuterium the smallest and hydrogen deuteride the intermediate value. As a consequence, the vibrational heat capacity will become measurable with deuterium at lower temperatures than for hydrogen deuteride which in its turn will show vibrational heat capacity at lower temperatures than hydrogen.

The data for ω_e and $x_e\omega_e$ also permit the calculation of the zero-point energies for the three molecules from the equation (4.26)

$$E_{v=0} = hc(\tfrac{1}{2}\omega_e - \tfrac{1}{4}x_e\omega_e),$$

giving the following values: H_2 : $E_{v=0}$ = 6183.5 cals., HD : 5366.4 cals. and D_2 : 4394.5 cals. Using the Beutler value for the dissociation energy, D_e, we obtain, by subtracting these values for the zero-point energies, the following values for the chemical heats of dissociation of the three hydrogen molecules, the value in each case referring to 0° K.

$$\begin{aligned} D_{H_2} &= 108.91 - 6.18 = 102.73 \text{ kcal.} \\ D_{HD} &= 108.91 - 5.37 = 103.54 \text{ kcal.} \\ D_{D_2} &= 108.91 - 4.39 = 104.52 \text{ kcal.} \end{aligned}$$

Similar, though less pronounced divergences, exist in isotopic compounds of any element. It will be shown that such differences in zero-point vibrational energy are of fundamental importance in the reactivity of molecular species, and, hence, are of importance in separations of isotopes depending on differences in reaction speed.

6. **Dipole Moments:** Within recent years a powerful new tool for the investigation of molecular structure has been developed based upon the determination of electrical dipole moments. If the center of action of the positive nuclei in a molecule coincides with that of the electrons in the molecule, we term the molecule *non-polar*. It will show no tendency to take up any definite position in an electric field. If the positive and negative centers of action do not coincide, the molecule is said to be *polar*. It can then be regarded as equivalent electrically to a rod negatively charged at one end and positively charged at the other. In an electrical field the molecule would suffer an orientation, the negative end arranging itself towards the positive pole and vice versa. Such molecules possess electrical dipole moments whose magnitude μ is given by the product of the charge on one end e and the distance s separating the charges

$$\mu = e.s. \tag{5.3}$$

Any molecule when placed in an electrical field will suffer a slight displacement of the electrons and nuclei in opposite directions, the extent of the displacement being proportional to the intensity of the field, and zero when the field is removed. We may speak of a moment thus produced as an induced electrical moment. If in a field of strength F the induced moment is αF then α is called the displacement polarizability of the molecule. The displacement of the electrons with respect to the nuclei towards the positive pole of the applied field may be called the electron polarization, P_e. As a result of the deformation of the electronic orbits the nuclei will be displaced with respect to one another. This is termed the atomic polarization, P_a. The extent of this displacement will be small compared with P_e. The orientation by a field of a molecule with permanent dipole moment gives rise to an orientation polarization, P_o.

The thermal agitation of the gas molecules will tend to nullify any orientation of molecules in an electric field. As the temperature increases, therefore, the orienting influence of the field decreases. The relation connecting these quantities was obtained by Debye in the expression

$$P = \frac{4\pi}{3} N \left(\alpha_0 + \frac{\mu^2}{3kT} \right). \tag{5.4}$$

The quantity α_0 in this equation represents the electronic and atomic susceptibilities and is independent of temperature, μ is the dipole moment, N is Avogadro's number, k the gas constant per molecule and T the absolute temperature. The quantity P is the molecular polarization of the substance. Its value can be determined from measurements of the dielectric constant, D, since, according to the Clausius-Mosotti Law

$$P = \frac{D - 1}{D + 2} \cdot \frac{M}{d} \tag{5.5}$$

where M is the molecular weight of the substance whose density is d. This relation is the analogue of the Lorenz-Lorentz formula for the molecular refractive power of a medium of refractive index, n,

$$P = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}. \tag{5.6}$$

Comparison of the two formulas shows that under conditions in which they are obeyed $D = n^2$.

The Debye expression can be expressed in the form

$$P = A + B/T, \tag{5.7}$$

where $A = \frac{4\pi}{3} N\alpha_0$ and $B = \frac{4\pi}{9} \frac{N}{k} \mu^2$.

By measuring the dielectric constant, and hence, P, at a series of temperatures the quantities A and B can be determined. For non-polar molecules there will be no effect of temperature, P will be constant and equal to the electronic and atomic polarization. If P varies with the temperature, B and hence μ can be determined from the slope of the plot of P against $1/T$.

The values of μ so obtained are of the order of magnitude, 10^{-18} e.s.u. This follows from the size of the electronic charge 4.80×10^{-10} e.s.u. and the normal molecular distance, 10^{-8} cm. The following are data of C. P. Smyth and Zahn for three gases, two non-polar and one polar.

TABLE 5.5

Dielectric Constants of Gases

Ethylene		Acetylene		Sulfur Dioxide	
$T°$ K.	$(D-1)v$	$T°$ K.	$(D-1)v$	$T°$ K.	$(D-1)v$
237.4	.001450	197.4	.001334	267.6	.009530
296.3	.001444	295.7	.001333	297.2	.008768
366.5	.001447	365.6	.001335	366.9	.007323
460.9	.001437	460.5	.001333	443.8	.006336
$A = 10.79$	$B = 0$	$A = 9.96$	$B = 0$	$A = 10.70$	$B = 16185$

In the table v refers to the volume occupied by 2.701×10^{19} molecules that is to say the Avogadro number per cc. at 0° C. and 760 mm. Since the gases studied are not ideal one cannot use the relation $v = T/273$ but must correct this quantity by means of van der Waals's equation. This was done for the data cited. The values of B derived, indicate that neither ethylene nor acetylene has an electric moment but that sulfur dioxide shows a value of B from which a moment $\mu_{SO_2} = 1.61 \times 10^{-18}$ can be calculated. The induced polarization A is nearly the same for the three substances.

The conclusions to which such studies lead would be beyond the scope of the present volume. A very useful summary of the work has been given by Sidgwick,[1] of which we shall cite some of the more elementary conclusions. Inert gases are non-polar. The diatomic elementary gases having similar atoms H_2, N_2, O_2 and probably Cl_2, Br_2 and I_2 are non-polar. Diatomic molecules with dissimilar atoms have dipole moments as in the case of HCl, HBr, HI and CO. Triatomic molecules of the type AB_2 should be non-polar if A is the central atom, the two bonds are the same and the molecule is linear. This is true of CO_2 and CS_2 which are therefore presumably linear. The polarity of SO_2 indicates non-linearity as do also infra-red spectra and other lines of evidence. When the bond is a single bond as in H_2O and H_2S, the molecule is always polar indicating that the molecule is non-linear. If one assumes an angle φ between the bonds the moment M should be equal to $2m \cos(\varphi/2)$

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[1] Sidgwick, The Covalent Link in Chemistry, pp. 138–198, Cornell University Press, 1933.

where m is the moment of a single bond A–B. The values of φ so obtained indicate the essential correctness, even with these molecules, of the concept of the tetrahedral angle developed by van't Hoff for the stereochemistry of carbon compounds.

Tetratomic molecules AB_3 with the A–B bonds single should be non-polar if all the atoms lie in a plane and all the valence angles are equal. On the tetrahedral model a triangular pyramid should be formed with A at the apex. The molecule should then be polar. This is true of ammonia, phosphine, arsine and the trihalides of phosphorus, arsenic and antimony.

Pentatomic molecules AB_4 should be non-polar on the tetrahedral or plane model. This is true of methane and the tetrachlorides of carbon, silicon and titanium, and the tetraiodide of tin. The plane molecule can be shown to be impossible because trans-methylene chloride CH_2Cl_2 should then be non-polar whereas it has a moment.

All the saturated paraffin hydrocarbons examined have been found non-polar. The moments of primary alcohols vary little in a homologous series. This is true also of a group of dialkyl ketones. The results in Table 5.5 indicate that symmetrical double and triple bonded hydrocarbons are non-polar, presumably linear molecules as indeed other evidence also indicates.

The examples cited show the potentialities of these studies of electric moment. By correlating them with the conclusions to be reached from Raman spectra, infra-red spectra, data from the scattering of X-rays and electrons, the chemist is accumulating an increasingly important body of evidence concerning the shape, size and spacial configurations of molecules.

Exercises (5)

1. Calculate the rotational energy per mole of para-deuterium at the absolute zero.

2. Using the rotational energies of para-hydrogen given in Table 5.1 show that the rotational heat capacity will pass through a maximum between 100° K. and 200° K.

3. What is the vibrational heat capacity of bromine at 100° C.?

4. Calculate the molecular polarization of benzene given that its density at 20° C. is 0.8790 and its refractive index is 1.5014.

5. Calculate the permanent moment of the ammonia molecule, given that the molecular polarizations at 60° and 175° C. are 51.2 and 39.5 respectively.

6. The electric moment of chlorbenzene is 1.52×10^{-18} e.s.u. Calculate the moment of ortho-dichlorbenzene, assuming the regular hexagon structure for benzene. The observed moment of the dichlorbenzene is 2.25×10^{-18} e.s.u. What angle between the chlorine-carbon bonds would be necessary to bring about agreement between the observed and calculated results?

CHAPTER 6

THE LIQUID STATE

THE liquid state is intermediate to the solid and the gaseous states. It results from the solid state, the transition occurring at the melting point, with absorption of the latent heat of fusion. It results from the gaseous state either by abstraction of heat energy from the gas or by compression of the gas. Fall of temperature accompanies the withdrawal of heat energy, the diminished kinetic energy of the molecules becoming insufficient to overcome their mutual attraction. Alternatively, compression of the gas brings the gas molecules into closer proximity to one another and thereby favors the operation of the attractive forces. Of the two factors, the lowering of temperature is the more important. For every gas there exists a **critical temperature** above which it is impossible to liquefy a gas by compression. The pressure which suffices to produce liquefaction at the critical temperature is known as the **critical pressure.** The volume occupied by the substance under the critical conditions of temperature and pressure is known as the **critical volume.**

We have already seen that the homogeneous distribution of a gas throughout the volume of the containing system is satisfactorily formulated in terms of individual molecules moving with velocities determined by the Maxwell distribution law. The van der Waals equation reveals the existence of molecular forces of attraction which account, in part, for the deviations from ideal behavior. These molecular forces, F, vary rapidly as the inverse power of the distance, d, between molecules, probably as the inverse seventh power, $F \propto 1/d^7$. The forces are therefore considerable at close proximity but fall away rapidly with increasing distance, so that their effective range is small. Molecules which come within this range of each other without the necessary kinetic energy to overcome these forces of molecular attraction tend to form a conglomerate of molecules which may be regarded as the incipient formation of a liquid. Were the velocities of all the gas molecules identical there would be a definite temperature at which all the gas molecules would form such a conglomerate, or liquid. This temperature would be the critical temperature. In actual gases, however, the critical temperature must be defined as the temperature in which the average kinetic energy of the molecules is equal to the summation of the work done against the attractive forces over the effective range.

Below the critical temperature, gas molecules with insufficient kinetic energy to overcome the attractive forces of a liquid conglomerate will become part of the liquid on collision. The molecules in the liquid will have, however, a distribution of velocities so that occasionally some of these molecules will have sufficient kinetic energy to escape from the liquid into the gas. Depending on which of the two processes predominates we have either condensation or evaporation. The rate of condensation obviously depends on the concentration of gas molecules and therefore on the gas pressure. Increase of gas pressure increases the concentration of gas molecules and therefore increases the liquefaction. When the rate of evaporation equals the rate of condensation we have a position of stability showing no net change with time. This condition is defined as an equilibrium and the gas pressure necessary to establish this condition is known as the vapor pressure. It obviously depends on the temperature, since this latter determines the distribution of velocities of both gas and liquid.

The molecules which escape from a liquid medium are those which have velocities in excess of the average velocities of the liquid molecules. Their escape causes a reduction in the average velocity of the remaining molecules. The temperature of the residue is consequently lowered. The heat necessary to re-establish the initial temperature is, of course, the latent heat of vaporization of the liquid.

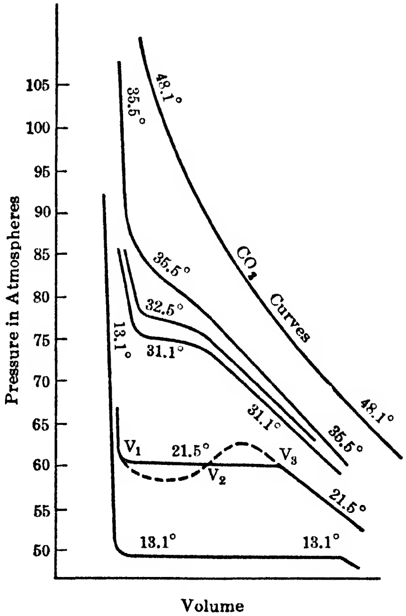

Fig. 6.1. p–v Isothermals

1. **Isothermal p-v Curves:** It is evident that, above and below the critical temperature, a difference of behavior will be noted on compressing a gas. Above the critical temperature, no liquid phase appears, no matter how high the pressure. Below the critical temperature liquid sooner or later makes its appearance. We may readily indicate this varied behavior by a diagrammatic representation of the pressure-volume relationships at various temperatures. The curve for a given temperature is known as a p–v isothermal. The diagram, Fig. 6.1, reproduces a number of such isothermals for carbon dioxide, whose critical temperature is 31.1° C. It

will be observed that above this temperature the curves are continuous and resemble the rectangular hyperbola demanded by Boyle's law. Below the critical temperature the curve is discontinuous. It exhibits three sections. The right-hand section of the curve corresponds to the gas compression curves above the critical temperature. The center horizontal section is the section in which both gas and liquid are present. It should be noted that the pressure is constant throughout a very considerable volume change. The pressure is, indeed, the vapor pressure of the liquid at the given temperature. The left-hand section of the discontinuous curves is the compression curve of the liquid alone, all the vapor having been converted by compression into the liquid state.

The diagram indicates that, the higher the temperature, the higher is the vapor pressure and the shorter is the region of coexistence of liquid and gas. This is true for all liquids. At the critical temperature, the discontinuity becomes a simple inflection in the curve. These p–v isothermals were established experimentally by Andrews for carbon dioxide. Similar diagrams may be obtained for other vapors and their liquids.

2. **Van der Waals's Equation and the p-v Isothermals:** We have already indicated that, by means of the van der Waals equation,

$$(p + a/v^2)(v - b) = RT, \qquad (6.1)$$

it is possible to interpret the p–v relationships of actual gases more accurately than is possible with the fundamental equation $pv = RT$. The van der Waals equation should therefore apply to the isothermals above the critical temperature and it is of interest to see how the values of a and b so obtained interpret the behavior below the critical temperature. Actually, test of this point shows that van der Waals's equation does not reproduce the discontinuous portions of the isothermals but gives a continuous curve of the form indicated by the dotted line in the 21.5° isothermal. This behavior may be better understood by employing the equation in the expanded form

$$v^3 - (b + RT/p)v^2 + av/p - ab/p = 0. \qquad (6.2)$$

This is a cubic equation and there are, therefore, three values of v for each value of p. In the 21.5° isothermal the three values are indicated as v_1, v_2 and v_3. They are three real values. As the temperature is raised these values, v_1, v_2 and v_3, become more nearly equal, until at the critical temperature, they become equal.

$$v_1 = v_2 = v_3 = v_c. \qquad (6.3)$$

Since the temperature and pressure are both critical, this value of v is the critical volume. Its value must be such that

$$(v - v_c)^3 = 0. \qquad (6.4)$$

Expansion of this equation gives

$$v^3 - 3v_cv^2 + 3v_c^2v - v_c^3 = 0. \tag{6.5}$$

If we equate the coefficients of v^2, v and $v^0(=1)$ in this equation with the corresponding coefficients in van der Waals's equation for the critical temperature and pressure

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{a}{p_c}v - \frac{ab}{p_c} = 0 \tag{6.6}$$

we obtain

$$3v_c = b + RT_c/p_c, \tag{6.7}$$

$$3v_c^2 = a/p_c, \tag{6.8}$$

and

$$v_c^3 = ab/p_c. \tag{6.9}$$

From (6.8) and (6.9) it follows that

$$v_c = 3b, \tag{6.10}$$

from (6.8) and (6.10) that

$$p_c = a/27b^2, \tag{6.11}$$

from (6.7), (6.10) and (6.11) that

$$T_c = 8a/27bR. \tag{6.12}$$

The experimental values of a and b obtained from Andrews's data for carbon dioxide were used to calculate the critical temperature and pressure by means of equations (6.10), (6.11) and (6.12). An agreement within twenty per cent of the experimental values of these latter constants was obtained. This agreement is evidence of the truth of the fundamental ideas involved in the van der Waals equation. The critical data furnish, moreover, one means of obtaining approximate values for a and b in the equation of state. By reason of the applicability of his equation, van der Waals suggested the term 'continuity of state' as indicating an essential continuity in the transition from one set of isothermals, above the critical temperature, where the conditions are indisputably gaseous, to those below the critical temperature where they are also liquid.

3. The Equation of Corresponding States: The equations (6.7), (6.8) and (6.9) of the preceding section can be utilized to give the following values of a, b and R in terms of the critical constants:

$$a = 3p_cv_c^2; \qquad b = \frac{v_c}{3}; \qquad R = \frac{8p_cv_c}{3T_c}. \tag{6.13}$$

Substituting these values in the van der Waals equation one obtains

$$\left(p + \frac{3p_cv_c^2}{v^2}\right)\left(v - \frac{v_c}{3}\right) = \frac{8p_cv_c}{3T_c}T. \tag{6.14}$$

Dividing by $p_c v_c/3$ there results

$$\left(\frac{p}{p_c} + \frac{3v_c^2}{v^2}\right)\left(\frac{3v}{v_c} - 1\right) = 8\frac{T}{T_c}. \tag{6.15}$$

This equation may now be written

$$(P + 3/V^2)(3V - 1) = 8T', \tag{6.16}$$

where

$$P = p/p_c; \qquad V = v/v_c \qquad \text{and} \qquad T' = T/T_c. \tag{6.17}$$

These fractions, P, V and T', are known respectively as the *reduced* pressure, volume and temperature. It will be noted that equation (6.16) is unlike the van der Waals equation in that it contains no constants characteristic of the substance in question. This equation should be equally applicable to all gas-liquid systems. It suggests the conditions, therefore, under which such different systems should be compared. They should be compared at equal values of P and V or P and T' or V and T', at equal reduced temperatures, volumes or pressures. One interesting illustration of the truth of this may be cited. In comparing the properties of different liquids it was found experimentally that regularities could be traced if the properties of the liquids were measured at the boiling point of the liquids. Thus, it was shown by Kopp that the molecular volumes of series of organic compounds were an additive function of their component atoms, the type, number and method of linkage, provided comparisons were made of the molecular volumes of the species at their own boiling points. Now, it happens that the boiling points of most liquids are at the same corresponding or reduced temperature, the boiling point on the absolute scale being approximately two thirds (more accurately 0.62) of the critical temperature on the absolute scale. Comparisons of properties at the boiling point are therefore in harmony with the theorem of corresponding states as here developed. The theorem does not depend on the van der Waals equation since other equations of state also may be shown to yield equations of corresponding states.

4. **Vapor Pressure:** In the p–v isothermals already discussed it has been shown that in the region of coexistence of liquid and gas, the pressure remains constant so long as the two states are present. Furthermore, as the temperature increases, these pressures, which are the vapor pressures of the liquid, also increase. This effect of rise in temperature on the vapor pressure of a liquid is in accord with the kinetic ideas already developed. A rise in temperature means an increased kinetic energy of the molecules of the liquid, so that a larger proportion will have a velocity which will carry them through the attractive forces operative in the surface layers of the liquid. Hence, a larger number will escape, with a resultant increase in the vapor pressure. Due also to the increased kinetic energy of the molecules, the field of molecular attraction will act

as though it were diminished, since the molecules of the liquid will be able to move farther apart before the molecular forces cause their return.

We can express the variation in vapor pressure with temperature with the aid of the principle of distribution of velocities discussed in a preceding chapter. Let us assume that, over a given temperature range, a molecule must reach the surface with an energy in excess of L, in order that it may leave the liquid for the gas phase. The number of such molecules will be proportional to the number in the whole liquid which have such an energy content. We saw in Chapter 3 that the number of molecules having an energy in excess of L is given approximately by the expression

$$n_L = ne^{-L/RT}. \tag{6.18}$$

On the assumptions made, therefore, we may set the vapor pressure, p, equal to this quantity multiplied by a constant proportionality factor, c, and obtain

$$p = c \cdot e^{-L/RT}, \qquad \text{or,} \qquad \ln p = \ln c - L/RT. \tag{6.19}$$

If this equation expresses the relationship between vapor pressure and temperature it is apparent that if we plot $\ln p$ as ordinates against $1/T$ as abscissas a straight line relationship must result. Actually, for graphical purposes, the equation is used with the logarithms to the base, 10, in which case $R \times 2.303 = 4.57$ and

$$\log p = \log c - L/4.57T. \tag{6.20}$$

Such a procedure actually does yield the straight line relationship anticipated provided the temperature range is not too great. It follows that the intercept on the pressure axis, i.e., the value for $1/T = 0$, gives the value of $\log c$. The slope of the straight line gives the value of $L/4.57$. That L cannot be constant over a wide range of temperatures is apparent for the reasons already cited in the first paragraph of this section. We may regard the quantity L as equivalent to the latent heat of vaporization. Indeed, we shall later show that the same relation may be derived thermodynamically for a liquid at low vapor pressures where the vapor obeys the gas laws, in which case the thermodynamic expression for the relation between heat of vaporization and pressure is given by the **Clapeyron-Clausius equation,**

$$\lambda = \frac{RT^2}{p}\frac{dp}{dT}, \qquad \text{or} \qquad \frac{d \ln p}{dT} = \frac{\lambda}{RT^2}, \tag{6.21}$$

which, on integration, gives the result,

$$\ln p = -\lambda/RT + \text{const.}, \tag{6.22}$$

an equation identical with that already deduced from approximate kinetic considerations. The value of λ is itself dependent on the temperature and, indeed, becomes zero at the critical temperature. Hence the limited applicability of such equations.

5. **Ramsay and Young's Rule:** It is a consequence of the theorem of corresponding states that, at corresponding temperatures, the corresponding pressures will be the same. This has been tested by Ramsay and Young and found true for a large number of liquids. If p_1 and p_2 are any two vapor pressures of a liquid at temperatures T_1 and T_2, then, the corresponding temperatures T_1/T_c and T_2/T_c must be the same for any other liquid at the vapor pressures p_1 and p_2. Hence $T_1/T_c \div T_2/T_c = T_1/T_2$ should be the same for all liquids. Ramsay and Young measured the temperatures at which the vapor pressures were 76 and 20 cm. respectively and found the ratio of these temperatures to be a constant, 1.11, for a large number of liquids. This rule is not universal. For liquid hydrogen the ratio is 1.23. For ethyl alcohol the ratio is 1.09.

6. **Trouton's Rule:** If the corresponding pressures of liquids are the same at corresponding temperatures a further interesting conclusion can be drawn from the Clapeyron-Clausius equation (6.21). For the boiling point, T_B, and employing the theorem of corresponding states

$$\frac{\lambda}{T_B} = R\frac{d\ln p}{dT_B/T_B} = R\frac{d\ln p}{d\ln T_B} = R\frac{d\ln p/p_c}{d\ln T_B/T_c}\,. \tag{6.23}$$

Consequently, the quantity λ/T_B should be a constant for all liquids. This rule was established empirically by Trouton, who showed that, as an average,

$$\lambda/T_B = 20.7 \text{ cals. per degree.} \tag{6.24}$$

This ratio is also only an approximate rule, deviations occurring with low boiling liquids, e.g., liquid hydrogen, and also for a number of groups of liquids, including water and especially the alcohols.

7. **Vapor Pressure and External Pressure:** In the preceding sections, vapor pressure has been considered with a liquid in contact with its saturated vapor alone. A condensed system, solid or liquid, may, however, exist under a pressure different from that of its own vapor. For example, if the vapor contains an indifferent gas, the total gas pressure is the sum of two pressures, that of the vapor and that of the foreign gas. This is, indeed, the normal circumstance in a vessel containing air admixed with vapor in equilibrium with the liquid. Under such circumstances, the vapor pressure of the liquid is different from that in the isolated liquid-vapor system. The equation connecting vapor pressure and external pressure was derived by Willard Gibbs in 1876.

At constant temperature, the change in vapor pressure dp with change in external pressure dP is equal to the ratio of the specific volume of the liquid v to that of its vapor V under the pressure p.

$$dp/dP = v/V. \tag{6.25}$$

Thus, the vapor pressure of any liquid is increased by compression of the liquid and the same is true also for solids. Since v/V is a very small fraction, it follows that, for all small values of dP, the variation in vapor pressure with external pressure is generally negligibly small. Thus, the vapor pressure of a liquid under its own saturated vapor pressure will not be sensibly different from that when the liquid is exposed to the pressure of the atmosphere. But, at the super-pressures now becoming familiar in technical work, variations in the vapor pressure will be manifest. Thus, under the pressure of an inert gas equal to 300 atmospheres pressure, the vapor pressure of water increases by about 20 per cent. In applying the equation to such high values of dP it is necessary to know the variation of v and V through the pressure region from p to P.

8. **Surface Tension:** The molecules at the surface of a liquid differ as regards the forces of molecular attraction from those in the interior of the liquid. In the latter case, the molecular forces are exerted equally in all directions. The molecules at the surface are under a force whose resultant is in the direction towards the main body of the liquid. The operation of molecular forces, even in a film, can be demonstrated by the formation of a continuous film of liquid inside a wire ring. Indeed, one may approach a definition of such forces by the study of such films. If one imagines a film of liquid bounded on three sides by a wire bent in the form of a U and on the fourth side by a movable rod, then, assuming the absence of friction, the tension of the film will tend to contract the film. A force, F, must be applied to the rod to maintain the film at its given size. If by means of the equation

$$F = 2\gamma l \qquad (6.26)$$

we equate this force, F, to the surface tension, γ, acting along the length of rod, l, on two sides of the film, we have a method of measuring surface tension. For, if the rod be moved through a distance x, so that the film is extended and its surface increased by $2xl$, it follows that the work done is

$$Fx = 2x\gamma l. \qquad (6.27)$$

For unit area increase it is apparent that γ ergs of energy will be required. The definition of surface tension that these considerations yield is that **surface tension is the force in dynes per unit length of surface of liquid in a direction parallel to the surface.**

This force exerted by a film is connected with the downward field of force in the surface of a mass of liquid. For, in any increase in the surface area of a given mass of liquid, molecules which were not subject to a resultant force have to be pulled up to the surface against the resultant force in order to create the new surface.

9. **Measurement of Surface Tension:** Two manifestations of surface tension are utilized for the indirect determination of surface tension, the rise of liquid in a capillary tube and the formation of drops of liquid at the ends of capillary tubes.

10. **Capillary Rise:** A liquid which wets a capillary tube will rise to a given height above the level of the horizontal surface of the liquid outside the tube. The surface tension γ acts at the circumference of the tube which, if of radius r, involves a total force of $2\pi r\gamma$. This force, at equilibrium, must balance the force exerted by the volume of liquid in the capillary above the level in the body of the liquid outside. If the capillary rise is h, the volume is $\pi r^2 h$ and the hydrostatic pressure must be $\pi r^2 hdg$ where d is the density and g is gravity. Equating the force of surface tension with that of hydrostatic pressure, $2\pi r\gamma = \pi r^2 hdg$, whence it follows that

$$\gamma = \tfrac{1}{2}rhdg. \tag{6.28}$$

Accurate determinations of surface tension by this method have been made by Richards and his students.[1]

11. **The Drop Weight Method:** Relative surface tensions in terms of a standard liquid of known surface tension may be obtained by determining the weight of drops of the liquids forming at the tip of a capillary tube. The surface tension is proportional to the weight of the drop formed. The exact theoretical relationship between surface tension and weight is a matter of very considerable controversy, so that, in practical use, the surface tension ratio of a given liquid and a standard liquid, e.g., water, is set equal to the ratio of the weights of the drops

$$\frac{\gamma_x}{\gamma_{H_2O}} = \frac{m_x}{m_{H_2O}}. \tag{6.29}$$

12. **Surface Tension and Temperature:** With rise in temperature the surface tension decreases, reaching a value of zero at the critical temperature. For the greater part of the temperature range the relation between surface tension and temperature is nearly linear. Near the critical temperature, the surface tension varies less rapidly with rise of temperature. It was shown by Eotvos and Ramsay and Shields that the variation of molecular surface energy with the temperature can be represented by an equation

$$\gamma(M/d)^{2/3} = k(T_c - 6° - T), \tag{6.30}$$

where M is the molecular weight and d the density of the liquid. M/d is a volume and therefore $(M/d)^{2/3}$ has the dimensions of a surface. It refers to surfaces containing equal numbers of molecules. Ramsay and

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[1] *J. Am. Chem. Soc.*, **37**, 1656 (1915); **46**, 1196 (1924).

Shields found that, for a number of liquids, k has the value 2.12. Such liquids are known as normal liquids.

13. **Molecular Association:** For a number of other liquids the experimental determinations give abnormal values of k. This result may be stated otherwise by pointing out that, if the normal value of $k = 2.12$ be employed, the value of M so deduced is abnormally high. Thus, for water, a value of M considerably higher than 18, the value for water vapor, is derived. This result indicates that such liquids contain associations of molecules. A similar behavior has already been referred to in the case of gases such as sulfur vapor which apparently did not obey the gas law. Those liquids which, from surface energy measurements, appear to be associated are also those which in other respects show abnormal behavior. They show abnormal values for the constant in Trouton's rule. They do not follow the Ramsay and Young rule. Water and the lower alcohols are conspicuous members of this group of abnormal or associated liquids. In general, the concept of association is linked with the presence in the molecule of a strong polar grouping.

14. **Density of Liquid-Vapor Systems:** The thermal expansion of a liquid with increase in temperature results in a decrease in density of a liquid with increasing temperature. At the same time the increased vapor pressure causes an increase in the concentration of the saturated vapor and hence in its density. As the critical temperature is approached the densities of liquid and vapor approach each other and finally become indistinguishable at the critical temperature. Cailletet and Mathias, in 1886, observed that the mean density of liquid plus saturated vapor was practically constant over a range of temperature. More accurately, the mean density d_m of the system, varying approximately linearly with the temperature, can be expressed by the equation

$$d_m = \tfrac{1}{2}(d_l + d_v) = d_0 + at. \qquad (6.31)$$

With such an equation it is obviously possible to obtain the critical density when the critical temperature is known. For still more accurate determinations of the critical volume, equations in higher powers of t may be used, e.g.,

$$d_m = d_0 + at + bt^2. \qquad (6.32)$$

Eyring has called attention to the significance of this approximate constancy of mean density. This is readily understood if, in a liquid-vapor system, there are holes whose volume per unit volume of liquid is equal to the volume of the molecules per unit volume of the saturated vapor phase in equilibrium at the temperature in question. The holes need not be of molecular dimensions. Eyring points out that this concept of holes in the interior of a liquid gives an approximate measure of the free volume, v_f, in the liquid, a quantity which is important for all phenomena in which motion of one part with respect to another is involved. Viscosity of liquids is one such property that will be later considered.

15. **Molecular Volumes of Liquids:** The volume occupied by a gram mole of a liquid is obviously dependent on the temperature of measurement since, as we have seen, the density decreases with temperature increase. Kopp compared molecular volumes at the boiling point, which can be seen to be of advantage since the boiling points of liquids are, as already pointed out, corresponding temperatures of many normal liquids. Kopp found that isomeric substances had practically equal molecular volumes. In an homologous series of organic liquids the addition of a CH_2 group produced a constant increase in the molecular volume. It is thus evident that, to a first approximation, the molecular volumes can be regarded as the sum of the atomic volumes of the constituents.

Such comparisons do not allow for the effect on the volume of the **internal pressure** of the liquid. That such pressures exist is evident from the presence in the van der Waals equation of the term a/v^2. Indeed, this quantity is actually an approximate measure of the internal pressure, p_i. For liquids, at moderate values of p, the term a/v^2 must be predominantly large. The evidence of surface tension is a further indication of the existence of internal pressures which have been estimated to be as high as hundreds of atmospheres. Comparisons of molecular volumes of liquids should therefore be made under comparable internal pressures, but the compressibility data and accurate values for the internal pressures would be required before these comparisons could be made.

16. **The Parachor:** Another function devised by Sugden, the parachor, tends to eliminate the internal pressure difficulty in comparing molecular volumes. In 1923 MacLeod showed that the following relation between the surface tension, γ, and liquid and vapor densities was approximately true:

$$\gamma/(D - d)^4 = C. \tag{6.33}$$

C was a constant independent of the temperature. The parachor P of Sugden is the product of the molecular weight, M, and the fourth root of the MacLeod constant

$$P = MC^{1/4} = M\gamma^{1/4}/(D - d). \tag{6.34}$$

Since the vapor density is negligible compared with the liquid density, the parachor is essentially the product of the molecular volume, v_l, of the liquid and the fourth root of the surface tension

$$P \sim v_l\gamma^{1/4} \tag{6.35}$$

and can be regarded as the molecular volume at comparable internal pressures. The value of the parachor is independent of temperature over a wide temperature range, and is found to be remarkably additive. The parachor for a molecule can thus be obtained from the sum of values representative of the constitutive elements. There are, however, effects of change of valence and of nature of bonds which sometimes introduce difficulties in its application.

17. **Orientation of Molecules:** The idea of the polar molecule is almost as old as the molecular theory itself. The basis of this idea is that the field of molecular forces of attraction does not proceed uniformly from the center of the molecule but may be concentrated in the neighborhood of one of the atoms composing the molecule. The oxygen atom has long been recognized as one whose field of force is not completely neutralized by the fields of force of neighboring atoms held in direct chemical combination with it. Formic acid, for instance, may be looked upon as having a large field of molecular attraction resulting in a high surface tension, high critical temperature, etc. Ethane molecules have a very small attraction for one another, as is evidenced by their physical constants. A molecule composed, so to speak, of both, namely, propionic acid, will then be a polar molecule, one in which the molecular force of attraction is more concentrated in one particular part, so that if these molecules are oblong in shape, the field of force around one end, the —COOH end, will be more pronounced. The existence of molecular orientation logically follows the concept of the polar molecule.

Further insight into the problem of orientation is obtained from a study of the behavior of insoluble films on liquid surfaces. It has long been known that insoluble oils form either lenses or extended films on water surfaces. The lenses form quite generally with pure hydrocarbon oils, while films are formed with insoluble substances which contain one or more polar groupings in the oil molecules. The fatty acids and their esters are typical oils forming films. Such oil films were soon found to reduce the surface tension of water very greatly when spread over the water surface.

Rayleigh, in 1890, observed that a definite minimum quantity of oil was required to produce a definite reduction of surface tension and he measured the quantities of oil in terms of the area covered. He also pointed out that certain surface properties of water are due to contamination with impurities such as grease. In the same year, Miss Pockels devised the technique of procuring clean surfaces by wiping the surface with barriers or strips of material which push the impurities in front of the strips, leaving a clean surface behind. If the barriers extended the whole width of a rectangular trough filled with water, the barriers resting on the edges and in contact with the water surface, an area of clean surface could be secured and maintained by resting the barrier at a definite position in the water surface. She also revealed the spreading of films on surfaces, even from solid bodies, by dusting the water surface. The spreading film pushed back the boundaries of the dusty area. She compared this outward pressure exerted by spreading films with osmotic pressure. She found that the surface tension of water was not perceptibly modified unless a certain quantity of oil was spread on a given surface.

Rayleigh confirmed this conclusion in 1899 and showed that the surface tension of water fell rapidly when the water area was reduced, for a given quantity of oil, below the critical area. He concluded that the oil molecules were floating objects, repelling one another when in a single layer in contact, and, therefore, that the point at which rapid decrease in surface tension arose corresponded to an area of film one molecule thick, now conveniently referred to as a *monolayer.*

A floating barrier separating an insoluble oil film surface from a clean surface can be regarded as a semi-permeable membrane. There is freedom of passage of the water molecules across the barrier, via the body of the water. Owing to the insolubility of the film no such free passage across the barrier is available to the oil. If an oil film enclosed by a floating barrier of length l exercises an outward pressure of F dynes per centimeter on the barrier, we can express this force in terms of the surface tension γ of the water on one side of the barrier and of γ_1 on the oil film side of the barrier, since for a displacement of the barrier, dx, we have

$$F \cdot l \cdot dx = (\gamma - \gamma_1) l \, dx. \tag{6.36}$$

Hence the force $F = \gamma - \gamma_1$, the difference in surface tensions on the two sides of the barrier.

From 1904 to 1913 numerous experiments on the properties of oil films and the development of technique were made by Devaux, who confirmed the maximum extension of films and the thickness of molecular magnitude. It was Langmuir, however, in 1916 who proceeded to the direct measurement of the force, F, and, *using pure substances* as oils for the monolayers, brought out quantitatively the dimensions of molecules.

The experimental method designed by Langmuir and employed subsequently in a long series of researches by N. K. Adam[1] is shown diagrammatically in plan and elevation in Fig. 6.2. A trough, A, is filled with water, separated into portions by two strips, B and C, of paraffined copper immersed in the water to half their thickness. Strip B is supported by the walls of the trough and makes contact with the sides. Strip C is fastened rigidly to a beam balanced on a knife edge, F, which is supported by a stand not shown in the diagram. On one end of the beam a pan is fastened on which weights can be placed, and a counterpoise weight is attached to the other end. Strip C does not touch the sides of the trough and is free to move in either direction, S or S'. When pure

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[1] N. K. Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, Oxford, Third Edition, 1942.

water is in contact with both sides of strip *C*, the balance is in its zero position, adjustment of the weights having been made so as to bring strip *C* directly under the knife edge. On placing an oil, which spreads over water, between strips *B* and *C*, the surface tension forces on *C* are upset; that of the pure water predominates and the strip tends to move in direction *S′*, but is prevented from doing so by adjustment of the weights on the balance pan. To stop the oil from getting past the ends of the strip *C*, two jets of air are played at points *D* and *D′*. These jets are maintained at constant speed, and any effect they have on strip *C* is adjusted in the first instance, before adding the oil to the water surface.

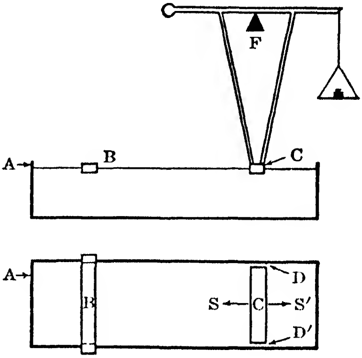

Fig. 6.2. Apparatus for Measurement of Film Characteristics

A description of the precautions that have to be taken, such as the assurance of an uncontaminated water surface, will not be detailed. The procedure to form the film consists in placing a known weight of the substance out of which the film is to be formed, dissolved in a few drops of benzene, on the surface between the strips *B* and *C*, the former being at the far end of the trough. After the benzene has evaporated, the strip *B* is gradually moved toward *C*. Provided a small enough quantity of substance has been used, no effect is noted on strip *C* until the area between *B* and *C* has been diminished beyond a certain point. After that, weights are placed in the pan to keep *C* in its zero position, the areas between *B* and *C* and corresponding weights being tabulated. The weights are expressed in dynes per unit length of *C*, measured in the direction *S′*, and the area, measured in square centimeters, is divided by $6.02 \times 10^{23} m/M$, where m is the weight of the substance composing the film and M its molecular weight. This gives the average area occupied by each molecule.[1]

The results obtained by Langmuir can best be illustrated by an example. For palmitic acid, the area per molecule at which a sharp change in F (dynes per cm.) occurred with compression of the surface is about 20.5 sq. Ångstroms = 20.5×10^{-16} sq. cm. per molecule (cf. Curve I, Fig. 6.3). Langmuir found that the area did not sensibly alter with variation in the number of carbon atoms in the chain from twelve to twenty-

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[1] For experimental exercises on the areas occupied by oil films see Mack and France, Laboratory Manual of Physical Chemistry, D. Van Nostrand Co., New York, 1934.

six. Now the molecular volume of palmitic acid is 300 cc., which is equivalent to 495 cubic Ångstroms per molecule. Dividing this by the observed area, we deduce a length of about 24.2 Ångstroms compared with a length and breadth of 4 or 5 Å. Change of CH_2 in the length of the hydrocarbon chain produces a change of molecular volume of 17.8 cc. = 29.4 cubic Å per molecule. This corresponds to a change in length of the chain of 1.43 Å per CH_2 group. This value deduced from molecular films is to be compared with the results of X-ray spectroscopy on solids containing hydrocarbon chains, from which a value of 1.26 Å is deduced. The difference may be due to differences in density of oil film and solid or to a tilt of the hydrocarbon in the film away from the vertical.

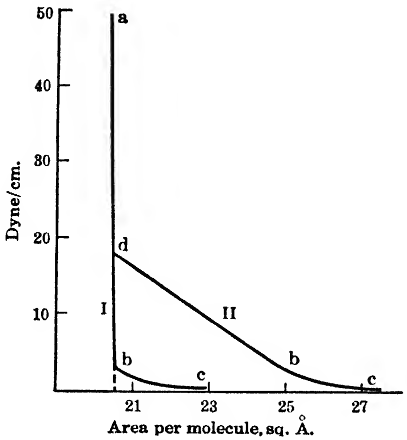


Fig. 6.3. Fatty acid films (I) on water, (II) on acid

Langmuir emphasized the polar characteristics of such film-forming molecules. He pointed out that a fatty acid molecule has a hydrophilic portion, the COOH group, and a hydrophobic portion, the hydrocarbon section. It is lateral adhesion between the hydrocarbon portions of the molecules which keeps the molecules out of the water, conferring insolubility. With small hydrocarbon sections as in the lower fatty acids, acetic, propionic acid, this adhesion between hydrocarbon sections is overcome by the attraction of the COOH groups by the water molecules. The attraction between COOH group and water determines the orientation of the fatty acid film, the polar COOH group being drawn into the water, leaving the outermost portion of the surface the hydrocarbon residue of the molecule.

Naming the polar group the head of the molecule (in the case of the fatty acids, the COOH group), it appears that the head occupies a greater area than the cross-section of the chain. Where the film is spread over distilled water, the cross-section of the chain gives the *effective* area, because of the different depths to which alternate molecules enter into the water. That this is so is shown by increasing the hydrogen-ion concentration of the water, which diminishes the attraction of the COOH group for the water and forces all these groups to the same level. Curve II shows the result obtained for any saturated fatty acid, spread over $N/100$ HCl solution. The larger area, 25×10^{-16} sq. cms., represents the cross-section of the polar group. Diminution in area increases the lateral pressure on the film molecules and forces the heads to different levels until the carbon chains are again in close contact, corresponding to a cross-section of 21 × 10^{-16} sq. cm. This is brought out by the break, *d*, in Fig. 6.3, curve II.

18. **Types of Film:** The work of Langmuir and its extension by Adam has revealed four types of films of oriented molecules in surfaces, dependent on the extent of lateral adhesion between the molecules. These are:

(1) The condensed or close-packed film, steeply oriented to the surface. The fatty acids and alcohols studied by Langmuir are such films.

(2) The gaseous film with separated molecules, independent in their motions.

(3) Liquid expanded films, with strong lateral adhesion but less close-packing than in the condensed films.

(4) Vapor-expanded films, with weak adhesion. These do not differ greatly in many respects from the gaseous films.

19. **Gaseous Films:** In these films the oriented molecules being separate have two degrees of freedom of kinetic motion to each of which we may ascribe an energy of $\frac{1}{2}kT$. By analogy with the fundamental gas law, $pv = RT$, we may write the equation of an ideal gaseous film in the form

$$F \cdot A = kT, \tag{6.37}$$

where F is the force directed laterally outwards from the film, A is the area of the film and k is $8.314 \times 10^7/6.02 \times 10^{23} = 1.372 \times 10^{-16}$ erg per degree per molecule. At room temperature kT has, therefore, the value $\sim 400 \times 10^{-16}$ erg per molecule and, since the latter has an area of $\sim 10^{-16}$ sq. cm., it follows that, if the unit of area is the square Ångstrom, k becomes 1.372 and $kT \approx 400$. A perfect gaseous film would exert a force F of one dyne per cm. at 400 square Ångstroms.

Adam found, by measurements of great delicacy, that the esters of dibasic acids, $C_2H_5OOC \cdot (CH_2)_n \cdot COOC_2H_5$, with $n = 10$ or 11, showed this behavior. With such films he found a curve on plotting FA against F entirely analogous to the pv-p curve for real gases. At low values of F the value of FA was 400. The curve showed an initial fall due to increasing lateral adhesion of the molecules, paralleling the effect of the van der Waals term a/v^2 in the case of gases. At higher values of F the curve rose again, paralleling the effect in gases of the volume term, v-b.

Hence, we may write the equation for an ideal gaseous film in the form

$$F = \gamma - \gamma_1 = cRT, \tag{6.38}$$

and the equation for real gaseous films

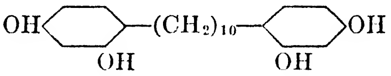
$$F = \gamma - \gamma_1 = -\frac{\alpha}{A^2} + \frac{RT}{A - \beta} \tag{6.39}$$

entirely analogous to the van der Waals equation. This equation for the lowering of the surface tension by gaseous insoluble films bears a close relation to empirical equations developed by Frumkin and by Syzskowski to interpret measurements of the surface tensions of solutions of the lower fatty acids. Frumkin's equation is of the form

$$F = \gamma - \gamma_1 = -\frac{\alpha}{A^2} - \frac{RT}{\beta}\ln\left(1 - \frac{\beta}{A}\right). \tag{6.40}$$

We may therefore conclude that soluble substances in solution give molecules in the surface layers which behave as do the molecules in gaseous insoluble films.

Various lines of evidence indicate that the gaseous film molecules lie flat on the water surface. This is most easily understood in the cases of molecules which have two polar extremities, as in the dibasic esters already mentioned, in molecules such as



and its tetra-acetate. Molecules such as oleic acid, containing a double bond in the middle of the molecule in addition to the polar COOH group at the end, form a gaseous film on acid permanganate solutions, owing to the affinity between permanganate and the double bond which is indicated by the oxidizing action of the permanganate at the double bond. On pure water surfaces, where this affinity is absent, oleic acid molecules form condensed films. It is obvious that the relative magnitudes of the lateral attractions and that between film and aqueous layer determine whether the film is gaseous or condensed.

20. **Transition from Gaseous to Liquid Films:** The plot of FA against F gives with dilute gaseous films, as we have seen, curves analogous to the pv-p curves of gases. Langmuir predicted, and Adam and Jessop found, curves for the force F against the area A analogous to the curves shown in Fig. 6.1 for p against v, showing the transition from gaseous to liquid state. Thus, with myristic acid at a temperature of 14.5° C., at surface areas greater than 1000 sq. Å, the curve is similar to that of a gaseous compression. Just below 1000 sq. Å, and down to about 200 sq. Å, the curve is horizontal, no change occurring in F ($= 0.2$ dyne per cm.) over this range of area. Below 200 sq. Å the value of F rises steeply with decrease of area. With tridecylic acid, the next lower acid, at 14.5° C. the horizontal portion occurs at $F = 0.3$ dyne per cm., between 600 and 100 sq. Å. With pentadecylic acid, the next higher acid, the horizontal portion of the curve occurs at $F = 0.1$ dyne per cm., over the wide area 2500 to 100 sq. Å. In each case the horizontal part of the curve corresponds to the horizontal portion of the p-v curve in which gas and

liquid are co-existent. In the case of films we assume the presence of both liquid areas of film and gaseous film. The value of F at the horizontal portion of the curve can be regarded as a surface film vapor pressure.

21. **Condensed Films:** These are the commonest, and owing to strong lateral adhesion they form one compact film or islands of film on the surface. Molecules seldom leave these islands. Two types have already been indicated in Fig. 6.3. The areas per molecule range from 20.5 sq. Å for the saturated fatty acids, 21.7 for the alcohols to 40.8 for cholesterol and 52 for the lecithin group. It is the nature of the end chain which determines the area, variation in length of carbon chain having small effect.

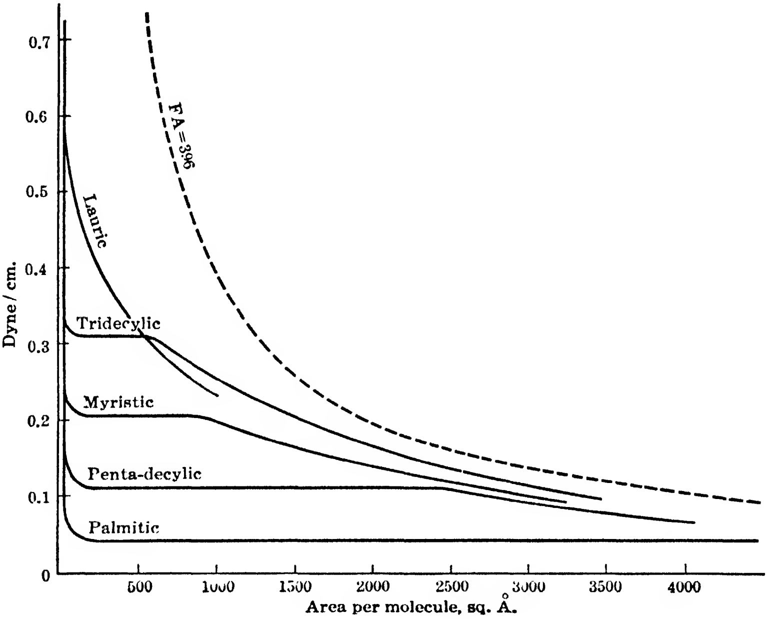


FIG. 6.4

These condensed films can show changes of state which may be regarded as allotropic forms of the films. Below 28° C. the octadecyl derivative of urea forms a stable structure which may be regarded as a solid with an area of 26 sq. Å at no compression. Above 28° C. the typical curve similar to I of Fig. 6.3 is obtained. The transition temperature is raised about 2° C. for each additional carbon atom in the chain.

22. **Expanded Films:** This type is intermediate in area and other properties between the gaseous and condensed films, and is found with

long-chain aliphatic substances. For a given acid, such as myristic acid between 2 and 35° C., the properties of the expanded film show a regular progression. At the lowest temperature the film is condensed, in the manner indicated by Curve II, Fig. 6.3. At the highest temperature the film is wholly expanded. At the intermediate temperatures the expanded curves pass, at higher pressures the higher the temperature, into a transition region where there is first a rapid decrease in area for slight change in pressure followed by a slower change which gradually merges into a condensed area curve. The transition region sets in, with myristic acid, at 43 sq. Å and 2 dynes per cm. at 7.2° C. and at 30 sq. Å and 18 dynes per cm. at 23° C.

Langmuir, in 1933, suggested that the upper, hydrocarbon, portion of such films should be regarded as a liquid phase resting on the water surface, with the lower interface against the water containing the water-soluble groups equal in number per unit area to the number of oil molecules and essentially a 'gaseous' film. On this view, Langmuir deduced that the outward spreading force per centimeter at the lower interface would be given by the expression:

$$F - F_0 = kT/(A - A_0), \tag{6.41}$$

where A is the observed area and A_0 a constant, F is the observed spreading force and F_0 the spreading force of the upper hydrocarbon portion of the film on water. For a pure hydrocarbon film on water, F_0 should be negative and Langmuir found that the curves for myristic acid could be represented by the expression:

$$(F + 11.2)(A - (12 + 0.178t^\circ \text{ C.})) = kT. \tag{6.42}$$

23. **Chemical Reaction in Monolayers:** The possibility of investigating the chemical reactions occurring in monolayers has been studied, largely by Rideal and his co-workers. As examples of such reactions we may cite the following: The hydrolysis of stearolactone by alkalies in a film closely resembles similar reactions in homogeneous systems. Irradiation of films of ergosterol appears to yield vitamin D. The rate of oxidation of unimolecular films of unsaturated fatty acids by potassium permanganate solutions depends on the degree of extension of the film. Compression, as we have seen, removes the unsaturated linkages from the surface, thus diminishing the opportunity for oxidation. The possibility of important biochemical applications is indicated by the studies of the digestion of monolayers of proteins by enzymes. Here also the extent of compression influences the rate of reaction, paralleling differences in the metabolism of resting muscle and of muscle in a stretched state.

In the field of sterol chemistry the study of monolayers has yielded interesting results. The older formulas for the sterol skeleton were shown to be incompatible with the areas occupied by such films when spread on water. The corrected formula (Fig. 6.5) for the skeleton is in best agreement with film data. Film studies also reveal the stereo-chemical arrangement of substituents in the sterol molecule. Thus, Schulman and Rideal showed that digitonin injected under a cholesterol monolayer increased the force *F*, at constant area, from 10 to over 60 dynes per cm. Langmuir, Schaefer and Sobotka studied the adsorption of digitonin by sterol monolayers on water and showed that solid films were formed with cholesterol, cholestanol and ergosterol while the films of *epi*-cholesterol, *epi*-cholestanol and of calciferol remained liquid. The differences in behavior between the natural sterols and the epi-sterols thus indicated, and paralleled in the formation or non-formation of digitonides in bulk, is attributable to the inversion of the hydrogen and hydroxyl substituents on carbon atom 3 of the sterol skeleton. The hydroxyl in the 3-position of an *epi*-sterol molecule forms an angle with the interface entirely different from the angle in a natural sterol because of the difference in position in reference to the median plane of the molecule.

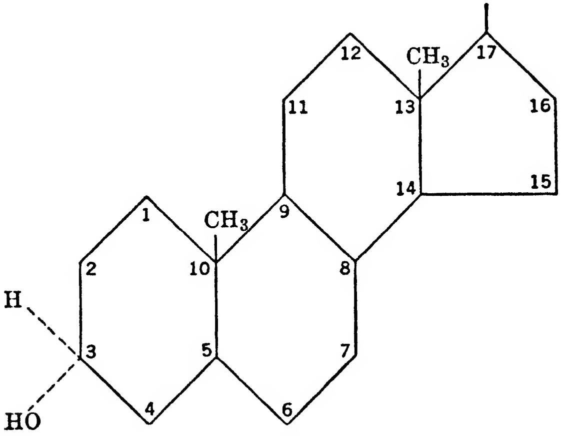


Fig. 6.5

Complex organic molecules such as the cellulose esters and synthetic polymers can also be studied by spreading on the surface of water or on alkali solutions. On the latter, denitration of nitro-cellulose occurs rapidly, so that the film is probably alkali cellulose. The quantitative force-area evidence indicates that the chains of hexose groups lie flat on the surface and that lateral adhesion of the individual cellulose chains is largely disrupted.

Proteins can be spread on water either from concentrated aqueous solution (Gorter, 1925) or from the solid material on a quartz fiber brought into contact with the water surface (Rideal, 1932). Coherent films are formed, which may be both solid and liquid. Langmuir has studied such films spread on water with 'cylinder oil' (a hydrocarbon oil which has been subjected to slight oxidation) as an indicator of the area of spreading. The cylinder oil forms a multi-layer which is visible to the eye due to its interference colors. The protein films can be determined as to their nature by the manner in which they spread or by placing an additional drop of cylinder oil in the center of the protein film. If the latter is solid the film will form with a serrated edge and be torn apart by the drop of cylinder oil in V-shaped wedge-like tearing. Liquid protein films have a circular outline and the cylinder oil added to the film center will spread circularly (Fig. 6.6).

Monolayers of fatty acids on water are very sensitive to the ion content of the water. Divalent ions tend to facilitate the formation of close-packed chains at 20.5 sq. Å area. Absence of ions tends to favor films with close-packed heads at 25 sq. Å area. Langmuir and Schaefer have examined the adsorption of Ba^{++}, Ca^{++}, Al^{+++}, and Cu^{++} by stearic acid films. A monolayer of pure stearic acid adsorbs the aluminum ion from solutions containing one part of the ion in 2×10^9 parts of water. A molten 'skim' of stearic acid is colored green when a film is spread on water containing one part of copper in 3×10^8 parts of water. The viscosities of stearic acid films on water undergo a progressive change due to adsorption of such ion impurities.

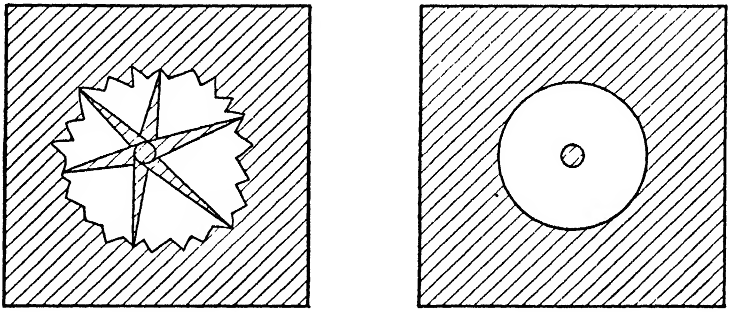

Solid Film Liquid Film

FIG. 6.6. Shaded Areas, Cylinder Oil; Clear Areas, Protein Film

24. **Built-up Films:** Blodgett in 1935 developed a method of building up successive monolayers on a solid surface, particularly layers of barium and calcium stearates on glass slides or polished chromium plated metal slides. The Langmuir trough technique was modified in important particulars. A waxed silk thread attached by metal clips to each side of the trough served as the boundary of the film. A monolayer of the substance to be studied was spread within the thread and then placed under con-

stant compression by deposition, outside the silk-thread barrier, of a 'piston' oil, using an oil such as oleic acid, which, so long as it is present in more than a monolayer (lenses of oil apparent on the water surface), gives a constant surface pressure of 29.5 dynes per cm. at 20° C. with a linear decrease with increasing temperature of 0.07 dyne per cm. per degree C. The underlying water is preferably kept on the alkaline side at pH $>$ 7.5. With stearic acid and calcium ions a calcium stearate soap film results.

On dipping a polished slide through such a film under compression nothing occurs in the first immersion. On withdrawing the slide, however, a calcium stearate layer attaches itself to the slide, —COOH group towards the glass or metal surface, hydrocarbon end uppermost. This latter is easily demonstrated because the resultant surface is hydrophobic. A second immersion adds another layer on the downward trip, hydrocarbon inside, —COOH group outside, and therefore hydrophilic. The second withdrawal duplicates the first producing a hydrophobic surface now three layers thick. In this manner any odd number of layers can be built up on the slide, 21, 41, 61, · · · 201 sequences in steps having been studied. These steps show vivid interference colors when viewed by white light. The thickness of the step-films can be measured by means of the interference of reflected monochromatic light and give values of film thickness corresponding to the values of the long spacings in fatty acids determined by X-ray diffraction measurements.

Langmuir, Schaefer and Sobotka utilized this built-up film technique to determine the thicknesses of sterol films. A single layer of sterol was superimposed on a Blodgett barium stearate step-film and, from the change in the position of the reflection maximum, using monochromatic light, the thickness of a single film of sterol could be accurately calculated. Similar use has been made of the built-up films in the study of single layers of proteins. It is possible, further, to study thus the biochemical activity of single films of proteins such as urease and trypsin to determine whether in the process of film formation denaturation of the protein occurs.

25. **Surface Tension of Liquid Metals:** Liquid metals have been found to possess higher surface tensions than are shown by any other class of liquids. As compared with a value of 72.75 dynes per cm. for water at 20°, those for the liquid metals are as follows: mercury, 480 at 0°; tin, 526 at 253°; lead, 453 at 350°; bismuth, 388 at 300°; antimony, 368 at 750°; cadmium, 600 at 500°; copper, 1103 at 1130° C. With most of these metals the surface tension decreases with increasing temperature but with cadmium, and especially with copper, the surface tension increases. Between 1130 and 1215° C. the increase in γ for copper is 0.74 per degree. These high surface tensions cause, of course, enormous

capillary rises, which can be utilized commercially for introducing liquid metals between two metals that it is desired to bond by a metal solder.

26. **The Structure of Liquids:** It has already been indicated that a liquid may be thought of as a very dense gas with molecules close together by reason of their forces of mutual attraction. The X-ray investigation of liquids initiated by Debye and Scherrer in 1916 shows, however, from the broad diffuse rings obtained with various liquids, that some arrangement of the molecules in a liquid similar to that found in the solid state must occur. Eyring has developed a theory of liquids which combines both points of view. The properties of the liquid are related to the free volume, v_f, which each molecule may be assigned in a given liquid. Thus, as indicated in Fig. 6.7, the free volume may be ascribed to the three-dimensional space in which the center of gravity of the molecule may move without the molecule colliding with its neighbors. This is different from the specific volume of each molecule, v_l, which is the molar volume, v, divided by the Avogadro number.

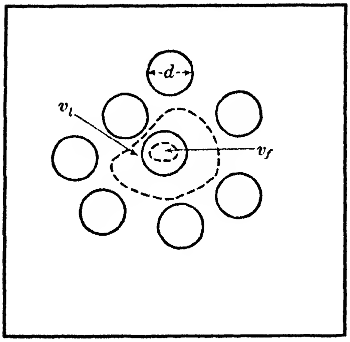


FIG. 6.7. The Free Volume v_f and the Specific Volume v_l

If a cubical arrangement of spherical molecules of a liquid be assumed, it is possible to relate the free volume with the specific volume. As shown in Fig. 6.8, the distance between the outside molecules is twice the cube root of the specific volume. If the diameter of the molecules be d then the motion of one (shaded in the diagram) relative to the others regarded as held stationary will attain a maximum value $2(v_l^{1/3} - d)$ in each dimension. The free volume is therefore the cube of this distance, or,

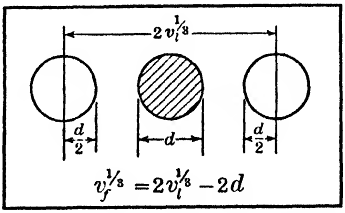


FIG. 6.8. Free Volume for Simple Cubic Packing

$$v_f = (2(v_l^{1/3} - d))^3 = 8((v/N)^{1/3} - d)^3. \qquad (6.43)$$

The diameter, d, can be expressed in terms of the van der Waals constant, b,

$$d = (3b/2\pi N)^{1/3} = 0.7816(b/N)^{1/3}. \qquad (6.44)$$

The properties of liquids can be expressed in terms of the free volume.

This applies to both thermodynamic and kinetic properties. As an example of the former we can cite the vapor pressure of a liquid, where the vapor is assumed to obey the ideal gas laws. A molecule taken from the vapor phase to the liquid phase is brought from a volume v_g to a volume v_f. In the latter the molecule is in a force-free field since there is a balance of all the attractions exerted on such a molecule in the interior of a liquid. The perfect gas laws may therefore be expected to apply to both the initial and final states. Hence the work involved in the compression is given by the expression $kT \ln (v_g/v_f)$ where k is the gas constant per molecule. This work may be equated to the heat of vaporization, λ, per molecule,

$$\lambda = kT \ln (v_g/v_f), \qquad \text{or,} \qquad v_f = v_g e^{-\lambda/kT}. \tag{6.45}$$

If the vapor pressure of the liquid is P, and the vapor obeys the gas laws $Pv_g = kT$ per molecule. Hence

$$P = kT/v_g = (kT/v_f)e^{-\lambda/kT}. \tag{6.46}$$

This expression gives an explicit value for c in Equation (6.19). Other thermodynamic properties of liquids may be stated thus in terms of the free volume of the liquid.

27. **Viscosity of Liquids:** The viscosity of liquids distinguishes itself from that of gases under ordinary compressions because the mean free path in liquids is so very much smaller than in gases. Viscosity implies resistance to flow. Flow through tubes whose diameters are large in comparison with the mean free path is known as Poiseuille Flow. For small rates of flow the motion is determined by Poiseuille's Law, which states that the volume, v, of fluid of viscosity, η, passing through the tube in time, t, under a pressure gradient $(p_2 - p_1)$ is given by the expression

$$v = \frac{\pi r^4}{8l\eta}(p_2 - p_1)t, \tag{6.47}$$

where r is the radius of the tube of length l. The experimental determination of viscosity of liquids depends on measurements of rate of flow through capillary tubes. Actually, relative viscosities are usually determined by measuring the time taken for a given volume of liquid to flow through the capillary tube of a viscosimeter, one type of which is shown in Fig. 6.9. This time is compared with the time taken for a standard liquid (generally water) for the same operation. If η and t are the viscosity and time taken for a liquid of density d, and η_w, t_w and d_w are the corresponding magnitudes for water, then,

$$\eta = \eta_w \frac{d \cdot t}{d_w \cdot t_w}. \tag{6.48}$$

This method of viscosimetry is evidently based on Poiseuille's law in an apparatus in which v, r and l are maintained constant. The density ratio d/d_w takes care of the variation in $(p_2 - p_1)$ since this is actually the head of liquid under which the flow takes place. The determinations are carried out at carefully controlled temperatures since, in the case of liquids, there is a marked decrease of viscosity with rise in temperature. At 100° C. the viscosity of water is only 15.8 per cent of its value at 0° C.; at 25° C. the viscosity is only 49.7 per cent of its value at 0° C. In this respect liquids differ markedly from gases which, as we have seen (3, 14), at low pressures, slightly increase in viscosity with increase of temperature.

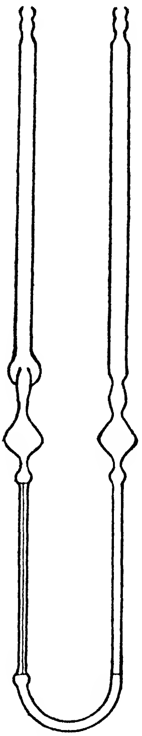


Fig. 6.9. Viscosimeter (Bingham)

The transition in viscosity from gas to liquid was shown by Phillips[1] who investigated the viscosity of carbon dioxide over a short temperature range at pressures from 1 to 100 atmospheres. In Fig. 6.10 are shown the isobars of the coefficients of viscosity at various temperatures. The 1-atmosphere isobar shows that the viscosity increases with the temperature in accordance with the kinetic theory of gases. In the neighborhood of this pressure also, Maxwell's law, that the coefficient of viscosity does not vary with the pressure, holds fairly well. The law, however, only holds as long as the gas approximates to the ideal condition. As the pressure is increased considerably, new factors come into play and the viscosity increases with increase in pressure. The 40-atmosphere isobar still shows a positive but slightly smaller temperature coefficient for the viscosity. The 60-atmosphere isobar indicates that viscosity is independent of the temperature. At this pressure and over the temperature range shown, the average volume of the carbon dioxide is some twenty-five times that of the space occupied by the molecules as calculated from van der Waals's b. The 70-atmosphere and higher isobars show negative temperature coefficients similar to the temperature coefficients of viscosity of liquids. Thus, the change in the property of viscosity varies continuously from gas to liquid.

The variation of viscosity with temperature shows wide variation from linearity; it was pointed out by Bingham that the reciprocal viscosity, $1/\eta$, or the *fluidity* showed, in general, a much more nearly linear variation with temperature. The importance of the fluidity as a measure

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[1] *Proc. Roy. Soc.*, **87A**, 48 (1912).

of fluid flow was increased by the observation by Batschinski that, in the case of sixty-six non-associated liquids, a linear relationship exists between the specific volume and the fluidity, expressible by the equation

$$v = a + \frac{b}{\eta}\cdot \tag{6.49}$$

Indeed, this expression is valid for the fluidity of liquids far above their boiling points, ether, ethyl acetate and benzene having been studied from 0° C. to temperatures of 100, 183 and 186° respectively. Associated liquids such as the alcohols show, however, deviations from this linear relation between volume and fluidity, the fluidity increasing more rapidly than the specific volume. The viscosity of associated liquids, therefore, decreases proportionately more rapidly than that of non-associated liquids.

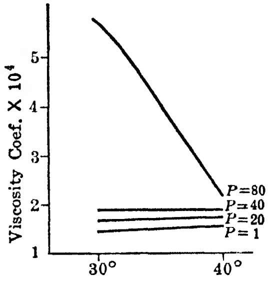


FIG. 6.10. Viscosity Coefficients of Carbon Dioxide

Numerous efforts have been made to relate the variation in viscosity with the temperature. The most recent efforts have indicated that the viscosity varies with temperature in an exponential manner, an equation of Andrade having the form

$$\eta = \eta_0 e^{\lambda/3.5kT}, \qquad \text{or} \qquad \log \eta = \lambda/3.5kT + \text{const.}, \tag{6.50}$$

where η_0 is independent of temperature and λ is the heat of vaporization per molecule. The constant, 3.5, in the equation varies between 3 and 4 for a large number of substances. Eyring has pointed out the reason for this regularity. The tightness of packing in a liquid hinders the flow of one molecule past another. Free volume is necessary for flow. To make a hole the size of one molecule requires work equal to λ. The exponential dependence on temperature seems to indicate that the unit process for viscous flow requires the formation of a hole one-third to one-fourth the size of a molecule. The flow appears to occur by the collision of two molecules followed by a rotation of the pair through 90°. This requires, geometrically, about the volume deduced from the Andrade equation. Associated liquids are exceptional in their behavior, with high and variable temperature coefficients. This is to be interpreted on the view that, in making the hole, it is necessary at the same time to break hydrogen bonds between molecules. Liquid metals also constitute an exceptional class as regards the above generalization. They have much smaller temperature coefficients. Eyring interprets this as involving the relative motion, not of atoms of the metals, but of ions and these are conspicuously smaller units. Indeed, if, for 3.5 in the Andrade expression, one substitutes 3 (volume of metallic ion/volume of metallic atom) the temperature variation of viscosity in metals is well reproduced.

The phenomenon of viscous flow in liquids is a particular case of the general phenomenon of reaction rates which will be discussed in detail in Chapter 15.

EXERCISES (6)

1. For pressure expressed in atmospheres and volume taken as unity at 0° C. and 1 atmosphere, the van der Waals constants for sulfur dioxide are, $a = 0.01338$, $b = 0.002516$. Calculate the critical temperature and pressure and compare them with the observed values of 157.2° C. and 77.7 atms.

2. The following are the vapor pressures of water at the temperature indicated:

T° C.	100	80	60	40
p(mms.)	760	355	149	55

Calculate the heat of vaporization.

3. Calculate the Trouton constant for water from the results of problem 2.

4. Using the Dieterici equation of state (3.62), find the relation between b and v_c.

5. In a tube of radius 0.129 mm. carbon disulfide rose to a height of 4.20 cm. The temperature was 19.4° C. when the density of the liquid was 1.264. Taking $g = 980.4$, find the surface tension in dynes per cm.

6. The molecular surface energy of formic acid decreases 0.902 per degree between 15° and 45° C. Assuming the Ramsay and Shields constant to have a value 2.12 calculate the association factor for formic acid.

7. The following are the densities of liquid and gaseous oxygen at the temperatures indicated:

T° C.	d_L	d_G
−210.4	1.2746	0.0001
−180.0	1.1415	0.0051
−154.5	0.9758	0.0385
−140.2	0.8742	0.0805
−129.9	0.7781	0.1320
−123.3	0.6779	0.2022
−120.4	0.6032	0.2701

Calculate the constants of the rectilinear diameter and hence the critical density if $T_c = -118.8$° C.

8. Calculate the viscosity of a liquid, whose density at 25° C. is 1.256, which took 28.8 secs. to travel through a viscosimeter as compared with water of density 0.997 taking 86.4 secs. The viscosity of water at 25° C. is 0.00891 poise (dyne sec./cm.^{2}).

9. The surface pressure of oleic acid is 29.5 dyne/cm. Calculate the pressure in atmospheres exerted by oleic acid on a molecular wall of thickness 25 Å.

CHAPTER 7

THE CRYSTALLINE STATE

The majority of substances can exist in solid forms which are bounded by plane surfaces so oriented to one another that the whole possesses some degree of symmetry. A substance in this state is said to be crystalline and the state is called the crystalline state of aggregation. All other solid bodies are classed as amorphous and are to be regarded as nothing other than liquids of great viscosity. Among such viscous fluids are glasses and certain resins.

That amorphous solids differ from liquids only in degree is demonstrated by the fact that on heating they lose, by imperceptible gradations, their rigidity and may become as fluid as water. The absence of a definite transition point renders it futile to attempt to distinguish such bodies as solid under one set of conditions and liquid under another. With crystalline solids, however, matters are very different. Every crystalline solid has a definite transition point at which it undergoes an *abrupt* change into a liquid with absorption of heat. Even under great pressures the transition from the crystalline to the liquid state invariably takes place abruptly when a definite temperature, which depends upon the pressure, is reached.

1. **Crystal Symmetry:** The various types of symmetry found in crystals include planes, axes and centers of symmetry. When a crystal has a plane of symmetry it may be divided by an imaginary plane into two parts which are mirror images of each other in that plane. An axis of symmetry is an axis of revolution of the crystal provided that during a complete revolution the crystal presents the same appearance more than once. The recurrence of the initial aspect of the crystal may be two, three, four or six times corresponding to rotations through 180°, 120°, 90° or 60°, yielding diad, triad, tetrad and hexad axes respectively. A center of symmetry is a point such that any line drawn through it will intersect the crystal surfaces at equal distances on either side.

2. **Classification of Crystals:** There are recognizable, on the majority of crystals, sets of faces similarly oriented with respect to the symmetry of the whole. Such a set is known as a *form*. Thus, the six faces of a cube together constitute a form, as do the eight faces of an octahedron. These forms can be gathered into groups which have the same axes, planes and centers—that is, the same elements—of symmetry. Such groups constitute the crystal classes, of which there are 32. Axes of reference

may be chosen for each of these classes such that the indices of all the faces of any one form are the same. When this is done, it is found that the crystal classes can be grouped into sets for which the axes are the same as regards equality or inequality of their lengths and of the angles they make with one another. These sets are the crystal systems, of which there are seven. These seven crystal systems with their axes are:

I. *The Triclinic or Anorthic System:* Three axes of unequal length all inclined at unequal angles other than 90°, 60°, 45° or 30°.

II. *The Monoclinic or Monosymmetric System:* Three axes of unequal length, one at right angles to the other two, which are inclined to one another.

III. *The Rhombic or Orthorhombic System:* Three axes of unequal length but at right angles.

IV. *The Tetragonal System:* Three rectangular axes, two of which are of equal length.

V. *The Trigonal System:* Three axes of equal length, forming equal angles (other than 90°) with one another.

VI. *The Hexagonal System:* Three axes of equal length lying in the same plane and inclined at 60° to each other and a fourth axis perpendicular to them and unequal to them in length.

VII. *The Cubic System:* Three equal rectangular axes.

3. **Crystal Form:** It has long been recognized that the external form of a crystal, though apparently dependent on the conditions during crystallization, possessed a constancy expressible in two ways. The first, called the *Law of Constancy of Angles,* states that the angles between the faces of a crystal are constant. The second, called the *Law of Rational Intercepts,* states that the distances from the origin cut on a given axis by the faces of a crystal stand to each other as small integers. The ratio of the intercepts of a given face on all the axes is constant. A given face is designated by the Miller indices which are the reciprocals of its intercepts on the various axes. A face parallel to a given axis has an infinite intercept and thus a Miller index of zero. The face of a cube may be referred to as a 100 face. The diagonal plane of a cube becomes a 110 face. The face of an octahedron has a Miller symbol, 111. Any planes parallel to these as well as other similar faces will have the same symbols since the choice of origin and axes is somewhat arbitrary.

4. **Space Lattice:** The discovery by Abbé Haüy that the fragments produced by the cleavage of larger crystals have the same form as the original crystal suggested that a repetition of the process would yield a fundamental unit, the unit cell, from which the crystal could again be built up. The unit cell would contain the minimum amount of material necessary to specify the crystal form and its elements of symmetry. An actual crystal may thus be conceived as a repetition of atoms or groups of atoms at definite intervals in directions corresponding to the axes of sym-

metry. The regular arrangement in space of the points which locate the centers of such atoms is called a space lattice.

5. **Types of Lattices. Cubic Lattices:** From purely geometrical considerations it has been possible to show that only fourteen kinds of simple space lattice are possible. The symmetry of these corresponds to the seven crystal systems. For the cubic system three different types of lattice are found shown in Fig. 7.1 and termed the simple, face-centered and body-centered. The differentiation between these latter may most easily be achieved in terms of the relative spacing of corresponding lattice planes. The planes to be considered are the 100 planes, the cube faces; the 110 planes, those perpendicular to a face diagonal and the 111 planes which are perpendicular to a cube diagonal. Taking d_{100}, the distance between successive 100 planes of the simple cubic lattice, as a, d_{110} becomes $a/\sqrt{2}$ and d_{111}, $a/\sqrt{3}$. When d_{100} for the face-centered lattice is a, the edge of the unit cell is $2a$ and d_{110} becomes $a/\sqrt{2}$ while d_{111} is $2a/\sqrt{3}$. Similarly for the body-centered lattice $d_{100} : d_{110} : d_{111} = 1 : \sqrt{2} : 1/\sqrt{3}$. Thus the 110 plane spacing particularizes the body-centered lattice while for the face-centered lattice it is the 111 plane spacing which is different.

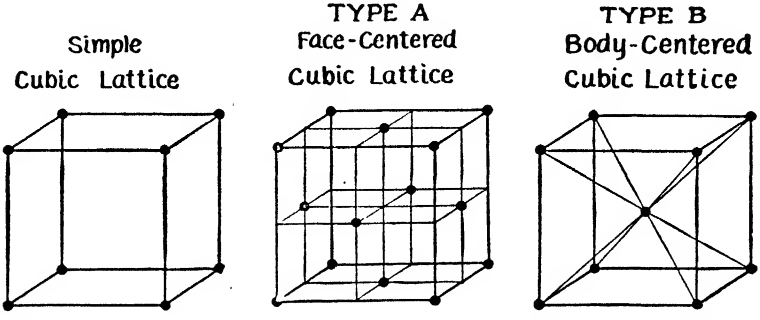


FIG. 7.1. Cubic Lattices

6. **X-rays and Crystal Structure:** In 1912 Laue in an effort to determine the wave length of X-rays suggested that a crystal might act as a diffraction grating and produce interference since the interatomic spacing in the crystal and the wave length of the X-rays had each been estimated to be of the same order of magnitude, 10^{-8} cm. Experiments by Friedrich and Knipping completely confirmed the suggestion. A typical Laue diagram for magnesium oxide is shown in Fig. 7.2. The analysis of such diagrams is rather complex and the subsequent discovery by W. H. and W. L. Bragg that crystals could be used as reflection gratings as well as transmission gratings following Laue led to considerable simplification.

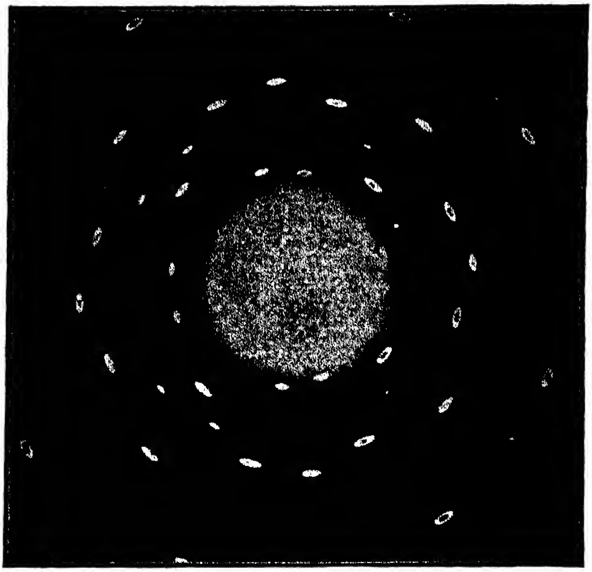


FIG. 7.2. Laue Diagram of Magnesium Oxide

7. The Bragg Equation: Consider Fig. 7.3 in which an incident beam of X-rays represented by A, A', A'', A''' of single wave length λ (AA_1), strikes planes p, p parallel to some face of a crystal. The spacing between the planes is d. Part of the beam AA_1 incident at a small angle θ

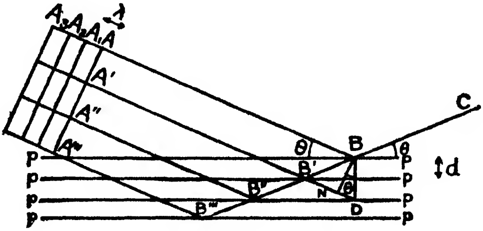


FIG. 7.3

is reflected at B along BC. Another part originating at A' will penetrate the crystal and be reflected at B' along the same direction $B'BC$. If the path $A'B'B$ differs in length from the path AB by a whole number, n, of wave lengths, the two beams from A and A' will reinforce each other at B and an intense diffracted beam will result along BC. The condition for this enhancement can be found geometrically. Extend $A'B'$ to D and rotated around one of its axes and exposed to X-rays at right angles to this direction. Various planes of the crystal are thus brought successively into suitable positions for diffraction to occur and corresponding spots in horizontal lines are produced on a cylindrical film which almost completely surrounds the crystal. The distance between lattice layers is then dependent on the distance between the horizontal lines.

The powder method devised by Debye and Scherrer and independently by Hull employs a fine crystalline powder, in which, when exposed to a narrow beam of X-rays, all the principal planes will be oriented in all directions and so a sufficiently large number will fulfil the requirements of the Bragg relation and lines corresponding to maximum reflection in the various orders can be registered on a photographic strip in a semicircle with the powder at the center. The powder photograph obtained with a substance of known crystal structure permits a calibration of the apparatus to be made. This method has been of particular value in determining the crystal structure of metals and alloys which cannot readily be obtained in large crystals.

10. **The Binding Forces in Crystal Structures:** A very large number of substances, both elements and compounds, inorganic and organic, have been examined by the X-ray method. It would be impossible to discuss all the results here. Since, however, only four types of binding have so far been recognized in crystals, all the results may be summarized in terms of these. The four types are: (*a*) the Covalent Bond; (*b*) the Ionic Bond; (*c*) van der Waals Forces; (*d*) the Metallic Bond.

11. **The Covalent Bond and van der Waals Forces:** The electron-pair bond, first postulated by Lewis and interpreted by quantum mechanics as two electrons of opposite spins, is probably the most frequently occurring bond in crystals. It is found in the non-metallic elements, in the majority of organic compounds and also in many inorganic compounds.

In the non-metallic elements each atom is joined by a covalent bond to one or more neighboring atoms such that each atom completes its octet of outer electrons. This number of nearest neighbors is called the *co-ordination number* of the atom and will be equal to the usual valence of the element. Thus, carbon in the form of diamond has a co-ordination number of four. These four atoms are arranged tetrahedrally to the central atom and the crystal thus has the zinc blende structure shown in Fig. 7.5 except that all the atoms are identical. The distance between the centers of neighboring atoms is 1.54 Å. The closeness of this value to that found for the $C-C$ bond in aliphatic structures is suggestive that the linkages in diamond are covalent. A diamond is thus a macromolecule. The strength of the bonds is probably responsible for the hardness of diamond. Close inspection of the diamond structure shows a series of hexagonal rings which are "puckered" such that one para atom is above and one below the plane of the other four atoms. Similar puckered rings are found in such saturated compounds as cyclohexane where single covalent bonds alone are present.

In Group V elements, the valence being three, each atom is attached by covalent bonds to three others, again yielding puckered six-membered rings. The crystals thus consist of layers and, since the valence of each atom is satisfied within the layer, there can be no covalent binding between layers. This situation resembles that found in graphite in which the carbon atoms form a layer lattice by mutual attachment to three others, the layers being 3.41 Å apart. The layers, however, are planar, consisting of flat hexagons, the C—C distance being 1.42 Å. Such flat rings are found in benzene, naphthalene and other aromatic hydrocarbons as well as in many of their derivatives which involve single and double covalent bonds.

The distance between successive layers in these layer lattices is far too great to correspond to a true chemical bond and the binding is attributed to van der Waals forces. Such relatively weak forces are easily overcome and the layers slide easily over each other accounting for the high lubricating property. These forces are easily overcome also by change in temperature; thus, the elements in Group O form crystals dependent on van der Waals forces alone and have correspondingly very low melting points.

Selenium, tellurium and plastic sulfur having six valence electrons can share electrons with two other atoms and thus form long chains which are held parallel by van der Waals forces. In rhombic sulfur the chains are found to extend to eight members only and these form puckered rings suggestive of the S_8 molecules found in sulfur vapor. Here then there is some evidence of the existence of a molecule as such in the crystal. With iodine, capable of forming only one covalent bond, the crystal is entirely molecular; the lattice is face-centered rhombohedral with an iodine molecule at each lattice point.

The formation of covalent bonds just discussed for atoms, with co-ordination numbers of 4, 3 and 2, does not appear to be probable for higher co-ordination numbers. Many inorganic compounds possess low co-ordination numbers and the linkages in the crystal are covalent, for example, hydrogen chloride, carbon dioxide, and the sulfides of tungsten and molybdenum. In sodium chloride, however, we have seen that the co-ordination number is six for each atom and an explanation on the basis of covalent bonds is impossible. Instead, electron octets are completed, not by sharing electrons, but by electron transfer between the atoms producing ions which are bound together by their mutual electrostatic attractions following Coulomb's law.

12. **The Ionic Bond:** Sodium chloride is a typical ionic lattice. The concept of a molecule in the lattice is entirely absent. The stoichiometric ratio of the ions in the crystal results solely from the requirement of

electrical neutrality requiring equal numbers of positive and negative ions. Ionic lattices can therefore be built up from complex ions containing more than one atomic species. Thus, the $CO_3^=$ and $SO_4^=$ ions occupy negative lattice points as a unit, surrounded by positive ions.

The systematic investigations of Goldschmidt have been directed towards the elucidation of structure of compounds of the general type MX, MX_2, MX_3, M_2X_3, and so on where M and X are atoms or ions. It is shown that the structure is determined by the ratio of the numbers, the ratio of the sizes and the properties of polarization of the atoms or ions. In each group, MX or MX_2, for example, only a limited number of structures are possible and a gradual transition from a typical ionic lattice to a purely covalent lattice is evident, following the decrease in co-ordination number. Figs. 7.6 and 7.7 illustrate some important structure types of compounds MX and MX_2. The fact that ion size can be used as a criterion of structure type indicates that the ions behave as spheres of definite size regardless of the crystal in which they are present. From measurements of optical refraction, Wasastjerna found the radius of the $O^=$ ion to be 1.32 Å. Study of the lattice dimensions of various metallic oxides permits a calculation of the sizes of the metal ions. Study of the halides then gives the sizes of the halogen ions and so forth. In this way data such as in Table 7.2 have been accumulated. It may be added that careful study has shown that ionic distances are not exactly additive but give a very good approximation to the lattice distances.

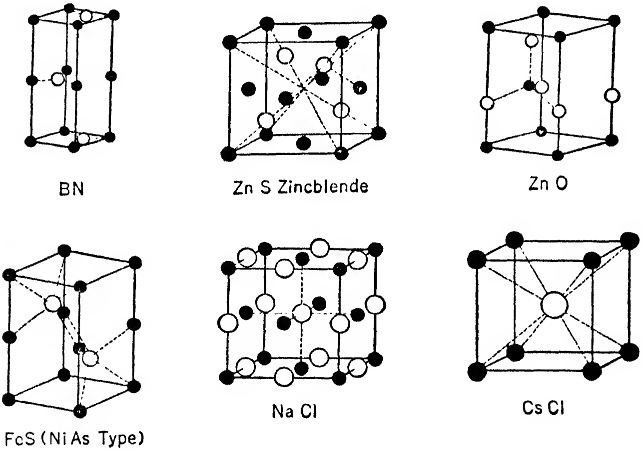
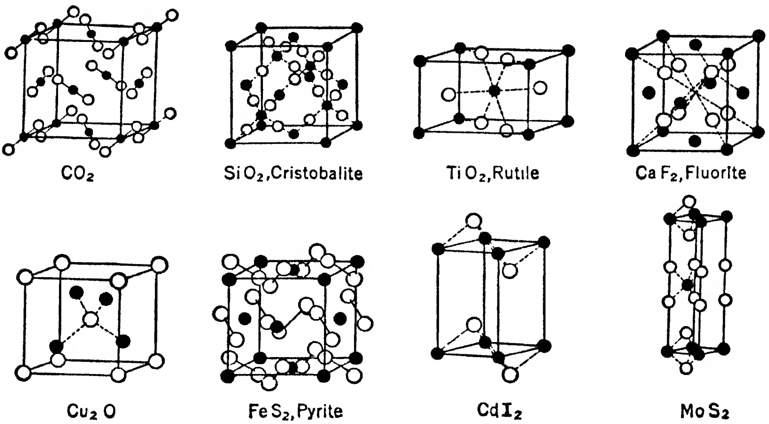


Fig. 7.6. Some Important Structure Types of Compounds MX

It would be expected that the size of the ion would differ from that


CO_2 SiO_2,Cristobalite TiO_2,Rutile CaF_2,Fluorite

Cu_2O FeS_2,Pyrite CdI_2 MoS_2

FIG. 7.7. Some Important Structure Types of Compound MX_2

TABLE 7.2

IONIC RADII IN ÅNGSTROMS

2−	1−	0	1+	2+	3+	4+
		He ~1.22	Li 0.68	Be 0.34		
O 1.32	F 1.33	Ne ~1.52	Na 0.98	Mg 0.78	Al 0.57	Si 0.39
S 1.74	Cl 1.81	A ~1.92	K 1.33	Ca 0.98	Sc 0.83	Ti 0.64
Se 1.96	Br 1.96	Kr ~2.1	Rb 1.48	Sr 1.15	Y 1.06	Zr 0.87
Te 2.18	I 2.19	Xe ~2.3	Cs 1.65	Ba 1.37	La 1.22	Ce 1.02

of the corresponding atom. Thus, for a cation, the positive charge causes the electrons to lie closer to the nucleus giving a smaller radius while, for an anion, the negative charge causes a mutual repulsion of the electrons and consequently a larger radius. Table 7.3 gives some covalent bond radii based on direct measurements such as for carbon and a combination with lattice data for appropriate compounds. Comparison of the size of Si^{++++}, 0.39 Å, with that of Si, 1.17 Å, and of F^-, 1.33 Å

TABLE 7.3

ATOMIC RADII IN ÅNGSTROMS

C 0.77	N 0.70	O 0.66	F 0.64
Si 1.17	P 1.10	S 1.04	Cl 0.99
Ge 1.22	As 1.18	Se 1.14	Br 1.14
Sn 1.40	Sb 1.36	Te 1.32	I 1.33

with that of F, 0.64 Å substantiates the expected effect of the ionic charge and shows, also, that positive ions in general will be smaller than negative ions. For efficient packing of ions the anions must surround the cations and simple geometry permits the calculation of the number of outer spheres required to surround and touch one sphere in terms of the ratio of the radii of the spheres. The co-ordination number is thus fixed by the ratio of the ionic radii and the crystal structure is simply a question of the packing of spheres.

The charge on an anion considered above as affecting the size of that ion as compared with the neutral atom will also have a corresponding effect on other neighboring ions. The positive field of a cation causes a tightening of the electrons of the anion decreasing thereby their polarizability, while the negative field of an anion loosens the electrons of the cation increasing the polarizability. Since cations are smaller than anions of the same structure, they exert the more intense field and have the greater polarizing power. The polarizing power thus increases with increasing charge and decreasing size. The cations such as Ag^+, Hg^{++}, which do not have an inert gas structure, would be expected to show high polarizing power. Thus, the valence bond in the halides of these ions is more nearly covalent in contrast to the electrovalence of the alkali halides.

In the more complex ions such as those of the oxy-acids, the ion itself has a definite structure. In NO_3^- and $CO_3^=$ the oxygen atoms are equilaterally placed with nitrogen or carbon at the center, all in the same plane. ClO_3^-, BrO_3^-, and $SO_3^=$ are pyramidal, the oxygens being in one plane. $PO_4^\equiv$, $SO_4^=$, CrO_4^-, ClO_4^-, and MnO_4^- are tetrahedral in oxygen with the other atom at the center. The crystal structure formed from one of these and a metallic ion again depends on the relative sizes of anion and cation; the dimensions of the crystal are determined by the possible packing.

The silicates present features diverging from those of the salts just discussed. In the silicates, silicon is always found between four oxygen atoms as the extended researches of W. L. Bragg have revealed. In the ortho-silicates there are independent SiO_4 groups, the oxygen atoms arranged tetrahedrally, and behaving like quadrivalent acid radicals. The oxygen atoms may, however, act as bridges between two silicon atoms and numerous possibilities result. Closed systems may be formed. Thus, two tetrahedra may be linked through one oxygen atom common to both silicons to yield Si_2O_7; three may form a ring Si_3O_9 and six may form Si_6O_{18}, also a ring. Chains or bands may be formed, of indefinite extension. If the edges of two tetrahedra are linked by two common oxygen atoms a chain $(SiO_3)_n$ is formed. Two chains linked side by side give a band with the composition $(Si_4O_{11})_n$. Metal ions can bind chains laterally. Sheets may be formed of linked tetrahedra, each tetrahedron sharing three corners. Such silicates as mica belong to this class, of composition $(Si_2O_5)_n$. If every corner of the tetrahedron is shared with other tetrahedra, the extension occurs in three dimensions and the composition is $(SiO_2)_n$. The various forms of silica are of this type. When aluminum replaces silicon in such lattices the tetrahedron acquires a negative charge and consequently positive ions can be incorporated in the structure. Feldspars are of this structure. Zeolites are more open structures, containing water molecules in the structure also.

Water molecules also enter into the architecture of some crystals. In the compound $BeSO_4 \cdot 4H_2O$ the water molecules are arranged tetrahedrally around the cation forming a co-ordinated positive ion. In $NiSO_4 \cdot 6H_2O$ six molecules surround the Ni^+. Similar observations extend to a number of the co-ordination compounds, discussed by Werner, involving ammonia, hydroxide, etc., as in $Cl_3Co(NH_3)_6$, etc. Among complex anions may be mentioned K_2PtCl_4 in which the anion $PtCl_4^=$ is planar and K_2PtCl_6 in which the anion $PtCl_6^=$ is octahedral, the six chlorine atoms being arranged at the corners of the octahedron with the platinum at the center. The crystal as a whole is of the calcium fluoride type, the potassiums in the location of the fluorine ions, the $PtCl_6^=$ ions replacing calcium.

13. The Metallic Bond: Metallic crystals are found to belong to one of three types, face-centered cubic, close-packed hexagonal or body-centered cubic. In the first two types the co-ordination number is twelve; in body-centered it is eight. It is obvious that covalent linkages due to electron-pair sharing are impossible. The crystal strength nevertheless could not be accounted for if van der Waals forces were the only binding. It is therefore apparent that a special type of binding must be present. The metal crystal is an assembly of positive ions, the electrons freed from the metal atoms forming a mobile "cloud" which binds the ions together. This view of the mobile electrons accounts for the high thermal and electrical conductivity of metals.

Since the only material units present are the metal ions the structure is again solely one of packing. Closest packing of spheres can occur in two ways. The only difference lies in the position of repetition. In the cubic close-packing, that is, face-centered cubic, the arrangement of the spheres is repeated every third layer. In the hexagonal close-packing alternate layers involve repetition. The body-centered lattice found in the alkali metals is a much looser type of packing. With such close-packed structures large numbers of "flow-planes" are present and the material is ductile and malleable and less liable to fracture under stress.

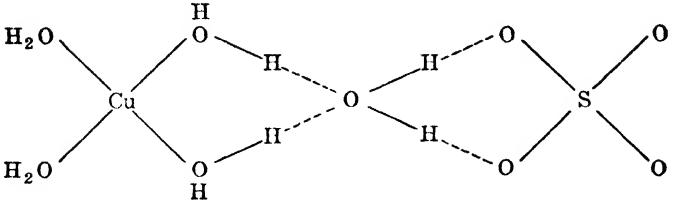
Substitution of one positive ion by another of the same size will have no effect on the structure; solid solution is thus a frequent occurrence.

Even though the substituting ion is larger than the one it replaces, the lattice can assume the strain up to a certain extent, but after a critical concentration the original lattice structure becomes modified. Thus copper, which is cubic packed, will dissolve about 32 per cent of zinc and zinc, which is hexagonal, will dissolve about 5 per cent of copper, without change of the respective lattices. Between the α and η-brasses so formed, three other different structures are found. Frequently changes in structure are associated with compositions corresponding to simple stoichiometric proportions. This does not, however, necessarily prove the presence of true compounds involving normal valences since in many cases the distribution throughout the lattice is not regular. An especially interesting case is typified by the cubic packed system Cu—Au. For Cu_3Au a well annealed crystal shows gold ions at the corners and copper at the face-centers, a so-called *superlattice.* If the crystal is melted and rapidly cooled again the ion distribution is quite random though the size and nature of the lattice remain the same. If Cu_3Au were a true compound such an order-disorder transformation should not be possible.

Despite the close-packed nature of the metals and alloys it is nevertheless found that atoms of the lighter elements which are therefore small can enter the spaces in the lattice without producing much change in the dimensions. Such interstitial structures are found in the borides, carbides and nitrides of manganese, chromium, iron and molybdenum.

14. **Hydrogen Bonds:** In the analysis of the structure of certain anions containing hydrogen, such as $H_2PO_4^-$ or HCO_3^-, measurements show that the distance between two oxygens from neighboring groups, 2.6 Å, is greater than could be expected from a normal bonding yet is less than would be expected if bonding were absent. It has been suggested that the linking is through a hydrogen atom which due to a movement of electrons is alternately attached to one or other oxygen atom causing a resonance between the alternate structures. Such a linkage is reasonably common and has been called a *hydrogen bond.* Unfortunately the position of the hydrogen atoms in a crystal cannot be directly found owing to their very low X-ray diffraction and so must be inferred, but it appears probable that the structure involves $-O-H-O-$ chains since, in ice, the distance between nearest oxygens is almost the same, 2.78 Å.

Water of crystallization in some cases may be accounted for by hydrogen bonds. Thus, in $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 7H_2O$, four molecules of water are in a plane around the copper ion and six are co-ordinated octahedrally around the nickel ion. The remaining water molecule connects the hydrated cation tetrahedrally with two oxygens of the anion. This may be represented in a plane as follows:

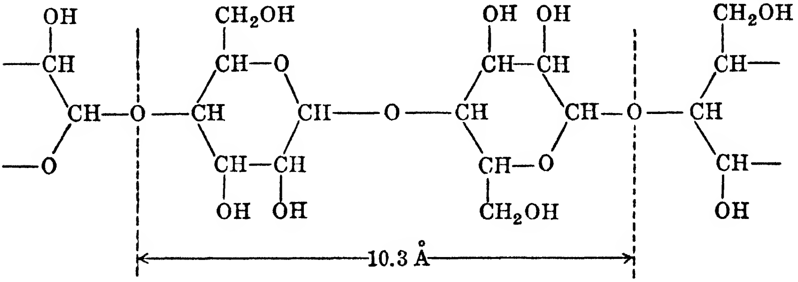


Hydrogen bonding may also be responsible for the structure found in the fatty acids. The lattice spacing corresponding to the chain length for the fatty acid is found to be almost twice as great as that for the pure hydrocarbon with the same number of carbon atoms. This bonding of two acid molecules through their carboxyl groups causes the fatty acids to be arranged essentially in bimolecular layers.

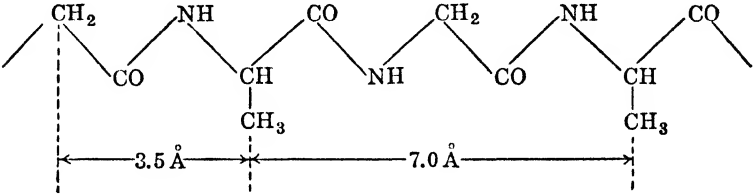
Finally, hydrogen bonds are responsible for holding together long chains of atoms such as are found in the fibers occurring in both the animal and vegetable kingdoms.

15. **Fiber Structure:** Simple microscopic examination of such fibers as cellulose, silk and wool shows them to be made up of threadlike units arranged almost parallel to each other. When a beam of X-rays is passed at right angles to the length through such fibers on to a photographic plate the resulting picture closely resembles a rotation photograph, showing that the fiber is built up of crystallites whose axes are aligned in the direction of the fiber length. When the beam of X-rays is parallel to the fiber length only diffuse rings are obtained, showing that the crystallites have random arrangement in all directions but that of their length.

Cellulose $(C_6H_{10}O_5)_n$. Haworth has shown chemically that cellulose consists of glucose residues joined in the 1.4 positions. The length of a cellulose unit by X-ray examination is 10.3 Å. This is precisely the length to be expected from atomic distances in covalent bonding for two glucose residues. The structure may therefore be represented as follows:

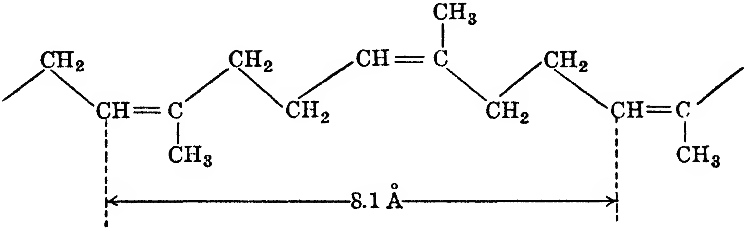


Silk, Wool and Hair. These are protein fibers, silk being made up of fibroin, and wool and hair of keratin. Simple hydrolysis yields amino acids. The proteins are thus long chains of these acids joined by the peptide linkage $-CO-NH-$. Fibroin consists of glycine CH_2NH_2COOH and alanine CH_3CHNH_2COOH and shows an axis length of 7.00 Å in agreement with the following structure:



Keratin is more complex than fibroin, having longer side-chains, and exists in at least two forms. One of these, β-keratin, obtained by simple stretching of the hair closely resembles fibroin in its X-ray analysis and is probably an extended chain of polypeptide units which repeat every 3.4 Å. Successive chains are held together normal to the chains by hydrogen bonds between $-NH$ of one chain and $-CO$ of an adjacent chain. Normal or α-keratin must have a folded structure, possibly a spiral fold of units containing the sequence $-CO \cdot NH \cdot CHR-$ with three such units in each turn of the spiral. This model would give the distance 5.1 Å as the significant lattice dimension and under tension can be shown to stretch, due to free rotation around the bonds, 100 per cent to 10.2 Å. This is just three times the repeating unit in the β form. This doubling in length is aided by heat and steam and may form the basis of the "permanent wave," or "trousers' crease." The reverse shrinkage is well known in woolens washed in hot water.

Rubber. Normal or unstretched rubber gives no definite X-ray pattern. On stretching, a pattern appears, indicating a unit 8.1 Å in length which corresponds to two isoprene C_5H_8 residues. Apparently



such a chain does not fold regularly like keratin, but in a random manner giving the diffuse X-ray pattern.

16. Isomorphism: We have already discussed in Chapter 1 the phenomenon of isomorphism, the almost complete identity of crystalline form among substances similar in chemical constitution. We saw that this observation of Mitscherlich was utilized by Berzelius in fixing atomic weight, and checking the results of analysis of the compounds. It was pointed out that the identity in form was not absolute, the distance between atoms varying slightly in one compound from that in the compound of the next analogue. This is illustrated by the following values of the axial ratios of the rhombic sulfates and selenates of the alkali metals measured by Tutton.

TABLE 7.4

THE AXIAL RATIOS OF THE ISOMORPHOUS SERIES $R_2\left(\frac{S}{Se}\right)O_4$

(R = alkali metal. The crystals are orthorhombic.)

Salt	Axial Ratios *a* : *b* : *c*
K_2SO_4	0.5727 : 1 : 0.7418
Rb_2SO_4	0.5723 : 1 : 0.7485
Cs_2SO_4	0.5712 : 1 : 0.7531
K_2SeO_4	0.5731 : 1 : 0.7319
Rb_2SeO_4	0.5708 : 1 : 0.7386
Cs_2SeO_4	0.5700 : 1 : 0.7424

Many pairs of isomorphous substances are capable of forming (*a*) solid solutions, when aqueous solutions of both are evaporated, (*b*) parallel growths, when a solution of one is evaporated on the surface of a crystal of the other, or (*c*) overgrowths, when a crystal of one is suspended in a saturated solution of the other. Unfortunately, such observations have sometimes been taken as the sole criteria of isomorphism whereas the question of relative solubility, or approximate equality of molecular volumes, may be a more important determining factor than the isomorphism. It appears from Goldschmidt's work on crystal types that the conditions for isomorphism are: (1) the formula of each substance must be of the same type, (2) the *relative* sizes of the structural units, atoms or ions, must be but little different and (3) the units must be linked by the same type of bond. If, in addition, the dimensions of the unit cells differ by less than 10 per cent, solid solution or overgrowths may be possible.

17. **Polymorphism:** It often happens that a substance can occur in more than one crystalline form. When this is the case, the substance is said to be polymorphic. The different polymorphic modifications ordinarily belong to different crystal systems, though there are exceptions. A familiar example is sulfur, which has a rhombic modification, stable up to 95.6°, and a monoclinic modification, stable between 95.6° and 119.25° (its melting point).

Polymorphism results from different space-lattice arrangements of the same chemical units, as is attested by the fact that the modifications usually belong to different crystal systems. The crystal structures have been worked out in only a few cases. Thus, carbon occurs as diamond and as graphite, the structures of which have already been discussed. Silver iodide occurs in a hexagonal and in a cubic form. In the first, it has the ZnO[1] structure and in the second, the ZnS structure. Ammonium chloride is an example of a substance having two modifications which both crystallize in the same system (the cubic). The high temperature modification has the sodium chloride structure and the low temperature modification has the caesium chloride structure.

Polymorphic modifications may or may not be interconvertible. When they are interconvertible (e.g., $S_{rh} \overset{95.6°}{\rightleftarrows} S_{monocl.}$), the change is said to be enantiotropic. When the change can only take place in one direction, that is, when one form is metastable under all conditions investigated, it is said to be monotropic, as Diamond → Graphite or Aragonite → Calcite. Since such forms as diamond and aragonite have remained as such through geologic ages, it is evident that the conversion of polymorphic modifications may be exceedingly slow. This is to be compared to the rapidity with which equilibrium is reached in the transition of solid to liquid. Further discussion of solid-solid transitions will be found in Chapter 11, "Phase Equilibria."

18. **Melting Point of a Solid:** The melting point of a solid may be defined as the temperature at which the solid is in equilibrium with the pure corresponding liquid; both forms of the substance can coexist at that temperature. As a general rule, a crystalline solid undergoes spontaneous transformation into the liquid phase when the melting point is reached; that is, a crystalline solid cannot be superheated. On the contrary, liquids are very readily cooled below the freezing point, which is identical with the melting temperature of the corresponding solid. If a liquid is carefully freed from suspended solid, especially particles of the corresponding solid, and if it is protected from vibrations and sudden changes, it may often be cooled many degrees below the freezing point. Under these conditions, the velocity of crystallization may be negligibly small; it is to this possibility that glasses owe their existence. Devitrification in glass is a manifestation of crystallization occurring in a supercooled liquid. At ordinary temperatures it occurs excessively slowly. The rate is increased by raising the temperature to a given degree.

Each polymorphic modification of a substance has its own particular melting point. For example, rhombic sulfur melts at 113° C. while monoclinic sulfur melts at 119.25° C. Consequently in giving a melting point, the polymorphic modification to which it refers should also be stated.

[1] This is sometimes referred to as the wurtzite type of ZnS as opposed to the zinc blende type.

19. **Forces Acting in Crystals:** It is generally assumed that the units of the crystal lattice are confined, as to motion, to vibrations about equilibrium positions in the lattice. This equilibrium results from the action of attractive and repulsive forces between the constituents of the lattice. The attractive force gives rise to the cohesion of the solid. It is clear that thermal expansion must take place against this force and will therefore be small when the cohesive force is large. Compression, on the other hand, must take place against the repulsive forces. Since, however, the two are normally balanced against one another, the repulsive force must be large and therefore the compressibility small, when the cohesive force is large. These two properties should therefore vary from one solid to another in the same way, and this is found to be the case. Thus, among the solid elements, the alkali metals are found to have the greatest compressibilities, and also the greatest expansion coefficients corresponding to minima in the cohesive forces. Two other properties, atomic (or molecular) volume and melting points, in all probability also bear a relation to the cohesive forces. A large cohesive force should result in a relatively small atomic volume and a high melting point. The small atomic volume obviously corresponds to a large attraction between the atoms. The melting point represents the limit to which a solid can be heated and maintain its form. Rise in temperature corresponds to the input of energy, some of which, as kinetic energy, works against the cohesive forces. If these forces are small, a relatively small input of energy and therefore a relatively low temperature is sufficient to overcome them and bring about destruction of the lattice and hence melting.

TABLE 7.5

LATTICE ENERGY IN KCAL. PER MOLE

	F	Cl	Br	I
Na	213	183	175	164
K	190	165	159	151
Rb	182	161	154	145

In the case of ionic lattices calculations have been made of the lattice energy, that is, the energy of formation from "gaseous ions" assuming the applicability of Coulomb's law for the electrostatic charges on the ions in crystals of known structure. To show the magnitude of these energies the values for some alkali halides are given in Table 7.5. Since the total heat of solution of such salts in water may be considered as made up of the lattice energy required to split the crystal into gaseous ions and the heat of hydration of the ions, lattice energy values may be tested indirectly with known heats of solution.

The motions of the structural units in crystals have been referred to so far as vibrations. It was suggested by Pauling in 1930 that certain abrupt changes in heat capacity, dielectric constant or thermal expansion with change in temperature could be accounted for by the assumption that the lattice units began to rotate freely. At low temperatures, the lattice forces presumably will only permit a partial to and fro rotation. As the temperature is increased a critical point will be reached at which a few units can rotate freely resulting in a weakening of the neighboring forces and permitting more or less general rotation. In many cases the onset of free rotation is accompanied by a polymorphic transition. Thus, HCl at −169.5° changes from orthorhombic to cubic; NH_4NO_3 changes at 125° from tetragonal to cubic. On the other hand NH_4Cl shows a transition to free rotation at −30° without change in crystal form.

20. **Heat Capacity of Crystals:** According to Dulong and Petit's law the atomic heat capacity of the elements is approximately 6 calories per degree. Kopp extended the law to compounds since, in postulating additivity of atomic heat capacities, the molecular heat becomes 6 *n* cals. per degree where *n* is the number of atoms in the molecule.

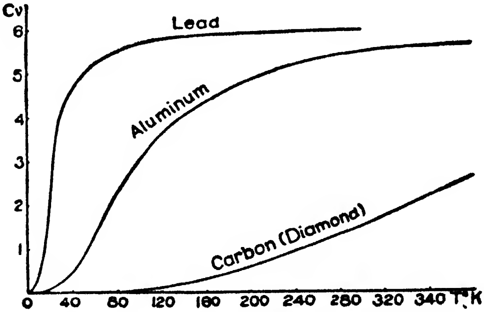


FIG. 7.8. Atomic Heats of Lead, Aluminum and Diamond

The value of 6 cals. per degree can be arrived at on the basis of the principle of equipartition of energy. The motion of the lattice units involving both kinetic and potential energies will require an energy of *RT* per mole per degree of freedom. For three degrees of freedom the energy will be $3RT$ or the heat capacity $3R = 6$.

The elements carbon, boron, silicon and many compounds show values for the heat capacity lower than expected on this basis. When the data are calculated by equation (3.45) for constant volume, instead of at constant pressure, the agreement with Dulong and Petit's law is somewhat better. The failure of classical equipartition here, as already found with gases, lies in the variation of the heat capacity with the temperature. In Fig. 7.8 are plotted values of atomic heat capacity against temperature for three typical substances. It will be seen that, for two of these, the heat capacity approaches a value in the neighborhood of 6 at the higher temperatures. As the temperature is lowered, a region is encountered in which the heat capacity falls off rapidly and, in the case of at least one substance (diamond) and probably of many, becomes immeasurably small at temperatures considerably above the absolute zero.

This behavior of solids with respect to heat capacity is easily understood once it is realized that the predominant type of motion in a crystal lattice is vibration of atoms, ions, radicals or molecules about the mean position in the lattice. We have already seen that vibratory motion is acquired in quanta of a particular frequency characteristic of the vibrator, and that the mean energy of a linear vibrator is:

$$\bar{\epsilon} = \frac{\epsilon}{e^{\epsilon/kT} - 1} = \frac{h\nu}{e^{h\nu/kT} - 1}.$$

Since the atoms in a crystal lattice can vibrate in three dimensions we can expect an average energy per atom equal to three times this quantity, or, for N atoms in a gram molecule of crystal,

$$\bar{E}_v = 3N\bar{\epsilon} = \frac{3Nh\nu}{e^{h\nu/kT} - 1} = \frac{3R\theta}{e^{\theta/T} - 1}, \tag{7.1}$$

where, as before, we make the substitutions $Nk = R$ and $\theta = h\nu/k$. We saw, also, that such an expression for the average energy leads to the expression for the heat capacity,

$$C_v = \frac{d\bar{E}_v}{dT} = 3R\frac{(\theta/T)^2e^{\theta/T}}{(e^{\theta/T} - 1)^2}. \tag{7.2}$$

The form of this equation satisfies the requirements of a formula to interpret observations on the heat capacity variation with temperature since the expression $(\theta/T)^2e^{\theta/T}/(e^{\theta/T} - 1)^2$ approaches zero as T approaches 0 and approaches unity as T becomes high with respect to θ. It was Einstein in 1907 who developed this expression for the heat capacity of solid bodies and found values of the characteristic temperature θ for a number of substances which satisfactorily interpreted the experimental values for C_v at different temperatures.

The substances which show a slow increase of heat capacity with temperature are those with high values of θ. Thus, diamond is found to have a θ value of 1860. Lead, on the other hand, has a value $\theta = 95$. That of aluminum is intermediate or 400. This signifies that, in the case of diamond and other substances with abnormal specific heats, such as boron and silicon, the quanta of vibrational energy are large and so cannot be acquired until relatively high temperatures are reached. It will be noted that these substances are all high melting substances.

Lindemann traced a relation between the value of θ and the temperature of melting, in which the vibration frequency ν was related to the melting point, T, by the expression

$$\nu = \frac{\theta}{h/k} = \text{const.} \times \sqrt{\frac{T}{mV^{2/3}}}, \tag{7.3}$$

where V is the volume and m the mass of the atom. Melting, upon this basis, is to be associated with the vibrations of the constituent atoms in the crystal, the mean energy of vibration at the melting point being sensibly that demanded by the Dulong and Petit law. In agreement with this view also is the low θ value for the low melting element lead.

The decrease in C_v with decrease in temperature in the lower temperature ranges given by the Einstein equation (7.2) is more rapid than that found experimentally. Debye has accounted for this by assuming that the units in a crystal lattice do not vibrate with only a single frequency, but, because of their interactions, with a spectrum of frequencies. By a summation of the Einstein type expressions for each of these frequencies Debye has represented C_v as a function of only one characteristic frequency, which is in close agreement with experiment for many solids. His result indicates, further, that at very low temperatures the heat capacity varies as the cube of the absolute temperature,

$$C_v = 77.93 \times 3R\left(\frac{T}{\theta}\right)^3 \text{ cal. deg.}^{-1} \text{ g. atom}^{-1}. \tag{7.4}$$

This has been verified for a number of substances. When the units in the lattice are themselves complex such as the oxygen acid anions, a distinction must be made between the Debye function applicable to the lattice vibrations of anions and cations and vibrations within the anion which can be represented by Einstein functions just as for the vibrations of atoms in gaseous molecules.

Lewis and Gibson showed that a large number of heat capacity data could be represented by a general equation of the form

$$C_v = f(T/\theta)^n. \tag{7.5}$$

In this case θ is chosen as the temperature at which $C_v = 3R/2$ calories, and is approximately one-quarter of the value of the Debye-Einstein $\theta = h\nu/k$. The simpler substances can be represented with a function in which $n = 1$. More complex molecules require fractional values of n. The value of n has no theoretical significance. The equation of Lewis and Gibson is of value for the simplicity with which the heat capacity variation may be plotted once n and the θ value are known.

21. The Vitreous State: It has already been stated in Section 18 that the glasses owe their existence to a slow rate of crystallization of the undercooled liquid. In the introduction to the chapter it was remarked that the difference between the glasses as "amorphous solids" and liquids was one of degree only. This must not be taken to infer a complete absence of structure in the glasses since X-ray analysis of the glasses as also of liquids shows quite definite evidence of structure in both.

Instead of the sharp diffraction of X-rays given by a crystal, a glass gives a diffuse halo at a displacement from the origin which depends on the wave length of the incident beam. By a modification of the Bragg method these distances can be related to "lattice" spacings. It has thus been possible to show that the structural unit in vitreous silica is almost identical with that in crystalline silica. The unit is SiO_4 and, in the crystal, each silicon atom is at the center of a tetrahedron of the four oxygens, each oxygen attached to two silicon atoms giving a three dimensional ring structure. In the glass the regular arrangement and complete orientation of the units is lost. Very small disturbances of the tetrahedral angles alone will give ring structures with more and less atoms in them than in the crystal so that in bulk the glass presents a randomness. In the organic glasses such as glucose and glycerol, ring structures are formed by hydrogen bonds which, becoming relatively stronger as the temperature is lowered, prevent movement of the molecules to the positions required for the crystal lattice.

Since the glasses are formed by cooling the liquid it is inevitable that the fundamental structure must be present also in the liquid but in an overall random way and it is this which is "frozen" when cooling occurs. That the converse of melting a crystal does not necessarily correspond to a transition from complete order in the crystal to complete disorder in the liquid is shown by the existence of the mesomorphic state.

22. **The Mesomorphic State:** Cholesteryl benzoate which is crystalline at room temperature undergoes on heating a sharp transition at 145.5° to a cloudy, viscous liquid, the mesomorphic state. This is stable up to 178.5° at which temperature it "melts" to a clear normal liquid. If the temperature is lowered the changes occur in the reverse order. The turbid liquid shows double refraction and gives interference patterns with polarized light, properties usually associated with anisotropic crystals.

Large numbers of organic compounds have been found to exhibit similar properties. They are all long chain molecules generally ending in an ester grouping. The molecules probably arrange themselves parallel to each other forming groups with more or less complete orientation in the group. The mesomorphic state consists of a distribution of such groups, the degree of randomness of the groups being variable. Two main types of phases have been recognized, smectic and nematic which differ mainly in the way they flow. Smectic phases are built up in layers and the flow is of a gliding nature. They give an X-ray pattern but in only one direction. Nematic phases have a lower viscosity, flow easily, are threadlike and give only a diffuse X-ray pattern. That these constitute varying degrees of random orientation of the oriented groups is perhaps best seen in the case of ethyl-anisal-*p*-amino-cinnamate which undergoes a first transition at 83° to a smectic phase consisting of very thick layers. At 91° this phase changes to a second smectic phase whose layers are much thinner. At 118° the layer structure changes to a nematic phase which at 139° finally "melts" to the liquid.

The implications of studies of the vitreous state and the mesomorphic state make inescapable the conclusion that structural orientation is not alone confined to crystals but may still be quite marked in liquids. Since frequently the distinction between a compressed gas and the corresponding liquid is not very marked it may well be that some regularity still persists and that only in dilute gases will complete randomness of molecular arrangement occur.

EXERCISES (7)

1. Silver has a face-centered cubic lattice and the distance between nearest atoms is 2.87 Å. Calculate the density.

2. If the second order reflection from a 100 plane of NaCl occurs at an angle of 11.9 degrees, calculate the wave length of the X-ray used.

3. TlCl has the CsCl structure. The molecular volume is 34.1 ccs. Calculate the lattice spacing.

4. Calculate the heat capacity of aluminum at 100° and 200° K. from the Einstein equation given $\theta = 400$.

5. Taking the Lindemann melting point constant as 2.80×10^{12}, find the characteristic vibration frequency for copper given its melting point as 1356° K. and atomic volume as 7.1 cc. Compare this with the observed value $\nu = 6.6 \times 10^{12}$ sec.$^{-1}$.

6. Show how the following data for the heat capacity of aluminum at low temperatures substantiate the Debye T^3 relation.

T° K.	19.1	23.6	27.2	33.5
C_v	0.066	0.110	0.162	0.301

CHAPTER 8

THE DIRECTION OF CHEMICAL CHANGE

It can be shown experimentally that, at a definite temperature and pressure, hydrogen and iodine will react to yield hydrogen iodide and that hydrogen iodide will also decompose to yield hydrogen and iodine. Evidently there is some intermediate state in which, under the given conditions, hydrogen, iodine and hydrogen iodide will all be present in fixed, definite and unchanging amounts. Towards this state, both hydrogen and iodine on the one hand and hydrogen iodide on the other, will tend to change if maintained under the working conditions. Such a final state, to which systems tend, is known as a **state of equilibrium.** The importance of the equilibrium state is obvious, since it determines the extent to which a chemical process may occur. It is necessary to possess means whereby such a state of equilibrium may be identified and the composition and quantities of the constituents of the system be determined. Furthermore, the variability of the equilibrium state with variation in the external conditions of temperature and pressure is an important phase of the general problem. It will be necessary, first of all, to examine some fundamental aspects of change.

1. **Spontaneous Processes:** We are quite familiar with a variety of processes, both physical and chemical, which will proceed of themselves, or as we may designate them, spontaneously occurring processes. Heat is spontaneously transferred from a hot to a cold body either by contact or by radiation. Uniformity of temperature throughout the system will eventually result. With a concentrated solution in contact with a more dilute solution, diffusion of the solute will spontaneously occur and continue until a uniform concentration results. Gases permeate a vacuum. Similarly, the inter-diffusion of two gases when brought together is another familiar phenomenon. An electric current will flow along a conductor when differences of potential manifest themselves, just as water will flow from a region of higher level to a lower level until a uniform level is secured throughout the system. Many chemical reactions occur spontaneously; ammonia and hydrogen chloride gas at ordinary temperatures when brought into contact will react to yield solid ammonium chloride. All such processes proceed of themselves; *they are also, of themselves, irreversible.* All are tending to a state of greater stability. The *velocity* with which such a position of greater stability is approached may vary widely. The *trend* in that direction is definite and cannot be reversed by the system of itself. Only by the employment of external agencies can

the direction of such processes be reversed. The final state which such a system attains is spoken of as a state of equilibrium. A system in such a state is characterized by the uniformity in the intensity of all its forms of energy. In reaching this finality many halting places may occur. The system in such case is in a state of *metastable equilibrium.* Thus, for example, hydrogen and oxygen at room temperatures are only apparently in equilibrium. In reality they are in partial or metastable equilibrium, as the introduction of a small amount of platinum black into the system would demonstrate. Water would result from the interaction of the gases. But, in no conceivable manner, without the intervention of external agencies, could the process be expected to reverse itself, to proceed from the water stage back to the state of the gas mixture. We might generalize such observations in the conclusion that: *spontaneously occurring processes are irreversible.*

2. **Reversibility:** Let us now examine the conditions under which we must operate in order to approximate to reversibility in the conduct of a process. The direction which any energy change takes is determined by the relative magnitudes of the intensity factors of the energy of the system and of its surroundings. At equilibrium the intensities of all the forms of energy are uniform. An infinitesimal variation in any one intensity factor will produce a change in that direction which will tend towards uniformity.

Imagine a pure liquid in equilibrium with its saturated vapor enclosed in a cylinder fitted with a piston the pressure upon which may be delicately adjusted. Let the apparatus be at constant temperature in a large reservoir from which the system may withdraw heat or to which it may give up heat. The piston will be stationary when the pressure on the piston is exactly equal to the pressure of the saturated vapor at the given temperature. Any displacement of the pressure on the piston, no matter how small, will cause a change to take place in the system, liquid-vapor. If the pressure on the piston be diminished infinitesimally, the piston will rise. The volume occupied by the saturated vapor will increase and hence a little of the liquid will evaporate to produce the saturation pressure. In doing this, heat will be abstracted from the reservoir. In this way, a process may be continuously operated, namely, the change from liquid to saturated vapor at a given temperature. The process will be exceedingly slow since the difference in the intensity factors is, under assumption, infinitesimally small. The process may also be reversed. Imagine a pressure on the piston infinitesimally greater than the saturated vapor pressure. The piston will, under such circumstances, compress the saturated vapor into a smaller volume, the supersaturation of the vapor which would thereby result being overcome by condensation of some of the vapor. By this reversal of the process vapor may be converted to liquid. Heat will be given up to the surrounding reservoir.

The energy expended in two such processes as we have just outlined may now be computed. Let the saturated vapor pressure at the constant temperature T be equal to p. In the first case let the pressure on the piston be $p - dp$, infinitesimally smaller than p. Let the volume change, dv, be infinitesimally small. The work expended by the system on the surroundings will be

$$(p - dp)dv = pdv - dp \cdot dv. \tag{8.1}$$

If dp and dv are infinitesimally small, the second factor $dp \cdot dv$ is an infinitesimal of the second order, negligible in comparison with $p \cdot dv$. Substantially therefore, the work done is $p \cdot dv$. In the second process considered, that of compression, the pressure on the piston must be slightly greater than p, say $p + dp$. Let the system, after the expansion, be compressed by such a pressure through a volume decrease $- dv$. The work done on the system will be

$$- (p + dp)dv = - (pdv + dp \cdot dv) \tag{8.2}$$

or $- p \cdot dv$ when second order infinitesimals are neglected. The system is now in its original condition, the heat changes paralleling the two processes having occurred and being demonstrably equal and opposite, provided that no accidental and irreversible processes have simultaneously occurred. For this, it is necessary to assume that the piston shall be both weightless and frictionless since, otherwise, irreversible changes, e.g., those due to friction, would doubtless have occurred. Such a process represents an ideal to which all naturally occurring processes may approximate without ever realizing. Such an ideal process, however, though not actually realizable, is, nevertheless, conceivable. From the mental conception and its consequences, definite conclusions may be reached. Such an ideal process is characterized by its complete reversibility in contrast to actual processes which will always contain elements of irreversibility to a greater or less degree. In the ideal process, all of the stages of the process may be repeated in inverse order in point of time, the net expenditure of energy by all the mechanical forces involved being zero on completion of the whole process.

One other example, involving another form of energy, may be cited to illustrate the concept of reversible processes and to show the approximation to the ideal process which may be achieved by a real process. The lead storage battery, when discharging, yields current at approximately 2 volts. After discharge, the process may be reversed by supplying current to the battery. As normally operated, the process of discharge and charge is accompanied by a number of irreversible phenomena, diffusion of electrolyte, heat losses and the like. The discharge of the battery may, however, be secured under conditions approximating to the ideal reversible process by opposing to the flow of current from the battery a current at a potential infinitesimally smaller than that of the battery. Under such circumstances current would be drawn from the battery in infinitesimally small amounts at minute speed and the factors of irreversibility in the process would be reduced to a minimum. At any moment by increasing the opposing potential infinitesimally beyond that of the battery the direction of current flow would be reversed, the battery would begin to charge. Furthermore, as in the previous case, the energy expenditure for any infinitesimal change in one direction will be exactly equal numerically to that expended in the reverse case. This type of reversible process is approximately obtained in the Poggendorf method of measurement of the electromotive forces of galvanic elements. The unknown potential is measured by opposing to it a potential of known magnitude, equality of potential being indicated by zero displacement of a galvanometer suitably placed in the electrical circuit. With such a system, very minute quantities of current could be drawn from a galvanic element and the actual conditions of energy change would approximate very closely to the ideal reversible conditions.

3. **Maximum Work:** It is characteristic of such ideal reversible processes that the external work performed by the system undergoing change is the maximum amount of work that the system is capable of accomplishing. It is very evident that, if all irreversible effects could be eliminated from a process, the efficiency of the process should be a maximum. This is actually true. It may be made the more evident from a reconsideration of some ideal processes. In the isothermal expansion of an ideal gas through an infinitesimal volume change, dv, the work done is pdv. The magnitude of this quantity is obviously dependent on the opposing pressure p. When p is zero, expansion against a vacuum, the work done is zero. As p is increased the work done, pdv, also increases. The value attains a maximum when the driving pressure of the gas is infinitesimally greater than the opposing pressure. For, if these two pressures are equal, no volume change can occur, and if the opposing pressure be infinitesimally greater than the gas pressure, contraction in volume of the system will result. The maximum external work is therefore done when driving and opposing forces differ infinitesimally. This condition is, we have seen, that demanded by an ideal reversible process at all stages of its operation. The external work performed in a reversible process is therefore the maximum work available in the conduct of the process. In the expansion process just discussed, the maximum work, W_r, done by the system is therefore

$$W_r = pdv. \tag{8.3}$$

For a finite volume change conducted isothermally and reversibly

$$W_r = \int_{v_1}^{v_2} p dv, \tag{8.4}$$

which, as we have previously shown for an ideal gas, equation 3.63, is

$$W_r = RT \ln v_2/v_1 = RT \ln p_1/p_2. \tag{8.5}$$

A little consideration will show also that the work done on the surroundings in an adiabatic expansion, equation (3.65)

$$C_v(T_1 - T_2) = \int_{v_1}^{v_2} pdv \tag{8.6}$$

also gives the maximum work available from the process.

4. **Cyclic Processes:** A system which, upon completion of a change or series of changes, is in its original state, is said to have completed a cycle. The whole process is known as a cyclic process. From the first law it follows that, since U is a single-valued function of its variables, dependent, therefore, only on the state of the system, independent of past history, for every cyclic process,

$$\Delta U = 0 = q - w. \tag{8.7}$$

If conducted at constant temperature the cycle is known as an isothermal cycle.

The cyclic process forms a useful method of studying the variation of matter when subjected to variations of energy content. The most celebrated of such cyclic processes is known as the Carnot Cycle.

5. **The Carnot Cycle:** This cycle comprises a four-stage process to which an ideal gas may be submitted. It was employed by Carnot to demonstrate the work available from a process of heat transfer. The cycle consists of four successive processes: (a) an isothermal expansion, (b) an adiabatic expansion, (c) an isothermal compression at the lower temperature produced in the previous adiabatic expansion and (d) an adiabatic compression whereby the ideal gas is restored to its original temperature, pressure and volume. The accompanying diagram represents the p–v relationships in such a cycle starting at the state represented by A at temperature T_2, with the sequence of changes already detailed carrying the gas through states represented by the lines (a) AB, (b) BC, (c) CD and (d) DA.

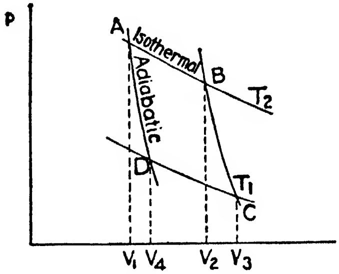


FIG. 8.1

The lines AB and CD represent the two isothermals, at the temperatures T_2 and T_1 ($T_2 > T_1$). The lines BC and DA represent the two adiabatics. Let the respective p, v, T magnitudes be for A, p_1, v_1, T_2, for B, p_2, v_2, T_2, for C, p_3, v_3, T_1 and for D, p_4, v_4, T_1.

We may follow the changes occurring in the several stages thus:

Stage I. The gas expands isothermally from A to B at temperature T_2. Heat q_2 is absorbed at temperature T_2 equal in amount to the work done by the system on the surroundings, since, for an ideal gas, the change in internal energy is zero.

$$q_2 = w_{\text{I}} = RT_2 \ln (v_2/v_1). \tag{8.8}$$

Stage II. The gas expands adiabatically from B to C. The heat absorbed is zero; hence the work done is

$$w_{\text{II}} = C_v(T_2 - T_1), \tag{8.9}$$

where $T_2 - T_1$ is the change in temperature resulting from the adiabatic expansion.

Stage III. The gas is compressed isothermally from C to D in a reservoir at T_1, whereby the heat q_1 is given up to the surroundings in amount equal to the work of compression

$$q_1 = w_{\text{III}} = RT_1 \ln (v_3/v_4). \tag{8.10}$$

Stage IV. The gas is compressed adiabatically from D to A. The work done on the gas is

$$w_{\text{IV}} = C_v(T_2 - T_1), \tag{8.11}$$

where $T_2 - T_1$ is the increase in temperature produced by the adiabatic compression.

The net heat absorbed by the gas in the whole cycle is, therefore,

$$q = q_2 - q_1 = RT_2 \ln (v_2/v_1) - RT_1 \ln (v_3/v_4). \tag{8.12}$$

From our knowledge of adiabatic expansions of an ideal gas we know that in the two adiabatic processes considered

$$C_v \ln (T_2/T_1) = R \ln (v_3/v_2) \quad \text{(Stage II)} \tag{8.13}$$

and

$$C_v \ln (T_2/T_1) = R \ln (v_4/v_1) \quad \text{(Stage IV).} \tag{8.14}$$

Hence

$$v_3/v_2 = v_4/v_1 \qquad \text{or} \qquad v_2/v_1 = v_3/v_4. \tag{8.15}$$

Hence

$$q = q_2 - q_1 = R(T_2 - T_1) \ln (v_2/v_1). \tag{8.16}$$

Similarly, the work done by the gas,

$$w = w_{\text{I}} + w_{\text{II}} - w_{\text{III}} - w_{\text{IV}} = R(T_2 - T_1) \ln (v_2/v_1), \tag{8.17}$$

which satisfies the condition for a cyclic process

$$w = q. \tag{8.18}$$

The work done may now be compared with the quantity of heat q_2 absorbed at the higher temperature T_2.

$$w = R(T_2 - T_1) \ln (v_2/v_1), \tag{8.19}$$

$$q_2 = RT_2 \ln (v_2/v_1). \tag{8.20}$$

Hence

$$w = q_2(T_2 - T_1)/T_2. \tag{8.21}$$

Now, since all the operations in the complete cyclic process possess the criterion of reversibility, we may conclude that the external work performed is the maximum work that can be accomplished in that cycle of operations, and the relationship may be written

$$W_{r,c} = q_2(T_2 - T_1)/T_2, \tag{8.22}$$

where $W_{r,c}$ refers to the work of the reversible cycle done by the system in the transfer of heat q_2 from temperature T_2 to T_1. It represents the maximum amount of work obtainable in an ideally conducted process. All real processes would yield a smaller amount of work.

For such a transfer of heat the fraction converted to useful work is independent of the mechanism employed provided the mechanism is reversible. For if we assume a reversible cycle which produces an amount of work $W'_{r,c}$ greater than $W_{r,c}$ obtained in the Carnot cycle, it follows that a quantity of heat q_2 will be taken from the reservoir at T_2 and a quantity $q_1'(< q_1)$ will be given to the reservoir at T_1, with the relationship,

$$q_2 - q_1' = W'_{r,c}. \tag{8.23}$$

By employing the Carnot cycle for an ideal gas in the reverse direction from that previously considered, a quantity of heat q_1 can be taken from the reservoir at T_1 and with the aid of a portion of the work $W'_{r,c}$, actually the quantity $W_{r,c}$, an amount of heat q_2 can be put back into the reservoir at temperature T_2. As a result of this compound cycle the only change in the system as a whole is that a quantity of heat $q_1 - q_1'$ has been taken from a reservoir at T_1 and converted into useful work $W'_{r,c} - W_{r,c}$ without causing any other permanent changes in the system as a whole. Experience teaches that such a machine is impossible. It is not in contradiction of the first law of thermodynamics since heat energy is consumed in the production of work.

6. **The Second Law of Thermodynamics:** The possibility of constructing such a machine is denied by the Second Law of Thermodynamics, based upon the experience of man in the search for such a machine. Were such a machine possible, whereby heat could be continuously converted

into work without compensation, an even more wonderful perpetual motion than that denied by the first law would be possible. It would be possible continuously to utilize the large heat reservoirs of our environment to supply the motive power of our universe. It would be possible, for example, to drive a ship with the store of heat energy available in the ocean in which the ship was placed. Such a perpetual motion machine, which Ostwald has called a perpetual motion machine of the second kind, is specifically denied by experience and has resulted in the enunciation of the Second Law of Thermodynamics. One possible formulation of the law is: for useful work to be produced from heat without compensation, a transfer of heat from a higher to a lower temperature is demanded. The fraction of heat converted into work is given by equation (8.22) and this is the maximum work available. It is therefore evident that whatever the reversible mechanism used for the heat transfer from a higher to a lower temperature reservoir the maximum work available is a constant.

With an engine working in a heat reservoir at its own temperature it is obvious that $T_2 - T_1$ and, therefore, $W_{r,c}$ must be zero. It follows also that the work done in an isothermal reversible cycle is equal to zero, since the internal energy does not change, $\Delta U = 0$, and, by the second law, the heat of the isothermal environment cannot be converted into useful work.

7. **Reversible Cycles:** Any reversible cycle can be shown to be equivalent to a sum of Carnot cycles. In the accompanying diagram, Fig. 8.2, let the continuous lines *AB*, *BA* represent the path of a reversible cycle. It is evident that the path from *A* to *B* may be traversed by a number of isothermals and adiabatics as shown. Similarly the return path may be so traversed. The broken line path *A* to *B* approximates the more closely to the continuous curve *AB* the more minute the individual isothermals and adiabatics become. The same holds true for the reverse path. By prolonging the isothermals back into the enclosed portion of the diagram it is evident that the area *ABA* may be regarded as made up of a large number of small Carnot cycles actually equal to the reversible cycle under consideration. In the summation, all those portions of the small isothermals and adiabatics within the actual cycle will be traversed once in the one direction, once in the reverse direction so that the net resultant

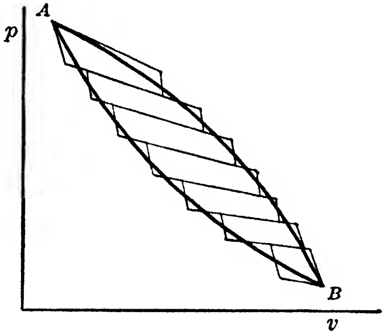


Fig. 8.2. The Reversible Cycle *ABA*

of such sections is zero. The properties of any reversible cycle will therefore be equal to the summation of the properties of all the Carnot cycles of which it may be regarded as composed.

8. **The Concept of Entropy:** In the discussion of the Carnot cycle and in the generalization of the conclusions therefrom for any reversible cycle, we saw that the heat q_2 taken isothermally from a reservoir at T_2 was related to the heat q_1 given up to the reservoir at T_1 and to the maximum work $W_{r,c}$ by means of the relation

$$q_2 - q_1 = w = W_{r,c} = q_2(T_2 - T_1)/T_2, \tag{8.24}$$

It follows, therefore, for any reversible cycle, that

$$(q_2 - q_1)/q_2 = (T_2 - T_1)/T_2, \tag{8.25}$$

or that

$$q_1/T_1 = q_2/T_2. \tag{8.26}$$

If the cycle is not reversible, if any irreversible effects are present resulting in the dissipation of heat, it is evident that the work done, w, must be less than $[(T_2 - T_1)/T_2]q_2$. Under such circumstances,

$$(q_2 - q_1)/q_2 < (T_2 - T_1)/T_2, \tag{8.27}$$

or

$$q_2/T_2 < q_1/T_1. \tag{8.28}$$

Regarded from the standpoint of the machine conducting the Carnot cycle the above expression for the equality of q_1/T_1 and of q_2/T_2 may be rearranged so that $+\ q$ represents heat absorbed by the machine. In such circumstances we have, for the Carnot cycle,

$$\frac{-\ q_1}{T_1} = \frac{q_2}{T_2}, \tag{8.29}$$

or

$$q_1/T_1 + q_2/T_2 = 0. \tag{8.30}$$

Similarly for an irreversible process

$$q_1/T_1 + q_2/T_2 < 0, \tag{8.31}$$

where again q_1 and q_2 are the heats absorbed by the machine at the two temperatures.

For each individual Carnot cycle into which a reversible cycle may be divided, the relationship (8.30) will hold. When the isothermal and adiabatic changes of each Carnot cycle are infinitesimally small, the summation of the Carnot cycles is equal to the reversible cycle ABA in the preceding diagram. For the Carnot cycles we therefore have

$$\Sigma(q/T) = 0, \tag{8.32}$$

where Σ represents the sign of summation; and when the changes are infinitesimal we have correspondingly

$$\oint \frac{\mathrm{d}q}{T} = 0, \tag{8.33}$$

where the circle through the integral implies integration over the whole cycle. The symbol dq is used for an infinitesimal amount of heat, the symbol d being thus used to remind us that the quantity dq is not, like dH or dU, a complete differential and that q is dependent on the path chosen, unlike ΔU and ΔH. This expression is applicable to any reversible cycle irrespective of its nature or the path by which it is achieved provided that this be a reversible path. In the preceding figure, where the cycle is achieved in two stages A to B and B to A, it is evident that

$$\oint \frac{\mathrm{d}q}{T} = \int_A^B \frac{\mathrm{d}q}{T} + \int_B^A \frac{\mathrm{d}q}{T} = 0. \tag{8.34}$$

Both of these integrals are evidently independent of the path taken from A to B or conversely from B to A. Both are therefore determined by the properties of the initial and final states A and B. They are therefore evidently equal to the change in some single-valued function of the variables of the states A and B of the system. Let us express this by the relationship

$$\Delta S = S_B - S_A = \int_A^B \frac{\mathrm{d}q}{T}, \tag{8.35}$$

whence it follows that

$$dS = \frac{\mathrm{d}q}{T}. \tag{8.36}$$

These expressions give us a definition of the entropy of a system. The increase ΔS, in the entropy, S, of a reversible process is the integral of all the heat changes which the system undergoes in passing from state A to state B, each heat change to be divided by the absolute temperature at which it occurred.

9. Entropy Change in Fusion and Vaporization: We can make our concept of entropy quite concrete by reference to the well-known processes of fusion of solids and vaporization either of liquids or solids. The fusion process occurs at a definite temperature T, the melting point; an amount of heat ΔH_F is absorbed equal to the latent heat of fusion per mole. The entropy change is obviously the quantity $\Delta H_F/T$ and we may express this in terms of the entropies of the solid and the liquid fusion product

$$\Delta S_F = S_{liq.} - S_{sol.} = \frac{\Delta H_F}{T}. \tag{8.37}$$

Similarly, for the vaporization process of a liquid or solid,

$$\Delta S_{vap.} = S_{vap.} - S_{liq.\ or\ sol.} = \Delta H_{vap.}/T. \tag{8.38}$$

This entropy change $\Delta S_{vap.}$ is identical with the Trouton constant (6, 6) and so we conclude that the process of vaporization of a normal liquid at its boiling point is accompanied by an increase of about 20.7 entropy units. These units are, quite obviously, calories per degree per mole.

10. Entropy Change in an Ideal Gas: The heat absorbed by an ideal gas in any process of change is given by the expression (2.5)

$$q = \Delta U + p\Delta v.$$

For infinitesimal changes,

$$dq = dU + pdv.$$

The corresponding entropy change becomes

$$dS = \frac{dq}{T} = \frac{dU + pdv}{T} = \frac{C_v dT + pdv}{T}, \tag{8.39}$$

since $dU = C_v dT$(2.14). If, as in the case of a monatomic gas, for example, C_v is independent of temperature, and remembering that for p we may write RT/v, we obtain

$$S = \int dS = C_v \int \frac{dT}{T} + R \int \frac{dv}{v} + const., \tag{8.40}$$

or,

$$S = C_v \ln T + R \ln v + const. \tag{8.41}$$

We can eliminate the unknown integration constant for any change in the entropy from state A to state B, since this will be the same in the two states and will disappear from the expression for entropy change, ΔS. Let us consider such a change, say in a monatomic gas, for which C_v is constant, occurring at constant temperature T, in which a volume change from v_A to v_B for one mole of gas occurs. Then,

$$\Delta S = S_B - S_A = R \ln (v_B/v_A). \tag{8.42}$$

Note that since $\ln (v_B/v_A)$ is a number and R the gas constant may have the dimensions, calories per degree per mole, the entropy change can in this case also be calories per degree per mole. Quite generally, entropy change is measured in energy units per degree per mole.

If equation (8.41) be expressed in the form

$$S = C_v \ln T + R \ln v + S_0, \tag{8.43}$$

where S_0 is the integration constant, the following transformation is possible in the case of an ideal gas. The volume v may be replaced by RT/p and, since $C_p - C_v = R$ (3, 17), there results

$$S = C_p \ln T - R \ln p + S_0', \tag{8.44}$$

where $S_0' = S_0 + R \ln R$.

Applying this expression to a mixture of ideal gases at partial pressures p_1, p_2, $\cdots$, it follows that the entropy of a mole of the gases in the mixture is given by equations of the form

$$S_1 = C_{p,1} \ln T - R \ln p_1 + S'_{0,1}, \tag{8.45}$$

$$S_2 = C_{p,2} \ln T - R \ln p_2 + S'_{0,2}. \tag{8.46}$$

For a mixture of n_1 moles at pressure p_1 with n_2 moles at pressure p_2,

$$S = n_1(C_{p,1} \ln T - R \ln p_1 + S'_{0,1}) + n_2(C_{p,2} \ln T - R \ln p_2 + S'_{0,2}). \tag{8.47}$$

If p is the total pressure, then, by Dalton's law, $p_1 = x_1 p$ and $p_2 = x_2 p$ where x_1 and x_2 are the respective mole fractions. Hence,

$$S = n_1(C_{p,1} \ln T - R \ln p - R \ln x_1 + S'_{0,1}) + n_2(C_{p,2} \ln T - R \ln p - R \ln x_2 + S'_{0,2}). \tag{8.48}$$

If the entropy of the mixture at the total pressure p be compared with the sum of the entropies of the pure gases each at pressure p, it is obvious that the entropy of mixing of ideal gases at constant pressure is

$$\Delta S = - n_1 R \ln x_1 - n_2 R \ln x_2. \tag{8.49}$$

Since x_1 and x_2 are fractions, it follows that the entropy change on mixing is a positive quantity.

11. **Entropy Change with Volume, Temperature and Pressure:** The preceding section shows at constant temperature $\Delta S = R \ln (v_B/v_A)$. Hence, if the volume change occurring is an isothermal compression then v_B is less than v_A and the entropy decreases in the process. If the volume change is an isothermal expansion the entropy of the system increases.

If the system be kept at constant volume the entropy change with change of temperature is given by the expression

$$\Delta S = S_B - S_A = \int_{T_1}^{T_2} C_v \frac{dT}{T} = \int_{T_1}^{T_2} C_v d \ln T. \tag{8.50}$$

To evaluate this integral it is necessary to know the variation of the heat capacity at constant volume with temperature. If this is known as an equation in powers of T (2, 21), this evaluation is possible. Otherwise graphical methods can be used as in (3, 27), C_v being plotted against log T and the area under the curve between two temperatures determined.

For a simultaneous change in volume and temperature at constant pressure we proceed as follows:

$$dS = \frac{dq}{T} = \frac{dU + pdv}{T} = \frac{dH}{T}, \tag{8.51}$$

$$S = \int dS = \int \frac{dH}{T} + const. = \int C_p \frac{dT}{T} + const., \tag{8.52}$$

or

$$\Delta S = \int_{T_1}^{T_2} C_p \frac{dT}{T} = \int_{T_1}^{T_2} C_p d \ln T, \tag{8.53}$$

the equation being solved again either mathematically or graphically. This latter equation is strictly applicable to all systems, not only ideal gases, since, in the application of the equation in this form, we do not have to use any equation of state connecting volume and pressure.

Alternatively equation (8.39) may be written $TdS = dU + pdv$. For an isothermal process it follows that

$$p = T(\partial S/\partial v)_T - (\partial U/\partial v)_T. \tag{8.39}$$

This expression may be differentiated with respect to temperature, the volume being assumed constant,

$$\left(\frac{\partial p}{\partial T}\right)_v = T\frac{\partial^2 S}{\partial T \partial v} + \left(\frac{\partial S}{\partial v}\right)_T - \frac{\partial^2 U}{\partial T \partial v}. \tag{8.54}$$

Since, at constant volume, $dS = C_v dT/T$, it follows that

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T} \quad \text{and} \quad \frac{\partial^2 S}{\partial T \partial v} = \frac{1}{T}\left(\frac{\partial C_v}{\partial v}\right)_T. \tag{8.55}$$

But $(\partial U/\partial T)_v = C_v$, whence

$$\frac{\partial^2 U}{\partial T \partial v} = \left(\frac{\partial C_v}{\partial v}\right)_T. \tag{8.56}$$

Hence from equations (8.54), (8.55) and (8.56)

$$(\partial S/\partial v)_T = (\partial p/\partial T)_v. \tag{8.57}$$

In a similar manner it may be shown that

$$(\partial S/\partial p)_T = -(\partial v/\partial T)_p. \tag{8.58}$$

12. Molal Entropies: The Nernst Heat Theorem or Third Law of Thermodynamics: With a knowledge of the heat capacities of substances over a range of temperatures from the neighborhood of the absolute zero upwards, together with numerical data on latent heats of change and the temperatures at which such transitions occur, one is in a position to determine the entropy of any substance in any state of aggregation within the range of temperature for which the data are available. The values thus obtained depend, however, on the entropy of the substance at the absolute zero. We may write our general expression for the entropy of a given substance in the form

$$S - S_0 = \int_0^T C_p \frac{dT}{T}, \tag{8.59}$$

where the quantity S_0 is the integration constant and is the entropy of the substance at the absolute zero. On the basis of a theorem first enunciated by Nernst in 1906, we are led to the conclusion that the entropy of any crystalline substance at the absolute zero may be arbitrarily assigned the value of $S_0 = 0$. This assumption is in accord with the Nernst heat theorem that the entropy change for chemical reactions involving crystalline solids is zero at the absolute zero,

$$\Delta S_0 = 0. \tag{8.60}$$

With this assumption the entropy of any crystalline substance at temperature T becomes

$$S = \int_0^T \frac{C_p}{T}\, dT. \tag{8.61}$$

The entropy of the liquid form of the same material at any temperature T becomes

$$S = \int_0^{T_F} \frac{C_{p(s)}}{T}\, dT + \frac{\Delta H_F}{T_F} + \int_{T_F}^T \frac{C_{p(l)}}{T}\, dT, \tag{8.62}$$

where T_F is the fusion temperature, ΔH_F the heat of fusion, $C_{p(s)}$ and $C_{p(l)}$ are the heat capacities of the crystalline and liquid states respectively. The entropy of a gas at temperature T becomes by similar processes of reasoning

$$S = \int_0^{T_F} \frac{C_{p(s)}}{T}\, dT + \frac{\Delta H_F}{T_F} + \int_{T_F}^{T_v} \frac{C_{p(l)}}{T}\, dT + \frac{\Delta H_v}{T_v} + \int_{T_v}^T \frac{C_{p(g)}}{T}\, dT, \tag{8.63}$$

where T_v is the vaporization temperature, ΔH_v is the latent heat of vaporization and $C_{p(g)}$ is the heat capacity of the gas. In these equations all quantities refer to one gram mole.

The importance of heat capacity measurements over a wide temperature range and for all states of aggregation can thus be realized. When such data are available, molal entropies at any temperature can be determined, the utility of which will emerge from subsequent discussion. The importance of entropies is such that other methods of determining these magnitudes have developed. We shall see (Sections 15 and 16) that the entropy change in a reaction can be related to the change in ΔH and the simultaneous change in free energy. The development of spectroscopy by the physicist has also permitted independent determinations of the molal entropy of substances (Section 8, 28). Table 8.1 contains a list of molal entropies at 25° C. and 1 atmosphere pressure for a variety of elements and compounds in various states of aggregation.

TABLE 8.1

MOLAL ENTROPIES AT 298° K. AND 1 ATMOSPHERE PRESSURE, CAL. DEG.$^{-1}$ MOLE^{-1}

H_2	31.23	$H_2O(l)$	16.9	S(rh.)	7.6
D_2	34.36	N_2O	52.58	S(monocl.)	7.8
HD	34.4	CO_2	51.07	Ag	10.0
O_2	49.03	NH_3	46.4	Pb	15.5
N_2	45.79	CH_4	44.35	Zn	9.8
Cl_2	53.31	C_2H_6	55.0	KCl	19.7
$Br_2(g)$	58.67	$n\text{-}C_4H_{10}$	74.4	AgCl	23.0
$I_2(g)$	62.29	$n\text{-}C_5H_{12}$	62.0	$PbCl_2$	33.2
$I_2(s)$	28.0	$n\text{-}C_7H_{16}$	78.5	HgCl	23.2
H	27.4	$n\text{-}C_8H_{18}$	86.0	$Hg(l)$	17.8
Cl	39.0	C_2H_4	52.3	$Hg(g)$	41.8
I	42.9	C_3H_6	63.1	Cu	8.2
HCl	44.64	C_4H_8	72.5	He	30.1
HBr	47.48	*cis* C_4H_8	73.0	Ne	34.9
HI	49.4	*trans* C_4H_8	71.2	Ar	37.0
CO	47.32	C_2H_2	48.0	Xe	40.5
NO	43.75	C (diamond)	0.6		
$H_2O(g)$	45.17	C (graphite)	1.3		

13. **Entropy Change in Irreversible Processes:** The transfer of heat from a hotter to a colder system constitutes a simple irreversible process. Let us imagine an isolated system consisting of two reservoirs at temperatures T_2 and T_1 ($T_2 > T_1$) and a machine, e.g., an ideal gas, by which heat may be transferred. By allowing the gas to expand isothermally in the reservoir of heat at T_2, an amount of heat q may be taken from the reservoir. The gas may now be allowed to expand adiabatically until a temperature T_1 is attained. By placing the gas in contact with the reservoir at T_1 and isothermally compressing, an amount of heat q may be communicated to the reservoir at T_1. The change in entropy of the gas is $q/T_2 - q/T_1$. The change in entropy of the reservoirs considered as a system is equal to $-q/T_2 + q/T_1 = q/T_1 - q/T_2$. Now, since T_2 is greater than T_1, we conclude that the conduction of heat from a reservoir

of high temperature to one of low temperature results in an increase of entropy of the reservoir system.

The expansion of an ideal gas from volume v_A to volume v_B against a vacuum is another irreversible process, in which, as already shown,

$$S_B - S_A = R \ln (v_B/v_A), \tag{8.42}$$

in which therefore an entropy increase of the gaseous system results.

We may generalize our conclusions with regard to entropy change in the following manner. In irreversible processes, the entropy of all the systems involved in the change is increased. In ideal reversible processes, the entropy of the system as a whole is unchanged. The change in entropy of any portion of such a system undergoing a reversible change is equal to the heat which such portion of the system absorbs divided by the absolute temperature at which the heat is absorbed.

14. **A Statement of the Second Law of Thermodynamics:** Since all real processes are irreversible we can express our conclusions with respect to the direction of spontaneous change in any system in the following form: *all naturally occurring processes are accompanied by an increase in entropy of the system.* Clausius combined this formulation of the second law of thermodynamics with the concept of energy conservation which is embodied in the first law by means of the famous aphorism: the energy of the universe is constant; the entropy of the universe tends towards a maximum.

15. **Free Energy:** Prior to the development of the concept of entropy the ideas embodied in the second law were formulated on the one hand in terms of 'free energy' as developed by Helmholtz and on the other in terms of 'thermodynamic potential' by Gibbs, which function subsequently was termed free energy by Lewis and Randall in their systematization of modern thermodynamics applied to chemistry.

These two thermodynamic functions may be defined in the following manner. The Helmholtz free energy, A, is defined by the expression,

$$A = U - TS, \tag{8.64}$$

and the Gibbs free energy function is defined by the equation,

$$F = H - TS. \tag{8.65}$$

The two free energies bear, therefore, the same relation to one another that the internal energy, U, bears to the heat content, H,

$$F = H - TS = (U + pv) - TS = A + pv. \tag{8.66}$$

For an isothermal change, these several thermodynamic functions may be related in the expressions,

$$\Delta A = \Delta U - T\Delta S \tag{8.67}$$

and

$$\Delta F = \Delta H - T\Delta S, \tag{8.68}$$

from which the relation follows,

$$\Delta F = \Delta A + p\Delta v. \tag{8.69}$$

For a reversible change at constant temperature T, the quantity $T\Delta S$ is equal to the heat, q, absorbed in the process. Also, from the application of the first law to such a reversible isothermal process,

$$\Delta U = q - W_r, \tag{8.70}$$

whence, it is seen that

$$\Delta A = (-W_r)_T, \tag{8.71}$$

which associates the change in Helmholtz free energy with the maximum work available in an isothermal reversible process. Lewis and Randall refer to the quantity A, therefore, as the maximum work function.

In a process at constant temperature and constant pressure it is obvious that the work w done by the system will be composite of two factors, that involved in the volume change, $p\Delta v$, and a residual quantity, w', which may be one of many energy quantities. A frequent form of energy obtained in the conduct of chemical processes is electrical energy. Radiant energy, in the form of light, may be produced. The quantity $p\Delta v$ is constant irrespective of the mode of conduct of the process. The magnitude of the quantity, w', on the other hand, will vary with the mode of conduct of the process. Thus, silver and iodine may be caused to react spontaneously to form silver iodide, for example, in a calorimeter at atmospheric pressure, with the performance of no other external work than that involved in the $p\Delta v$ term. In this case the reaction results in the evolution of 15 kcal. of heat per mole of silver iodide formed. On the other hand, the same reaction can be effected in a galvanic cell, with silver and iodine electrodes in a saturated solution of silver iodide in potassium iodide, in which case there is a net absorption of heat equivalent to 0.75 kcal. since, in addition to the $p\Delta v$ term, the external work performed by the system includes electrical energy equal to 15.75 kcal. per mole of silver iodide formed.

The greater the degree of irreversibility there is in the mode of conduct of the process, the smaller will w' be. The more the process approximates to reversible conditions the greater will w' be, and, in the limit, with a completely reversible process, it will become equal to its maximum value, w_r'. Hence, for a completely reversible isothermal process at constant pressure,

$$W_r = p\Delta v + W_r' = -\Delta A. \tag{8.72}$$

Since from equation (8.69), $\Delta F = \Delta A + p\Delta v$, it follows immediately that

$$W_r' = -\Delta F. \tag{8.73}$$

The decrease in Gibbs free energy, ΔF, is therefore the net work done by the system, operating reversibly, exclusive of the work $p\Delta v$ done against the external pressure. It is this free energy which is normally the preferred free energy function since most chemical experiments are carried out under constant pressure conditions. For reactions at constant volume and constant pressure it is obvious that $\Delta A = \Delta F$.

16. **The Relation between Helmholtz Free Energy and Entropy:** Differentiation of the equation (8.64) for the Helmholtz free energy, $A = U - TS$, yields

$$dA = dU - TdS - SdT. \tag{8.74}$$

Applying the equation of the first law, $dq = dU + pdv$, and restricting the external work to the mechanical work due to the volume change, it follows that

$$dA = dq - pdv - TdS - SdT. \tag{8.75}$$

If dq is supplied reversibly, it is equal to TdS and hence,

$$dA = -pdv - SdT. \tag{8.76}$$

Therefore, for a reversible change at constant volume, $(dv = 0)$,

$$\left(\frac{\partial A}{\partial T}\right)_v = -S. \tag{8.77}$$

Further, at constant temperature, $dA = -pdv$, or, for an ideal gas in which $pv = RT$, for a volume change, v_1 to v_2,

$$\Delta A = -\int_{v_1}^{v_2} pdv = RT \ln \frac{v_1}{v_2} \cdot \tag{8.78}$$

These equations are applicable to physical changes occurring in the system, exclusive of chemical reaction, the amounts of the constituents of the system present being assumed unaltered in the changes occurring.

17. **Free Energy Change with Temperature and Pressure:** Differentiation of the equation $F = H - TS$ yields

$$dF = dH - TdS - SdT \tag{8.79}$$

and, since $H = U + pv$ and $dH = dU + pdv + vdp$, it follows that

$$dF = dU + pdv + vdp - TdS - SdT. \tag{8.80}$$

From equation (8.51), $dU + pdv = TdS$, and thus

$$dF = vdp - SdT. \tag{8.81}$$

For processes at constant temperature, $SdT = 0$ and

$$dF = vdp \qquad \text{or} \qquad (\partial F/\partial p)_T = v, \tag{8.82}$$

while for processes at constant pressure, $vdp = 0$ and

$$dF = -SdT \qquad \text{or} \qquad (\partial F/\partial T)_p = -S. \tag{8.83}$$

For a finite pressure change from p_1 to p_2 with an ideal gas

$$dF = vdp \qquad \text{or} \qquad \Delta F = \int_{p_1}^{p_2} vdp = RT\int_{p_1}^{p_2}\frac{dp}{p} = RT\ln\frac{p_2}{p_1}\cdot \tag{8.84}$$

18. **The Gibbs-Helmholtz Equation:** For a reversible change from state A to state B, at constant pressure, it follows from equation (8.81) that

$$dF_A = -S_AdT \qquad \text{and} \qquad dF_B = -S_BdT.$$

By subtraction,

$$d(F_B - F_A) = -(S_B - S_A)dT \tag{8.85}$$

or

$$d(\Delta F) = -\Delta SdT. \tag{8.86}$$

At constant pressure, therefore,

$$\left(\frac{\partial(\Delta F)}{\partial T}\right)_p = -\Delta S. \tag{8.87}$$

If this value for ΔS is introduced into equation (8.68) it follows that

$$\Delta F - \Delta H = T\left(\frac{\partial\Delta F}{\partial T}\right)_p\cdot \tag{8.88}$$

A corresponding derivation, employing the Helmholtz free energy in the form

$$dA = -SdT,$$

yields the analogous expression, applicable to an isothermal reversible change at constant volume,

$$\Delta A - \Delta U = T\left(\frac{\partial\Delta A}{\partial T}\right)_v\cdot \tag{8.89}$$

These two alternative forms of the Gibbs-Helmholtz equation relate the change in internal energy ΔU and the change in heat content ΔH to the corresponding changes in free energy and their temperature coefficients. Applied to reversible galvanic cells they permit the determination of the change in heat content accompanying the cell reaction from measurements of the electromotive force E and the temperature coefficient of electromotive force $d\mathrm{E}/dT$. At constant pressure

$$-\Delta F = n\mathrm{FE}, \tag{8.90}$$

where $n\mathrm{F}$ is the number of coulombs of electricity yielded by the cell reaction, F is a faraday of electricity, and the cell is operated under such circumstances as will yield the maximum electrical work. The Gibbs-Helmholtz equation assumes the form

$$-n\mathrm{FE} - \Delta H = -n\mathrm{F}T\left(\frac{\partial \mathrm{E}}{\partial T}\right)_p$$

or

$$n\mathrm{FE} + \Delta H = n\mathrm{F}T\left(\frac{\partial \mathrm{E}}{\partial T}\right)_p. \tag{8.91}$$

From such measurements of galvanic cells we obtain our most direct measure of free energy change.

This equation enables us also to calculate ΔH, the change in heat content which occurs when the chemical reaction yielding the electrical energy takes place. Thus, the Weston standard cell, which, as we have seen, is utilized as the standard of electromotive force, is found to have an electromotive force of 1.0183 volts at 20° C. (= 293° K.) and also has a temperature coefficient of − 0.00004 volt per degree at that temperature. The chemical process which takes place when this energy is supplied is expressed by the equation

$$\mathrm{Cd} + \mathrm{Hg_2SO_4} + 8/3\mathrm{H_2O} = \mathrm{CdSO_4{\cdot}8/3H_2O} + 2\mathrm{Hg}.$$

It follows, therefore, that the change in heat content, ΔH, for this process is given by the expression

$$\begin{aligned}\Delta H &= -(2 \times 23{,}060 \times 1.0183) + (2 \times 293 \times 23{,}060 \times -0.00004)\\ &= -46{,}964 - 541\\ &= -47{,}505 \text{ calories.}\end{aligned}$$

The factor, 23,060, is used to express the result in calories, since F is obtained from Faraday's law as 96,494 coulombs. 1 volt coulomb = 1 joule = 0.2389 cal. Hence (96,494 coulombs × 1 volt) 0.2389 = 23,060 calories. The cell change involves 2 gram equivalents. Hence the factor, $n = 2$, in the expression.

19. **Free Energy and Activity:** For ideal gas systems, at constant temperature, $dF = vdp$ may be employed in the form

$$F = RT \ln p + \text{constant}, \tag{8.92}$$

since RT/p may be substituted for v and the integration performed. For non-ideal systems it would be necessary to know v as a function of the pressure before the expression $\int dF = \int vdp$ could be integrated. This means that a knowledge of the equation of state for the substance would be required. Lewis, however, introduced an empirical function, the *activity*, which we shall designate by a designed to take account empirically of the non-ideality of gaseous systems and indeed of solutions also. The substitution of an empirical coefficient a for p means that, for any gas, we can write RT/a in place of v. Our free energy expression then becomes

$$F = RT \ln a + \text{const.}$$

or

$$F = RT \ln a + F^0, \tag{8.93}$$

where F^0 is the integration constant or is the free energy in an arbitrarily defined standard state to which reference is made under any other conditions with the aid of the activity factor a. Any change in free energy will therefore be given by the expression

$$\Delta F = RT \ln a_2/a_1 \tag{8.94}$$

where a_2 and a_1 are the activities in states 2 and 1 analogous to the pressures p_2 and p_1 in the equation (8.84). We shall see that this concept of activity has found extended use in the treatment of non-ideal gaseous systems and solutions.

20. **Thermodynamic Equilibrium:** A condition of equilibrium may be defined by stating that a system is in equilibrium when it shows no change of state in any particular with time. The system must be in a state of absolute rest. A state of partial equilibrium is familiar to every one. A mixture of hydrogen and oxygen at room temperature is one such example already discussed in an earlier section.

A state of absolute rest is difficult to determine experimentally. This fact may be illustrated by the case of the mixture of hydrogen and oxygen just cited. If, for example, such a gas mixture were stored over mercury at room temperature, no change in volume would be noted over long periods of time. This does not mean, however, that no chemical change is occurring. Let it be assumed that 10^6 molecules of hydrogen and half this number of oxygen molecules are reacting per second. A simple calculation, employing for the Avogadro number, $N = 6.02 \times 10^{23}$ molecules per gram molecule, will reveal that it would require a period of observation extending over 2×10^6 years before a volume contraction of 1 cc. could be observed. It is very evident, therefore, that any thermodynamic criteria for a state of absolute rest or of chemical equilibrium would be extremely valuable if not absolutely necessary.

The thermodynamic functions of entropy and free energy may be utilized to provide such criteria of equilibrium. It has already been indicated that the conduct of a reversible process actually produces a succession of equilibrium states each differing infinitesimally from the next. In an isolated system, as already shown (Section 8, 8), the entropy remains unchanged, that is,

$$dS = 0, \tag{8.95}$$

which therefore becomes a criterion of equilibrium in such a system. Since in an isolated system q and w are zero it follows that ΔU is also zero, and so the criterion of reversibility may be stated in the form,

$$(\partial S)_{U,v} = 0. \tag{8.96}$$

This criterion applies also to equilibrium in an adiabatic system. For a reversible process, also, in which there is no exchange of energy with the surroundings other than that involved in the volume change,

$$dF = -SdT + vdp, \tag{8.81}$$

whence, for such reversible changes at constant pressure and temperature,

$$dF = 0$$

or

$$(\partial F)_{p,T} = 0. \tag{8.97}$$

Similarly, for the Helmholtz free energy change dA, which from equation (8.76) is equal to $-pdv - SdT$, it follows that

$$(\partial A)_{v,T} = 0 \tag{8.98}$$

is a characteristic of small reversible changes occurring in a system at equilibrium.

A system which is not in equilibrium tends to proceed spontaneously towards the state of equilibrium. Spontaneously occurring processes are accompanied by an increase in the entropy of the system. A maximum value for the entropy of the system is reached when the system attains equilibrium. When this condition is reached $dS = 0$. From the thermodynamic expression, applicable to systems at constant pressure and temperature,

$$\Delta F = \Delta H - T\Delta S, \tag{8.68}$$

since ΔH is constant at constant temperature and characteristic of the process of change, the increase of entropy of a spontaneous process at constant temperature and pressure is accompanied by a decrease in free energy to a minimum value when equilibrium is attained. When this condition is reached $(\partial F)_{p,T} = 0$.

Such a condition of equilibrium may be more readily understood by consideration of an equilibrium process, e.g., white and gray tin at the transition temperature, 18° C. and 1 atm., in a galvanic cell. Under such circumstances, the electromotive force of the cell is zero, and no transformation occurs. When an external electromotive force $d\mathrm{E}$ is imposed on the cell disturbing the equilibrium obtaining in the cell system, the free energy change is expressed by the equation

$$dF = -n\mathrm{F}d\mathrm{E}. \tag{8.90}$$

As before, nF is the number of coulombs of electricity involved, F being the faraday. The smaller the value of dE the smaller is the free energy change, dF, and the smaller the disturbance of the equilibrium. As dE approaches zero so does dF approach zero. If the reaction occurring could be performed exactly at equilibrium ($dE = 0$), then the change of free energy would be zero.

Even for processes involving change of temperature and pressure at equilibrium the free energy change is zero. For example, consider an equilibrium between two states of matter, a liquid in equilibrium with its saturated vapor. The expression

$$dF = vdp - SdT \tag{8.81}$$

may be employed. If equilibrium can obtain at temperature T and pressure p and also at $T + dT$ and $p + dp$ respectively, an infinitesimal displacement of the system from its equilibrium by changing pressure alone at constant temperature T or of temperature alone at constant pressure p involves the two free energy changes

$$dF = vdp \quad \text{and} \quad dF = -SdT. \tag{8.83}$$

A simultaneous change of p and T by the amounts dp and dT necessary to the establishment of a new state of equilibrium satisfies the condition

$$dF = vdp - SdT = 0. \tag{8.99}$$

It is evident that one could thus proceed by a series of infinitesimal steps from a given position of equilibrium in a liquid-vapor system at pressure p_1 and temperature T_1 to a new position of equilibrium at pressure p_2 and temperature T_2, each step in the process involving zero free energy change and, hence, for the overall process, $\Delta F = 0$.

Quite generally, therefore, for all processes occurring at equilibrium,

$$\Delta F_{eq.} = 0. \tag{8.100}$$

21. **The Clapeyron-Clausius Equation:** The variation in pressure with temperature in an equilibrium between two states of matter may be deduced, with the aid of the free energy relation, $dF = 0$, just obtained and from equation (8.57) for entropy change with volume. Applying this latter expression in the form

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T \tag{8.57}$$

to the process of vaporization, it is to be noted that the pressure p is independent of the volume. Furthermore, the infinitesimal dS/dv may be replaced by the expression $\Delta S/\Delta v$ which refers to one mole of the substance in question. Hence, for the vaporization of any substance,

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta v}. \tag{8.101}$$

For any system in equilibrium, since $\Delta F_{eq.} = 0$, $\Delta S = \Delta H/T$. Equation (8.101) therefore becomes

$$dp/dT = \Delta H/T\Delta v. \tag{8.102}$$

In this equation ΔH is actually the latent heat of vaporization λ of the substance so that

$$dp/dT = \lambda/T\Delta v. \tag{8.103}$$

This expression, which is quite generally applicable, can be transformed into a familiar form when applied to vapors sufficiently dilute that the equation $pv = RT$ can be assumed to hold and the volume of the vapor is large compared with that of the condensed system. In such case, the equation becomes

$$\frac{dp}{dT} = \frac{\lambda}{T(v_g - v_l)} \tag{8.104}$$

or, neglecting v_l,

$$\frac{dp}{dT} = \frac{\lambda}{T \cdot \dfrac{RT}{p}} \tag{8.105}$$

or

$$\frac{dp/p}{dT} = \frac{\lambda}{RT^2} \tag{8.106}$$

or

$$\frac{d \ln p}{dT} = \frac{\lambda}{RT^2}. \tag{8.107}$$

22. **The Statistical Nature of the Second Law:** The second law of thermodynamics applies only to macroscopic systems, those containing large numbers of molecules. The laws relating to the pressure exerted by a gas and the work which it may perform or to the position of equilibrium in a given system are not applicable to systems containing but few molecules. The restrictions on the direction of change embodied in the second law are the consequence of the statistics of large aggregations of molecules. The probability is 1/2 that a given molecule may be found at a given instant in a particular half of a given container. The probability is $(1/2)^2$ that two molecules will be so found simultaneously. When there are N molecules in the system the probability that N will be so found has decreased to $(1/2)^N$. For one mole of gas where $N = 6.02 \times 10^{23}$ this probability is a vanishingly small quantity. That is to say, the presence of all the gas molecules in one half of the container, while possible, is also a very improbable state and the distribution of the molecules throughout the vessel in a manner approaching uniformity of distribution is a state of high probability. We know that a change from the first to the second condition which would occur spontaneously would

be accompanied by an increase in entropy of the system. For such reasons, Boltzmann (1896) associated the entropy of the system with its thermodynamic probability, W, this being defined as the ratio of the probability of an actual state to one of the same volume and total energy having a completely ordered arrangement of its molecular constituents. The relation may be generally formulated by the expression $S = f(W)$. Now since, in the case of two systems, the entropy of the combined system S is obtained by adding the individual entropies, S_1 and S_2, whereas the probabilities must be multiplied, $W = W_1 \times W_2$, it is evident that the functional relation between the two must be logarithmic and we may write

$$S = k \ln W + \text{constant.} \qquad (8.108)$$

Boltzmann found that the constant k was equal to the gas constant per molecule ($= R/N$), where N is Avogadro's number. If the entropy depends only on the thermodynamic probability then the constant is zero and $S = k \ln W$. This condition was envisaged by Planck with the result that, at the absolute zero of temperature, where a completely ordered atomic or molecular arrangement might, in favorable circumstances, be expected to prevail in a crystal, the probability W would be unity and the entropy corresponding would be zero.

It is a well-known result of the laws of chance that the random tossing of a coin yields, in an increasing number of trials, a number of heads and of tails which progressively approach equality. The chance of a head resulting in a random toss is one half. Similarly there is an equal probability that a white or a black ball will be withdrawn from a bag in a single trial if there is one white and one black ball in the bag, or if there are an equal and large number of each in the bag. The chance is 1/2, or 10/20, or 1000/2000, if there are 2, 20, or 2000 balls, equally distributed between black and white, in the bag. This result may be expressed thus: the chance that a white ball will be withdrawn in a random trial is equal to the number of white balls divided by the total number of balls.

It is a further consequence of the laws of chance that, in the withdrawal of two balls simultaneously from a bag containing an equal number of white and black balls, there is twice as great a chance that the pair will be black and white as that the balls will be two whites or two blacks. This is well known to two players A and B who have matched coins after tossing, since there are two ways in which heads and tails can result, A head B tail or A tail B head, whereas there is no such distinction when two heads or two tails result from the toss. This conclusion comes close to the statistical interpretation of equilibrium in an idealized chemical system, e.g., the formation of diatomic molecules from an equal number of two isotopic atomic species. On the laws of chance it would be expected that an equal number of hydrogen and deuterium atoms would combine to yield H_2, HD and D_2 in the ratio 1 : 2 : 1. This is approximately true, especially at high temperatures, and would lead to an equilibrium constant, $K = [HD]^2/[H_2][D_2] = 4$ to which value this reaction system tends as the temperature is raised.* A similar example

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* The student must be careful not to generalize this conclusion for all systems. It does not apply to $H_2 + I_2 = 2HI$ in the normal range of investigation. The individual characteristics of the molecules determine this. The choice of isotopic atoms was deliberate, to avoid such different characteristics as far as possible.

of statistical distribution in a more complex molecular system has been recorded by Calingaert and his co-workers in the case of metal alkyls. Thus, an equimolar mixture of lead tetraethyl and lead tetramethyl could be converted by interchange of radicals to $PbMe_4$, $PbMe_3Et$, $PbMe_2Et_2$, $PbMeEt_3$, and $PbEt_4$ in the approximate molecular ratio 1 : 4 : 6 : 4 : 1 which will be recognized as the numerical coefficients of the expansion $(a + b)^4$, or the relative probabilities of their presence in a statistical mixture if the two radicals are statistically equal.

In the application of statistics to the problems of thermodynamics and of equilibrium use is made of the Boltzmann distribution equation (Section 3, 11) according to which the number of molecules having an energy ϵ is given by the expression $n_\epsilon = ne^{-\epsilon/kT}$ where n is the total number of molecules. It is evident that the total number of molecules is actually the summation of the quantity $ne^{-\epsilon/kT}$ for all values of ϵ between zero and infinity. This may be written in the form

$$\sum_i ne^{-\epsilon_i/kT} \qquad \text{or} \qquad n\sum_i e^{-\epsilon_i/kT},$$

where the summation extends over all values of the energy states ϵ_i. If the energy ϵ_i can be taken up in more than one way the fraction $e^{-\epsilon_i/kT}$ has to be increased by a factor, g_i, the "statistical weight," which is the number of ways in which the energy ϵ_i can be achieved. The summation then becomes $\sum_i g_ie^{-\epsilon_i/kT}$. By reasoning analogous to that involving the white and black balls already considered it will be also evident that the probability, $P(\epsilon_i)$, that a molecular system has the energy ϵ_i in a single state will be given by the ratio of the number having that energy to the total number or

$$P(\epsilon_i) = \frac{ng_ie^{-\epsilon_i/kT}}{\sum_i ng_ie^{-\epsilon_i/kT}} = \frac{g_ie^{-\epsilon_i/kT}}{\sum_i g_ie^{-\epsilon_i/kT}}.^1 \tag{8.109}$$

23. The Partition Function: The summation term $\sum_i e^{-\epsilon_i/kT}$ which enters into the denominator of the expression for $P(\epsilon_i)$ is an important quantity which may be related to the various thermodynamic quantities, internal energy, heat content, heat capacity, free energy and entropy. It has been variously called the state-sum, sum-over-states and distribution function but recently the term partition-function has been most frequently employed. We may assign it the symbol f and define it explicitly:

$$f = \sum_i e^{-\epsilon_i/kT} = e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT} + \cdots + e^{-\epsilon_i/kT}, \tag{8.110}$$

where the summation extends over all the possible energy states of the system, each term multiplied, where necessary, by its statistical weight, g_i.

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[1] There are various methods whereby such an equation can be more or less rigorously derived. The interested student may be referred to Pease, Equilibrium and Kinetics of Gas Reactions, Chap. III, Princeton University Press, Princeton, N. J., 1942; or Treatise on Physical Chemistry, 3rd ed., Vol. I, Chaps. III and IV, D. Van Nostrand Co., New York, N. Y., 1942; H. Eyring and J. Walter, *J. Chem. Educ.*, **18**, 73 (1941).

24. Internal Energy and the Partition Function: The internal energy of a molecular system in excess of that possessed by it at the absolute zero is given by the expression,

$$U - U_0 = N_0\epsilon_0 + N_1\epsilon_1 + N_2\epsilon_2 + \cdots + N_i\epsilon_i, \qquad (8.111)$$

where N_0, N_1, $N_2 \cdots N_i$ are the numbers of molecules possessing the energies ϵ_0, ϵ_1, ϵ_2, $\cdots$, ϵ_i. Since $N_i = N \cdot P(\epsilon_i) = N \cdot e^{-\epsilon_i/kT}/f$ where N is the total number of molecules,

$$U - U_0 = \frac{N}{f}e^{-\epsilon_0/kT} \cdot \epsilon_0 + \frac{N}{f}e^{-\epsilon_1/kT} \cdot \epsilon_1 + \cdots + \frac{N}{f}e^{-\epsilon_i/kT} \cdot \epsilon_i. \qquad (8.112)$$

Now by differentiating f with respect to temperature,

$$\frac{df}{dT} = e^{-\epsilon_0/kT} \cdot \frac{\epsilon_0}{kT^2} + e^{-\epsilon_1/kT} \cdot \frac{\epsilon_1}{kT^2} + \cdots + e^{-\epsilon_i/kT} \cdot \frac{\epsilon_i}{kT^2} \cdot \qquad (8.113)$$

Hence, for 1 mole, where N is the Avogadro number,

$$U - U_0 = \frac{N}{f}kT^2\frac{df}{dT} = NkT^2\frac{d\ln f}{dT} = RT^2\frac{d\ln f}{dT} \cdot \qquad (8.114)$$

25. Heat Capacity and the Partition Funcion: The internal energy per mole can be expressed in the form $U = U_0 + RT^2 d\ln f/dT$. Now since $(\partial U/\partial T)_v = C_v$, it follows that, at constant volume,

$$C_v = \frac{\partial}{\partial T}\left(RT^2\frac{\partial \ln f}{\partial T}\right)_v \cdot \qquad (8.115)$$

26. Equilibrium, Free Energy, and the Partition Function: In an equilibrium $A \rightleftarrows B$ the equilibrium constant K_c will be given by the ratio of the number of molecules per unit volume in the various energy states of B to the number in the various energy states of A in the same volume. That is,

$$K_c = \frac{n\sum\limits_i e^{-\epsilon_{B_i}/kT}/v}{n\sum\limits_i e^{-\epsilon_{A_i}/kT}/v} = \frac{f_B/v}{f_A/v} = \frac{f_B}{f_A} \cdot \qquad (8.116)$$

This is to be compared with the expression applicable to an ideal gas system (10.5) $K_c = c_B/c_A$. Also, it will be shown in (10, 7) that the equilibrium constant in such a system can be related to the standard free energy change ΔF^0 by the expression $\Delta F^0 = -RT\ln K_c$, where $\Delta F^0 = F_B^0 - F_A^0$, the difference of the free energies of B and A in the standard state. It is evident that we can, by identification of terms on the right and left of the equation, written in the following form,

$$F_B^0 - F_A^0 = -RT\left(\ln\frac{f_B}{v} - \ln\frac{f_A}{v}\right) \qquad (8.117)$$

derive the expression for the free energy in the standard state

$$F^0 = -RT\ln\frac{f}{v} \cdot \qquad (8.118)$$

Now since $F = RT \ln C + F^0$ it follows that

$$F = RT \ln \frac{N}{v} - RT \ln \frac{f}{v} = RT \ln \frac{N}{f} = - RT \ln \frac{f}{N} \cdot \qquad (8.119)$$

The Helmholtz free energy $A = F - RT$; hence,

$$\begin{aligned} A = - RT(\ln f - \ln N + 1) &= - kT(N \ln f - N \ln N + N) \\ &= - kT(N \ln f - \ln N!) \end{aligned} \qquad (8.120)$$

since, by Stirling's formula, $\ln N! = N \ln N - N$. Hence,

$$A = - kT \ln \frac{f^N}{N!} \cdot \qquad (8.121)$$

27. **Entropy and the Partition Function:** From the thermodynamic relation $A = U - TS$ or from the relation $(\partial A/\partial T)_v = - S$ it follows that the expression for entropy in terms of the partition function is

$$S = \frac{U - A}{T} = RT \frac{d \ln f}{dT} + k \ln \frac{f^N}{N!} \cdot \qquad (8.122)$$

28. **Evaluation of the Partition Function:** To evaluate a partition function of a molecular system it is necessary to know the energies which a molecule may possess in virtue of its translational, rotational and vibrational degrees of freedom and its electronic excitation, if any. The energy levels of a molecule may be expressed in terms of four quantum numbers, one for each type of energy. This includes translational energy which ordinarily is treated classically but can equally well be treated in terms of quanta. As we have seen for vibrational energy, the two modes of treatment are equivalent for small quanta or high temperature. The total partition function for the several energy forms becomes

$$f = \sum_{t, r, v, e} e^{-E_{t, r, v, e}/kT}, \qquad (8.123)$$

the summation being extended over all possible combinations of the quantum numbers. This is only possible to any degree of completeness in a very few cases and so it is customary to use approximate methods in practice. To a good approximation the energy may be expressed as a sum of the energies of each type.

$$E_{t, r, v, e} \approx E_t + E_r + E_v + E_e. \qquad (8.124)$$

To this approximation, the partition function becomes

$$\begin{aligned} f = \sum_{t, r, v, e} e^{-(E_t+E_r+E_v+E_e)/kT} &= \sum_t e^{-E_t/kT} \\ &\times \sum_r e^{-E_r/kT} \sum_v e^{-E_v/kT} \sum_e e^{-E_e/kT} = f_t f_r f_v f_e \end{aligned} \qquad (8.125)$$

or the product of partition functions for each of the types of energy.

29. **Approximate Partition Function for Translational Motion:** If translational energy in three degrees of freedom be expressed in terms of three integral quantum numbers p, q, and r, the translational energy of a

particle of mass m moving in a rectangular box with sides a, b and c in length is, by quantum mechanics,[1]

$$E_{p,q,r} = \frac{h^2}{8m}\left\{\frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{r^2}{c^2}\right\}. \tag{8.126}$$

The partition function for translational motion then becomes

$$f_t = \sum_{p=1}^{\infty} e^{-p^2h^2/8ma^2kT} \sum_{q=1}^{\infty} e^{-q^2h^2/8mb^2kT} \sum_{r=1}^{\infty} e^{-r^2h^2/8mc^2kT}. \tag{8.127}$$

To a close approximation, since the quanta are small, the summations may be replaced by an integration and since

$$\int_0^{\infty} e^{-p^2h^2/8ma^2kT} = (2\pi mkT)^{1/2}a/h \tag{8.128}$$

it follows that

$$f_t = (2\pi mkT)^{3/2}abc/h^3 = (2\pi mkT)^{3/2}V/h^3, \tag{8.129}$$

where $V = abc$ = the volume of the box.

30. **Approximate Partition Function for Rotational Motion:** The rotational energy of a diatomic molecule is given by equations (4.20) and (4.21)

$$E_r = J(J + 1)h^2/8\pi^2 I$$

and the statistical weight factor, g_i, is equal to $2J + 1$, where J is the rotational quantum number. Hence, the partition function becomes

$$f_r = \sum_{0}^{\infty}(2J + 1)e^{-J(J+1)h^2/8\pi^2 IkT}. \tag{8.130}$$

At high temperatures the summation may be replaced by an integral so that

$$f_r = \frac{8\pi^2 IkT}{h^2}. \tag{8.131}$$

For the case in which the two halves of the molecule are identical, the quantum mechanical treatment shows that only alternate values of J are allowed. The partition function is, therefore, obtained by a summation over half the levels only, and gives

$$f_r = \frac{8\pi^2 IkT}{2h^2}. \tag{8.132}$$

In general, for a linear molecule, the expression becomes

$$f_r = \frac{8\pi^2 IkT}{\sigma h^2}, \tag{8.133}$$

where the symmetry number σ is 2 if both halves of the molecule are alike and otherwise σ is unity. The symmetry number is the number of equivalent ways of orienting the molecule.

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[1] Glasstone, *Text Book of Physical Chemistry*, p. 859, D. Van Nostrand Company, New York, 1940.

For a non-linear molecule with principal moments of inertia, A, B and C, a corresponding development gives

$$f_r = \frac{8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}}{\sigma h^3}. \tag{8.134}$$

The symmetry number, σ, is again determined by the number of equivalent ways of orienting the molecule in space as can be seen from the following values: $\sigma_{H_2O} = 2$; $\sigma_{NH_3} = 3$; $\sigma_{C_2H_4} = 4$; $\sigma_{CH_4} = 12$; $\sigma_{C_6H_6} = 12$.

31. **Approximate Partition Function for Vibrational Motion:** A molecule containing n atoms has $3n - 6$ vibrational degrees of freedom if it is non-linear, and $3n - 5$ if it is linear. Each vibrational degree of freedom may be considered as a harmonic oscillator. The energy for such an oscillator has already been given in Section 5, 4, and the corresponding partition function is

$$f_v = (1 - e^{-h\nu_i/kT})^{-1}. \tag{8.125}$$

For i vibrational degrees of freedom the approximate partition function for vibrational motion becomes the product of the functions for each vibration,

$$f_v = \prod_{i=1}^{i=3n-x} (1 - e^{-h\nu_i/kT})^{-1}, \tag{8.136}$$

where the required frequencies, ν_i, are obtained from infra-red and Raman spectra of the molecule.

32. **Partition Function for Electronic Energy:** This function is directly calculated from the observed electronic energy levels of the molecule using the relation

$$f_e = \sum_e g_e e^{-E_e/kT}. \tag{8.137}$$

In chemical reactions, the electronic energy levels are in general too high in energy above the ground state to contribute materially to the partition function at ordinary temperatures. Most molecules have $^1\Sigma$ ground states and the electronic partition function is usually unity. For molecules having multiplet ground states, such as nitric oxide, oxygen and the hydroxyl radical, the partition function must be suitably modified. It is especially to be remembered that a multiplet ground state modifies correspondingly the rotational partition function, replacing the single energy level by a multiplicity of levels.

33. **Gas Pressure and the Partition Function:** As an example of the applicability of the partition function, the pressure of a gas composed of non-linear molecules can be calculated. From the preceding it is evident that, ignoring electronic energy levels, the partition function for such an n-atomic molecule becomes

$$f = \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} v \right\} \left\{ \frac{8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}}{\sigma h^3} \right\} \times \left\{ \prod_{i=7}^{i=3n} (1 - e^{-h\nu_i/kT})^{-1} \right\}. \tag{8.138}$$

The partition function is a function of the mass, moments of inertia, frequencies of vibration, symmetry of the molecule, temperature and volume. From the thermodynamic relation (8.78),

$$p = -\left(\frac{\partial A}{\partial v}\right)_T,$$

it follows that, for an ideal gas, since all terms other than v are independent of the volume

$$p = kT\frac{\partial}{\partial v}\ln\frac{f^N}{N!} = NkT\frac{\partial}{\partial v}\ln f = \frac{NkT}{v} = \frac{RT}{v}. \qquad (8.139)$$

For a gas obeying van der Waals's equation, with potential energy of interaction between the molecules, the translational partition function would be modified by the substitution for v of the term $(v - b)$ and multiplication of the function by $e^{a/vRT}$. The pressure so calculated would have the familiar form of the van der Waals equation.

34. **Partition Functions for Liquids and Solids:** For these states of matter the translational and rotational terms disappear in the partition function and are replaced by vibrational terms in which the frequencies are functions of volume and temperature. There will also be an interaction term of the general form $e^{-E(v,T)/RT}$ analogous to the term $e^{a/vRT}$ of the van der Waals gas. The calculation of the partition function follows that for a gas when this interaction term has been introduced.

35. **The Ortho-Para-Hydrogen Equilibrium and the Partition Function:** The equilibrium

$$H_{2\,\text{ortho}} \rightleftarrows H_{2\,\text{para}}$$

may well serve as a simple example of an equilibrium $A \rightleftarrows B$ discussed in Section 8, 26. The simplification arises from the fact that all the forms of energy other than that of rotation are alike in the two types of hydrogen molecule, so that the equilibrium constant becomes

$$K_c = \frac{f_{r(\text{para})}}{f_{r(\text{ortho})}} = \frac{\sum\limits_{J=0,2,4\ldots}(2J+1)e^{-J(J+1)h^2/8\pi^2IkT}}{\sum\limits_{J=1,3,5\ldots}3(2J+1)e^{-J(J+1)h^2/8\pi^2IkT}}. \qquad (8.140)$$

The factor 3 in the denominator is a special term to take account of the multiplication of levels due to nuclear spin. For ortho states with odd rotational levels the factor is $(i + 1)\ (2i + 1)$ where i is the spin quantum number, 1/2 in the case of hydrogen. For the para state, with even rotational levels, the factor is $i(2i + 1) = 1$ for $i = 1/2$. By summation of these terms the values for the percentage of para-hydrogen in the equilibrium mixture shown in Table 5.1 were calculated.

The application of the partition function to the determination of equilibrium in a simple chemical reaction, e.g. $2H \rightleftarrows H_2$ will be given in Chapter 10.

EXERCISES (8)

1. Calculate the maximum work which may be accomplished by an ideal gas in expanding from 10 atm. to one atmosphere pressure at 27° C.

2. What would be the final temperature of the gas if the same amount of work as in question 1 had been done in an adiabatic expansion?

3. What is the maximum work which can be obtained from the transfer of 500 calories from a reservoir at 127° C. to one at 27° C.?

4. The latent heat of fusion per gram of methane is 14.5 cal. The melting point is −184° C. Calculate the molar entropy of fusion.

5. Test Trouton's rule with the following vaporization data:

	Butane	CS_2	Ether	Pyridine
Latent heat per gram	87.5	84.1	83.9	107.4
Boiling Point ° C.	0.6	46.25	34.5	115.3

6. Calculate the entropy change when one mole of an ideal gas is heated at constant volume from 25° C. to 100° C.

7. Calculate the entropy change when one mole of an ideal gas is heated at constant pressure from 25° C. to 100° C.

8. Calculate the molal entropy of ammonia at 25° C. and half an atmosphere pressure.

9. The reaction $Zn + 2AgCl = ZnCl_2 + 2Ag$ under certain conditions gave an E.M.F. at 0° C. of 1.015 volt. The E.M.F. diminished as the temperature rose by 0.000402 volt per degree. Calculate the heat of the reaction.

10. Calculate the change in free energy per mole of an ideal gas expanding from 10 atm. to 1 atm. pressure at 27° C.

11. Calculate the free energy change for the reaction $N_2 + 3H_2 = 2NH_3$ at 25° C. given that the heat of reaction is 10,940 cal. per mole NH_3.

12. Calculate with the aid of the partition function the percentage of para-hydrogen in an equilibrium mixture of ortho- and para-hydrogen at 100° K.

CHAPTER 9

SOLUTIONS

The properties of matter so far considered have been those of pure substances. A solution is a homogeneous molecular mixture of two or more substances. It is important to study the properties of solutions in relation to the properties of the constituents. For this purpose, only solutions containing two substances will be considered here and, for convenience, the substance in excess will be called the solvent and the other the solute, although there is no fundamental difference between their rôles. Since a solution is homogeneous it must exist in one of the three states of aggregation. Thus there are gaseous, liquid and solid solutions. The ensuing treatment will consider examples of liquid solutions; the application of the results need not however be confined to liquid solutions but will be general for all types.

The properties of a pure substance have been shown to depend on two of the three variables, temperature, pressure and volume, the third being fixed by the equation of state. For a solution there is another variable, the composition. A variety of methods of expressing composition are in practical use differing only in the units used, but alike in that the composition is stated as a ratio of one constituent to the other or to the resulting solution. The most useful composition unit for the present purposes is termed the *mole fraction.* It is the number of moles of one constituent divided by the total number of moles of all constituents present. The sum of the individual mole fractions of all constituents is thus unity.

The properties of solutions which are to be considered will be shown to depend on the number of molecules present rather than on the nature of the molecules. These properties should therefore be related to each other. Ostwald has called them the colligative properties and van't Hoff was the first to demonstrate their interrelations thermodynamically. They are also referred to as osmotic properties of solution since they include osmotic pressure in addition to vapor pressure, freezing point and boiling point.

1. **Vapor Pressure Lowering:** It has been known for many years that the vapor pressure of a solution containing a non-volatile solute was lower than that of the pure solvent. In 1848 von Babo and again in 1858 Wüllner concluded that at a given temperature the relative vapor pressure lowering was proportional to the concentration of the solution.

This work had employed aqueous solutions of salts and, for reasons which will appear later, the factor of proportionality was difficult to discover. It remained for Raoult in 1888 using various organic solutes and solvents to establish the generalization that bears his name, Raoult's Law, namely, that the relative lowering of the vapor pressure is proportional to the mole fraction of solute and independent of the temperature. If p_0 represents the vapor pressure of pure solvent and p that of the solution, $p_0 - p$ is the lowering of the vapor pressure and $(p_0 - p)/p_0$ is the relative lowering. According to Raoult,

$$\frac{p_0 - p}{p_0} = \frac{n}{n_0 + n} = x, \quad (9.1)$$

where n_0 is the number of moles of solvent, n the number of moles of solute and x is the mole fraction of solute. An alternative form of this expression may be obtained as follows:

$$1 - p/p_0 = x, \quad (9.2)$$

whence

$$p/p_0 = 1 - x = x_0, \quad (9.3)$$

where x_0 is the mole fraction of solvent. This relation is essentially Henry's Law. Henry found that the solubility of a gas in a liquid is proportional to the pressure of the gas. In the above equation x_0 is simply the solubility of the solvent in the solution. Raoult's and Henry's laws are therefore merely alternative ways of expressing the same idea, that the vapor pressure of a constituent of a solution is proportional to the relative number of its molecules in the solution. An illustration of the applicability of Raoult's law, over a complete range of composition, is given in Fig. 9.1 which shows the partial vapor pressures of ethylene dibromide and propylene dibromide as linear functions of

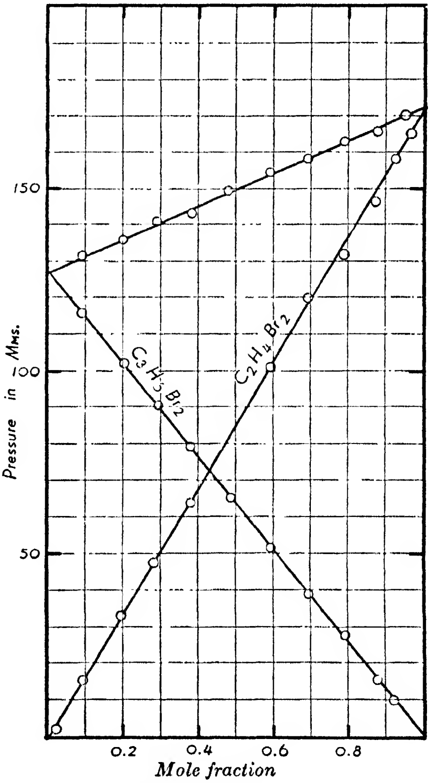

FIG. 9.1. Vapor Pressure of Ethylene and Propylene Dibromides

their mole fractions in the solution. The total vapor pressure of the solution must also be linear.

2. Ideal Solutions: An ideal solution may be defined as one which obeys Raoult's law over the whole range of composition and at all temperatures. The reason for the latter proviso will appear later. It is instructive to consider the requirements necessary for two constituents to form an ideal solution. The partial pressure of a constituent over a solution is determined in part by the "escaping tendency" of that constituent and in part by its concentration. If, in a solution, the forces acting between two molecules of solvent, two molecules of solute and between a molecule of solvent and one of solute are the same, the forces which hold any molecule in the solution are exactly the same as those which hold it in the pure liquid. The escaping tendency of any molecule is thus the same from the solution as from the pure substance. Its partial pressure will then depend solely on the composition of the solution. Hence for a constituent A of a solution

$$p_A = kx_A. \tag{9.4}$$

The proportionality factor is easily recognized as the vapor pressure p_A^0 of pure A at the temperature in question since in pure A the mole fraction x_A is unity. Hence

$$p_A = p_A^0 x_A, \tag{9.5}$$

which is identical with Raoult's law. It is to be expected then, that for an ideal solution, the two constituents shall have similar intermolecular forces. This necessitates that the constituents shall be miscible in all proportions since the environment of the solute and solvent molecules in the solution is similar to that in the pure solute and pure solvent. Furthermore, on mixing the constituents, no change in the partial volumes of either species can occur and, also, for the liquid constituents the total energy of the solution will be the sum of the energies of the constituents. It follows therefore that there will be no heat of mixing for substances in the liquid state. For a solid solute it will be shown that allowance must be made for its heat of fusion and, for a gas, its heat of condensation.

It should be observed that constancy of environment to the solute molecules in a solution can also be obtained by dilution with solvent so that the solute environment is solely solvent. Thus Raoult's law may be expected to hold at high dilutions of any solution. For solutions of electrolytes in water it may be necessary to go to concentrations as low as 0.0001 M before this is achieved. It is this latter alternative that was used by van't Hoff in his theoretical treatment of solutions and which consequently restricts his results to dilute systems.

Having deduced a fundamental relation for one of the colligative properties of ideal solutions there remains only to show how the others are related to it. For this, the law may be used in the above form $p_A = p_A^0 x_A$, or in other forms, for example, taking logarithms

$$\ln p_A = \ln p_A^0 + \ln x_A, \tag{9.6}$$

or differentiating

$$d \ln p_A = d \ln x_A. \tag{9.7}$$

3. **Freezing Point and Solubility:** It is well to realize at the outset that the determination of both a freezing point and of a solubility involves a study of the equilibrium existing in a saturated solution. They are alternative ways of studying the same phenomenon. An aqueous solution is at the freezing point when it is in equilibrium with ice. The solution is saturated with ice and the concentration of water in the solution represents the solubility of the ice. A general relation for the dependence of solubility on temperature thus furnishes equally information on freezing points.

Consider two liquids A and B capable of forming an ideal solution. Let a solution in which the mole fraction of A is x'_A be undercooled to a temperature T, below the freezing point without solidification occurring. The solution being ideal, Raoult's law gives $p'_A = p_A^0 x'_A$ for the partial pressure p'_A of A over the solution, where p_A^0 is the vapor pressure of pure A as a metastable liquid at the temperature T. The solution is supersaturated with A and, upon seeding with a crystal of A, solid A will crystallize, reducing the mole fraction of A in the solution to x_A, and the vapor pressure over the solution to p_A, the proportionality factor between them being as before. Thus $p_A = p_A^0 x_A$. Since the solid A is now in equilibrium with the solution it will possess the same vapor pressure, that is $p_A = p_A^s$. Hence $p_A^s = p_A^0 x_A$. Taking logarithms and differentiating with respect to temperature yields

$$\frac{d \ln p_A^s}{dT} - \frac{d \ln p_A^0}{dT} = \frac{d \ln x_A}{dT}. \tag{9.8}$$

By the Clapeyron-Clausius equation (8.107)

$$\frac{d \ln p_A^s}{dT} = \frac{\lambda_s}{RT^2} \quad \text{and} \quad \frac{d \ln p_A^0}{dT} = \frac{\lambda_v}{RT^2}, \tag{9.9}$$

where λ_s and λ_v are the heats of sublimation and vaporization of the solid and liquid respectively. The difference between them is the heat of fusion λ_f. Thus

$$\frac{\lambda_s}{RT^2} - \frac{\lambda_v}{RT^2} = \frac{\lambda_f}{RT^2} = \frac{d \ln x_A}{dT}. \tag{9.10}$$

Integrating between the temperature limits T_0, the freezing point of pure A and T, that of the solution, gives

$$\int_1^{x_A} d\ln x_A = \frac{\lambda_f}{R}\int_{T_0}^{T}\frac{dT}{T^2}$$

or

$$\ln x_A = \frac{\lambda_f}{R}\cdot\frac{T - T_0}{TT_0} = \frac{\lambda_f}{R}\frac{(-\Delta T_f)}{TT_0}\,. \tag{9.11}$$

This is an ideal solubility equation. It has been assumed in the integration that the heat of fusion is independent of temperature. A more accurate equation could be obtained by taking account of this variation, using Kirchhoff's equation relating it to the heat capacities of the solid and liquid.

The equation (9.11) shows that the solubility in an ideal solution increases with an increase of temperature. This will be true for both constituents of the solution. Hence there exists a temperature at which the solution is saturated with both constituents. It is termed the eutectic temperature. Johnston and his co-workers have studied numerous mixtures of ortho, meta and para disubstituted benzene derivatives, systems which might be expected to behave ideally and have found that the above equation allows accurate calculation, not only of the three binary eutectics but also the ternary eutectics. Table 9.1 contains the observed and calculated eutectic temperatures for the case of the dinitrobenzenes.

TABLE 9.1

System	Eutectic Temperature Observed	Calculated
ortho-para	101.7	100.1
meta-para	78.3	77.8
ortho-meta	63.0	62.8
ternary	58.1	57.0

The equation (9.11) also demands that a substance with a higher melting point should be less soluble at a given temperature than one with a lower melting point but similar heat of fusion. This is illustrated in Table 9.2 for the nitroanilines.

TABLE 9.2

Solute	Melting Point	Solubility in mole fraction at 50° C. Ideal	Acetone
o-nitroaniline	69.3	0.725	0.656
m-nitroaniline	111.8	0.230	0.312
p-nitroaniline	147.5	0.186	0.238

The third column lists the values of the solubility calculated from the ideal equation, while the fourth column gives the observed solubilities in acetone.

Since the freezing point of a liquid is the temperature at which liquid and solid are in equilibrium, it is the temperature at which the vapor pressure is that of the solid. By Raoult's law, the partial pressure of a constituent of a solution is lower than that of the pure constituent and hence, for a solution to freeze, a lower temperature will be required and the presence of a solute causes a freezing point depression. The extent of this depression may be seen from the ideal equation above. Calling ΔT_f the freezing point depression, the equation may be rearranged to give

$$\Delta T_f = \frac{RTT_0}{\lambda_f}(-\ln x_A), \tag{9.12}$$

where x_A is the solubility in mole fraction of the solid which crystallizes at the temperature T, its melting point and heat of fusion being T_0 and λ_f respectively. In the usual determinations of a freezing point depression A is then the solvent. If x_B is the mole fraction of solute the equation gives

$$\Delta T_f = \frac{RTT_0}{\lambda_f}(-\ln(1 - x_B)) = \frac{RTT_0}{\lambda_f}(x_B + \tfrac{1}{2}x_B^2 + \tfrac{1}{3}x_B^3 + \ldots). \tag{9.13}$$

For dilute solutions x_B is a small fraction and the higher powers may be neglected; the difference between T and T_0 is also small and the product TT_0 may be replaced by T_0^2. Writing x_B as approximately n_1/n_0, the ratio of moles of solute to moles of solvent there results

$$\Delta T_f = \frac{RT_0^2}{\lambda_f} \cdot \frac{n_1}{n_0} \cdot \tag{9.14}$$

The molal concentration c, that is, the number of moles of solute dissolved in 1000 g. solvent is given by $c = (n_1/n_0)(1000/M_0)$, where M_0 is the molecular weight of the solvent. Hence

$$\Delta T_f = \frac{RT_0^2}{\lambda_f} \cdot \frac{M_0}{1000} \cdot c = K_f c, \tag{9.15}$$

where

$$K_f = \frac{RT_0^2}{\lambda_f} \cdot \frac{M_0}{1000} \tag{9.16}$$

is a constant for a given solvent and is termed the molal freezing point constant. Table 9.3 gives the values of the freezing point constant for a number of solvents. The last solvent camphor is unusual in having a relatively high molecular weight and melting point and low heat of fusion and giving therefore a large freezing point depression. On this account

TABLE 9.3

Solvent	K_f
Water	1.858
Acetic acid	3.90
Benzene	5.12
Naphthalene	6.9
Cyclohexane	20.2
Camphor	40

Rast suggested its use as a solvent in the micro-determination of molecular weights of organic compounds.

4. **Boiling Point:** The boiling point of a liquid is defined as the temperature at which the vapor pressure is equal to atmospheric pressure. Since the vapor pressure of a solution of a non-volatile solute is lower than that of the pure solvent, the boiling point of the solution will be higher than that of the solvent. The boiling point elevation must be sufficient to raise the vapor pressure of the solution due to the temperature rise by an amount equal to the lowering of the vapor pressure by the solute. Expressed mathematically, the vapor pressure of a solution is a function of both temperature and composition $p = f(T, x)$, whence the change in vapor pressure for a simultaneous change in temperature and composition will be given by the relation

$$dp = \left(\frac{\partial p}{\partial T}\right)_x dT + \left(\frac{\partial p}{\partial x}\right)_T dx. \tag{9.17}$$

In the boiling point determination the pressure is constant, namely atmospheric, that is, $dp = 0$. Hence

$$\left(\frac{\partial p}{\partial T}\right)_x dT = -\left(\frac{\partial p}{\partial x}\right)_T dx. \tag{9.18}$$

Dividing throughout by p

$$\left(\frac{\partial \ln p}{\partial T}\right)_x dT = -\left(\frac{\partial \ln p}{\partial x}\right)_T dx. \tag{9.19}$$

Now the variation with temperature of the vapor pressure of a liquid of fixed composition is given by the Clapeyron-Clausius equation, while the variation with composition at constant temperature is given by Raoult's law, that is,

$$\left(\frac{\partial \ln p}{\partial T}\right)_x = \frac{\lambda_v}{RT^2} \qquad \text{and} \qquad \partial \ln p = \partial \ln x.$$

Hence

$$\frac{\lambda_v}{RT^2} dT = -\left(\frac{\partial \ln x}{\partial x}\right)_T dx = -\frac{dx}{x} = -d \ln x. \tag{9.20}$$

Integrating from pure solvent to solution gives

$$\int_1^x d\ln x = -\frac{\lambda_v}{R}\int_{T_0}^{T}\frac{dT}{T^2}$$

or

$$\ln x = -\frac{\lambda_v}{R}\cdot\frac{T - T_0}{TT_0} = -\frac{\lambda_v}{R}\cdot\frac{\Delta T_b}{TT_0}. \tag{9.21}$$

Using the same approximations as for the freezing point depression there results

$$\Delta T_b = \frac{RT_0^2}{\lambda_v}\cdot\frac{M_0}{1000}\cdot c = K_b c, \tag{9.22}$$

where T_0 is the boiling point of the solvent whose heat of vaporization is λ_v and whose molecular weight is M_0. Table 9.4 gives the values of the molal boiling point constant of several solvents.

TABLE 9.4

Solvent	K_b
Water	0.52
Methyl alcohol	0.82
Ethyl alcohol	1.19
Acetone	1.73
Benzene	2.62
Carbon tetrachloride	5.0

5. **Osmotic Pressure:** The process of osmosis was first observed in 1748 by Abbé Nollet, who showed that if a solution of sugar be placed in a vessel which is closed below by an animal membrane and dipped in a vessel of water, the latter will diffuse through the membrane and cause the solution to rise in the containing vessel. The phenomenon may be illustrated by the use of the apparatus shown in the accompanying diagram (Fig. 9.2). A glass vessel *A* which has a long narrow tube attached to it (a thistle tube serves the purpose) is closed at the bottom by a piece of parchment paper, *C*, filled with a sugar solution and supported in a vessel of water. The column of liquid in the tube, *B*, will be seen to rise until the hydrostatic pressure produced just counter-balances the force tending to cause water to enter the vessel. This pressure is known as the osmotic pressure and is caused by the force tending to bring about equilibrium between the pure solvent and solution which in the absence of a membrane results in mixing by diffusion and the production of a homogeneous solution. Osmotic pressure is, then, the excess pressure which must be put on a solution to bring it into equilibrium with

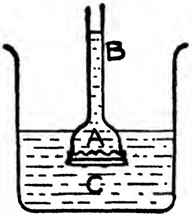

FIG. 9.2

the solvent. Between 1826 and 1848 Dutrochet and Vierodt made some quantitative measurements using pigs' bladders as semipermeable membranes and first recognized the significance of osmotic pressure in physiological processes. Moritz Traube, following the analogy in behavior shown by Graham to exist between animal and colloidal substances, first showed that certain inorganic precipitates of a colloidal nature could act as semipermeable membranes. Pfeffer (1877) carried out a series of reliable quantitative measurements using porous clay cells in the pores of which was deposited a membrane of $Cu_2Fe(CN)_6$. The modern work of Morse and Frazer and their students in America, of the Earl of Berkeley and of Hartley in England, and that of other workers have supplied experimental data which have served as a basis for theoretical treatment.

The theoretical treatment of osmotic pressure began with van't Hoff who made use of the experimental data obtained by Pfeffer to confirm his generalizations. van't Hoff believed that there exists an analogy between the osmotic pressure of a dilute solution and the gaseous pressure that the solute would exert if it existed in the form of a gas in the volume occupied by the solution. As will be seen from the data of Table 9.5 obtained by Pfeffer for sugar solutions, osmotic pressure is directly proportional to concentration, a relation corresponding to Boyle's law for gases. Moreover, the change in osmotic pressure with temperature, as van't Hoff showed from Pfeffer's data, is given by the law of Gay-Lussac for gases. van't Hoff showed therefore that the perfect gas equation

$$PV = nRT \qquad \text{or} \qquad P = cRT \tag{9.23}$$

expressed the relation between osmotic pressure, concentration and temperature.

TABLE 9.5

THE OSMOTIC PRESSURE OF SUCROSE (PFEFFER)

Concentration in Per Cent	Osmotic Pressure in Atmospheres	Ratio of Osmotic Pressure to Concentration
1	0.686	0.68
2	1.34	.67
4	2.75	.68
6	4.04	.67

The analogy between osmotic pressure and gas pressure rests on the observation that R has the same numerical magnitude in the van't Hoff osmotic equation as in the ideal gas equation. More accurate data of Morse and Frazer, and Berkeley and Hartley have shown that, at higher concentrations (above 0.2 molar), the proportionality factor between osmotic pressure and the temperature-composition product, increases markedly with increasing concentration. Morse observed that if the composition was expressed as a molality, that is, in moles per 1000 g. of water instead of per liter of solution, the proportionality factor remained more nearly constant. This change in the method of expressing the composition, in terms of the solvent rather than of the solution as a whole, has been likened to the $(v - b)$ correction factor to the ideal gas equation as suggested by van der Waals. It will be shown later, however, that, at very high concentrations, even the use of molalities is not satisfactory; the osmotic pressure calculated in terms of concentration expressed in molality and the gas constant R is considerably in excess of the observed value.

If, following van't Hoff, the solute in a liquid solution is in the gaseous state then a gas should have zero heat of solution while for a liquid and a solid the heats of solution would be the heat of vaporization and sublimation respectively. It has been shown above, however, that in the ideal cases the heat of solution of a gas (see the boiling point relation) is equal to its heat of condensation, the heat of solution of a solid (see freezing point relation) is its heat of fusion while the heat of solution of a liquid is zero. The solute, therefore, must be present in the liquid state. Although the van't Hoff mechanism is thus not justified, his results are found to be applicable at low concentrations.

There appears to be no completely satisfactory mechanism which will account in all cases for osmosis. It seems advisable therefore to consider the phenomenon merely as one alternative manifestation of the tendency of solvent to pass spontaneously into solution. When contact between solvent and solution is established through the vapor phase this passage can occur by distillation since the vapor pressure of the solvent is higher than that of the solution. When contact is made between the liquids through a membrane which is permeable only to solvent and impermeable to solute, the passage occurs by osmosis. A parallel between these two modes can be seen from a realization that the surface of a solution of a nonvolatile solute is itself a semipermeable membrane allowing solvent molecules alone to enter the vapor phase. Since, as has been shown by Gibbs, the vapor pressure of a liquid is increased by an increase of external pressure on the liquid, in order to prevent distillation of solvent from pure solvent to solution it would be necessary either to subject the solution to an increased pressure sufficient to raise its vapor pressure to that of the solvent, or to subject the solvent to a "negative" pressure sufficient to lower its vapor pressure to that of the solution. It is these pressures that are the equivalent of the osmotic pressure of the solution.

6. **Osmotic Pressure and Vapor Pressure:** Consider the enclosed system shown in Fig. 9.3. Solvent and solution are separated by a semipermeable membrane acting as a piston upon which a pressure P may be applied to counteract the osmotic pressure π of the solution. The whole

system is then in equilibrium, solvent and solution having the same vapor pressure p. The thermodynamic criterion for the equilibrium of the solvent between solution and vapor gives

$$dF \text{ (solution)} = dF \text{ (vapor)}, \qquad (9.24)$$

whence

$$V_0 dP = v_0 dp, \qquad (9.25)$$

where V_0 and v_0 denote the molar volumes of pure solvent in the solution and vapor respectively. Therefore

$$dP/dp = v_0/V_0, \qquad (9.26)$$

which is the Gibbs relation (6.25). Since P acts in opposition to the osmotic pressure, π, $dP = -d\pi$ and $d\pi/dp = -v_0/V_0$. Assuming that the gas laws apply to the vapor, $v_0 = RT/p$, whence

$$d\pi = -(RT/V_0)\, d \ln p. \qquad (9.27)$$

Integrating between limits set by solvent and solution, noting that the osmotic pressure of the solvent is zero, there follows

$$\pi = -(RT/V_0) \ln p/p_0. \qquad (9.28)$$

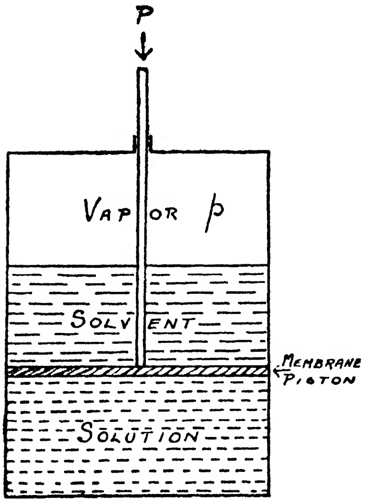

FIG. 9.3. Osmotic Equilibrium between Solvent and Solution

Since the only assumption made in deriving this relation is that the vapor obeys the gas laws, the equation is equally well applicable to non-ideal as to ideal solutions. Table 9.6 gives a comparison between the osmotic pressures observed by Frazer and Myrick and those calculated by means

TABLE 9.6

OSMOTIC PRESSURE IN ATMOSPHERES OF SUCROSE AT 30° C.

Molal Conc.	π obs.	π calc.	π ideal
0.1	2.47	2.47	2.44
1.0	27.22	27.0	24.40
2.0	58.37	58.5	48.32
3.0	95.16	96.2	71.85
4.0	138.96	138.5	94.80
5.0	187.3	183.0	117.7
6.0	232.3	231.0	140.1

of the equation from the vapor pressures measured by Berkeley, Hartley and Burton of cane sugar solutions at 30° C., which, as will be seen later, are not ideal solutions.

Considering the experimental difficulties in the determinations of both osmotic and vapor pressures the concordance is excellent, indicating the generality of the equation.

7. Osmotic Pressure and Concentration: The dependence of osmotic pressure on concentration may easily be found for ideal solutions by combining the above general relation with Raoult's law. Since $\ln p/p_0 = \ln x_0$, where x_0 is the mole fraction of solvent in an ideal solution, the osmotic pressure equation becomes

$$\pi = -(RT/V_0) \ln x_0. \quad \text{(Ideal)} \tag{9.29}$$

Making similar approximations for dilute solutions to those used in the consideration of the freezing point lowering there results

$$\pi = \frac{RT}{V_0}\frac{n_1}{n_0}\cdot \quad \text{(Morse)} \tag{9.30}$$

Since n_0V_0 is the volume of solvent in a solution containing n_1 mols of solute, n_1/n_0V_0 is akin to a molal concentration and the equation is similar to the Morse modification of van't Hoff's law. At high dilution molal and molar concentrations become identical and van't Hoff's law results

$$\pi = RTc. \quad \text{(van't Hoff)} \tag{9.31}$$

TABLE 9.7

$C_2H_4Br_2$ IN $C_3H_6Br_2$ AT 85° C.

Mole fraction	π from Vapor Pressure	π Ideal	π Morse	π van't Hoff
0.147	55	51	55	47
.222	86	80	91	69
.298	114	113	136	90
.412	173	171	224	121
.526	240	241	351	151
.620	319	313	520	173
.720	414	412	820	198
.800	525	522	1280	218
.860	649	640	1960	232
.915	827	806	3440	241

Table 9.7 shows the applicability of these equations to the ideal system of ethylene and propylene dibromides previously considered. The osmotic pressures in atmospheres are calculated first from the

measured vapor pressures and then in turn by the ideal, Morse and van't Hoff equations.

The concordance between the values in the second and third columns substantiates the ideal equation. The last column shows that the van't Hoff law must be restricted to high dilutions even for an ideal system while column four shows the Morse modification to be a marked over-correction of the deviations in van't Hoff's equation.

The applicability of the ideal equation to the non-ideal sucrose system may be judged from the fourth column of Table 9.6 where the values calculated by the ideal equation were included for comparison. The observed pressures are increasingly higher than those calculated as the concentration increases, being almost one hundred per cent higher as saturation is approached.

8. **Molecular Weight Determination:** The ideal equations which have been derived for the various colligative properties, either in the exact or the more approximate form, involve the concentration of the solute. If, therefore, the magnitude of any colligative property is measured for a known weight of solute, the molecular weight may be calculated on the assumption that the solution is ideal, which, in the general case, means sufficiently dilute.

The freezing-point depression is the easiest of all the colligative properties to measure with accuracy in fairly dilute solution. The expression (9.15) previously derived for freezing-point depression is

$$\Delta T_f = K_f c,$$

where c is the number of moles of solute dissolved in 1000 g. of solvent. If, therefore, w grams of solute of molecular weight M are dissolved in W grams of solvent

$$M = \frac{1000 \cdot w \cdot K_f}{W \cdot \Delta T_f} \cdot \qquad (9.32)$$

In a similar manner the molecular weight of solute may be related to the other colligative properties. It must be observed however that the above two equations are only approximations for dilute solutions, even of constituents which would form ideal solutions. At higher concentrations of such ideal solutions, the accurate expression involving the mole fraction should be used and account must be taken of the change in the heat of fusion of solvent with temperature, since the temperature change may be quite large.

It should be noted that since the above relation assumes the validity of Raoult's law and since, in using the latter, mole fractions would be obtained by using the molecular weight of the solvent as vapor, the molecular weight of a solute calculated from any of the colligative properties of the solution is the molecular weight it would have in the vapor phase. Furthermore, since the molecular weight of the solvent appears only in the molal freezing point constant K_f and is there in the form of M_0/λ_f, which ratio is the reciprocal of the latent heat of fusion per gram, the determination of molecular weights in solution is independent of the molecular weight of solvent.

9. **Non-Ideal Solutions:** The deductions so far made, except where otherwise specified, have assumed that the solutions considered were ideal. If, in a binary solution of two constituents A and B, the intermolecular forces are not the same, deviations from the ideal, for all the colligative properties, are to be expected. Thus, for example, if the attraction between a molecule of A and a molecule of B is less than that between two molecules of A or two molecules of B, the molecules of each species will be squeezed out of the liquid phase into the vapor phase and the measured partial pressure of each will be higher than that calculated by Raoult's law. Such deviations are termed positive deviations and are illustrated in Fig. 9.4.

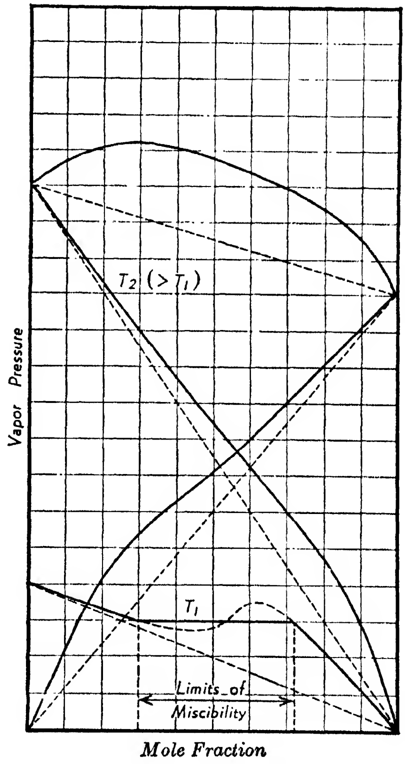

FIG. 9.4. Positive Deviation from Raoult's Law (Schematic)

It is obvious from the figure that the partial pressure curve for a given constituent becomes asymptotic to the ideal (dotted) line as the mole fraction approaches unity. This is true since here the solution is dilute and Raoult's law should be approximately obeyed. As the mole fraction approaches zero, however, the solution is very concentrated, the deviation from ideality will be marked and the partial pressure curve makes a definite angle with the ideal line. Curves for systems showing positive deviation thus have a definite bulge for the higher solute concentrations. At lower temperatures the decreased kinetic energy of the molecules will be less and less able to overcome the mutual attractions and the positive deviation would be expected to increase, that is, the bulge in the curve would become more pronounced and might tend to give a maximum and a minimum. This however does not happen, but, instead, the solution separates into two layers with a common vapor phase and hence a constant vapor pressure so long as the two layers exist.

Water and methyl alcohol is a typical system showing a small positive deviation. The total pressure of the system rises steadily from that of pure water to that of the alcohol. With ethyl alcohol the deviation is more marked and a small maximum appears in the total pressure. In neither case however does a separation into two layers occur with decreasing temperature since the solutions freeze first. With the higher alcohols, for example, butyl alcohol, a flat maximum appears in the total pressure curve and two liquid layers can be obtained even at the boiling point of the pure alcohol.

When the intermolecular forces between a molecule of A and one of B are greater than those for two molecules of A or for two molecules of B, each species becomes held in the liquid phase by the other and the escaping tendency to the vapor phase is reduced. The observed vapor pressure will be less than that calculated by Raoult's law; the system will show negative deviations. Fig. 9.5 illustrates a typical system showing negative deviations. The total vapor pressure curve sags below the ideal line and frequently will possess a marked minimum. Such selective attraction between molecules of opposite species is the same as a tendency to compound formation. The limit to negative deviation will thus occur when a stable compound may be formed. The total pressure curve will have sagged until it reaches a zero value at the composition corresponding to the compound. If only one compound is formed the partial vapor pressure curve of either constituent will be com-

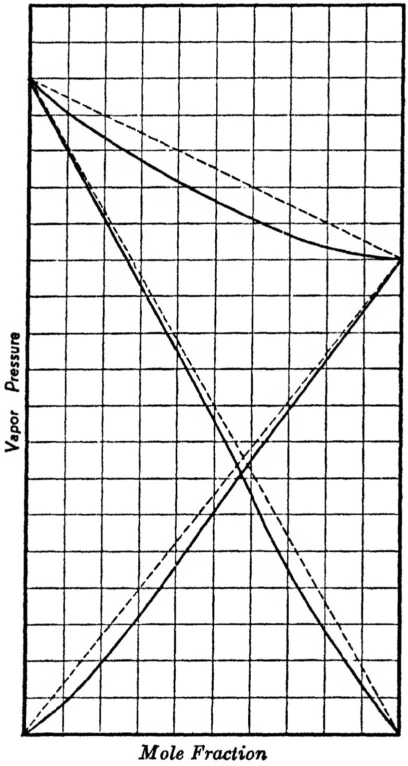

FIG. 9.5. Negative Deviation from Raoult's Law (Schematic)

posed of two parts touching the abscissa at the composition of the compound. Examples of systems showing negative deviations are hydrochloric or nitric acid and water, acetone and chloroform, or aniline and phenol. In the latter case a definite compound is isolable. From acetone and chloroform no compounds can be isolated while in the acid solutions it is probable that hydrates are formed. The term compound formation used as an explanation of negative deviation should not necessarily be interpreted to mean the production of a chemically stable compound. Any loose association such as might result from a mutual orientation of polar bodies would give rise to negative deviations. It is in fact significant that negative deviations are usually found where both constituents are polar. This is especially true in aqueous solutions of electrolytes where a polarization of the dipole water molecules occurs, due to the electrical fields around the ions.

It must be realized that, in general, when there exists a tendency to compound formation there will also be differences in the mutual attractions between like species which would give rise to positive deviations. When the former predominates, the latter is obscured and a net negative deviation is found. That the two effects may exactly counterbalance is shown in the case of ethyl acetate or ethyl ether and water [1] which thus behave ideally. Since the magnitudes of the positive and negative deviations depend on temperature it would be expected that such pseudo-ideal solutions would behave ideally only over a limited temperature range. Ethyl acetate and water show a freezing point depression curve that is ideal up to the limit of their solubility. This covers the temperature range from zero to $-2°$ C. It seems probable that the system would not be ideal at temperatures far removed from this. It is on this account that the definition of ideal solutions given earlier stated that Raoult's law must be obeyed at all temperatures.

The effect which these deviations would have on the other colligative properties can easily be seen. Since a solution will be saturated with one constitutent at a certain temperature when the partial pressure of that constituent is equal to the partial pressure of the solid form at that temperature, a solution showing a positive deviation from Raoult's law will be saturated by a lower mole fraction than for the ideal case; a solution showing a negative deviation requires a higher mole fraction to build up the vapor pressure to the ideal value. In a similar manner, a negative deviation from Raoult's law will parallel an increased freezing-point depression, boiling-point elevation and osmotic pressure above the ideally calculated values. In confirmation of this, Kendall has shown a progressive increase in the solubility of dimethyl pyrone in various acids as solvents in order of increasing acid strength. Table 9.8 gives

[1] Kendall, *Trans. Faraday Soc.*, **33**, 4 (1937).

the actual data and shows the increasing tendency for compound formation as the strength of the acid increases, reflected in the increased negative deviation from Raoult's law and increased solubility.

TABLE 9.8

SOLUBILITY OF DIMETHYL PYRONE AT 40° C.

Solvent	Mole Per Cent
Acetic acid	40.2
Formic acid	46.8
Chloracetic acid	50.6
Dichloracetic acid	53.5
Trichloracetic acid	54.3

Such systems showing negative deviations from Raoult's law and correspondingly abnormal values of the other colligative properties were known to and studied by van't Hoff, especially aqueous solutions of inorganic acids and bases, and most salts. To surmount the difficulty that the colligative properties were abnormally large in comparison with the values calculated from the ideal equations, van't Hoff suggested the inclusion in those equations of an empirical factor i. Thus the van't Hoff osmotic pressure equation became

$$\pi = iRTc. \tag{9.33}$$

Arrhenius first showed the factor i not to be constant but to increase as the dilution increased, and accounted for it by his ionic theory. In so doing Arrhenius virtually assumed that the non-ideality was only apparent and that if the partial dissociation of the electrolyte was taken into account no deviations would be found. This assumes that the ions, the undissociated electrolyte and the solvent are ideal and consequently the substitution of their true concentrations in Raoult's law or its equivalent should give satisfactory agreement. This is not found to be true and, as will be discussed later, ions in particular are far from being ideal constituents. It is interesting to note that when a strong salt solution (2–4 M) is used as a solvent instead of water, the ideal equations are obeyed up to concentrations of solute one hundredfold greater than those when water alone is the solvent.[1] The use of a salt solution as solvent for another salt as solute automatically produces the ideal environment for the solute in that the forces acting between the particles in the solvent are similar to those in the solution, yielding an electrical environment for the solute ions which will be constant so long as the solvent salt is in large excess.

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[1] Brönsted, *Z. physik. Chem.*, **103**, 307 (1922).

The assumption by Arrhenius that the constituents of solutions of electrolytes are ideal is similar to that which is made, probably even more frequently, in the interpretation of molecular weight determinations in systems showing positive deviation. In such systems application of the usual equations which were derived for dilute ideal systems will give apparent molecular weights greater than the true values. This is frequently interpreted as indicating an association of the solute. While it may be true in some cases that association does occur, the evidence is by no means certain and in many cases is due simply to the application of an approximate ideal equation to a non-ideal system. It may be repeated, as already shown, that freezing-point depression measurements, for example, yield molecular weights for the solute as vapor and such evidence for association, even if true, is not indicative of the condition of the solute in the solution, although if the solute is associated as vapor it will probably also be associated in solution. The unequivocal interpretation of apparent molecular weights obtained from measurements of the colligative properties of solutions is extremely difficult.

EXERCISES (9)

1. The specific gravity of a 10 per cent K_2SO_4 solution at 20° C. is 1.0817. Calculate the molar, molal, normal and mole fraction compositions.

2. A solution of 2.47 g. ethyl benzoate in 100 g. benzene has a vapor pressure at 80° C. of 742.6 mm. Benzene at this temperature has a vapor pressure of 751.86 mm. Calculate the molecular weight of ethyl benzoate.

3. Given that the density of benzene at 80° C. is 0.8149, calculate the osmotic pressure of the solution in question 2.

4. The vapor pressure of propylene dibromide at 85° C. is 128 mm. That of ethylene dibromide is 172.6 mm. Calculate the concentration of a solution for which the partial vapor pressure of each constituent is the same.

5. The latent heat of fusion of benzene is 30.5 cal. per gram. The melting point of benzene is 5.4° C. Calculate the molecular freezing point lowering.

6. The latent heat of fusion of anthracene is 38.7 cal. per gram. The melting point is 217° C. Calculate its solubility in terms of mole fraction in an ideal solution at 25° C.

7. 4.04 g. benzoic acid lowers the freezing point of 100 g. acetic acid 1.215°. 4.725 g. benzoic acid lowers the freezing point of 100 g. benzene 0.983. If the molecular freezing point lowerings of acetic acid and benzene are 3.9° and 5.1° respectively, calculate the apparent molecular weight of benzoic acid in each solvent.

8. How accurately in degrees must a thermometer be readable in order to obtain a molecular weight around 200 accurate to one per cent if one gram is dissolved in 100 g. water (*a*) for a freezing point, and (*b*) for a boiling point determination?

9. What is the ratio of the vapor pressures of two solutions containing respectively 1 and 0.36 mole H_2SO_4 in 100 g. water, if the mean value of the van't Hoff factor i in this range is 2.22?

10. The observed osmotic pressure of a molal solution of sucrose in water at 30° C. is 27.22 atm. The vapor pressure of water at 30° C. is 31.824 mm. Calculate the vapor pressure of the sucrose solution.

11. 0.4559 g. iodine raised the boiling point of 30.14 g. ether from 35° to 35.126° C. The heat of vaporization of ether is 90 cals. per gram. Calculate the molecular weight of iodine.

12. The observed osmotic pressure of a 2.0 molal solution of sucrose in water at 30° C. is 58.37 atms. Calculate the freezing point of such a solution.

CHAPTER 10

CHEMICAL EQUILIBRIUM

THE relationship between equilibrium and the driving force of chemical reactions has already been discussed. The development of this relationship has been gradual. Bergmann who compiled 'Tables of Affinity' (1775) was unaware of the concept of equilibrium except as the affinities of the elements were modified by different physical conditions. His order of affinities was different 'in fire' and 'in water.' Wenzel, however, in 1777, suggested that quantity as well as chemical nature affected the rate of chemical action but this suggestion was apparently unnoticed until long afterwards.

The next important step in the development of the subject came in 1799, when Berthollet suggested that large quantity of a material might overcome a weak affinity, and pointed out that the sodium carbonate deposits of Egypt might have been formed from calcium carbonate and salt, the great masses of the latter serving to reverse the usual reaction. This is certainly very nearly a "mass law," but unfortunately Berthollet himself confused the situation by maintaining that mass could affect not only the direction of a reaction but also the ratio in which the substances combine. This brought him into difficulties with the law of definite proportions, just then being placed on a firm experimental basis, and in the ensuing controversy Berthollet's conclusions were discredited.

Advances resulted when quantitative experimental investigations began to supplement hypothetical assertions. The investigations of Rose suggested the importance of quantity in affecting chemical action; Wilhelmy in 1850 made the first quantitative study of the rate of a chemical reaction; Malaguti showed in 1853 that many reactions are reversible, and others added individual facts upon which a theory could be built.

Finally, Berthelot and St. Gilles in 1862–3 carried out an extensive investigation of the equilibrium between acetic acid, ethyl alcohol, ethyl acetate, and water, and showed that their data could be represented mathematically by the identical expression which the present "mass law" would give for this reaction.

It remained, however, for Guldberg and Waage in 1864–7 to enunciate the generalization which expresses essentially what is called the "law of mass action," and to point out clearly the general reversibility of chemical reactions, and the conditions which exist at equilibrium. Guldberg and

Waage stated essentially that the rate at which a substance reacts is proportional to its "active mass," and that the rate of a chemical reaction is proportional to the product of the active masses of the substances reacting; thus, if we consider the reaction,

$$A + B = C + D, \tag{10.1}$$

the rate of the reaction at any given time, from left to right, is given by the expression

$$V_1 = k_1 \times A_A \times A_B, \tag{10.2}$$

where A_A, etc., represent the active masses of A and B present at that time.

If the reaction is reversible, the rate of the opposing reaction is then

$$V_2 = k_2 \times A_C \times A_D. \tag{10.3}$$

If both reactions occur simultaneously, a condition will eventually be reached in which $V_1 = V_2$, when, from equations (10.2) and (10.3), we have

$$\frac{k_1}{k_2} = K = \frac{A_C \times A_D}{A_A \times A_B}. \tag{10.4}$$

Equilibrium is thus considered as a dynamic condition, in which two opposing reactions occur at equal rates, and the "equilibrium constant," K, is simply the ratio of the two separate velocity proportionality constants.

Guldberg and Waage recognized the difficulty introduced by the use of the term "active mass," and pointed out that apparently "molecular concentration" could be substituted therefor in the case of dissolved or gaseous substances, and that the active mass of a solid may be considered as constant.

THE CONDITION OF EQUILIBRIUM IN A CHEMICAL REACTION

1. **The Reversibility of Chemical Reactions:** Numerous experimental investigations have demonstrated the reversibility of particular chemical reactions, and have determined the condition of equilibrium under different conditions of temperature and pressure. Furthermore, the application of the principles of thermodynamics to the energy changes accompanying chemical reactions has led to noteworthy advances in our knowledge of the relations existing at equilibrium, and many important technical chemical processes owe their existence to these advances in theory. In the older literature the term 'reversible reactions' is frequently limited to reactions which have been experimentally carried out in opposite directions. There is no reason to believe, however, that any reaction is not reversible, at least for the purpose of theoretical considerations. The

fact that an equilibrium may lie so far on the side of complete reaction in one direction as to fail of experimental measurement, or the fact that the *rate* of chemical reaction in a given case may be so slow as to prevent the establishment of equilibrium under the conditions investigated, need not prevent us from considering the condition which must prevail at equilibrium in these same reactions. Every reaction will be considered reversible, proceeding eventually to a state of equilibrium determined by the temperature, the pressure, and the proportions of the reacting substances.

2. **Chemical Equilibrium from the Standpoint of Kinetics:** The Mass Law as derived by Guldberg and Waage was based essentially upon consideration of the kinetics of chemical reactions. For a reaction between gases, an expression equivalent to equation (10.4) may be derived (Chap. 15, Section 9) from theoretical considerations, based upon the kinetics of moving gas particles and simple assumptions concerning the relation between the collisions of the reacting species and their chemical reaction. Thus, for the reaction,

$$H_2 + I_2 = 2HI,$$

we can derive an expression for the Law of Mass Action of the form

$$\frac{[C_{HI}]^2}{[C_{H_2}][C_{I_2}]} = K_c, \tag{10.5}$$

which may also be written in terms of the partial pressures of the reacting gases, thus:

$$\frac{p_{HI}^2}{p_{H_2} \times p_{I_2}} = K_p. \tag{10.6}$$

We may generalize this result for the reaction,

$$aA + bB = cC + dD,$$

and obtain, by the same type of reasoning,

$$\frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} = K_p. \tag{10.7}$$

The equilibrium constant K may be regarded as the ratio k_1/k_2 between the velocity constants of the forward and opposing reactions. Where both of these velocities are measurable the value of K may be deduced. This was done by Bodenstein in the case of hydrogen iodide and good agreement was found between this ratio and actually determined values of the equilibrium constant. Furthermore, from the value of K and the velocity constant of the reaction in one direction, the velocity in the reverse direction may be deduced.

3. Chemical Equilibrium from the Standpoint of Thermodynamics: From the form of the expressions already given for the equilibrium constant it is evident that the constant is determined by the nature of the reaction as expressed in the equation. A reaction may follow a course quite different from that indicated by the reaction equation and, in many cases, follows a quite obscure or even unknown course. It is desirable, therefore, to have some other method of approach to the problem of the equilibrium state and this is to be found, as already indicated in Chapter 8, in the thermodynamic method.

From equation (8.84), for a change in free energy between two pressure limits p_1 and p_2, $\Delta F = RT \ln (p_2/p_1)$. Use of this expression leads to a deduction of the law of mass action for a gaseous system obeying the perfect gas laws.

Consider two equilibrium systems, I and II (Fig. 10.1), at the same temperature, T, each containing *different* mixtures of the gases, hydrogen, oxygen and water vapor, both mixtures being, however, in the state of equilibrium. Let the two systems be so large that removal of small quantities of the reacting species does not alter their composition appreciably; let them be contained in vessels provided with membranes each of which is permeable to one of the respective gases and no other, and leads to a cylinder provided with a piston by means of which a given component of the mixture may be withdrawn or added to the system. With the aid of these two vessels a series of changes are made so chosen that, at the end, the initial state of the system will be reproduced. The operations will therefore be units in a complete cycle. Since the thermodynamic functions U, A, and F are independent of previous history, functions only of the state of the system at the given moment, it is characteristic of such cyclic processes, when conducted isothermally and reversibly, that these several functions are unchanged upon completion of the cycle. For an isothermal and reversible cycle, the sum of all the free energy changes is equal to zero, $\Sigma \Delta F = 0$.

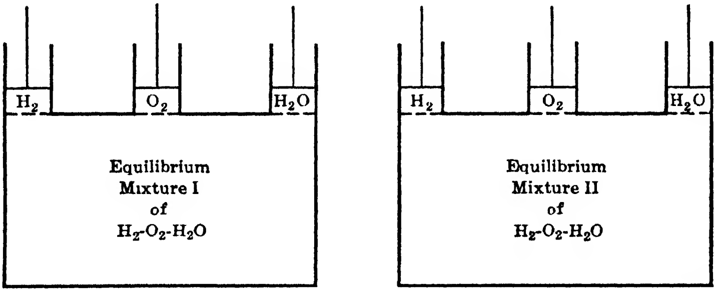

FIG. 10.1

The cycle to be performed in this case is the removal of 2 moles of hydrogen and 1 mole of oxygen from I, expansion to the pressures of these gases in II, insertions of these gases in II, reaction there to form water vapor, removal of 2 moles of water vapor from II, conversion to the partial pressure of water vapor prevalent in I and insertion of the vapor in I followed by its reaction at equilibrium to form hydrogen and oxygen. If we assume that the two systems are so large that removal of small quantities of the reacting species does not alter the prevailing compositions in I and II appreciably we shall disturb the equilibrium negligibly.

Step (1): Withdraw 2 moles of hydrogen and 1 mole of oxygen at the respective partial pressures p_{H_2} and p_{O_2} at which they are present in the equilibrium system I. The free energy increase for this step is evidently zero since the condition of equilibrium is not measurably disturbed, that is, $\Delta F_1 = 0$.

Step (2): Change reversibly the pressures of the two gases to p'_{H_2} and p'_{O_2} at which they exist in the equilibrium system II. The free energy increase for this step is

$$\Delta F_2 = 2RT \ln \frac{p'_{H_2}}{p_{H_2}} + RT \ln \frac{p'_{O_2}}{p_{O_2}}, \tag{10.8}$$

since 2 moles of hydrogen and 1 mole of oxygen are involved.

Step (3): Introduce the gases into the equilibrium system II. Since this does not measurably disturb the equilibrium, we have again zero free energy change, $\Delta F_3 = 0$.

Steps (4), (5) and (6): Carry out a similar series of steps by which 2 moles of water vapor are removed from system II, the partial pressure changed from p'_{H_2O} to p_{H_2O}, and introduced into system I.

$$\Delta F_4 = 0; \qquad \Delta F_5 = 2RT \ln (p_{H_2O}/p'_{H_2O}); \qquad \Delta F_6 = 0.$$

Now from the relation $\Sigma \Delta F = 0$ it follows that,

$$2RT \ln \frac{p'_{H_2}}{p_{H_2}} + RT \ln \frac{p'_{O_2}}{p_{O_2}} + 2RT \ln \frac{p_{H_2O}}{p'_{H_2O}} = 0. \tag{10.9}$$

Or, rearranging,

$$RT \ln \frac{p'^2_{H_2O}}{p'^2_{H_2} \times p'_{O_2}} = RT \ln \frac{p^2_{H_2O}}{p^2_{H_2} \times p_{O_2}}, \tag{10.10}$$

whence,

$$\frac{p'^2_{H_2O}}{p'^2_{H_2} \times p'_{O_2}} = \frac{p^2_{H_2O}}{p^2_{H_2} \times p_{O_2}}. \tag{10.11}$$

Now the two systems chosen were *any* two systems in which hydrogen, oxygen and water vapor were in equilibrium at the given temperature. Hence, for *all* such systems the expressions relating their partial pressures will be equal. Hence, we may write for all such equilibrium systems

$$\frac{p^2_{H_2O}}{p^2_{H_2} \times p_{O_2}} = K_p, \tag{10.12}$$

which expression is none other than the expression for the law of mass action, for gases which obey the gas law, identical with that derived by kinetic methods.

We may generalize this result for any reaction in a dilute gaseous system of the form

$$aA + bB + \cdots = cC + dD + \cdots$$

and obtain the expression already given in equation (10.7).

4. **The Mass Action Law Applied to Dilute Solutions:** A similar expression results for all equilibria occurring in a dilute solution whose vapor obeys Henry's law and the ideal gas law. The procedure is identical with the preceding except that the two equilibrium systems are liquid and the transfer of each solute from one concentration to the other is done by first vaporizing it from the solution. Alternatively, use may be made of the osmotic work involved in the transfer of material from one concentration to another. In either case the final result is that

$$\frac{x^c_C \times x^d_D}{x^a_A \times x^b_B} = K_x, \tag{10.13}$$

where x is the mole fraction of the substance in question. If the solution be sufficiently dilute we may write

$$\frac{c^c_C \times c^d_D}{c^a_A \times c^b_B} = K_c, \tag{10.14}$$

where c is the molecular concentration, expressed as moles of solute per 1,000 grams of solvent.

5. **The Relationship between K_p, K_x and K_c:** In gaseous systems which obey, approximately, the gas laws, we may derive the relations existing between these several forms of the equilibrium constant for the general reaction

$$aA + bB = cC + dD.$$

If P represents the total gas pressure, then the mole fraction of any constituent, e.g., x_A is given by the expression $p_A = x_A P$. Hence, for K_p we may write

$$K_p = \frac{x^c_C \times x^d_D}{x^a_A \times x^b_B} P^{(c+d-a-b)}, \tag{10.15}$$

whence

$$K_p = K_x \times P^{(c+d-a-b)} \tag{10.16}$$

and

$$K_x = K_p \times P^{(a+b-c-d)}. \tag{10.17}$$

It is at once evident that, for a reaction without change in the number of molecules, as, for example,

$$H_2O + CO = H_2 + CO_2$$

the two quantities K_x and K_p are equal since $a + b = c + d$. For a reaction involving a change in the number of molecules, as, for example,

$$2CO + O_2 = 2CO_2$$

it is evident that, in this case, $K_x = K_p \times P$, since $a + b - c = 2 + 1 - 2 = 1$.

For ideal gases, the relationship between p and c is derived from the fundamental equation $pv = nRT$ and, since $n/v = c$, where c is the concentration in moles per litre, it follows that $p = cRT$. Hence

$$K_p = \frac{c_C^c \times c_D^d}{c_A^a \times c_B^b} \times (RT)^{(c+d-a-b)} \tag{10.18}$$

or

$$K_p = K_c \times (RT)^{(c+d-a-b)} \tag{10.19}$$

or

$$K_c = K_p \times (RT)^{(a+b-c-d)}. \tag{10.20}$$

Here, also, K_c and K_p are numerically equal for gas reactions involving no change in the number of molecules. They differ by the factor $(RT)^{(a+b-c-d)}$ when $a + b - c - d$ is not equal to zero.

In the case of homogeneous equilibria in liquid systems, K_p is, obviously, not employed. In this case either K_x or K_c are used to express the equilibrium conditions.

6. **Activity and Equilibrium:** In the discussion of free energy in Chapter 8 its relationship to the empirical function, activity, was defined by the equation (8.93):

$$F = RT \ln a + F^0,$$

where F^0 is a constant which may be arbitrarily defined in reference to some standard state. The use of the activity concept in a general specification of equilibrium may be shown by the following consideration. Consider the reaction:

$$aA + bB = cC + dD.$$

Applying the definition of activity to each reactant and resultant:

$$(F - F^0)_A = a\,RT \ln a_A; \qquad (F - F^0)_B = b\,RT \ln a_B;$$
$$(F - F^0)_C = c\,RT \ln a_C; \qquad (F - F^0)_D = d\,RT \ln a_D.$$

The total free energy change resulting from the disappearance of reactants and production of resultants will be:

$$[(F - F^0)_C + (F - F^0)_D - (F - F^0)_A - (F - F^0)_B] = RT \ln \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}.$$

This may be simplified into:

$$\Delta F - \Delta F^0 = RT \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}, \qquad (10.21)$$

where $\Delta F = F_C + F_D - F_A - F_B$ and $\Delta F^0 = F^0{}_C + F^0{}_D - F^0{}_A - F^0{}_B$. For a reaction system in equilibrium, ΔF must be zero. Hence

$$-\Delta F^0 = RT \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}, \qquad (10.22)$$

where a now represents the equilibrium activity value. However, since the F^0 values are constants, ΔF^0 is also a constant.

Hence

$$K_a = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}, \qquad (10.23)$$

an equation, identical in form with those previously derived but having the advantage of being exact and of general applicability.

For the majority of gaseous reactions and for those reactions in solution which do not involve electrolytes the difference between K_a and either K_p or K_x is negligible. For gas reactions at high pressures as will be shown, K_p is not constant while K_a, were data available for its calculation, would be found constant under all conditions. Its value would be approximately that found for K_p at high temperatures and low pressures, when the reacting gases are most nearly ideal. The absolute necessity of using K_a in considering ionic equilibria will be shown in Chapter 14.

7. The Free Energy Increase Accompanying a Gaseous Reaction: An expression of extraordinary utility giving the increase of free energy in a reaction between gases will now be derived. We shall examine the increase of free energy which occurs when 2 moles of hydrogen and 1 mole of oxygen at their respective partial pressures p_{H_2} and p_{O_2} react to form 2 moles of water vapor at the partial pressure, p_{H_2O}, at a constant temperature, T. Again we shall make use of a large equilibrium box containing these several gases in equilibrium with one another at pressures p'_{H_2}, p'_{O_2} and p'_{H_2O}. The box is to be regarded as fitted with semipermeable membranes, cylinders and pistons as formerly. The mode of conduct of the reaction is as follows:

Step 1: Change the pressure of two moles of hydrogen and one mole of oxygen respectively from p_{H_2} and p_{O_2} to p'_{H_2} and p'_{O_2}, the change being conducted isothermally and reversibly. The increase of free energy is given by the expression

$$\Delta F_1 = 2RT \ln \frac{p'_{\mathrm{H}_2}}{p_{\mathrm{H}_2}} + RT \ln \frac{p'_{\mathrm{O}_2}}{p_{\mathrm{O}_2}}\,. \tag{10.24}$$

Step 2: Introduce these gases through their respective semipermeable membranes into the equilibrium box. Simultaneously, withdraw from the box 2 moles of water vapor through its own semipermeable membrane. During this process the hydrogen and oxygen introduced react in the box to form water vapor thus keeping the composition of the reservoir only infinitesimally different from the equilibrium condition. Since the partial pressures of the gases introduced and withdrawn are equal to the corresponding pressures in the reservoir, none of the processes occurring in Step 2 involves any change in free energy, that is, $\Delta F_2 = 0$.

Step 3: Change, isothermally and reversibly, the partial pressure of the 2 moles of water vapor from $p'_{\mathrm{H}_2\mathrm{O}}$ to $p_{\mathrm{H}_2\mathrm{O}}$, the pressure of the water vapor in the reaction under study. As before, this involves a free energy increase

$$\Delta F_3 = 2RT \ln \frac{p_{\mathrm{H}_2\mathrm{O}}}{p'_{\mathrm{H}_2\mathrm{O}}}\,. \tag{10.25}$$

Hence, for the total reaction we have

$$\Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3 = 2RT \ln \frac{p'_{\mathrm{H}_2}}{p_{\mathrm{H}_2}} + RT \ln \frac{p'_{\mathrm{O}}}{p_{\mathrm{O}_2}} + 2RT \ln \frac{p_{\mathrm{H}_2\mathrm{O}}}{p'_{\mathrm{H}_2\mathrm{O}}}$$

or, rearranging,

$$\begin{aligned} \Delta F &= RT \ln \frac{p^2_{\mathrm{H}_2\mathrm{O}}}{p^2_{\mathrm{H}_2} \times p_{\mathrm{O}_2}} - RT \ln \frac{p'^2_{\mathrm{H}_2\mathrm{O}}}{p'^2_{\mathrm{H}_2} \times p'_{\mathrm{O}_2}} \\ &= RT \ln \frac{p^2_{\mathrm{H}_2\mathrm{O}}}{p^2_{\mathrm{H}_2} \times p_{\mathrm{O}_2}} - RT \ln K_p. \end{aligned} \tag{10.26}$$

From this equation, it is evident that the free energy increase, which results when hydrogen at 1 atmos. partial pressure reacts with oxygen at 1 atmos pressure to yield water vapor at 1 atmosphere pressure, is given by the expression

$$\Delta F^0 = -RT \ln K_p. \tag{10.27}$$

In general, for the equation

$$aA + bB = cC + dD$$

$$\Delta F = RT \ln \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} - RT \ln K_p \tag{10.28}$$

or if $p_A = p_B = p_C = p_D = 1$,

$$\Delta F^0 = -RT \ln K_p. \tag{10.29}$$

In this expression we have a method, auxiliary to that already given (the determination of electromotive forces of suitable cell reactions), for determining the free energy increase of a chemical reaction. All that is necessary for the calculation is an experimental measurement of equilibrium at the temperature in question. Given such, we can determine the value of ΔF for a given reaction under given conditions and can then predict whether or not the reaction can occur spontaneously, since spontaneous change can occur only in the direction of free energy decrease. A negative value of ΔF, therefore, for a chemical reaction written in a given sense indicates that spontaneous reaction is possible in that sense; a positive value indicates that the reaction can occur spontaneously only in the opposite sense.

THE VARIATION OF EQUILIBRIUM CONDITIONS WITH TEMPERATURE, PRESSURE AND CONCENTRATION

8. **The Le Chatelier-Braun Principle:** A state of equilibrium in a chemical reaction is determined by the temperature, pressure, and proportions of the substances present. Changes in the condition of equilibrium are brought about by a change in one or more of the variable factors involved.

Qualitatively, these changes may be predicted by the use of the theorem of Le Chatelier-Braun, which may be stated as follows: *If a change occurs in one of the factors determining a condition of equilibrium, the equilibrium shifts in such a way as to tend to annul the effect of the change.* From this statement, it follows that the effect of an increase in temperature, all other factors remaining constant, is to shift an equilibrium in the direction in which absorption of heat occurs, as this change would tend to annul the effect of the heat added in changing the temperature; the effect of an increase in pressure will be to shift the equilibrium in the direction in which a decrease in volume occurs, as this change would tend to annul the effect of the increased pressure; an increase in the concentration of one of the substances present at equilibrium will shift the equilibrium in such a way as to tend to decrease the concentration of that substance. This principle is an extremely useful one, and serves not only for purely qualitative predictions, but also as a check upon the quantitative results in which errors of calculation may appear.

9. **The Effect of Temperature upon Chemical Equilibrium:** Quantitative information as to the effect of temperature may be obtained by a suitable combination of two expressions already derived for the free energy increase of a chemical reaction. The relation between the increase of free energy and the increase in heat content is given by the expression (8.88)

$$\Delta F - \Delta H = T\left(\frac{d(\Delta F)}{dT}\right)_p .$$

Combining this expression with equation (10.28) we obtain

$$\frac{d(\Delta F)}{dT} = -\frac{\Delta H}{T} - R \ln K_p + R \ln \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}. \tag{10.30}$$

Also, from equation (10.28) by differentiating with respect to temperature, we obtain[1]

$$\frac{d(\Delta F)}{dT} = -R \ln K_p - RT\frac{d \ln K_p}{dT} + R \ln \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}. \tag{10.31}$$

Combining equations (10.30) and (10.31), it follows that

$$RT\frac{d \ln K_p}{dT} = \frac{\Delta H}{T} \tag{10.32}$$

or

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \tag{10.33}$$

and, since, $\Delta H = -Q_p$, where Q_p is the heat evolved when the reaction is conducted at constant pressure, it follows that

$$\frac{d \ln K_p}{dT} = -\frac{Q_p}{RT^2}. \tag{10.34}$$

Since $K_p = K_c(RT)^{-n}$ where $n = a + b - c - d$ we may write $\ln K_p = \ln K_c - n \ln RT$, whence

$$\frac{d \ln K_c}{dT} - \frac{n\, d \ln RT}{dT} = -\frac{Q_p}{RT^2} \tag{10.35}$$

or

$$\frac{d \ln K_c}{dT} = -\frac{Q_p}{RT^2} + \frac{n}{T} = -\frac{Q_p - n\,RT}{RT^2} = -\frac{Q_v}{RT^2}, \tag{10.36}$$

since, as already shown (Chapter 2), $Q_p = Q_v + n\,RT$. Similarly, since $K_p = K_x \times P^{-n}$

$$\frac{d \ln K_x}{dT} + \frac{d \ln P^{-n}}{dT} = -\frac{Q_p}{RT^2}. \tag{10.37}$$

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[1] In performing this derivation we use the relation $d(uv) = udv + vdu$. Hence $d(RT \ln K_p)/dT = R \ln K_p - RTd \ln K_p/dT$. Note, also, that, since p_A, p_B, p_C and p_D are all arbitrarily chosen

$$RT\left(d \ln \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} \Big/ dT\right) = 0$$

since p_A, p_B, p_C and p_D are independent of temperature.

For reactions at constant pressure, P, the second term is independent of temperature. Hence

$$\frac{d \ln K_x}{dT} = -\frac{Q_p}{RT^2}. \tag{10.38}$$

10. **The Equation of the Reaction Isochore:** van't Hoff derived this expression for the relationship between K_p and temperature. The expression may be brought into a form more suitable for use in short temperature ranges over which it may be assumed that $\Delta H = -Q_p$ is constant and independent of the temperature. Under such circumstances the integration yields

$$\ln K_p = -(\Delta H/RT) + C, \tag{10.39}$$

where C is an unknown integration constant. This unknown constant can be eliminated by taking two values of T, whence $\ln K_{p_1} = -(\Delta H/RT_1) + C$; $\ln K_{p_2} = -(\Delta H/RT_2) + C$, or

$$\ln K_{p_1} - \ln K_{p_2} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{10.40}$$

After change to common logarithms and insertion of the numerical value of R the expression becomes

$$\log K_{p_1} - \log K_{p_2} = -\frac{\Delta H}{4.57}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{10.41}$$

This equation is widely used for the calculation of the effect of temperature upon equilibrium in cases where the heat of reaction is known, and also for the calculation of the heat of reaction where the equilibrium constant is known at more than one temperature. Even if ΔH is really dependent upon temperature the equation usually gives approximately correct results if the interval between T_1 and T_2 is not too great.

11. **The Nernst Approximation Formula:** The variation of ΔH with temperature is generally representable by an expression in ascending powers of T of the form

$$\Delta H = \Delta H_0 + qT + \tfrac{1}{2}rT^2 + \tfrac{1}{3}sT^3 + \cdots, \tag{10.42}$$

in which case the expression for K_p becomes

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_0}{RT^2} + \frac{q}{RT} + \frac{1}{2}\frac{r}{R} + \frac{1}{3}\frac{s}{R}T + \cdots, \tag{10.43}$$

and, by integration,

$$\ln K_p = -\frac{\Delta H_0}{RT} + \frac{q}{R}\ln T + \frac{1}{2}\frac{r}{R}T + \frac{1}{6}\frac{s}{R}T^2 + \cdots + C. \tag{10.44}$$

Since $\Delta F^0 = -RT \ln K_p$, we obtain the expression

$$\Delta F^0 = \Delta H_0 - qT \ln T - \tfrac{1}{2}rT^2 - \tfrac{1}{6}sT^3 \cdots - C'T. \qquad (10.45)$$

Because the variation of ΔH with temperature requires laborious measurements of specific heats and since also it is necessary still to obtain a value of C from at least one experimental determination of equilibrium, Nernst, in 1906, from considerations based upon his famous 'Heat Theorem,' set up an expression which approximately expresses the variation of K_p with temperature. The expression runs thus:

$$\log K_p = \frac{Q_p}{4.57T} + \Sigma n \, 1.75 \log T + \Sigma nC.^{1} \qquad (10.46)$$

Here, $\Sigma n = c + d - a - b$; the values of C for a number of the simpler gases are to be found in the subjoined table.

TABLE 10.1

CONVENTIONAL CHEMICAL CONSTANTS

H_2	1.6	HCl	3.0	N_2O	3.3	CH_4	2.5
N_2	2.6	HBr	3.2	NH_3	3.3	C_2H_6	2.6
O_2	2.8	HI	3.4	H_2O	3.6	C_2H_4	2.8
Cl_2	3.1	CO	3.5	H_2S	3.0	C_2H_2	3.2
Br_2	3.2	CO_2	3.2	CS_2	3.1	C_6H_6	3.0
I_2	3.9	NO	3.5	SO_2	3.3	CCl_4	3.1

12. **The Effect of Pressure upon Chemical Equilibrium:** The qualitative effect of pressure is given by the Le Chatelier-Braun principle. The effect of an increase of pressure is to shift the equilibrium in the direction in which a diminution in volume occurs. It follows, therefore, that increase of pressure has no effect on reactions which occur without change in the number of molecules.

The variation of the equilibrium constant with pressure can be studied with the aid of the free energy equation (10.28)

$$\Delta F = RT \ln \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} - RT \ln K_p.$$

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[1] *Note:* The Nernst school has normally employed the approximation formula in the form

$$\log K_p = -\frac{Q_p}{4.57T} + \Sigma n \, 1.75 \log T + \Sigma nC.$$

In this case K_p is defined as $\dfrac{P \text{ reactants}}{P \text{ resultants}}$ and Σn as equal to $a + b - c - d$. The differences are contained in these definitions of K_p and Σn.

The free energy increase is the difference of two energy quantities, F_1 and F_2, which characterize the initial and final energy states of the system, independent of the manner of their attainment, in this case independent therefore of the pressure in the equilibrium box. Similarly, since p_C, p_D, p_A and p_B are arbitrarily defined and independent of the pressure, it follows that K_p must also be independent of the pressure. Note, however, that this only applies in so far as the above equation is applicable. Reference to the deduction of this expression will show that, in its derivation, the gas laws were assumed. Hence, the expression is only valid so long as the gas laws are obeyed. Over this range, however, the value of K_p should be sensibly constant. With both ideal and non-ideal systems, the equilibrium constant K_a is independent of pressure.

The effect of pressure in shifting the position of equilibrium and the constancy of K_p over moderate pressure ranges in which the gas laws may be said to apply, can both be illustrated by the data on equilibrium in the gas reaction involved in the technical synthesis of ammonia at elevated pressures by passage of the reactants, nitrogen and hydrogen, over catalysts such as iron containing small amounts of acidic and basic oxides (Al_2O_3, KOH). The data given are due to Larson and Dodge.[1]

TABLE 10.2

PER CENT OF NH_3 IN EQUILIBRIUM WITH A 1 : 3, $N_2—H_2$ MIXTURE

Temperature ° C.	Pressures in Atmospheres						
	10	30	50	100	300	600	1000
325	10.38						
350	7.35	17.80	25.11				
375	5.25	13.35	19.44	30.95			
400	3.85	10.09	15.11	24.91			
425	2.80	7.59	11.71	20.23			
450	2.04	5.80	9.17	16.36	35.5	53.6	69.4
475	1.61	4.53	7.13	12.98	31.0	47.5	63.5
500	1.20	3.48	5.58	10.40	26.2	42.1	—

It will be noted that K_p is constant over a greater pressure range the higher the temperature. This would be expected since the higher the temperature the more nearly ideal is the behavior of gases.

HOMOGENEOUS EQUILIBRIUM IN THE GASEOUS PHASE

A number of examples will now be discussed, for which experimental measurements of the equilibrium position have been made and with which

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[1] *J. Am. Chem. Soc.*, **45**, 2918 (1923); **46**, 367 (1924).

TABLE 10.3

EQUILIBRIUM CONSTANT

$$K_p = \frac{p_{NH_3}}{p_{N_2}{}^{1/2} \times p_{H_2}{}^{3/2}}$$

Temperature ° C.	Pressures in Atmospheres						
	10	30	50	100	300	600	1000
350	0.0266	0.0273	0.0278				
375	0.0181	0.0184	0.0186	0.0202			
400	0.0129	0.0129	0.0130	0.0137			
425	0.00919	0.00919	0.00932	0.00987			
450	0.00659	0.00676	0.00690	0.00725	0.00884	0.01294	0.02328
475	0.00516	0.00515	0.00513	0.00532	0.00674	0.00895	0.01493
500	0.00381	0.00386	0.00388	0.00402	0.00498	0.00651	

the relationships established in the preceding theoretical treatment can be illustrated.

13. **Reactions without Change in the Number of Molecules:** These systems are independent of the total pressure so long as the gas laws apply. The classical example was studied by Bodenstein, the formation and decomposition of hydrogen iodide,

$$H_2 + I_2 = 2HI.$$

If a represent the number of moles of H_2 taken at the start of the reaction, b the number of moles of I_2, $2x$ the number of moles of HI formed after equilibrium has been reached, and P the total pressure, we have, for the equilibrium partial pressures,

$$p_{H_2} = \frac{(a - x)P}{a + b}; \qquad p_{I_2} = \frac{(b - x)P}{a + b}; \qquad p_{HI} = \frac{(2x)P}{a + b}.$$

Hence

$$K_p = \frac{p^2_{HI}}{p_{H_2} \times p_{I_2}} = \frac{4x^2}{(a - x)(b - x)}. \tag{10.47}$$

The equilibrium has been very carefully studied by Taylor and Crist[1] from both directions, of combination and decomposition. In Table 10.4 are given data for a typical temperature. The values in the last column are the equilibrium constants corrected for the hydrogen lost by diffusion through the walls of the quartz reaction cells during the experiments.

The variation of the equilibrium constant with temperature was

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[1] A. H. Taylor Jr. and R. H. Crist, *J. Am. Chem. Soc.*, **63**, 1377 (1941).

TABLE 10.4

EQUILIBRIUM DATA, $2HI = H_2 + I_2$

Temperature = 698.6° K.; $K = 1.812 \pm .005 \times 10^{-2}$

Mole/cc. H_2 start $\times 10^5$	Mole/cc. I_2 equil. $\times 10^5$	Mole/cc. H_2 equil. $\times 10^5$	Mole/cc. HI equil. $\times 10^5$	K $\times 10^2$	$K_{corr.}$ $\times 10^2$
Combination					
1.1148	0.17069	0.29070	1.6482	1.827	1.803
1.1354	.12500	.35600	1.5588	1.831	1.807
1.1337	.07378	.45647	1.3544	1.835	1.812
1.0678	.23360	.22523	1.6850	1.853	1.829
1.0667	.31292	.18313	1.7671	1.835	1.808
Decomposition					
	.04789	.04789	0.3531	1.840	1.812
	.11409	.11409	.8410	1.840	1.813
	.04953	.04953	.3655	1.832	1.809

found to be in agreement with that calculated by Murphy[1] from the partition functions of hydrogen, iodine and hydrogen iodide based on spectroscopic data and is given by the equation,

$$-R \ln K = 734.05/T - 1.5741 \ln T + \tfrac{1}{2}(1.6266 \times 10^{-3})T - \tfrac{1}{6}(2.973 \times 10^{-7})T^2 + 12.6934. \quad (10.48)$$

14. **The Water Gas Equilibrium:** This reaction, expressed by the equation

$$CO_2 + H_2 = CO + H_2O - 9.81 \text{ kcal.},$$

is of technical importance in the fuel bed of producers, water gas generators and the like. It is also the basis of a process for the technical production of hydrogen. At a temperature of 1000° C. the equilibrium constant,

$$K_p = \frac{p_{CO} \times p_{H_2O}}{p_{CO_2} \times p_{H_2}}, \quad (10.49)$$

has a value of 1.69. In agreement with the Le Chatelier-Braun principle, since the reaction as written is endothermic, high temperatures favor the presence of carbon monoxide and steam, low temperatures the formation of hydrogen. In accordance with this, water gas, which is made by the

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[1] G. M. Murphy, *J. Chem. Phys.*, **4**, 344 (1936).

action of steam on coke, should be produced at a high temperature to prevent excess of steam converting carbon monoxide to carbon dioxide. The fuel bed is accordingly maintained over 1000° C. On the other hand, in the production of hydrogen by passing water gas and steam over oxide catalysts it is desired to obtain from the gas a mixture as low in carbon monoxide and as high in hydrogen as possible. Accordingly the catalyst is maintained in the temperature region 450–500° C.

From the Nernst Approximation Formula, the variation of log K_p with temperature is given by the equation

$$\begin{aligned}\log K_p = \log \frac{p_{CO} \times p_{H_2O}}{p_{H_2} \times p_{CO_2}} &= -\frac{9810}{4.57T} + (3.5 + 3.6 - 3.2 - 1.6)\\ &= -\frac{9810}{4.57T} + 2.3. \qquad (10.50)\end{aligned}$$

This yields the values, $K_{\text{N.A.F.}}$ in Table 10.5. It is to be noted that in reactions without change in the number of molecules, the term, Σn 1.75 log T, disappears, but ΣnC does not do so, since each molecule has its own individual C value. The values so calculated are not very close to experiment. Owing to the technical importance of the reaction, more exact formulas have been derived, notably by Haber and by Lewis and Randall in which the heat capacity data for the reactants permit a determination of the variation of ΔH with temperature as in equation (10.42) and the corresponding expression for ln K_p (10.44). The equilibrium has also been studied with the aid of partition functions by Kassel.[1] The values so calculated, (K_{Kassel}), agree excellently with the best experimental results ($K_{\text{exp.}}$).

TABLE 10.5

EQUILIBRIUM DATA IN THE WATER GAS REACTION

$K = [CO][H_2O]/[CO_2][H_2]$

T° K.	700	773	800	873	900	973	1000	1173	1200
$K_{\text{exp.}}$	—	0.20	—	0.38	—	0.62	—	1.31	
K_{Kassel}	0.111	—	0.247	—	0.451	—	0.719	—	1.41
$K_{\text{N.A.F.}}$	0.167	—	0.414	—	0.82	—	—	—	3.24

15. **Reactions in which the Number of Molecules Changes:** Reactions belonging to this class include a number of important gas reactions, as, for example, the oxidation of carbon monoxide, hydrogen and sulfur dioxide, the dissociation of nitrogen tetroxide and the Deacon chlorine

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[1] Kassel, *J. Am. Chem. Soc.*, **56**, 1838 (1934).

process. The synthesis of ammonia also belongs to this class as well as the synthesis of methyl alcohol,

$$CO + 2H_2 = CH_3OH.$$

16. **The Dissociation of Carbon Dioxide and Water Vapor:** The reactions,

$$CO + \tfrac{1}{2}O_2 = CO_2 \qquad \text{and} \qquad H_2 + \tfrac{1}{2}O_2 = H_2O$$

ordinarily go practically to completion. At the temperature of flames, however, both carbon dioxide and water vapor are measurably dissociated. The extent of dissociation will vary with the pressure. Thus, in the case of carbon dioxide, we have

$$K_p = \frac{p_{CO} \times p_{O_2}{}^{1/2}}{p_{CO_2}}. \tag{10.51}$$

If α is the fraction of each mole of carbon dioxide dissociating at an equilibrium pressure P, there will be $1 - \alpha$ moles of carbon dioxide, α moles of carbon monoxide and $\alpha/2$ moles of oxygen, a total of $1 + \alpha/2$. Hence

$$K_p = \frac{\left(\frac{\alpha}{1 + \alpha/2}P\right)\left(\frac{\alpha}{2(1 + \alpha/2)}P\right)^{1/2}}{\left(\frac{1 - \alpha}{1 + \alpha/2}P\right)} = \frac{\alpha^{3/2}P^{1/2}}{\sqrt{2}(1 - \alpha)(1 + \alpha/2)^{1/2}}. \tag{10.52}$$

For small values of α compared with unity, we may write this equation

$$\alpha = KP^{-1/3}. \tag{10.53}$$

Hence, in this case, and in the case of water vapor, the dissociation varies inversely as the cube root of the total pressure. The higher the temperature, the greater the dissociation. Carbon dioxide at atmospheric pressure is 0.0142 per cent dissociated at 1100° C. and 0.4 per cent at 1450° C. Water vapor at atmospheric pressure is 0.01 per cent dissociated at 1100° C. and 1.8 per cent at 2000° C.

17. **The Dissociation of Nitrogen Tetroxide:** Nitrogen tetroxide is appreciably dissociated at 0° C.,

$$N_2O_4 = 2NO_2,$$

and the amount of dissociation increases rapidly with increasing temperature. The experimental measurement of the equilibrium conditions is simple. The measurements usually involve the determination of the density of the gas, and, as the method is one of the most frequently used in studying equilibria in gas reactions in which the total number of molecules changes, it may be considered in some detail.

The density (g./liter) of any gas which obeys the gas laws is given by the equation

$$d_t = \frac{MP}{RT}, \tag{10.54}$$

where M is the molecular weight and P the total pressure. This density we may call the theoretical density, d_t. If dissociation occurs, the volume will increase in proportion to the increase in the total number of molecules, and, since the total weight remains constant, the density will decrease in the same proportion. In the case of one mole N_2O_4, if α is the fraction dissociated, $1 - \alpha$ will be the number of moles of undissociated gas, and 2α will be the number of moles of NO_2. The total number of moles will be $1 + \alpha$, and the observed density will bear the relation to the theoretical density: $d_0/d_t = 1/(1 + \alpha)$. Rearranging, we have

$$\alpha = (d_t - d_0)/d_0. \tag{10.55}$$

The dissociation constant K_p is given by the equation

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1 + \alpha}P\right)^2}{\left(\frac{1 - \alpha}{1 + \alpha}\right)P} = \frac{4\alpha^2 P}{(1 - \alpha^2)}. \tag{10.56}$$

In this case the dissociation (α) varies, when the dissociation is small, inversely as the square root of the pressure.

It should be noted that if a substance dissociates into n molecules instead of 2 as in the case above, the equation becomes

$$\alpha = \frac{d_t - d_0}{(n - 1)d_0}. \tag{10.57}$$

Table 10.6 presents some data obtained by Verhoek and Daniels[1] at 25°, 35° and 45° C. The values of K_p, besides showing some individual variations, show a general decrease as the pressure increases. This is probably due to deviation of the gases from ideality. Extrapolation to zero pressure gives the true K_p values as 0.1426 at 25° C.; 0.3183 at 35° C.; and 0.6707 at 45° C. The former corresponds to $\Delta F^0_{298} = 1154$ cals. The average heat of dissociation $\Delta H = 14.6$ kcal.

18. **The Oxidation of Sulfur Dioxide:** The equilibrium in this reaction

$$SO_2 + \tfrac{1}{2}O_2 = SO_3$$

is important for the "contact" process of manufacture of sulfuric acid. The experimental method has usually consisted in passing a mixture of

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[1] *J. Am. Chem. Soc.*, **53**, 1250 (1931).

TABLE 10.6

EQUILIBRIUM DATA, $N_2O_4 = 2NO_2$

N_2O_4	25°		35°		45°	
moles/liter $\times 10^3$	P atm.	K_p	P atm.	K_p	P atm.	K_p
6.28	0.2118	0.1419	0.2382	0.3174	0.2662	0.6771
12.59	.3942	.1340	.4396	.2978	.4896	.6185
15.85	.4843	.1290	.5378	.2859	.5985	.5993
19.84	.5996	.1412	.6623	.3032	.7349	.6280
29.68	.8623	.1261	.9470	.2792	1.0474	.5934

sulfur dioxide and oxygen, or air, over a catalyst of finely divided platinum, analyzing the exit gases after rapid cooling. Bodenstein and Pohl carried out very careful determinations of the equilibrium over a range of temperature from 500° to 800° C. Their data show that the equilibrium constant corresponds to that required by the equation

$$K_p = \frac{p_{SO_3}}{p_{SO_2} \times p_{O_2}{}^{1/2}}, \tag{10.58}$$

where the variation of K_p with the temperature is expressed by the equation (Lewis and Randall)

$$\ln K_p = \frac{22,600}{RT} - \frac{21.36}{R}.$$

In technical practice, it is desired to bring about as completely as possible the oxidation of the sulfur dioxide, possible variables being the composition of the mixture, the temperature and the pressure. It is instructive to write the equation as follows

$$\frac{n_{SO_3}}{n_{SO_2}} = K_p\sqrt{\frac{n_{O_2}}{N} \times P}, \tag{10.59}$$

where N refers to the total number of moles of gas present, and n with a subscript the moles of the individual gases. The term on the left of the equation should have, for commercial operation, a value of the order of 50–100, which represents 98 to 99 per cent efficiency of oxidation. Obviously, the ratio n_{SO_3}/n_{SO_2} will increase with increase in total pressure, but only proportionally to the square root of the total pressure, so that a great gain in efficiency is not to be expected from pressure change. The effect of the excess oxygen, n_{O_2}, is also clear from the equation. If n_{O_2} should be extremely small, it might reduce the efficiency of oxidation considerably, but unless this is the case, changes in n_{O_2} do not alter appreciably the n_{SO_3}/n_{SO_2} ratio; for an increase in n_{O_2} also increases N, and the n_{SO_3}/n_{SO_2} ratio is proportional only to the square root of this ratio. If n_{O_2} is increased by adding *air* (essentially one O_2 to four N_2), the ratio of n_{O_2}/N may be *decreased* instead of increased, and the efficiency of oxidation affected unfavorably. Obviously, therefore, with a moderate excess of oxygen and at moderate pressures, the only way in which a high equilibrium value of the n_{SO_3}/n_{SO_2} ratio may be obtained is by operating under temperature conditions for which K_p has a high value. Technically, the reaction is carried out so that the temperature of the gas issuing from the reaction system is about 425° to 450° C., where K_p has values of about 400 and 200 respectively.

19. The Combination of Nitrogen and Hydrogen: The reaction

$$N_2 + 3H_2 = 2NH_3$$

originally studied by Haber constitutes today one of the major processes of industrial nitrogen fixation. Since the reaction involves a decrease in volume, ammonia production is favored by high pressure. This effect has already been mentioned and can be clearly seen from the following. If from an initial mixture of one mole of nitrogen to three of hydrogen a fraction, α, of the former is converted into ammonia, we have at equilibrium, $1 - \alpha$ moles nitrogen, $3(1 - \alpha)$ moles hydrogen and 2α moles ammonia or a total of $4 - 2\alpha$ moles. Hence, at a total pressure P,

$$K_p = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3} = \frac{\left(\dfrac{2\alpha}{4 - 2\alpha} P\right)^2}{\left(\dfrac{1 - \alpha}{4 - 2\alpha} P\right)\left(\dfrac{3(1 - \alpha)}{4 - 2\alpha} P\right)^3}$$

$$= \frac{16\alpha^2(2 - \alpha)^2}{27P^2(1 - \alpha)^4}. \qquad (10.60)$$

[illegible] all conversions, that is, $\alpha \ll 1$, it may be seen that α^2 is proportional or α is proportional to P. Table 10.2 shows data, in the lower e range at high temperatures where the conversion is small, which e this proportionality. At higher pressures and therefore with nversions the expression shows a smaller pressure dependence

reaction being exothermic, the production of ammonia is favored temperature. That equilibrium be established sufficiently rapidly e temperatures for which an effective conversion is obtained, must be used. Optimum conditions in commercial operation temperatures of 450–500° C. and pressures ranging from 200 to m.

20. The Equilibrium $H_2 \rightleftarrows 2H$: This reaction is of importance in the production of atomic from molecular hydrogen. It may be employed also as a simple illustration of the use of approximate partition functions in the calculation of chemical equilibria. In terms of these partition functions the equilibrium constant is given by the expression

$$K = \frac{(f_H)^2}{f_{H_2}}. \qquad (10.61)$$

The partition function f_H for atomic hydrogen involves the translational partition function, with no rotational or vibrational terms, and, in addition, a term which takes into account the fact that there is in the atom an unpaired electron, with a spin, $i = \frac{1}{2}$, which therefore contributes $2i + 1 = 2$ to the total function. For the molecule, there will be, in addition to the translational term, one rotational and one vibrational term. Thus, the equilibrium constant becomes

$$K = \frac{\left[\dfrac{(2\pi m_1 kT)^{3/2}V}{h^3N} \times 2\right]^2}{\dfrac{(2\pi m_2 kT)^{3/2}V}{h^3N} \cdot \dfrac{8\pi^2 IkT}{\sigma h} \cdot (1 - e^{h\nu/kT})^{-1}} e^{-\Delta U_0^0/RT}. \qquad (10.62)$$

In the translational terms both in the numerator and denominator there appears the Avogadro number N. This number plays a role analogous to the symmetry factor σ in the rotational partition function. It is inserted because one mole of any gas contains N atoms or molecules and these are indistinguishable one from another. For one mole of gas at a pressure of 1 atm. at the standard state it is apparent that V can be replaced by RT. The final exponential term $e^{-\Delta U_0^0/RT}$ is the Boltzmann factor expressing the ratio of atoms to molecules when the potential energy difference between them in the standard state is equal to ΔU_0^0 at the absolute zero.

The numerical value of K can therefore be calculated on ins the appropriate values for the several quantities involved: $m_1 =$ 6.02×10^{23}; $m_2 = 2 \times 1.0076/6.02 \times 10^{23}$; $I = 0.467 \times 10^{-40}$ 5, Section 1); $\sigma = 2$; $h\nu/k = 6100$ (Chapter 5, Section 4); ΔU_0^0 kcal. (Chapter 5, Section 5). At 2000° K. this gives a value $= 3.9 \times 10^{-6}$. An exact calculation using the best available scopic data for hydrogen gives a value for $K_{2000} = 2.94 \times 10$ approximate calculation gives therefore the correct order of m for the equilibrium constant.

The extent of dissociation as determined from Langmuir mental observations and as calculated statistically by Giauque temperatures is shown in Table 10.7.

TABLE 10.7

PERCENTAGE DISSOCIATION OF MOLECULAR HYDROGEN AT 1 ATM.

$T°$ K. =	1000	2000	2500	3000	3500
Obs. (Langmuir)	—	0.17	1.6	7.2	21
Calc. (Giauque)	1.3×10^{-7}	0.086	1.31	8.1	29.7

CHEMICAL EQUILIBRIUM IN THE LIQUID PHASE

21. **Esterification Equilibria:** One of the first experimental investigations of equilibrium was that of Berthelot and Pèan de St. Gilles on the reaction between acetic acid and ethyl alcohol. They proved it to be reversible, and showed that their equilibrium data could be represented mathematically by the equation

$$K = \frac{\text{moles ester} \times \text{moles water}}{\text{moles acid} \times \text{moles alcohol}}\,. \tag{10.63}$$

Alcohol and acetic acid were mixed in varying proportions in sealed glass tubes, and heated at temperatures in the neighborhood of 200° C. until no further change in composition was brought about by further heating. The mixtures were analyzed for acetic acid, and the composition of the entire mixture calculated from this measurement. If a represents the number of moles of alcohol taken, b the number of moles of acetic acid, and α the number of moles of ester (or water) formed, the experiments showed that at equilibrium the proportions of all constituents present are quite closely given by the equation

$$K = \frac{\alpha^2}{(a - \alpha)(b - \alpha)}, \tag{10.64}$$

[illegible] has the numerical value of 4.0. Table 10.8 gives the results of [illegible] xperiments, showing the values of α determined experimentally, [illegible] calculated from the above equation. The agreement is prob-[illegible] in the experimental error.

[illegible] lot and Pèan de St. Gilles found the value of the equilibrium [illegible] to be practically independent of the temperature, in accord [illegible] nown fact that the heat of reaction must be very close to zero, [illegible] indirectly by consideration of the heats of combustion of alco-[illegible] acid, and ethyl acetate.

[illegible] quilibrium constants for esterification reactions have been [illegible] perhaps more frequently than is the case for any other type of [illegible] n liquid systems (excluding ionic equilibria), and the literature [illegible] alues for the equilibrium constants for the reactions between

TABLE 10.8

Moles Acetic Acid Taken a	Moles Alcohol Taken b	Moles Ester Formed α (Found)	Moles Ester Calculated α
1.0	0.05	0.05	0.049
1.0	0.18	0.171	0.171
1.0	0.33	0.293	0.301
1.0	0.50	0.414	0.423
1.0	1.00	0.667	0.667
1.0	2.00	0.858	0.850
1.0	8.00	0.966	0.970

nearly all of the common acids and alcohols. One or two cases are of special interest in illustrating the application of the mass law.

It has been shown by Menschutkin that esters of tertiary alcohols decompose usually into acid and unsaturated hydrocarbon, and the equilibrium conditions for such reactions have been studied by Konowalow and by Nernst and Hohmann. The latter authors measured the equilibrium of the reaction between amylene and the chlorinated acetic acids, their results on trichloracetic acid at 100° C. being characteristic. The reaction proceeds according to the equation

$$CCl_3COOH + C_5H_{10} = CCl_3.COOC_5H_{11},$$

and we may write for it the mass law expression in mole fractions:

$$K_x = \frac{x \text{ ester}}{x \text{ acid} \times x \text{ amylene}}. \tag{10.65}$$

If 1.0 mole of acid is mixed with a moles of amylene, and if α represents the moles of ester formed when the reaction has reached equilibrium, we may write

$$K_x = \frac{\alpha \times N}{(a - \alpha)(1 - \alpha)},$$

where N represents the total number of moles. Table 10.9 c[illegible] comparison of the values for α found experimentally for several [illegible] a, and also those calculated from the mean value of the equilib[illegible] stant. It is clear that there is very fair agreement between the [illegible] and calculated values.

A comparison of these data with those for the reaction [illegible] acetic acid and ethyl alcohol brings out an interesting differe[illegible] havior. In the latter case the moles of ester present at e[illegible] increase rapidly with increasing moles of alcohol added, and [illegible] unity as the number of moles of alcohol becomes large. In the [illegible] reaction between amylene and acid, the number of moles of ester changes very slowly with an increase in the number of moles of amylene. This arises because an increase in a in the amylene reaction also increases N and therefore α is much less affected by the increase in a. This does not hold true in the case of the alcohol experiments.

TABLE 10.9

EQUILIBRIUM DATA

$(CCl_3COOH + C_5H_{10} = CCl_3COOC_5H_{11})$

Moles C_5H_{10} a	Moles CCl_3COOH	Moles Ester α (Found)	Moles Ester α (Calculated)
2.15	1.0	0.762	0.762
4.12	1.0	0.814	0.821
4.48	1.0	0.820	0.826
6.63	1.0	0.838	0.844
6.80	1.0	0.839	0.845
7.13	1.0	0.855	0.846

CHEMICAL EQUILIBRIUM IN HETEROGENEOUS SYSTEMS

22. **Gas-Solid Equilibria:** In the case of heterogeneous reactions, for example, between gases and solids, a knowledge of the saturated vapor pressure of the solid constituents enables one to refer the reaction to that taking place in the homogeneous gas phase. A simple typical heterogeneous reaction may be used by way of illustration, the oxidation of sulfur to sulfur dioxide. This reaction may occur either as a heterogeneous reaction between solid sulfur and oxygen or as a homogeneous process between sulfur vapor and oxygen. For the latter, it is evident that

$$K_p = \frac{p_{SO_2}}{p_S \times p_{O_2}}. \tag{10.67}$$

In the heterogeneous system with solid sulfur continuously present it is apparent that the partial pressure of the sulfur will remain constant throughout the reaction process and be equal to π_S, the saturated vapor pressure of sulfur at the given temperature. The equilibrium constant of the heterogeneous reaction will therefore be

$$K_p = \frac{p_{SO_2}}{p_{O_2} \times \pi_S} \tag{10.68}$$

or since π_S is constant at constant temperature,

$$\frac{p_{SO_2}}{p_{O_2}} = K_p \times \pi_S = K_p'. \tag{10.69}$$

It is therefore evident that the equilibrium condition of heterogeneous reactions, K_p', can be deduced by inserting in the mass action expression the partial pressures (or concentrations) of the reactants present only in the gaseous phase. The solid phases present influence the numerical value of the equilibrium constant.

The variation of this constant with temperature can similarly be associated with the variation of the equilibrium constant of the homogeneous reaction with temperature. In the example cited

$$K_p \text{ (homogeneous)} = \frac{K_p' \text{ (heterogeneous)}}{\pi_S} \tag{10.70}$$

or

$$K_p \cdot \pi_S = K_p'.$$

Now, from the discussion in Section 9,

$$\frac{d \ln K_p}{dT} = -\frac{Q_p}{RT^2}, \tag{10.34}$$

and, from the Clapeyron-Clausius equation (8.107)

$$\frac{d \ln \pi_S}{dT} = \frac{\lambda_S}{RT^2}, \tag{10.71}$$

where λ_S is the latent heat of vaporization of solid sulfur. Hence,

$$\frac{d \ln K_p \cdot \pi_S}{dT} = \frac{d \ln K_p'}{dT} = -\frac{Q_p - \lambda_S}{RT^2} = -\frac{Q_p'}{RT^2}. \tag{10.72}$$

The quantity, Q_p', is the calorimetrically determined heat of reaction between solid sulfur and oxygen to form sulfur dioxide. The variation of K_p' with temperature is similar to that obtaining in the homogeneous system. For short intervals of temperature over which Q' may be regarded as constant the integrated form may be employed.

$$\ln \frac{K_1'}{K_2'} = \frac{Q'}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right). \tag{10.73}$$

As in the case of homogeneous equilibria, Nernst also suggested an approximation equation for the variation of K_p' with temperature which has the form:

$$\ln K_p' = \frac{Q_0}{RT} + \Sigma n 1.75 \ln T + \frac{\Sigma\beta}{R} T + \ldots + \Sigma n I. \tag{10.74}$$

In its more usual form, as an approximation, this gives

$$\log K_p' = \frac{Q_p'}{4.57T} + \Sigma n 1.75 \log T + \Sigma n C, \tag{10.75}$$

where the Σn refers to the algebraic summation of the components, resultants positive, reactants negative, existing in the gaseous state alone, C to the integration constants of the vapor pressure equation, employing common logarithms, for the substances existing only as gases in the reaction process, the so-called Conventional Chemical Constants of Nernst.

23. **The Dissociation of Silver Oxide:** This dissociation has been measured by Lewis in the lower range of pressures and by Keyes and Hara over a much wider range. The data have been used by Pollitzer to illustrate the use of the Nernst equation with numerical data shown in the following equation:

$$\log K_p = \log p_{O_2} = -\frac{13{,}130}{4.57T} + 1.75 \log T - \frac{0.010T}{4.57} + 2.8. \qquad (10.76)$$

The agreement with the data of Lewis is shown in the following table.

TABLE 10.10

p_{O_2} (atm.)	$T_{\text{obs.}}$	$T_{\text{calc.}}$
20.5	575	567
32.0	598	594
203.0	718	733

Lewis and Randall express the experimental data by means of the equation

$$\frac{\Delta F}{T} = -R \ln K = -\frac{7240}{T} - 1.0 \ln T + 21.95. \qquad (10.77)$$

Similarly, in the dissociation of calcium carbonate, $\log K_p' = \log p_{CO_2}$. For the decomposition of solid ammonium hydrosulfide to yield gaseous ammonia and hydrogen sulfide, Isambert showed that, at equilibrium, $K_p' = p_{NH_3} \cdot p_{H_2S}$. In the dissociation equilibria involving salt hydrates, for example, in the reaction,

$$CuSO_4.5H_2O(s) = CuSO_4.3H_2O(s) + 2H_2O(g),$$

the equilibrium constant, $K_p' = p^2_{H_2O}$. With two solids and two gases, as in the reactions,

$$\begin{aligned} Fe(s) + H_2O(g) &= FeO(s) + H_2(g), \\ 3FeO(s) + H_2O(g) &= Fe_3O_4(s) + H_2(g), \end{aligned}$$

the equilibrium constant in each case is given by the expression

$$K_p' = p_{H_2}/p_{H_2O}.$$

24. **Gas-Liquid Reactions:** The considerations given in the preceding section apply equally well to systems in which the condensed phase is a

liquid. Here, also, the expression for K_p' contains the partial pressures of those constituents which appear in the gaseous phase only. Thus, in the reaction

$$2H_2O(g) + S(l) = 2H_2S(g) + SO_2(g),$$

the equilibrium constant

$$K_p' = \frac{p^2_{H_2S} \times p_{SO_2}}{p^2_{H_2O}}. \tag{10.78}$$

This reaction has been investigated by Randall at the boiling point of sulfur. The mean value for K_p' at $T = 718°$ K. with the partial pressures in atmospheres, was 1.54×10^{-3}. The corresponding magnitude

$$\Delta F_{718} = -RT \ln K_p' = 9240 \text{ cals.}$$

EXERCISES (10)

1. The velocity constant of the hydrolysis of ethyl acetate at 25° C. is 2.50×10^{-4} liter mole^{-1} min.$^{-1}$. The reverse esterification reaction has a velocity constant of 6.25×10^{-5}. Calculate the equilibrium constant.

2. A 1 : 3 N_2-H_2 mixture at 50 atms. pressure and 350° C. contains at equilibrium 25.11 per cent ammonia. Calculate the equilibrium constant in terms of mole fractions.

3. From the data in Table 10.3 calculate the standard free energy change for ammonia synthesis at 500° C.

4. The heat of the reaction $H_2 + \frac{1}{2}O_2 = H_2O(l)$ is 68.36 kcal. at 25° C. With the help of the data in Table 8.1 calculate the equilibrium constant.

5. At 27° C. and 1 atmosphere pressure the equilibrium constant in terms of concentrations expressed in moles per liter for the reaction $N_2O_4 = 2NO_2$ is 0.0017. At 111° C. the value is 0.204. Calculate the heat of dissociation.

6. K_p at 980° C. for the reaction $CO + H_2O = CO_2 + H_2 + 10{,}500$ cals. is 1.60. Calculate the composition of a water gas formed from equal volumes of CO and steam at 1200° C.

7. The following values of K_p for the reaction $I_2 = 2I$ were found at the temperatures indicated:

K_p	0.0114	0.0474	0.165	0.492	1.23
$T°$ C.	800	900	1000	1100	1200

Calculate the heat of dissociation of iodine and thence the conventional chemical constant of atomic iodine.

8. Water vapor at atmospheric pressure is 0.01 per cent dissociated at 1100° C. Calculate the dissociation constant.

9. 729 mm. of a mixture of dry HCl and O_2 containing 34.1 per cent HCl was allowed to react to equilibrium at 430° C. At equilibrium 81 per cent of the HCl had decomposed. Calculate the equilibrium constant for the Deacon chlorine process, K_p, in atmospheres.

10. The percentage dissociations of H_2 at 2000 and 2200° K. and one atmosphere pressure are respectively 0.112 and 0.392. Calculate the heat of dissociation and the standard free energy change at 2000° K.

11. The following are data for the water gas equilibrium $H_2 + CO_2 = CO + H_2O$:

T° C.	500	600	700	800	900	1000
K_p	0.20	0.41	0.63	0.93	1.29	1.66

At what temperature will the standard free energy be zero?

12. From the data in Table 10.9 calculate K_x for the formation of the amyl ester of trichloracetic acid.

13. The heat of formation of steam is 57.83 kcal.; of NH_3 is 10.94 and of NO is − 21.5. Calculate the equilibrium constant for ammonia oxidation to NO at 1000° C.

14. The equilibrium constants for the reaction $H_2 + D_2 = 2HD$ at 400 and 700° K. are 3.494 and 3.800. Show that the heat of reaction is comparable with the difference of the zero-point energies of the reactants, namely 155 cals.

15. The equilibrium constant at 20° C. for the reaction:

$$H_2 + D_2 = 2HD \text{ is } K_1 = 3.27;$$

for

$$H_2O + D_2O = 2HDO,\ K_2 = 3.18;$$

and for

$$H_2O + HD = HDO + H_2,\ K_3 = 3.4.$$

Calculate the constant for the reaction $H_2O + D_2 = D_2O + H_2$.

16. The dissociation pressure of NH_4SH into NH_3 and H_2S at 9.5° C. is 175 mm. and at 25.1° C. is 501 mm. Calculate the heat of dissociation. Using this value for the heat of dissociation calculate the dissociation pressures at 9.5° and 25.1° C. using the Nernst approximation formula.

17. The heat of dissociation of $CaCO_3$ is 42.52 kcal. Calculate the equilibrium partial pressure at 300° K.

18. The heat absorbed in the reduction of zinc oxide by carbon to give CO is 89.6 kcal.; that for K_2CO_3 giving CO and potassium is 235 kcal. Show by the Nernst approximation formula why the two reductions occur at about the same temperature.

19. The ratios of the pressures of water vapor in equilibrium with $BaCl_2 \cdot 2H_2O$ and pure water are 0.1905 at 18.5° C. and 0.3204 at 43.5° C. Calculate the heat of hydration of barium chloride per mole of crystal formed.

CHAPTER 11

PHASE EQUILIBRIA

In addition to the chemical equilibria in homogeneous and heterogeneous systems already discussed, equilibria are possible in each state of aggregation in the system as well as between two or more such states. Many of these equilibria involve processes of physical change as, for example, that between a vapor and a solid or liquid. All such equilibria can be studied with the aid of two fundamental principles known as the Distribution Law and the Phase Rule. It will be seen that these are sufficient for systematizing many of the equilibrium phenomena involved when temperature, pressure and concentration are the determining factors.

THE DISTRIBUTION LAW

Consider a heterogeneous system consisting of two parts A and B, each homogeneous throughout, termed the phases of the system. If a third substance X, which is soluble in each phase, is added to the system, it will distribute itself between the two phases in a particular manner to yield a heterogeneous equilibrium. Thermodynamically, the criterion of the existence of this equilibrium will be the identity of the free energies of X, in the two phases. Hence, if to the system, A, B and X already in equilibrium, a very small amount of X be added the change in the free energy of X in phase A brought about by the slight change in the amount of X present in phase A will exactly balance the corresponding free energy change in phase B. The free energy change has been shown to depend, in the general case, on the activity of the substance by the relation: $dF = RT\,d\ln a$ or, for an ideal solution, on its concentration: $dF = RT\,d\ln c$. The distribution of X will be such as to yield

$$dF_A = dF_B, \tag{11.1}$$

where the subscripts refer to the phase in which the free energy change of X is measured. It follows therefore, by substitution, that:

$$RT\,d\ln a_A = RT\,d\ln a_B \tag{11.2}$$

whence

$$d\ln a_A = d\ln a_B \tag{11.3}$$

which upon integration gives

$$\ln a_A + k_1 = \ln a_B + k_2, \tag{11.4}$$

where k_1 and k_2 are the integration constants.

This equation may be written

$$a_A/a_B = constant \qquad (11.5)$$

which states that the distribution of a substance between two phases will be such that its activity in one phase is proportional to its activity in the other.

This is a generalized form of the distribution law applicable to any pair of phases of a heterogeneous system, regardless of the states of aggregation of the phases. Since, for ideal solutions or for very dilute solutions of non-ideal constituents, the activity is identical with the concentration, the law is frequently stated in terms of concentration thus:

$$C_A/C_B = constant. \qquad (11.6)$$

The applicability of the law to specific systems has been known for a long time. Thus, Henry's law, already discussed, is the particular form of the general statement in its application to the solubility of a gas in a liquid. Nernst[1] was the first to generalize the treatment of distribution, pointing out, however, that a constant distribution ratio is to be expected only when the concentrations of the same molecular species in each phase are considered. When due allowance is not made for the possibly different molecular conditions of the distributed substance in the two phases, apparent deviations from the distribution law will be found.

1. **Apparent Deviations. Solvation:** If the distributed substance X combines with one phase, forming solvates, and is normal in the other phase, the molecular condition of X in the two phases is not identical. However, a constant concentration ratio will still be found. Thus if C_A and C_B are the concentrations of distributed molecules in phases A and B and C_S is the concentration of solvent molecules S in phase A while C_C is the concentration of solvate molecules formed in phase A, the distribution law would give

$$C_A/C_B = K_1. \qquad (11.7)$$

The law of mass action applied to the homogeneous solvate equilibrium in phase A, namely

$$X + nS = X \cdot S_n$$

would give

$$C_C/C_A(C_S)^n = K_2. \qquad (11.8)$$

For dilute solution, C_S is large and is not altered appreciably by the solvation. It may therefore be considered a constant, and incorporated in K_2, giving

$$C_C/C_A = K_2'. \qquad (11.9)$$

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[1] *Z. physik. Chem.*, **8**, 110 (1891).

Combining the K_1 and K_2' equations yields

$$(C_A + C_C)/C_B = K_1(K_2' + 1) = K. \tag{11.10}$$

Now $(C_A + C_C)$ is the total concentration of the distributed substance in phase A. Hence the ratio of the total concentrations in phases A and B is constant. The numerical value K is not the same as would be obtained from a consideration of the same molecular species of X in the two phases, namely K_1, but the constancy is unaffected by the solvation.

2. **Association:** Reference to Fig. 11.1 will indicate the proper method of reasoning. Let X represent the molecular species common to both phases, and let it be associated in one phase to form double molecules, indicated as $(X)_2$. Analysis of the phase marked I gives us the concentration of X in that phase, represented by C; but analysis of phase II gives, not the concentration of X, which is necessary for testing the distribution law, but a concentration C_1 made up from both associated and non-associated molecules. The necessary term may be derived however by the application of the mass law to the equilibrium occurring in phase II. If α' represents the fraction that has undergone association then $(1 - \alpha')C_1$ is the concentration of simple molecules and $C_1(\alpha'/2)$ is the concentration of complex molecules. The law of mass action gives for the association constant

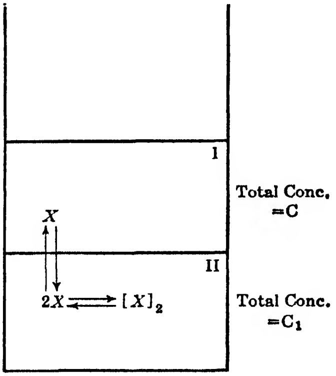

Fig. 11.1. Distribution Diagram for an Associated Compound

$$\frac{\alpha' C_1}{2(1 - \alpha')^2 C_1^2} = K, \tag{11.11}$$

whence the concentration of simple molecules is

$$(1 - \alpha')C_1 = \sqrt{\alpha' C_1/2K} \tag{11.12}$$

and the distribution ratio

$$k = \frac{C}{(1 - \alpha')C_1} = \frac{C}{\sqrt{\alpha' C_1/2K}}, \tag{11.13}$$

whence

$$C/\sqrt{\alpha' C_1} = k'. \tag{11.14}$$

It will be seen that if the association were into molecules three times the weight of the simplest molecule, the radical would become a cube root, and, in more general terms, for association into a molecule $(X)_n$ the denominator would become an *n*th root.

3. **Dissociation:** In like manner, if the distributed substance X undergoes a dissociation in one phase:

$$X = Y + Z$$

and α is the degree of dissociation, the concentration of the undissociated X will be $C_1(1 - \alpha)$ when C_1 is its total concentration in that phase. The distribution ratio would thus become:

$$C/C_1(1 - \alpha) = K. \tag{11.15}$$

Considering therefore only the simpler cases of dissociation of a binary compound and association into double molecules, the following general formulas have been developed:

$$\left.\begin{array}{l}\text{Phase I, neither association nor dissociation,}\\ \text{Phase II, neither association nor dissociation,}\end{array}\right\}\frac{C}{C_1} = K;$$

$$\left.\begin{array}{l}\text{Phase I, dissociation occurring,}\\ \text{Phase II, no molecular change occurring,}\end{array}\right\}\frac{C(1 - \alpha)}{C_1} = K;$$

$$\left.\begin{array}{l}\text{Phase I, no molecular change occurring,}\\ \text{Phase II, association occurring,}\end{array}\right\}\frac{C}{\sqrt{C_1\alpha'}} = K;$$

$$\left.\begin{array}{l}\text{Phase I, dissociation occurring,}\\ \text{Phase II, association occurring,}\end{array}\right\}\frac{C(1 - \alpha)}{\sqrt{C_1\alpha'}} = K.$$

In these general formulas, C and C_1 represent the concentrations as analytically determined, α and α' the degrees of dissociation and association as determined by independent methods; and the further assumptions are included that the degree of dissociation follows the mass law and that the distributed species is the simple molecule.

In several of the cases to be discussed, an algebraic simplification is possible for cases where association occurs. In benzene and similar hydrocarbons it happens that association is frequently complete or nearly so; the value of α' therefore becomes almost one, so that the ratio becomes

$$C/\sqrt{C_1} = K, \tag{11.16}$$

thus rendering unnecessary any quantitative knowledge of the association equilibrium.

A study by Hendrixson[1] of the distribution of benzoic acid between water and benzene illustrates the applicability of the distribution law in a complex case and shows its utility in the determination of equilibrium constants. For this discussion let

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[1] *Z. anorg. Chem.*, **13**, 73 (1897).

C_W = the total concentration in the aqueous phase,
C_B = the total concentration in the benzene phase,
α = the degree of electrolytic dissociation in water,
α' = the degree of association in benzene,
k = the distribution ratio of simple molecules,
K_D = the electrolytic dissociation constant in water,
K_A = the association constant in benzene.

It follows from the above that:

$$K_D = \frac{C_W\alpha^2}{1-\alpha} \tag{11.17}$$

and

$$k = \frac{C_W(1-\alpha)}{C_B(1-\alpha')}, \tag{11.18}$$

whence

$$C_B(1-\alpha') = C_W(1-\alpha)/k \tag{11.19}$$

or

$$\alpha' C_B = C_B - C_W(1-\alpha)/k. \tag{11.20}$$

Hence

$$K_A = \frac{\alpha' C_B}{2(1-\alpha')^2 C_B^2} = \frac{C_B - C_W(1-\alpha)/k}{2[C_W(1-\alpha)/k]^2}\,. \tag{11.21}$$

Assuming that K_D is known and that K_A is constant, values of C_W and C_B from two experiments (lines 1 and 7) of Table 11.1 are inserted in the equation and the value of the distribution ratio k is found to be 0.71. With this known, the values of K_A may be calculated at each concentration. K_D has been taken as 6×10^{-5}.

TABLE 11.1

DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE AT 10°. $k = 0.71$

C_W mole/liter	C_B mole/liter	α	K_A
1.758×10^{-3}	5.94×10^{-3}	0.169	458
2.304	9.76	0.149	459
3.372	19.37	0.125	440
4.608	36.24	0.104	450
7.299	89.28	0.0866	452
9.964	166.2	0.0747	454
11.54	224.8	0.0695	459

4. **Real Deviations:** In the foregoing discussion the assumption has been made that the solutions of the distributed species in each phase are

ideal. If this is not so, the concentration ratio must be replaced by the activity ratio. A particular case of the necessity for this latter treatment occurs where the distribution of an electrolyte is being considered under such conditions that electrolytic dissociation takes place. The detailed consideration will be taken up in a later chapter.

The restriction to ideal solutions is not alone sufficient. The condition for an ideal solution of the distributed species X in a phase A is that similar intermolecular forces exist between two molecules of X, two molecules of A and between a molecule of X and a molecule of A, thus giving a constant environment to the solute molecules. If X is also ideal in phase B then the forces between molecules of A must be the same as those between molecules of B, that is, A and B would form an ideal solution. They could not therefore exist as two separate phases. The restriction therefore must be to very dilute solutions of X in the two phases where the constant environment is that of the solvent molecules alone in each phase.

A further complication lies in the mutual solubility of the two phases between which the distribution takes place. In general, the two phases will not be completely mutually insoluble and hence the distribution will not be between two pure substances A and B but rather between two solutions, one of B in A and the other of A in B. The presence of the distributed substance may markedly alter this mutual solubility and to an extent dependent upon its own concentation. The experimental determination of the distribution ratio for varying total amounts of the distributed substance present will involve consideration therefore of the changing solvents. No quantitative method is available for this in the general case, so that determinations are to be restricted to dilute systems when the change in the mutual solubility of the phases is negligible.

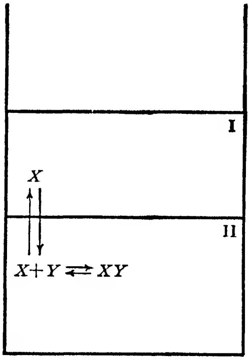

FIG. 11.2. Distribution Diagram for a Compound Undergoing Combination.

5. Study of Other Equilibria by Means of Distribution Experiments: It will be readily seen that distribution experiments are applicable to a variety of other chemical equilibria as well as to association or dissociation. If X in Fig. 11.2 represent a substance whose distribution coefficient between two phases can be determined, and if it is capable of entering into a reversible reaction with a second substance Y in one of the phases, the constants of this second equilibrium can be easily evaluated from a series of distribution experiments; analysis of the upper phase for its content of X will give the concentration of uncombined X in the lower phase from the distribution ratio previously determined, and analysis of the lower phase for X will give its total concentration as X and XY, from which the concentration of XY follows. Since the total concentration of Y is the amount taken, and its proportion in XY follows from knowledge of the composition of that compound, the concentration of uncombined Y is likewise known, and with X, Y and XY known in the lower phase the constants of the equilibrium can be immediately calculated.

In accordance with this principle, Kuriloff studied the equilibrium

$$\text{naphthol} + \text{picric acid} \rightleftarrows \text{naphtholpicrate}$$

in benzene solution. Roloff studied the action of bromine on potassium bromide in forming the polybromide KBr_3, and Jakowkin studied the formation of similar polyiodides and the interesting case of the hydrolysis of chlorine:

$$Cl_2 + HOH \rightleftarrows HCl + HClO.$$

Dawson, by studying the distribution of ammonia between chloroform and aqueous solutions of copper sulfate, was able to show the existence of the compound $CuSO_4.4NH_3$ in the aqueous phase together with certain dissociation products. Farmer has, in like manner, determined the hydrolysis of the barium salt of hydroxyazobenzene by distribution experiments between benzene and water. The method is one of very wide applicability, though it is unquestionably true that in many instances the conclusions are complicated by the fact that there are several equilibria occurring in each phase.

6. **The Process of Extraction:** Probably the commonest use to which the distribution principle is put in ordinary laboratory practice is the process of extraction. Organic compounds in particular are easily removed from inorganic materials by extracting the aqueous solution with ether or similar organic solvent; the distribution ratio of most organic bodies is largely in favor of the ether phase, whereas that of inorganic bodies is almost wholly in favor of the aqueous phase, so that repeated extraction with ether will give a nearly perfect separation in the majority of instances. It is frequently possible to increase the ratio in the desired direction by addition of another compound which depresses the dissociation of the substance being extracted; an organic acid of moderate strength, for example, can be most advantageously extracted from water after addition of a strong inorganic acid, which by its excess of hydrogen ion will convert the organic acid chiefly into undissociated molecules, which are soluble in the ethereal phase whereas the ions are not. An organic base, by the same reasoning, is most easily extracted in the presence of a strong inorganic base. The addition of neutral bodies such as salts will also in many cases lower the solubility of the organic

compound in water (the so-called salting-out effect) and thus favor the extraction by the ether.

In the majority of extraction processes there has been no extended study of distribution constants, degree of association, dissociation or combination, but the most appropriate extracting agent has been found by the method of trial. There is, however, in all cases, a general principle of great value which can be applied in determining the best method of extraction with a given quantity of extracting liquid, for it can be shown that extraction by means of several fractions of the liquid is more complete than if the whole liquid be used in a single extraction.

If the distribution ratio is known for the materials contained in a given extraction, it is possible to derive a generalized formula which will show the amount still unextracted after a given number of operations. Let W cc. of a solution containing x_0 g. of a substance be repeatedly extracted with L cc. of a given solvent. After the first extraction, let x_1 represent the number of grams remaining unextracted. The concentration in the extracting phase will then be $(x_0 - x_1)/L$ and in the original solution x_1/W. The distribution ratio K will then be, by definition,

$$\frac{x_1}{W} \div \frac{x_0 - x_1}{L} = K, \tag{11.22}$$

whence

$$x_1 = KW \times \frac{x_0 - x_1}{L} = x_0 \frac{KW}{KW + L} \cdot \tag{11.23}$$

After a second extraction x_2 g. remain in the original solution; the equation takes then the corresponding form

$$x_2 = x_1 \frac{KW}{KW + L} \cdot \tag{11.24}$$

If now the former value for x_1 be substituted in the equation,

$$x_2 = x_0 \frac{KW}{KW + L} \cdot \frac{KW}{KW + L} = x_0 \left[\frac{KW}{KW + L}\right]^2 \cdot \tag{11.25}$$

Putting the equation now in a generalized form, after the nth extraction, the residual quantity x_n is as follows:

$$x_n = x_0 \left[\frac{KW}{KW + L}\right]^n \cdot \tag{11.26}$$

Inspection of this generalized formula shows that for the residue x_n to be very small, the distribution constant K should also be small (i.e., the distribution ratio toward the phase being extracted should be small), and the number of extractions, n, should be large.

THE PHASE RULE

The most useful generalization relating to the physical and chemical reactions which occur in heterogeneous systems is the phase rule of Willard Gibbs.[1] Its fundamental value was not at once recognized. It is owing to the subsequent adoption of the phase rule by Roozeboom, Ostwald and van't Hoff that it has become generally known to chemists and physicists as a principle of the widest applicability, of the highest value in the classification of heterogeneous equilibria and of the greatest reliability in the settlement of disputed points. It has the advantage over others of our commonly accepted generalizations in that it contains no assumptions based upon theory, such as the molecular hypothesis, the kinetic theory, theories of constitution of matter or of chemical reaction, and is therefore not subject to revision or rejection as our views of these matters may change.

7. **The Phase Rule:** The phase rule of Gibbs is stated in terms of the number of phases present in a system at equilibrium, the number of components from which the system can be built up, and the number of conditions (pressure, composition or temperature) which may be varied without causing a change in the number of phases. The phase rule may be very simply expressed by the equation

$$F = C - P + 2, \tag{11.27}$$

in which C stands for the number of components of the system, P the number of phases present, and F the degree of freedom, or the variance, of the system.

8. **Equilibrium:** An equilibrium exists in any system under a fixed set of conditions when the parts of the system do not undergo any change of properties with the passage of time, provided that the parts of the system have these same properties when the same conditions are again arrived at by a different procedure. It is this provision which makes possible the distinction between stable equilibrium and metastable equilibrium; in both cases the system may be capable of maintaining itself perhaps indefinitely without change, but in the case of metastable equilibrium an alteration in the method of producing the system will give us an entirely new set of properties. Supercooled water at $-1°$ C. is in metastable equilibrium. Ice at $-1°$ C. is in stable equilibrium. The distinction lies in the fact that this second system may be produced by cooling water or by heating ice from lower temperatures, while the first can never be produced by warming ice.

The phase rule applies to systems in true equilibrium and only when they are in true equilibrium. The numbers and classes of phases de-

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[1] Gibbs, *Transactions Connecticut Acad.*, 1874–1878; also in Gibbs's Collected Scientific Papers, Longmans, Green and Co., 1906.

termined by the rule are not necessarily true for systems not in equilibrium. It is possible to have ice, water and water vapor in a tumbler many degrees above 0° C., and the experience does not contradict the phase rule; it indicates only that we frequently drink the liquid before equilibrium has been attained. Nor does the phase rule give any indication of the speed with which equilibrium is attained; it is limited to the statement of the existing conditions when equilibrium has been attained.

9. **Phases:** *A phase is any part of a system which is homogeneous throughout, is bounded by a surface and is mechanically separable from the other parts of the system.* Such a phase is necessarily in one of the three physical states of aggregation, gaseous, liquid or solid. Since all gases are found to be mutually soluble, it follows that there can be only a single gaseous phase in any system under consideration; with liquids complete solubility is by no means always the case, and there may therefore be several liquid phases present in certain systems; the same is true for solids. However many liquids or solids may have been formed under varying conditions from the components of a given system, in no case has the number of liquid phases coexisting at equilibrium been found greater than the number of the components in the system, and the number of coexistent solid phases at equilibrium cannot exceed the number of components by more than two, as will be shown later. A phase may be of fixed or variable composition, continuous as in a gaseous phase or discontinuous as is general in a solid phase. Gibbs, in introducing the term phase, states that it refers "solely to the composition and thermodynamic state of any body without regard to its quantity or form."

10. **Components:** The concept of the components is frequently less easily grasped than the other necessary concepts. This is, perhaps, because of a double use to which we put the term. It is necessary to derive, in the first place, the *number of components,* in order to have a numerical value to substitute for the term C in the phase-rule equation; it is also necessary to name the *individual components* in terms of which the composition of the various phases is to be expressed. The number of components must have a perfectly definite value, derivable in a systematic manner, and subject to no arbitrary desire on the part of the investigator. The individual components on the other hand, while limited in number as stated, may be chosen at will within certain limits, as will be shown.

The *number of components* of a system at equilibrium is defined as *the smallest number of independently variable constituents by means of which the composition of each phase may be mathematically expressed.* In accordance with this definition it is possible, though it is not the usual practice, to determine this number without any reference to what the individual components may be. This may be done, for example, by determining the value of C in the equation when the other variables

(F and P) are known. It is also possible to arrive at the number empirically, from analysis of all the phases present; if they are all of the same composition (under varying conditions), the system is of one component, if the phases present can be produced from any two phases, the system is of two components, while if more phases are necessary to express the composition of any one, the number of components is represented by that number of phases. More commonly, however, the number of components is deduced from knowledge as to the physical or chemical changes which the system undergoes. Thus, if the decomposition of calcium carbonate by heat is being studied, it is known that the phases present consist of a gaseous phase composed chiefly of CO_2 with whatever traces of $CaCO_3$ and CaO are capable of volatilization, and two solid phases, CaO and $CaCO_3$. It is clear that from two components, most simply CO_2 and CaO, the composition of each of these three phases may be expressed in the usual terms of percentage by weight, or in terms of other units; a smaller number (one) is incapable of doing this. In expressing the composition of the solid CaO, the amount of CO_2 is zero; neither zero values nor negative values however are excluded by the definition given. If we now consider what *individual components* shall be chosen in discussing this system, it would be wisest to choose CO_2 and CaO, since minus quantities will then not enter into any statement of composition and graphical representation will be most simple. It happens that, in this instance, each phase is of invariant composition, but in some two component systems the composition of some phase, namely, a solution, may vary from 0 per cent of component A and 100 per cent of component B to 100 per cent of A and 0 per cent of B.

The number of components of a system may differ also with the conditions under which its equilibria are being studied. Thus, water is regarded as a one-component system because, under the ordinary conditions of experimentation, the three phases found (ice, liquid and vapor) may all be expressed as composed of water alone; but, if temperatures are raised until the dissociation of water has begun, according to the equilibrium

$$2H_2O \rightleftarrows 2H_2 + O_2,$$

it would no longer be possible to express all possible compositions in terms of water; for, if excess hydrogen or oxygen be introduced, the composition of the vapor phase can be expressed only in terms of two components, hydrogen and oxygen, whose concentrations can be independently varied. *The number of components then, while always definite, may vary with the condition of the system,* and is arrived at in accordance with the definition given; the *individual components may be chosen according to convenience from among the substances taking part in the equilibrium.*

It is upon the basis of the number of components that systems are classified for phase-rule study as one-component systems, two-component systems, etc.

11. **Degree of Freedom (Variance of a System):** In the application of the phase rule, the independently variable conditions which are taken into consideration are three in number—*temperature, pressure,* and *composition.* This restriction of the types of independent variables to three is of course arbitrary; usually, the effects of gravitation, of electrical condition, of surface energy and of light absorption are purposely excluded. It is necessarily true that these variables may have an effect upon the equilibrium existing between various phases, but in large numbers of cases their effect is negligibly small; in the cases where their effect is large, the phase rule as here given affords but small help, as in the field of colloid chemistry, where surface energy is the most influential factor. If only these three variables are considered, it follows that when these three are known the system may be regarded as defined; that is, a complete statement of the properties of each phase is implied by the statement of the three variables. Thus, to state that a gaseous system contains 50 per cent each of carbon dioxide and nitrogen at 20° C. and 760 mm. pressure of mercury, defines the system in that any other sample of these gases made up according to the same conditions will be identical with the first in all properties except mass.

It is however not necessary in all cases to fix as many as three conditions in order to define the system under observation, and it is precisely the number of these variables which must be arbitrarily fixed in order completely to define the system, that is called the *degree of freedom* of that system. The mixture of gases mentioned above is obviously a system with three degrees of freedom, since a statement of a temperature, a pressure and a concentration was necessary; if the system to be defined is a saturated solution of sodium chloride with excess solid and vapor, we need mention only the desired temperature or pressure (one degree of freedom), while for a system of ice, water and vapor no further statement of condition is necessary. The specific application of this principle will appear in the examples to be studied; it will suffice for the present to state the customary nomenclature, which is to describe systems with no degree of freedom as *invariant,* those with one degree of freedom as *univariant,* those with two as *bivariant,* and so on for other multivariant systems. The possibility for a system to have a variance greater than three, where only temperature, pressure and composition are the variables, lies in the fact that, for multicomponent systems, knowledge of the concentration of more than one component is necessary in order to state the composition; thus, in a solution containing three components, the composition with respect to two must be stated before the composition of the solution is known.

12. Derivation of the Phase Rule: With the various terms of the phase rule discussed, a brief statement of its method of derivation may be made. The rigorous thermodynamic derivation which Gibbs made is abstract and difficult. The following is not given as a rigorous derivation, but is nevertheless useful in showing in a general way the method of derivation which Gibbs used.

It has previously been shown that the degree of freedom (F) of a system is the number of variables which must be arbitrarily fixed in order to define the system. It follows simply enough that the number of such variables must be equal to the total number of variables of the system minus the number of variables which are defined by the system itself; that is,

$$F = (\text{total variables of the system}) - (\text{defined variables}).$$

A numerical statement of these two terms in the equation, if it can be put in such fashion as to include only the number of phases and number of components, will give the phase rule equation.

The total number of variables can easily be calculated. They may be the variables of temperature, of pressure and of composition. There can be but one temperature and one pressure throughout a system at equilibrium, so that the temperature and pressure variables total two. The composition variables however may be numerous. In each phase the composition may vary, and within each phase the number of variations in composition is equal to the number of components less one, i.e., to $(C - 1)$, since for two components we may vary the percentage composition with respect to one of them and derive the second by difference, and for three components by similar reasoning we may vary two. The total number of composition variables in all the phases is therefore $P(C - 1)$, and the total number of variables of all kinds is greater by the two variables of temperature and pressure, so that the total number of variables to be set in the equation above is $P(C - 1) + 2$.

In order to calculate the second term, the number of variables defined by the system itself, Gibbs introduced the concept of the thermodynamic or chemical potential which each component possesses, and which is the intensity factor of the chemical energy of that component. In a system at equilibrium this chemical potential of each component must be the same in each phase, just as for thermal equilibrium the temperature, which is an intensity factor, must be the same in all parts. The potential of a given component in a given phase is a function of the temperature, the pressure and the composition of that phase and an equation exists relating the potential to those three variables.[1] One

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[1] It is worth noting that the actual *mass* of the phase plays no part in the equation, and hence has no influence upon the equilibrium. This is a fundamental

form of such an equation for a substance distributed between two phases is the general distribution law. A similar equation exists for this same component in each other phase, giving a number of equations equal to P; but since the potential is the same in each case, it follows mathematically there will be only $P - 1$ independent equations for that component. The fact that these equations may have a form and value unknown to us is of no importance; the essential is that there are $P - 1$ relationships which actually define the potential of that component in the system. Since what is true for one component is true for all, there are $C(P - 1)$ relationships existing in the system which define the chemical potential of all the components, and hence define the equilibrium.

It remains only to insert these two terms in the equation given above:

$$F = [P(C - 1) + 2] - [C(P - 1)] = C - P + 2. \quad (11.28)$$

SYSTEMS OF ONE COMPONENT

When a system consisting of a single component is considered, it follows, by substitution in the phase-rule equation, that it is bivariant if it exists in but one phase, univariant if it exists in two phases, and invariant if it exists in three. Since the number of phases cannot be less than one, the degree of freedom of such a system cannot exceed bivariance. The independent variables are limited to the pressure and the temperature, since all phases are alike in composition.[2] If it is assumed that such a system can have but one vapor phase, one liquid phase, and one solid phase, the following classification may be made, in which the symbols V, L, and S stand respectively for vapor phase, liquid phase and solid phase:

Bivariant	Univariant	Invariant
V	$L + V$	$S + L + V$
L	$S + V$	
S	$L + S$	

More than a single vapor phase cannot be present, since gases or vapors are always mutually soluble, and more than a single liquid phase is also unknown, though it is possible to regard liquid crystals as constituting a second liquid; of solid modifications (polymorphic forms) there may be a

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feature of heterogeneous equilibria. It was recognized before the statement of the phase rule, and finds expression for example in the well-known tenet that in mass-law equilibria the "active mass" of the solid is constant.

[2] This statement is true only in a restricted sense. The amount of material per unit volume, or density, of course varies from phase to phase, and the density (or specific volume) may therefore be regarded as a third independent variable. The familiar diagram of the pressure-volume relations of the gaseous and liquid state, showing the equality of volumes at the critical point, is the commonest example in which the volume is treated as an independent variable.

large number. If a second such solid form exists, the number of possible equilibria is increased by seven, since it can exist alone or in contact with each of the other three forms or in contact with each of the three combinations of two forms; the existence of a third solid form will of course increase the number of possible systems still more. It does not follow however that all of these systems which may be conceived as algebraical possibilities shall be capable of experimental realization; sometimes such equilibria can be shown to be necessarily false, and in many other cases the experimental requirements of temperature or pressure cannot be met.

13. **Water:** It is well known concerning this substance that the liquid has a vapor pressure which increases with the temperature (amounting to 760 mm. of mercury at 100°, which is its boiling point) until the temperature reaches 374° C., at which point it undergoes the critical phenomena; that, upon cooling, it freezes to form ice at 0° under atmospheric pressure, which solid also has a small but measurable vapor pressure; and, lastly, that this freezing point is lowered by increased pressure. The statement of these well-known facts implies the following phase equilibria: (1) liquid water and its vapor, in which the vapor pressure increases with the temperature, (2) ice and vapor, in which the vapor pressure and temperature bear a similar relationship, (3) solid and liquid, in which the melting point decreases with pressure increase, and (4) solid, liquid and vapor, existing together only at a fixed temperature of approximately 0° C. In these four equilibria, pressure and temperature are the only variables mentioned; in this system there can be no variations in composition, since each phase is wholly water under all conditions. The quantitative data for these relationships are given in the following table.

TABLE 11.2

EQUILIBRIUM PRESSURES FOR WATER

Temp. C.	Water ⇄ Vapor	Ice ⇄ Vapor	Ice ⇄ Water
	$L \rightleftarrows V$	$S \rightleftarrows V$	$S \rightleftarrows L$
− 20		0.770 mm. of Hg	1970 kg. per sq. cm.
− 15		1.237 " " "	1590 " " " "
− 10	2.144 mm. of Hg	1.947 " " "	1130 " " " "
− 5			610 " " " "
0	4.579 " " "	4.579 " " "	1 atmosphere
+ 20	17.539 " " "		
+100	760.00 " " "		
+200	15.3 atmospheres		
+300	84.6 "		
+374	217.5 "		

The same data are shown schematically in Fig. 11.3, in which the pressure is written as ordinate and the temperature as abscissa. Three curves result, representing the three univariant equilibria. The curve COt_c represents the equilibrium between liquid water and vapor, and is the so-called *vapor pressure curve for water*. For every temperature there exists one pressure, and only one, which can be exerted by the system, and for each pressure one temperature and only one at which equilibrium can be maintained, which is simply the more lengthy way of stating that the system consisting of liquid water and vapor is univariant, and that the selection of a temperature defines the pressure or the selection of a pressure defines the temperature. If, at a given temperature, a pressure is maintained above that indicated on the line Ot_c, the vapor will be compressed wholly into the liquid phase; or, if the pressure is maintained below the equilibrium pressure, the liquid will wholly evaporate. The upper end of the vapor pressure curve is the critical point t_c at a temperature of +374° C. and a critical pressure of 217.5 atmospheres.

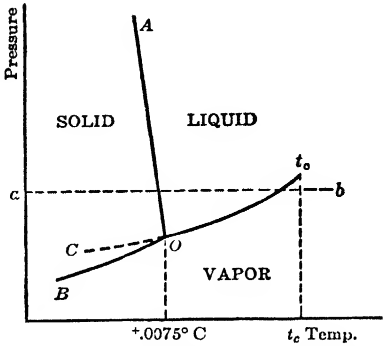

FIG. 11.3. *p-t* Diagram for Water (Schematic)

The point O represents the temperature at which water ordinarily freezes. With sufficient care however water may be cooled considerably below this temperature without the formation of ice, and from such experiments a prolongation OC of the vapor pressure curve has been drawn to represent the still perfectly definite relations of pressure to temperature. The extent of this prolongation is, however, indeterminate; the point C therefore represents no definite end to the curve. Throughout the whole course of the section OC the system water + vapor is metastable, in that it will, on contact with a nucleus of ice or sometimes without such contact, change into the system ice + vapor.

The curve OB in Fig. 11.3 represents the equilibrium curve for ice + vapor, and is spoken of as the *vapor pressure curve of ice* or sometimes as its *sublimation curve*. Its lower end B is assumed to be at the absolute zero of temperature. The experimental figures for this curve place the curve below that for water + vapor (OC) throughout its course, but its steeper curvature brings about an intersection of the two at a temperature very close to 0°. The positions of the two curves OB and OC may be used to explain the stability relationships of the two systems. If, at some constant temperature below that of the point *O*, ice is set in one vessel and water in a second under a bell-jar, the vapor pressure of the system water + vapor will be greater than that of the other, and as a result vapor passing from the liquid will solidify upon the ice until the liquid has entirely disappeared. In such a case it is obvious that the unstable system is the system with the higher vapor pressure.

The intersection of the two curves at the point *O* represents a new equilibrium. Ice and vapor are in equilibrium, water and vapor are in equilibrium, and the vapor is the same in pressure in both cases; it follows then that ice and water must also be in equilibrium, and the curve representing that equilibrium (*OA*) must pass through the point *O*, which is therefore the intersection of three curves. Roozeboom first suggested that such a point be called a "triple point." It represents an invariant condition, in which neither pressure nor temperature can be changed without the elimination of a phase. The temperature and pressure corresponding to this triple point have been carefully determined; the pressure is 4.579 mm. of mercury and the temperature +0.0075°. This temperature differs from the normally assumed value of the freezing point, 0° C. It is the freezing point of the system under its own vapor pressure of 4.579 mm. of mercury, whereas the value of 0° C. is the freezing point under an external pressure of one atmosphere. As is seen in the next paragraph, increased external pressure lowers the freezing point. At this temperature and pressure, and only here, can a system consisting of water be maintained in the three coexisting states of ice, liquid and vapor.

The triple point *O* has been shown to be the origin of the curve *OA*, representing the equilibrium between ice and liquid in the absence of vapor. It has long been known that the melting point of ice, that is, the equilibrium temperature, is altered by pressure. Whether an increase of pressure will raise or lower the melting point may be easily deduced from Le Chatelier's theorem; since, in the case of water, the liquid has a smaller volume than the solid (i.e., is denser), increased pressure at constant temperature results in liquefying ice. The curve *OA* is therefore inclined upward toward the pressure axis, so that at any temperature represented upon it an increased pressure (measured upward) brings the system into the region of liquid alone; or, otherwise stated, the freezing point is lowered by increased pressure.

It has been found that at high pressures there exist several polymorphic forms of ice, differing from the common variety in density, heat of formation, crystalline structure and other physical properties. Tammann was the first to discover that, at sufficiently high pressures, new modifications of ice appear, and his work together with that of Bridgman[1]

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[1] *Z. anorg. Chem.*, **77**, 377 (1912); *Proc. Nat. Acad. Sci.*, **47**, 441 (1912); *Z. physik. Chem.*, **86**, 513 (1914); *J. Chem. Phys.*, **5**, 964 (1937).

gives a fairly complete picture of the phase relations which exist. There are at least six polymorphic forms of ice, known as ice I (the common form), ice II, ice III, ice V, ice VI, and ice VII the positions of which in the *p-t* diagram are shown in Fig. 11.4. The relationships of ice IV are not clearly known, and it is not included in the sketch. Each of the six forms has definite limitations of pressure and temperature within

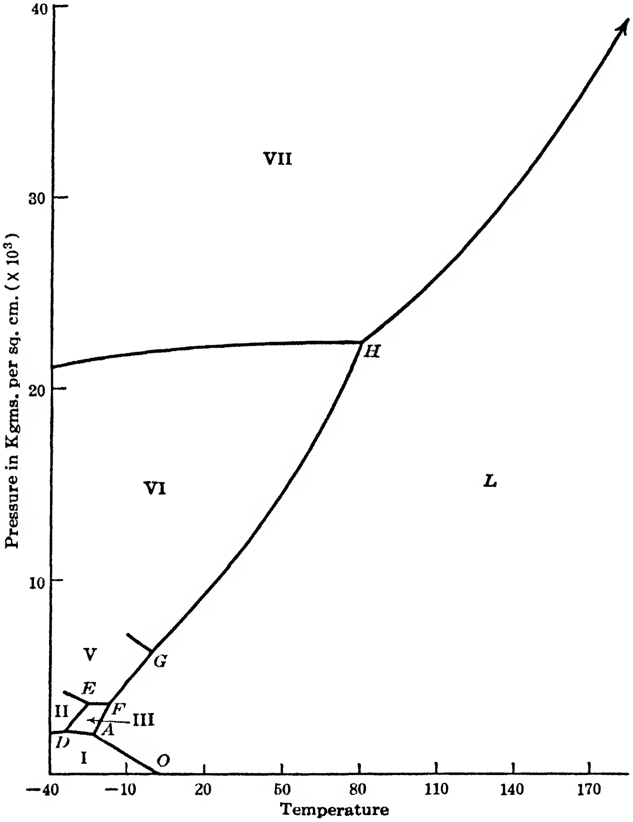

Fig. 11.4. *p-t* Diagram for Water at High Pressures

which it can exist as a stable form, at the boundaries of which it can exist in stable equilibrium with other forms and outside of which it can have only metastable existence. These boundary curves represent univariant equilibria, in the same sense as the curves studied in Fig. 11.3. Wherever three such boundary curves meet there exists a triple point, at which three phases coexist at the invariant temperature and pressure indicated. These triple points are of course all at pressures at which the vapor phase cannot exist, and consist of various combinations of two solid phases with the liquid and of three solids with each other. The entire list of such invariant equilibria is given in Table 11.3 in the order of increasing pressures, including the triple point for ice, water and vapor previously discussed.

TABLE 11.3

TRIPLE POINTS IN THE ONE-COMPONENT SYSTEM: WATER

Position in Fig. 11.4	System	Type	Temperature	Pressure in Kgm. per Sq. Cm.
O........	Ice I—liquid—vapor	S_1—L—V	+ 0.0075°	(4.579 mm.)
A........	Ice I—ice III—liquid	S_1—S_2—L	−22.0°	2115
D........	Ice I—ice II—ice III	S_1—S_2—S_3	−34.7°	2170
E........	Ice II—ice III—ice V	S_2—S_3—S_5	−24.3°	3510
F........	Ice III—ice V—liquid	S_3—S_5—L	−17.0°	3530
G........	Ice V—ice VI—liquid	S_5—S_6—L	+ 0.16°	6380
H........	Ice VI—ice VII—liquid	S_6—S_7—L	81.6	22400

14. **Sulfur:** Sulfur occurs in two crystalline modifications, rhombic sulfur and monoclinic sulfur; these have a transition temperature (96°) at which they are in equilibrium with each other. Each possesses a melting point, that of the rhombic being approximately 114° and that of the monoclinic about 120°. The liquid form of sulfur undergoes some rather remarkable changes in color and viscosity when heated, and boils at 444.7° C. On rapid cooling of very hot molten sulfur a brownish gum is obtained, called plastic sulfur, which slowly changes into a hard brittle substance, while if sulfur only slightly above its melting point is quickly cooled, the yellow substance is at once formed; these two quickly cooled products differ considerably in their solubility in carbon disulfide, the latter being much the more soluble; they contain varying amounts of a quasi-solid called amorphous sulfur.

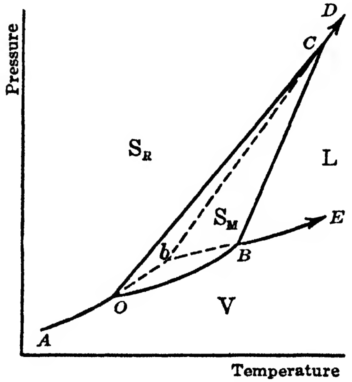

FIG. 11.5. *p-t* Diagram of Sulfur (Schematic)

These relationships are shown qualitatively in Fig. 11.5. The right-hand part of the diagram (curves *OB*, *BE* and *BC*) will be recognized as nearly duplicating the diagram for water; *OB* is the sublimation curve for monoclinic sulfur (univariant equilibrium $S_M \rightleftarrows V$), *BE* is the vapor pressure curve for liquid sulfur (univariant equilibrium $L \rightleftarrows V$), and their intersection at *B* is the triple point for the invariant equilibrium $S_M - L - V$, the temperature being 120°. *BC* is the fusion curve for monoclinic sulfur; since the solid form is denser than the liquid, as is the case in the majority of instances, the curve slopes upward away from the pressure axis. At *C* there is a second triple point, at which rhombic sulfur, monoclinic sulfur and liquid are in equilibrium; the temperature is 151° and the pressure 1320 kgm. per sq. cm.; the curve *CD* is the fusion curve for rhombic sulfur. For relationships not met with in the study of water we look to the left of the diagram, where we find the curve *AO* indicating the vapor pressure of rhombic sulfur. The point *O* is the transition temperature of the two solid forms, 96°, and is a triple point at which the two solids and vapor are in invariant equilibrium; it is also the point of intersection of the curve *OC*, which is the transition curve of the two solids. Since the two solids alone make up a univariant system, it follows that the transition temperature must vary with the pressure. Arguing backward from the diagram to the facts, it may be deduced from the slope of *OC*, by Le Chatelier's theorem, that rhombic sulfur is more dense than monoclinic; the densities are 2.04 and 1.93. The greater slope of the curve *OC* brings about its intersection with *BC* at the triple point *C* already mentioned. This series of curves, if drawn to accord with the experimental data, makes a division of the entire pressure-temperature diagram into four areas, one each for the vapor, liquid sulfur, rhombic sulfur and monoclinic sulfur; the area for the stable existence of monoclinic sulfur, *OBC*, is completely enclosed by the other three.

In addition to the stable equilibria discussed above, there are several metastable equilibria indicated by the dotted lines of Fig. 11.5. With the metastable vapor-pressure curve of the liquid, *Bb*, we are already familiar from our study of water. In the metastable curve *Ob*, the prolongation of *AO*, is represented the possibility of heating a solid above its transition point into a second solid; this phenomenon is common, and is due to the slow rate of the molecular rearrangements necessary for a change in crystalline form. The intersection *b* will be recognized as the metastable melting point of rhombic sulfur, at 114°. From this melting point, which is of course a triple point, the metastable fusion curve (*bC*) of rhombic sulfur into liquid runs upward to *C*, above which it is continued as the stable fusion curve *CD* mentioned earlier.

There are four bivariant equilibria, represented in the diagram by areas within which a single phase can exist and within which *both* the temperature and the pressure may be varied; there are six univariant equilibria, represented by lines, indicating two coexisting phases, which may have *either* temperature or pressure varied at will, but not both; and finally there are four invariant equilibria (one being metastable), represented by the points of intersection and indicating that the three coexisting phases can have neither temperature nor pressure altered. The list of univariant and invariant equilibria follows:

TABLE 11.4

EQUILIBRIA OF SULFUR

Univariant Equilibria		Invariant Equilibria			
Line	Phases Present	Point	Phases	Temp.	Pressure
AO (*Ob*)	S_R—V	*O*	S_R—S_M—V	96°	
OB	S_M—V	*B*	S_M—L—V	120°	
EB (*Bb*)	L—V	*C*	S_R—S_M—L	151°	1320 kgm.
BC	S_M—L	*b* (metastable)	S_R—L—V	114°	
OC	S_R—S_M				
DC (*Cb*)	S_R—L				

Alexander Smith and his coworkers established that, in the liquid state, as also in the vapor state, sulfur consists of two forms in dynamic equilibrium; to these Smith gave the names sulfur lambda (S_λ) and sulfur mu (S_μ). Sulfur λ has a molecular formula S_8 and is the principal constituent immediately above the melting point. It is practically insoluble, as a solid, in carbon disulfide at −80° C. which permits its separation from a less complex form of sulfur, S_π, which has the formula S_4, is present in small amounts in liquid sulfur, and is readily soluble in carbon disulfide at −80° C. With rise of temperature above the melting point there is, at about 170° C., a marked rise in the quantity of S_μ in the liquid. This is an amorphous sulfur and is insoluble in carbon disulfide at room temperature where both S_λ and S_π are freely soluble. The quantities of these three forms present at various temperatures are shown in Table 11.5. The increase in viscosity of liquid sulfur above

TABLE 11.5

CONSTITUENTS OF LIQUID SULFUR

Temperature	S_μ	S_π	S_λ
120	0.1	3.6	96.3
140	1.3	5.0	93.7
170	13.3	5.8	80.9
200	28.6	6.3	65.1
220	32.2	5.3	62.7
445	36.9	4.0	59.1

170° with a maximum around 200° has been ascribed to the presence of colloidally dispersed S_π in the liquid as solvent. S_λ is known to consist of 8-membered puckered rings of sulfur atoms lying in two planes. The conversion to the high temperature liquid is assumed to involve rupture of these rings and formation of long chain aggregates.

15. **Liquid Crystals:** We have already pointed out (Chap. 7) that a large number of substances exhibit the phenomenon of two transitions, first to liquid crystals and, at a higher temperature, to a liquid of entirely normal character.

Viewing the liquid crystals as an independent type of phase, they may be fitted into the phase-rule diagram as shown in Fig. 11.6. The point *O* represents the triple point for solid, liquid crystals and vapor, and is called simply a transition point without any new specific name; the point *B* is the triple point liquid crystal, liquid, vapor, and is named the melting point, being entirely analogous to the melting point as usually defined.

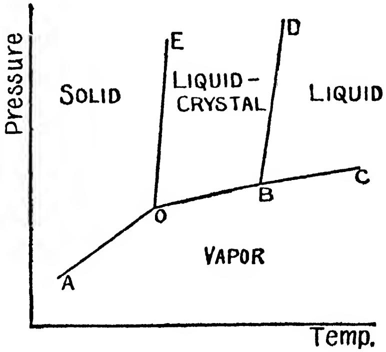

Fig. 11.6. One Component System including Liquid-Crystal Phase

SYSTEMS OF TWO COMPONENTS

In passing to the study of systems of two components, it will be well to consider certain general facts as to the components, independent variables, and phases. A system belongs to this class if it is possible to express the composition of all the phases in terms of two substances, and not less than two. The haphazard choice, however, of any two pure substances may not be depended upon to give merely a two-component system, but may also give rise to three-component systems, depending upon the nature of the substances taken. If the two substances employed give rise to no phases except such as are intermediate in composition between the two substances taken, the system will conform to the requirements for a two-component system; thus, the formation of solutions, which are always intermediate in composition between their components, introduces no new complication, nor does the formation of any *additive* compound from the two substances. Sodium sulfate and water, for example, may form, in addition to phases composed of the simple constituents, a solution of the two and may also form several hydrates, such as $Na_2SO_4 \cdot 10H_2O$; the system is of two components, by application of the rule. If, on the other hand, the two substances form compounds other than those of an additive nature, the system cannot be regarded as of two components; e.g., bismuth nitrate and water form by hydrolysis phases consisting of basic nitrates, such as $2Bi_2O_3 . N_2O_5 . H_2O$, whose composition cannot be expressed in terms of bismuth nitrate and water nor of any other two substances derivable from them; the system is, therefore, of three components.

The independent variables in two-component systems are three in number; in addition to the pressure and temperature, the composition of phases may also vary independently, through the formation of solutions. In order to make a complete representation of these three variables graphically, it is necessary to use diagrams in three dimensions, leading to surfaces and volumes in addition to the points, lines and areas occurring in two-dimensional representation. However, it is possible to study many of the relationships satisfactorily in two-dimensional graphs by choosing two of the three variables for representation, where the third is assumed constant or ignored because of its quantitatively small effect upon the equilibria. We shall therefore represent the conditions in this section by use of the three possible two-variable combinations, giving what are spoken of as *p-t* diagrams, *p-c* diagrams and *t-c* diagrams, where *p*, *t* and *c* stand respectively for pressure, temperature and composition.

By application of the phase-rule equation, it follows that for two-component systems, four coexisting phases give rise to invariant equilibrium, three coexisting phases to univariant equilibrium, two coexisting phases to bivariant equilibrium, and one phase to trivariant equilibrium. Trivariance is here possible, since variations in composition may occur in addition to variation in pressure and temperature. Of gaseous phases there can never be more than one present; of liquid phases, two is the maximum number thus far observed in coexistence; and of solids, there may coexist any number possible under the statement of the phase rule, consisting of pure components in their various polymorphic forms, of additive compounds, or of solid solutions.

THE EQUILIBRIUM: VAPOR-BINARY LIQUID

The equilibrium between a vapor and a two-component liquid, known as a binary solution, has a variance of two. At constant temperature, therefore, the vapor pressure depends on the composition. This dependence has already been discussed for ideal solutions by Raoult's law and the positive and negative deviations exhibited by non-ideal solutions indicated. It must be observed that, in general, the liquid phase will differ in composition from the vapor phase. Exceptions to this will be noted as they occur.

16. Binary Distillation. Mutually Soluble Components: Since the boiling point of a solution is that temperature at which the total vapor pressure of the solution is equal to the atmospheric pressure, the problem of binary distillation resolves itself into a consideration of the univariant equilibrium between vapor and liquid at constant pressure. The temperature-composition relations for an ideal system are shown in Fig. 11.7. The upper curve gives the composition of the vapor phase; the lower curve that of the liquid phase in equilibrium with it at each temperature. A liquid of composition X will boil at a temperature T_1 evolving a vapor whose composition is Y, that is, a vapor richer in component A than was the liquid. The liquid upon continued boiling thus becomes more concentrated in component B and its boiling point rises, say to T_2. Condensation of the vapor evolved between the two temperatures will yield a liquid richer in the more volatile constituent than the original liquid X used. By repeating the process of fractional distillation, a more or less complete separation of the components may be obtained.

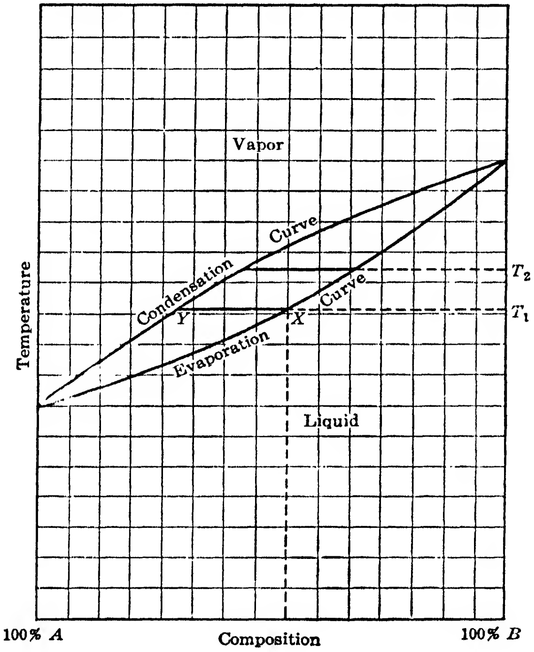

Fig. 11.7. Boiling Point Diagram for Liquid-Vapor Equilibrium

The efficiency of this separation will depend primarily upon the establishment of equilibrium between vapor and liquid. To aid this, use is made of "rectifiers" or "fractionation columns," devices in which the vapors pass countercurrently to a portion of the condensate returned as a reflux to the still. Intimate contact between vapor and liquid is obtained by having the vapor bubble through the liquid on trays or plates equally spaced throughout the column. Such a plate, on which equilibrium is established, is termed a theoretically perfect plate or simply a theoretical plate. In practice, plates will usually have only from 60 to 90 per cent efficiency. A simple graphical method for the calculation of the number of theoretical plates necessary for a given separation of a binary solution has been developed by McCabe and Thiele,[1] which will also show the compositions of liquid and vapor on each plate.

17. Maximum and Minimum Boiling Points: In discussing the deviations from Raoult's law, examples were shown where the total pressure at constant temperature might have a minimum or a maximum value. These solutions must therefore show a maximum or a minimum boiling point. At these points the vapor and liquid have the same composition. Such a solution would distill completely without change either in composition or temperature and might give the appearance of being a pure substance or a compound of the two components. The term *azeotropic solution* has been applied to such systems. That they are not pure substances is easily shown by the fact that if the pressure is changed not only does the temperature change but also the composition of the azeotropic solution.

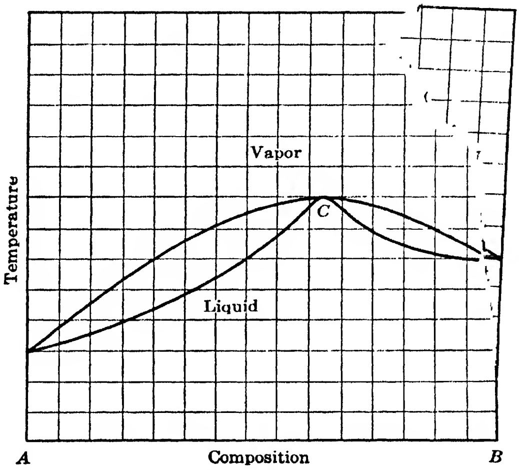

FIG. 11.8. Maximum Boiling Point

Fig. 11.8 represents the temperature-composition relations in an azeotropic solution showing maximum boiling point. Thus, to the

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[1] *Ind. Eng. Chem.*, 17, 605 (1925).

left of the maximum C, the vaporization is similar to that previously discussed in the ideal case, the vapor being richer in the more volatile component than the liquid. Upon continued boiling, the temperature of the solution will rise towards the maximum boiling point and the composition of the solution change to the azeotropic composition. Similar considerations apply to the portion of the curve to the right of C. Hulett and Bonner[1] have shown the usefulness of the azeotropic solution of hydrochloric acid as an acidimetric standard. Continued distillation of a solution of hydrochloric acid of any concentration finally gives a residue of the azeotropic composition, known for all normal working pressures. From such a solution standard acid solutions are readily prepared.

Fig. 11.9 represents a system showing a minimum boiling point exemplified by water and ethyl alcohol, the azeotropic solution containing 95 per cent alcohol. The diagram will show that if a dilute aqueous solution of alcohol is distilled, the vapors evolved are richer in alcohol than the liquid. Repeated fractionation of the condensed vapors will finally yield the azeotropic solution. Pure alcohol could only be obtained by starting initially with a solution containing more than 95 per cent, but this is impracticable due to the small range of temperature between the minimum b.p., 78.13°, and the pure alcohol 78.3° C.

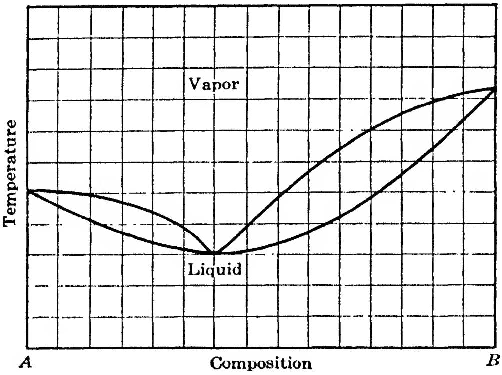

Fig. 11.9. Minimum Boiling Point

A single distillation cannot therefore cause complete separation into pure components in a system showing either maximum or minimum boiling points. The azeotropic solution will always be one of the products. A further slight separation can be obtained from the azeotropic solution by a distillation at some other pressure. Alternatively

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[1] *J. Am. Chem. Soc.*, **31**, 390 (1909).

the addition of a third component may so alter the volatility characteristics that separation is possible. Thus acetone and methyl alcohol, besides having boiling points differing by only 9° C., form an azeotropic solution with a boiling point only half a degree lower than that of acetone. Addition of a saturated aqueous solution of sodium thiosulfate so lowers the partial pressure of the alcohol that acetone may be readily obtained as a distillate.

18. **Partially Miscible Components:** A solution showing positive deviation from Raoult's law will in general, at some lower temperature, separate into two phases. The boiling point diagram corresponding to this condition is represented in Fig. 11.10. Provided both phases are

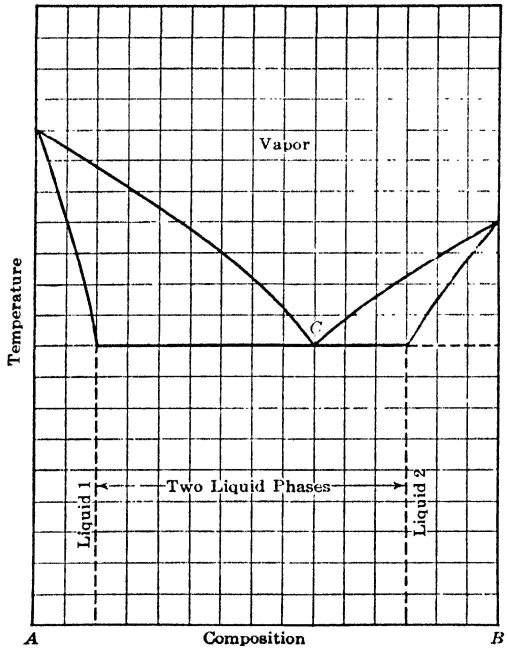

FIG. 11.10. Partially Miscible Components

present the boiling point and composition of the vapor C will remain constant. The system however is not azeotropic since no definite relation exists between the vapor composition C and the total composition of the liquid. In many cases the boiling point of the mixture lies below that of either pure component. It is upon this fact that the use of steam distillation depends, the addition of water as steam lowering the boiling point. Use could equally well be made of any chemically inert gas.

THE EQUILIBRIUM: LIQUID-LIQUID

19. Upper Consolute Temperatures: Phenol and Water: When phenol and water are brought together at room temperature and in suitable proportions, two liquid phases result together with a vapor. The two liquid phases formed at room temperature differ in that one of them is water with a small proportion of phenol and the second is chiefly phenol with a small proportion of water; as the temperature rises, the proportion of phenol increases in the aqueous phase and the proportion of water increases in the phenol phase, until, at 65.85°, the two liquid phases have identical composition. Table 11.6 contains figures taken from Hill and Malisoff's[1] experiments. Fig. 11.11 shows the curve obtained. At any fixed temperature, such as 30°, the composition of the two liquid phases is necessarily fixed, the system being invariant, and the points are indicated by A and A'; the isothermal line joining them is spoken of as a *tie-line*, and the two solutions are called conjugate solutions.

TABLE 11.6

THE SYSTEM: PHENOL-WATER

Temperature °C.	Wt. Per Cent Phenol in Phase L_1	Wt. Per Cent Phenol in Phase L_2
20	8.36	72.16
25	8.66	71.28
30	9.22	69.90
35	9.91	67.63
57.30	14.87	—
59.20	—	55.76
62.74	19.35	—
65.24	—	44.09
66.01	29.13	—
65.90	31.35	—
65.86	32.79	—
65.84	—	34.23

If now, at this temperature, 50 per cent each of phenol and water are brought together, the composition of the complex will be represented by the point x; the complex will form two liquids of the compositions A and A'. The relative quantities of these phases formed may be calculated geometrically from the diagram; the weight of phase A formed will be the fraction $xA'/(xA' + xA)$ of the total, and that of A' will be $xA/(xA' + xA)$ so that the ratio of the weights of A to A' will be that of the lengths of the lines xA' to xA; the weight of each is inversely proportional to the displacement of its composition from the composition of the total complex.

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[1] *J. Am. Chem. Soc.*, 48, 918 (1926).

The effect of rising temperature upon this system is to increase the mutual solubility: the curve *A'B'C* shows an increase in the concentration of phenol and the curve *ABC* an increase in that of water. At the point *C*, the curves merge into each other without discontinuity. What have been conjugate solutions at lower temperatures have now become a single solution; the temperature at which this phenomenon occurs is called the *consolute temperature*, or *critical solution temperature* (t_c). At higher temperatures, water and phenol are mutually soluble in all proportions, and the system can consist of but one liquid phase; below the consolute temperature, the mutual solubility is limited. No solution therefore can exist having composition indicated by points within the area *A–B–C–B'–A'*, but such compositions can lead only to two conjugate solutions of composition lying upon the curves at the intersections with the isothermal tie-lines.

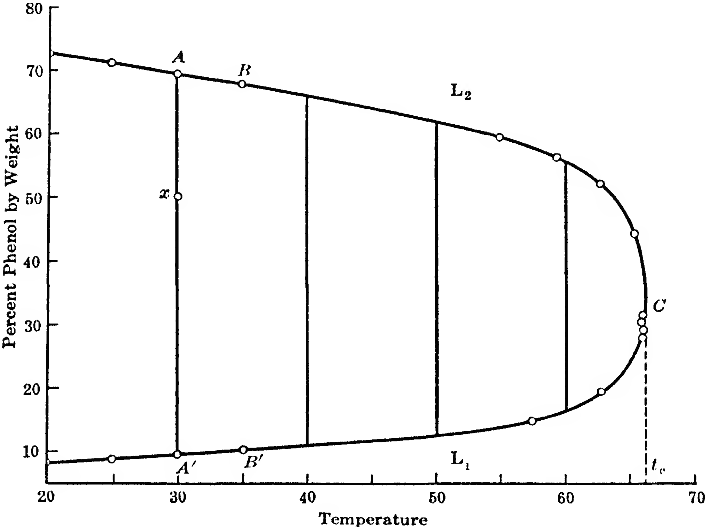

FIG. 11.11. *t-c* Diagram for the System Phenol-water

20. Lower Consolute Temperature: Tri-ethylamine and Water: In a certain number of cases, the solubility curves for two-liquid phases approach each other with diminishing temperature, and meet at a lower consolute temperature which is analogous to the upper consolute temperature discussed previously. Tri-ethylamine and water, Fig. 11.12, were found by Rothmund to show this behavior.

21. Completely Closed Solubility Curves: Nicotine and Water: With a knowledge of solubility curves closed at higher temperatures and others

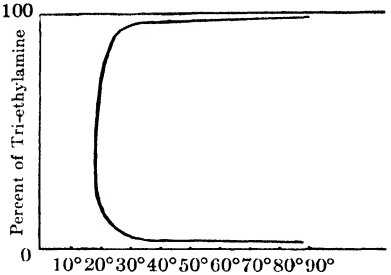

Fig. 11.12. *t-c* Diagram for the System, Tri-ethylamine-Water

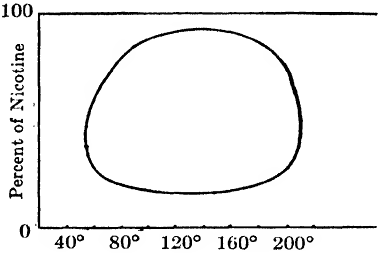

Fig. 11.13. *t-c* Diagram for the System, Nicotine-Water

closed at lower temperatures, it is natural to look for cases where the curves are closed at both temperatures, i.e., systems with both upper and lower consolute temperatures. Fig. 11.13 represents the curve for nicotine and water which shows this behavior. Many of the ethers of ethylene glycol show the same behavior with water.[1]

22. **Conjugate Liquids Without Consolute Points:** There is a very large number of conjugate liquid pairs which possess neither an upper nor a lower consolute temperature. This is the case with ether and water and with chloroform and water; it is probably the case with any pair whose mutual solubility is very low. As temperatures are lowered in such cases, a point is reached at which a solid phase appears; where water is one of the components, this occurs not far below 0°, since the concentration of the second component in the water and its effect upon the freezing point are small. There are, therefore, four phases present ($S - L_1 - L_2 - V$) and the system is invariant; if subjected to a cooling environment, ice continues to form until the aqueous layer has completely disappeared, and the system of conjugate solutions cannot exist at any lower temperature. If, on the other hand, the temperature be raised, a point will finally be reached at which one of the liquids, namely, that one rich in the more volatile component, is at its critical state; the vapor above it has reached not only the same relative composition as the liquid phase, but also the same density, and the two-component liquid phase disappears in the same fashion as at the critical temperature for a one-component system. Ether and water are known to behave thus.

THE EQUILIBRIUM: SOLID-LIQUID

23. **Pure Components as Solid Phases, with a Single Liquid:** We shall develop a diagram of an entirely general nature for this case and afterward show that it indicates, at least qualitatively, relations which

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[1] *J. Am. Chem. Soc.*, **48**, 451 (1926).

are met with in the determination of melting points and of the solubility of solids in liquids, as well as in the manufacture of metallic alloys. Treating our systems as prepared under the pressure of their own vapor, or under atmospheric pressure, and omitting the vapor phase from consideration, we may use Fig. 11.14 to represent the temperature-composition relations of the system $S_1 - S_2$. Here the point R represents the freezing point of pure S_1; as increasing quantities of S_2 are added, the freezing point falls along the curve RC, which therefore represents the equilibrium of S_1 with the liquid phase. In like manner M is the freezing point of S_2 and MC its freezing-point curve. Since, in all cases, the freezing point of a component which exists in the solid phase in pure condition is lowered by the presence of a second component in its solution,

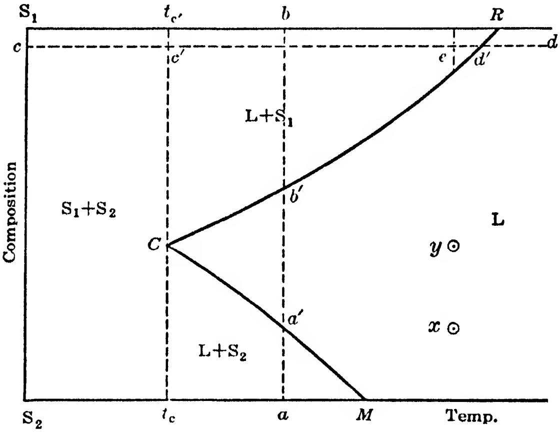

FIG. 11.14. The System $S_1 - S_2$. The Solid Phases are Pure Components, with One Liquid Phase Present

the two curves must take the general direction here indicated and must intersect at some point C, which will be discussed later; our freezing-point diagram therefore must show discontinuity, and the two branches to the curve represent respectively S_1 as solid phase in equilibrium with liquid and S_2 as solid phase in equilibrium with liquid.

The diagram for a solubility curve such as CR is here given in its simplest form; it will frequently show wide variations from the simple form indicated here, the only unvarying condition being that it necessarily begins at the point of intersection C and ends at the melting point R. It may, for example, show a discontinuity in direction at some intermediate point; this is evidence of a change of phase and must represent (since compound formation is here left out of discussion) that the solid phase has a transition point from one polymorphic form to another. The curve for the equilibrium of silver nitrate (solid phase) and water shows such a transition point at 160°; that for ammonium nitrate (solid phase) and water shows breaks at 32°, 82.7°, and 125.6°. Moreover, the curve sometimes fails in part of its course to maintain its slope toward the axis of the solid component with temperature rise. A slope in this direction means an increase in solubility with rising temperature; but numerous instances exist in which the solubility decreases with rising temperature, well-known cases being calcium chromate in water and calcium citrate in water. Maximum and minimum points in the solubility curve are also by no means uncommon. All of these directions and changes of direction can be derived from van't Hoff's law whenever the thermal data are available; the solubility curve is ascending at a given point when the heat of solution in the saturated solution is negative at that point, is descending when the heat of solution is positive at that point, and is neither ascending nor descending (which is the condition at a point of maximum or minimum solubility) when the heat of solution is zero. In applying this law, however, it is necessary to remember that the heat of solution which governs the direction of the equilibrium by its sign is the heat of solution at *saturation*, i.e., the heat developed by the last increment entering the solution. van't Hoff's law has to do with a displacement of an equilibrium by thermal means; it is clear that what may happen in a system not yet in equilibrium (i.e., not yet saturated) is altogether irrelevant. A recollection of this method of applying the law is essential if one is to avoid error. For example, it is common knowledge that when water is poured upon solid potassium hydroxide, much heat is evolved; if one deduced therefrom that the solubility of the compound decreased with the temperature, the error would be flagrant. The initial heat of solution is positive; it may be that the total heat of solution is positive; but the final heat of solution, representing the dissolving of the last increment entering the solution at the saturation point, is negative, and hence a rise of temperature will result in the dissolving of another increment.

In Fig. 11.14, a solubility curve such as *C–R* represents saturation or equilibrium conditions; it separates two regions in which solutions may occur, stable or metastable. The area to the right of the curve *C–R* is the region of unsaturated solutions; that to the left is the region of metastable supersaturated solutions. A phase-rule distinction between these three types of solutions is not only simple, but is the only logical one. A saturated solution is one in equilibrium with the solid phase, and is therefore unaffected by addition of more solid phase; an unsaturated solution is one which will dissolve more solid phase if it be added, and a supersaturated solution is one which, being metastable, will precipitate solid phase from its own composition and fall to the point of saturation if a nucleus of the solid phase be added. All concepts of degrees of saturation must always refer to a particular solid or saturating phase (S_1 in the case of the curve C–R), since a solution in equilibrium with one phase is quite capable of entering into new relations of saturation with respect to some second phase.

The intersection of the two solubility curves (C), called the *eutectic point,* is the most interesting point of the diagram. Since the curve RC represents solutions saturated with S_1, and MC solutions saturated with S_2, the intersection must represent a solution saturated with both solids. The system represented by this point consists of two solid phases, solution and vapor, and is called a *quadruple point*; by the phase-rule equation, it is an invariant point. A solution to be in equilibrium with both solids can have therefore only the eutectic composition C and can exist in stable equilibrium only at the eutectic temperature, t_c. Rise of temperature above t_c results in the disappearance of one or both solid phases, and fall of temperature in the disappearance of the liquid. The eutectic point may be defined in terms of these phenomena; it is an invariant temperature at which the phase reaction of the system, upon removal of heat without change of temperature, results in the disappearance of the liquid phase.

In a system including a eutectic we have a simple and widely used means of securing a constant temperature. If two solids, properly chosen as to their solubility relations, are brought together in the eutectic proportion or any proportion approximating the same, they will begin the process of dissolving which, being endothermal in all common cases for both solids, reduces the temperature to the eutectic temperature. If, now, the system is well enough insulated so that heat can reach it from without only at a moderate rate, and is well stirred so that solution of the solids can occur quickly and temperature inequalities be eliminated, it will remain constant at the eutectic temperature until one of the solids has dissolved completely. With proper apparatus, extremely constant temperatures result; but, it does not follow that the equilibrium will be reached at all if the apparatus is unsuited. Thus, the eutectic temperature for sodium chloride and water is − 22.4°, and a coarse mixture of the two solids, ice and salt, gives a reasonably effective freezing mixture for the household ice-cream freezer; but it is doubtful if this mixture, poorly insulated from the outside and warmed from the inside, practically free from stirring and with the salt and ice poorly mixed, ever gets within many degrees of − 22°; that is, no equilibrium is reached. But, if snow and fine salt be put in a Dewar flask and well stirred, a perfectly constant temperature may be maintained for hours; equilibrium is really attained.

Systems of two components which are represented diagrammatically by Fig. 11.14 are very numerous. They include many pairs of organic compounds and of inorganic compounds; salts with water fall into this class in numerous instances, and the solubility curve of a salt as given in the various solubility tables is usually a section, more or less complete, of one of the curves of the diagram; metallic alloys occasionally fall into this class, as well as the iron-carbon alloys, in which only one of the components is a metal. In Table 11.7 are given three typical cases of systems which may be represented by Fig. 11.14.

In the case of alloys, the conditions at the eutectic are of importance, not only as determining the lowest melting point for the metallic pair but also as affecting the structure and physical properties of the solid alloy. If some composition other than the eutectic composition be taken and the molten metallic solution cooled, upon reaching the freezing-point curve *RC* or *MC* in Fig. 11.14 (dependent on whether S_1 or S_2 is in excess), crystals of the one component begin to form throughout the liquid mass. When the temperature has dropped to the eutectic temperature, t_c, it will there remain constant and crystals of both S_1 and S_2 will form in the eutectic ratio and continue to form until the mass is entirely solid. This crystallization of the two solids in a continuously uniform ratio fills in the interstices between the crystals previously formed with a conglomerate which, though truly a mixture, is remarkably uniform in character. By the methods of metallography, such metallic surfaces can be examined under the microscope; under high magnification the eutectic mixture shows its heterogeneity, as in Fig. 11.15*a*, but its approximation to homogeneity as shown in Fig. 11.15*b* is such that in metallographic work it is looked upon as a "structural element" as if it were a single phase.

TABLE 11.7

SOLUBILITY CURVES WITH EUTECTICS

Point	Cyclohexane: Benzene		Silver Nitrate: Water		Lead: Silver	
	Temp.	Per Cent Cyclohexane	Temp.	Per Cent Silver Nitrate	Temp.	Per Cent Silver
M	+ 5°	0	0°	0	327°	0
	− 5.2	17.04				
	−11.3	28.26				
	−26.9	52.88				
	−36.2	65.05				
C	−(44)	(75)	−7	46.2	305	2.3
	−37.1	78.55	+5	56.3	460	10
	−31.2	84.56	20	67.8	535	20
	−16.5	88.34	40.5	76.8	648	50
	− 6.7	93.42	135	92.8	875	85
R	+ 6.2	100	208	100	960.5	100

24. **Compounds as Solid Phases, without Congruent Melting Points:** Systems of this type introduce few considerations not already advanced. They are, however, extremely common; whenever any two components show a high degree of solubility, it is probable that there is more or less

(*a*)
Magnified 500 times

(*b*)
Magnified 150 times

FIG. 11.15. Ag-Cu Alloy, Slightly to the Cu Side of the Eutectic Point (73% Ag, 27% Cu)

Diagrams by courtesy of
Prof. D. P. Smith and Mr. J. L. Whitten

compound formation in the liquid phase, and frequently one or more of these compounds will form solid phases as well; the formation of solid hydrates of salts, for example, is very common. The classical instance of a system of this type is given by sodium sulfate and water. The composition-temperature diagram is shown schematically in Fig. 11.16. The curve *AB* is the freezing-point curve for ice, which ends at the eutectic *B*(– 1.2°); here the other solid phase is the decahydrate, $Na_2SO_4 . 10H_2O$, which is an additive compound formed of the two components. The solubility curve for the decahydrate rises with the temperature up to 32.4°, which is its transition temperature (*F*) to the anhydrous form and the distinctive point of this diagram. The curve for the anhydrous sulfate shows a solubility diminishing with rise of temperature up to about 125° where it reaches a minimum value, afterwards rising until the temperature is 234°. Here (point *G*) occurs a transition from the common crystalline form, which is rhombic, to a polymorphic monoclinic form which has a diminishing solubility up to 365°, which is the critical temperature of the solution; the concentration of the salt in the liquid phase is here very low and the critical temperature is practically that of pure water. The four solid phases occurring in equilibrium with solution along this curve are represented by *W* (ice), S_{10} (decahydrate), S_r (rhombic anhydrous salt) and S_m (monoclinic anhydrous form).

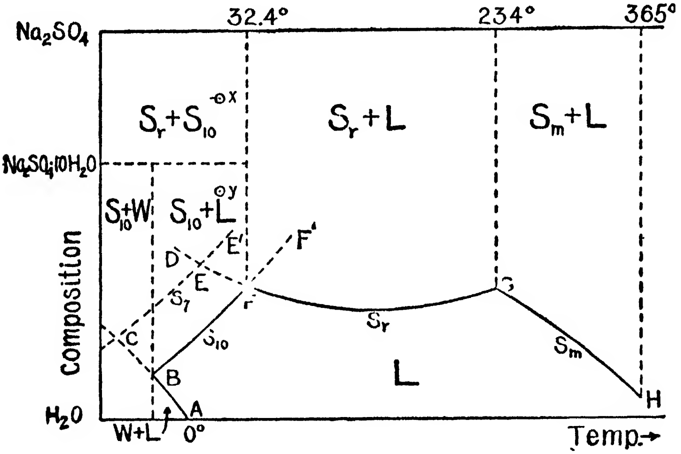

FIG. 11.16. *t-c* Diagram for the System, Sodium Sulfate-Water

The solubility curve for the decahydrate *BF* has been carried some distance beyond the transition temperature of 32.4°, to the point *F'*. Here, as in all cases of solubility, the solubility of the metastable body is higher than that of the stable body, so that if a crystal of the anhydrous salt is put into the solution of the composition F' the solubility drops to F with a simultaneous drop of temperature, since the precipitation of the solid is an endothermic reaction. The solubility curve of the rhombic anhydrous salt, GF, has also been prolonged a considerable distance into the metastable region, as shown by FD, and the ice curve AB has been extended to C. In this metastable region to the left of BF a second hydrate, of the formula $Na_2SO_4 \cdot 7H_2O$, has been found, having a solubility curve CE; it is itself metastable and gives rise to a metastable eutectic with ice at $-3.55°$ (C) and a metastable transition point to the anhydrous salt, E, at 24.2°.

The complete system, $Na_2SO_4 - H_2O$, shows the five quadruple points or invariant points B, C, E, F and G. B and C will be recognized at once as eutectics. E, F and G are transition points, of which we will discuss one (F) in some detail. The point F represents the stable transition point of the decahydrate to the rhombic anhydrous form, the phase reaction being the following: $Na_2SO_4 \cdot 10H_2O \rightleftarrows Na_2SO_4 +$ solution. The change from left to right represents a partial fusion, since the solid hydrate changes to a solution plus a second solid; such a transition is sometimes called an *incongruent melting point*, to distinguish it from a true or congruent melting point, which will be discussed with our next type of system. While not a melting point in the exact sense, it is nevertheless a change of great practical usefulness, since it occurs at an invariant temperature and therefore gives a convenient means of obtaining a definite and constant temperature. If a sample of the hydrate be subjected to the influence of a higher temperature, it will maintain this constant temperature F until the transformation is complete. Richards has found the temperature to be 32.383°, as carried out in an open vessel. This is not exactly the quadruple point, which, by definition, must be under the natural vapor pressure of the system. The transition points of this and other hydrates give us one of our most convenient methods of obtaining fixed points for the standardization of thermometers. Another method involving eutectics has already been mentioned. Such transition points are also of use in making constant-temperature baths for experimental work. Further, since the transition from anhydrous salt to hydrate is an exothermic change, such materials find use as thermophores or heat-producing mixtures for warming purposes; thus, a quantity of sodium acetate and water, if heated above its transition point and allowed to cool, forms a metastable saturated solution of the anhydrous salt and water, but, upon crystallization of the stable hydrate being started by agitation or other means, the temperature will rise to the transition temperature (58°) of the compound $NaC_2H_3O_2 \cdot 3H_2O$ and remain at that temperature until all the heat of transformation has been evolved.

25. **Compounds as Solid Phases, with Congruent Melting Point:** In a large number of systems in which additive compounds exist, it is found that these compounds not only possess a transition point such as has been described above, but also possess the property of melting sharply and distinctly into a liquid of the same composition as the solid. Such bodies are said to possess a *congruent melting point,* and possess a solubility curve quite different from those previously discussed. Phenol and aniline fall into this class, and will serve as our example. In this system three different solid phases appear, namely, aniline, phenol, and a compound of the formula $C_6H_5NH_2 \cdot C_6H_5OH$. These give rise to three solubility curves which are represented in Fig. 11.17 by the three curves *de*, *ab*, and *bcd*.

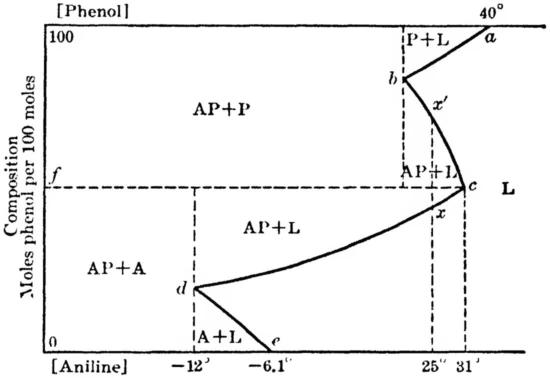

FIG. 11.17. The System, Phenol-Aniline (Schematic)

The composition of the solutions is given in molar percentages, which is always the most logical method of representing composition and is here of especial convenience where the composition of compounds is to be deduced. The point *d* in Fig. 11.17 is a eutectic, from which originates the solubility curve for the compound, *dc*; the solubility increases with temperature up to 31° and a composition of 50 molar per cent of aniline and of phenol, that is, a 1 : 1 molar ratio. This is, from the diagram, the point of maximum temperature at which the compound can exist in equilibrium with solution; the solution, it will be seen, has here the same composition as the solid. This point, invariant in that there are present three phases and that the restriction is imposed that solution and solid shall have the same composition, is the congruent melting point: it is also spoken of as a *dystectic,* in contradistinction to a eutectic, it being the highest melting point and the eutectic the lowest. From *c* the curve is retrograde to the point *b*, which is a second eutectic with compound and phenol as the two solid phases.

A curve of this character, showing a maximum temperature and a retrograde direction upon one branch, is considered proof of both the occurrence and the composition of a compound;[1] the composition is read directly from the ordinate (here 1 : 1 of phenol and aniline) and is therefore known without the necessity for the isolation and analysis of the solid. In many cases the separation of a solid for analysis is difficult or impossible; in such cases the phase-rule evidence is invaluable. Our knowledge of compound formation in alloys, for example, is very largely based upon evidence of this type.

In the study of systems composed of a salt and water, many examples of hydrates are found which melt congruently and have diagrams built upon the type of Fig. 11.17. The system ferric chloride-water is perhaps the most striking instance of multiple congruent melting points. There are four stable hydrates, $Fe_2Cl_6.12H_2O$,[2] $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6.5H_2O$ and $Fe_2Cl_6.4H_2O$, all possessing congruent melting points. Fig. 11.18 represents the system graphically.

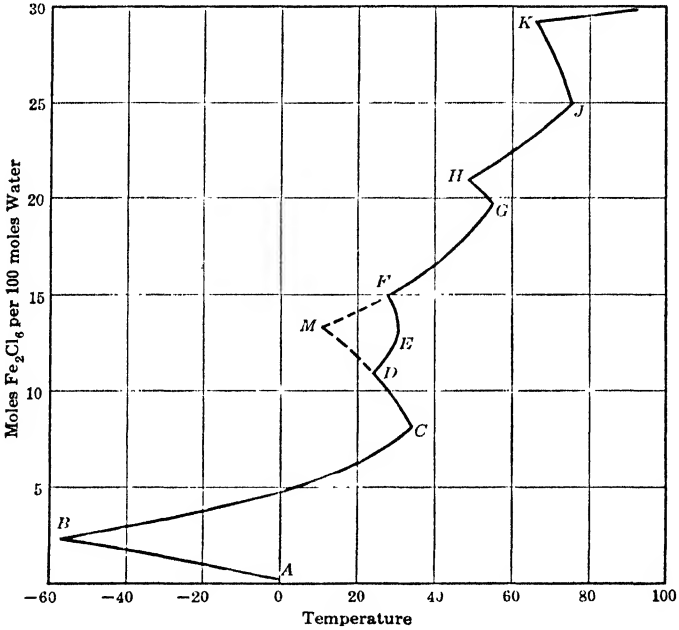

Fig. 11.18. The System, Ferric Chloride-Water (Schematic)

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[1] An exception to this reasoning is the occurrence of a maximum freezing point of a *solid solution*, which will be discussed later.

[2] The double formula Fe_2Cl_6 is used in order to avoid fractional coefficients for the water.

In systems like the above, in which only one of the components is appreciably volatile (here the water), very interesting phase changes occur upon isothermal evaporation. Let us assume that an unsaturated solution of ferric chloride and water be maintained at a constant temperature of 31°; the point is represented by x in Fig. 11.19. Isothermal evaporation will lead to the following systems: solution saturated with $Fe_2Cl_6.12H_2O$ at points between (1) and (3); solid $Fe_2Cl_6.12H_2O$ at point (2); unsaturated solution between (3) and (4); solution saturated with $Fe_2Cl_6.7H_2O$ between (4) and (6); solid $Fe_2Cl_6.7H_2O$ at point (5); unsaturated solution between (6) and (7) and finally solution saturated with $Fe_2Cl_6.5H_2O$ at (7) leading to solid $Fe_2Cl_6.5H_2O$ with no further liquefaction.

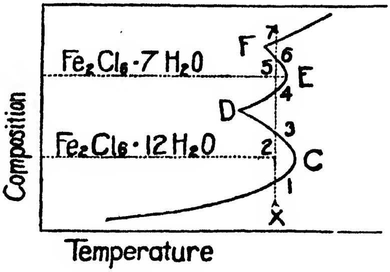

Fig. 11.19. Isothermal Evaporation in the System, Ferric Chloride-Water

26. **Solid Solutions as Solid Phases; A Single Solid Solution Present:** Abnormalities in the freezing-point curves of certain systems led van't Hoff to the view that the solid being precipitated was not a pure component, but a solid phase of variable composition to which he gave the name *solid solution.* Brief reference to solid solution has been made in the chapter on solutions. A definition of such a substance is simple; it is to be viewed as a phase and therefore homogeneous, and of variable composition and therefore a solution, existing in the solid state. The concept of a solid solution occasionally gives difficulty, but if approached *de novo* it is no more difficult (and also no less difficult) than the concept of a liquid solution. It is the idea of homogeneity in a body in which we know that there is more than one substance present that gives the difficulty; and it is true that to admit salt water as homogeneous is perhaps impossible philosophically and no less so if one prefers to think in terms of the molecular hypothesis. But salt water is homogeneous if defined empirically; that is, heterogeneity has not been demonstrated experimentally, and the treatment of it as homogeneous under the phase rule brings about no contradictions. In exactly the same manner, a solid solution is regarded as homogeneous for the same empirical reasons.

In dealing with liquid solutions, we have learned that, in some two-component systems, the liquids show complete mutual solubility, giving rise to but a single liquid phase, while other systems, in which there is limited solubility, form two liquid phases bearing conjugate relation to each other. The same conditions prevail for solids; the two components may dissolve mutually in all proportions, forming only a single solid solution, or may possess limited solubility and form two solid solutions which are conjugate. Extending our use of the term conjugate beyond its application to two liquid solutions, it will be seen that we may have the conjugate relation between a liquid and a solid solution and also between two solid solutions. We shall give our attention first to cases where the conjugate phases are a liquid solution and a solid solution.

Our problem being to trace the course of the equilibrium between a solid (albeit a solid solution) and a liquid phase, it is obvious that, to show the changes of concentration with the temperature, a freezing-point curve can be constructed. In our previous attention to freezing-point curves we have assumed, in accordance with the laws of dilute solution, that the freezing point of a solid is always lowered by the presence of a second component in the liquid phase. This assumption is justified, by the laws of thermodynamics, as long as the solid phase is a pure component; but there is no foundation for any such generalization when the solid phase is a solid solution. In this case, the freezing point of the solid solution may be either lower than that of the pure component, equal to it or higher, and all three possibilities are known. Fig. 11.20 is designed to demonstrate qualitatively these three conditions.

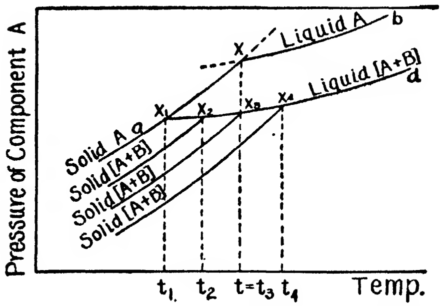

FIG. 11.20. Vapor Pressure of Component *A* in Solid and Liquid Phases

Let us consider the vapor pressure of the component *A* alone (i.e., its so-called partial pressure) in a system composed of *A* and *B*. The curve ax is the vapor-pressure curve of the pure solid and bx that of the pure liquid phase, the two intersecting at x; this relationship for a single component has previously been shown. Let us now consider that the liquid phase has an amount of *B* added to it; the curve representing the vapor pressure of *A* in this solution must fall below the curve for pure liquid *A*, since the vapor pressure of *A* is always lowered by a second component. The curve for this solution, dx_1, intersects ax at the point x_1, and the point of intersection is the freezing point, at which the vapor pressure of *A* in the two phases is the same, that being a necessary condition for equilibrium. The point x_1 is, by the diagram, necessarily at a temperature t_1 lower than t, which accords with the rule that where the solid phase is the pure component its freezing point is always lowered by a second component in the solution. Let us now consider however that the solid phase which forms is a solid solution containing varying quantities of *B*; the curves representing the pressure of *A* in these solid solutions fall below ax a distance dependent on the amount of *B* present in the solid phase. The intersections of these curves for the solid phase with that for the liquid phase (dx_1) are the freezing points, where the pressure of *A* in both phases is the same; and it will be seen that, according as the solid phase contains little or much *B*, the freezing point is below t (t_2), equal to it (t_3) or above it (t_4).

As to the concentrations in the phases at these various points, it can be shown thermodynamically, as it has been shown experimentally, that the following rule holds: if the concentration of the second component is greater in the liquid phase than in the solid phase, the freezing point is lowered (x_1 and x_2), and if it is greater in the solid phase, the freezing point is raised (x_4).

What has been shown for solid solutions in which A is the predominating component may also be shown where B predominates; it follows then that in a general system $A - B$ where solid solution occurs, the freezing point of each solid phase may be lowered, the freezing points of each may be raised, or one may have its freezing point raised and the other have it lowered. There will therefore be three types of curves necessary to express these three cases.

Let us now recapitulate what has been learned about systems consisting of a liquid phase and single solid solution, so that we may be in position to interpret complete diagrams: (1) there will be a liquid solution and solid solution bearing a conjugate relation to each other, and of course two separate curves will be necessary to show the composition of these two phases; (2) since only one solid phase and one liquid phase have been postulated, and only one vapor phase is possible, there can not be more than three phases present, and no invariant points, which require four phases (eutectics, transition points, etc.), can appear; (3) the freezing points of a pure component may be either raised or lowered by the second component, giving rise to three types of curves.

In Fig. 11.21 have been drawn schematic representations of complete systems fulfilling these requirements. Curve I illustrates the case where each component has its melting point lowered by the second. The curve *agcfe* represents the composition of the liquid phase, and is called the *liquidus curve*; the dotted line *abcde* is the curve for the solid phase, called the *solidus curve*, and the tie-lines show the conjugate relation. The position of these two curves with reference to each other fulfills the rule developed above; at a given temperature t, the liquid phase f contains more of A than does the solid phase d which therefore has a lower melting point than that of pure B, (e), and likewise the liquid g contains more of B than does the solid phase b, in accordance with which its melting point is lower than that of pure A (a). The point c bears a superficial resemblance to a eutectic, but is in no sense to be regarded as such, since it is not an invariant point; it is correctly described as a minimum melting point, which is a characteristic point in systems of the type in which each component has its melting point lowered by the other. Mercuric bromide and iodide give curves represented by Curve I, Fig. 11.21, with a minimum point at 59 molar per cent $HgBr_2$ and 216.1°.

The other two types of curves obtained are shown in Fig. 11.21 as Curves II and III. Curve II represents the case where the melting point of A is depressed by B, but that of B raised by A; hence the liquid

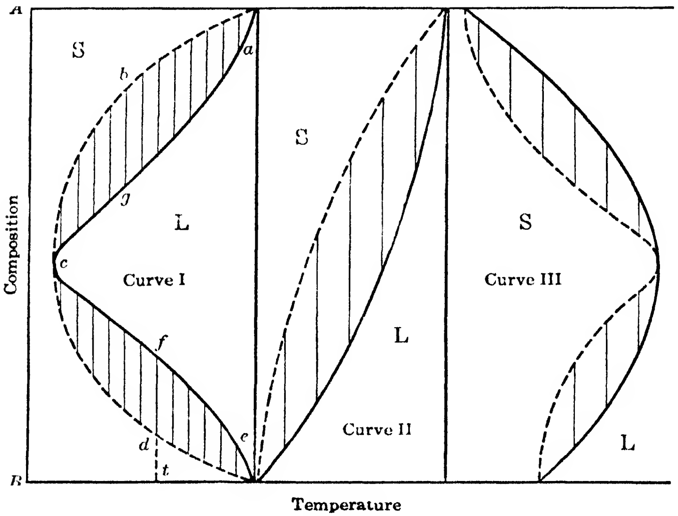

FIG. 11.21. The System *A* – *B*; Solid Phase, a Single Solid Solution

phase at all temperatures is richer in *B* than is the solid phase, to account for melting points lower than that of *A*. Curve III represents the elevation of the melting points of both components, leading to a maximum melting point; the position of the liquidus and solidus curves will be found to accord with the rule relating to concentrations in the two phases with the rise in freezing point.

27. Solid Solutions as Solid Phases; Two Solid Solutions Present: When the two components show a limited solubility in the solid phase, a number of new relations appear. In the first place, these two solid solutions will bear a conjugate relation to each other. Secondly, if the temperature limits of this conjugate curve extend up to the temperatures where liquids exist, there will be two solids and a liquid coexisting which, with the vapor phase, make four phases and give rise to an invariant point which meets the definition of a eutectic or transition point. Further, either of these solid solutions alone may be in conjugate relation to the liquid phase giving rise to conjugate solidus-liquidus curves such as have been shown in Fig. 11.21.

When the solidus-liquidus curves show a minimum melting point, like that of Fig. 11.21, Curve I, the existence of two solid solutions produces a eutectic at this point; the condition is shown in Fig. 11.22. Here the liquid of minimum freezing point, *b*, is in equilibrium with the two solid solutions of composition *d* and *e*, as shown by the tie-line *dbe*. This corresponds to a eutectic. Indeed, the system may be compared with the simplest melting-point diagram, that of Fig. 11.14, and the single distinction is that the liquid phases in Fig. 11.22 are conjugate with solid solutions, represented by *aef* and *cdg*, whereas in Fig. 11.14 they are conjugate with the pure components. Potassium nitrate and thallium nitrate are an example of this class.

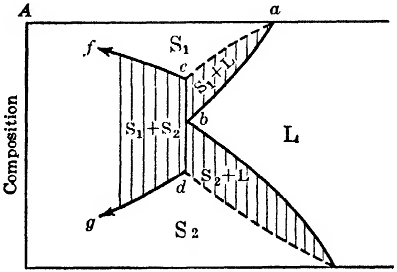

Fig. 11.22. The System $A - B$; Solid Phases, Two Solid Solutions with Eutectic

When the solidus-liquidus curves rise from the melting point of one component to that of the second, the system may be represented by Fig. 11.23. Here the juncture of the conjugate curve for the solid solutions ($fe - gb$) with the conjugate solidus-liquidus curves ($ad - ae$) produces an invariant condition where the phases are the two solid solutions e and b, the liquid solution d and vapor. This corresponds to a transition point, as shown earlier in Fig. 11.16; it is marked by the appearance of a new solid phase, whether one cools the system $S_1 + L$ or warms the system $S_2 + L$, and by a discontinuity of the solubility curve at d. Silver nitrate and sodium nitrate offer an illustration of this type of curve; the transition temperature is 217.5°, at which temperature the liquid d contains 19.5 molar per cent of sodium nitrate, and the solid solutions b and e 26 per cent and 38 per cent respectively.

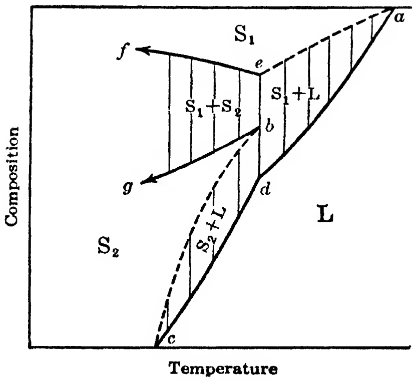

Fig. 11.23. The System $A - B$; Solid Phases, Two Solid Solutions with Transition Point

28. **Cooling Curves:** The commonest method of determining the nature of the solid is by a study of the cooling curve for the system, a method proposed by Tammann and almost universally used in the study of alloys, where the mechanical isolation of a solid phase is out of the question. It is clear that if a heated system is allowed to cool with a constant outside temperature environment, the loss of heat will depend upon the heat radiation of the system as a whole, including the container,

and the heat changes occurring within the system as a result of alteration in the chemical equilibrium with the temperature. Keeping these two factors in mind, let us plot schematically a cooling curve for a system like that of Fig. 11.14, starting with a complex x; in Fig. 11.24 we will plot the results, using time and temperature as coordinates. The system is composed of liquid and vapor and is therefore bivariant, so that its temperature may fall without producing any phase reaction; the cooling curve therefore beginning at a will be a smooth curve. At the temperature at which the solution reaches saturation however, solid phase appears and heat is produced by that phase reaction so that the direction of the cooling curve is altered and the rate of cooling lessened; b, the point of discontinuity, is the saturation temperature. The system now consists of three phases and is univariant, permitting the fall of temperature to continue until the eutectic temperature is reached; here occurs, at c, a second discontinuity in direction, and what is most important, the temperature will remain constant (the system being now of four phases and invariant) until the liquid has entirely disappeared, the positive heat of formation of the eutectic solids compensating for the loss of heat by radiation. When the liquid has finally disappeared, the system becomes univariant and a cooling curve *de* for the solids follows.

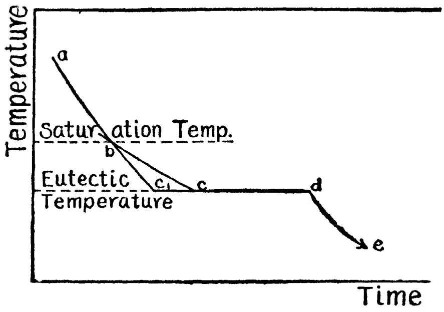

FIG. 11.24. Cooling Curve for a Two Component System

The cooling curve has revealed certain "arrests," b and c, indicating temperatures pertinent to the study of the system; by repetition under altered circumstances it may also be made to reveal the desired composition of the solid phase. It is the time of the eutectic halt (i.e., the time interval $c - d$) which may be made to give this information. It is obvious that the duration of the eutectic halt depends upon the quantity of liquid components which change to solid and thus produce the heat which halts the cooling. If amounts of A and B of the same total weight as in the first experiment be taken, but now of the eutectic composition as y in Fig. 11.14, there will be no "arrest" at any point until the eutectic temperature is reached and the halt will be extended to its maximum, namely, c_1d, Fig. 11.24. That composition therefore which gives the maximum eutectic halt establishes the composition of the solid phases at the eutectic. In like manner, a halt will occur at other invariant points, such as a transition point; but if a composition of a compound having a congruent melting point is taken, there will be no eutectic halt, since, as previously pointed out, such a compound acts like an independent component and can therefore have no eutectic. The relationship of the eutectic halt to the composition of these solid phases is rendered clearer by Figs. 11.25 and 11.26, in which the duration of the eutectic halt with the composition is plotted directly below the temperature-composition plot; it will be seen that the maximum eutectic halt shows the eutectic composition, and zero eutectic halt shows the composition of pure components and congruently melting compounds. By more extended thermal methods it becomes possible to determine the composition of compounds which do not melt congruently and of solid solutions as well; such methods have been invaluable in the study of metallography.

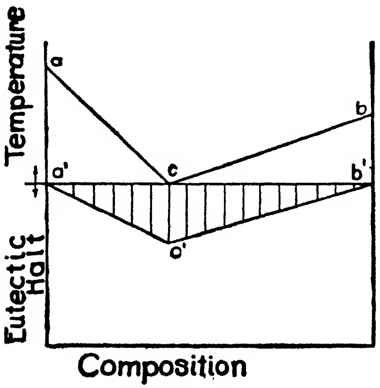

Fig. 11.25. Eutectic Halt, Showing Composition of Eutectic Solids

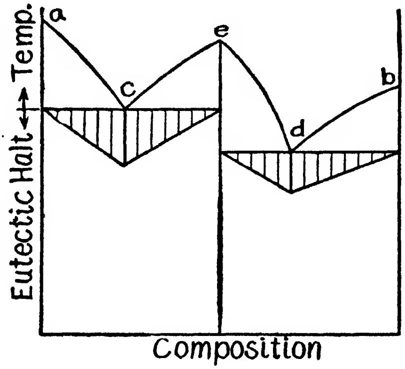

Fig. 11.26. Eutectic Halt, Showing Composition of Compound and of Eutectic Solids

THE EQUILIBRIUM GAS-SOLID

Of the three possible diagrams to represent the equilibria between gas and solid phases, namely, the pressure-composition (*p-c*), pressure-temperature (*p-t*) and temperature-composition (*t-c*) diagram, we shall select the first two as most instructive, and as an example will choose a system consisting of a salt and water, where hydrate formation occurs. If we keep the water small enough in amount so that no liquid phase occurs, the possible phases consist of water vapor, anhydrous salt, and as many hydrates as occur. Copper sulfate forms a number of hydrates, namely, $CuSO_4\ H_2O$, $CuSO_4.3H_2O$ and $CuSO_4.5H_2O$. The pressure-temperature relations are shown in Fig. 11.27. It must be stated that anhydrous $CuSO_4$ may be kept in contact with water vapor of certain pressures and temperatures without the slightest formation of a hydrate—a fact of primary importance in freeing our minds from the erroneous impression that this compound (or any substance) is a perfect dehydrating agent. The diagram therefore shows an area for the bivariant equilibrium $CuSO_4 + H_2O$, within which both pressure and temperature may be altered simultaneously without altering the number of phases; the formulas $CuSO_4$ + vapor are printed in this area. If, however, the pressure of water vapor is increased, there comes, for each temperature, a point at which the hydrate $CuSO_4.H_2O$ forms; since three phases are now present, the system is now univariant, and the curve *OC* represents the pressures and temperatures for that equilibrium. The curve is commonly spoken of as the dissociation curve for the monohydrate, since it represents the dissociation pressure of the reaction $CuSO_4.H_2O \rightarrow CuSO_4 + H_2O$ (vapor). If we desire to speak of it as a vapor-pressure curve, it is the vapor-pressure curve for the system $CuSO_4.H_2O - CuSO_4 -$ vapor, and not, correctly speaking, for the hydrate alone; for this hydrate has no vapor-pressure curve, but, on the contrary, a vapor-pressure area above the curve. In this area, again, the two-phase system is bivariant, and is bounded above by the vapor-pressure curve for the system $CuSO_4.H_2O - CuSO_4.3H_2O -$ vapor. The other areas and vapor-pressure curves may be read from the figure; some of the data are given below.

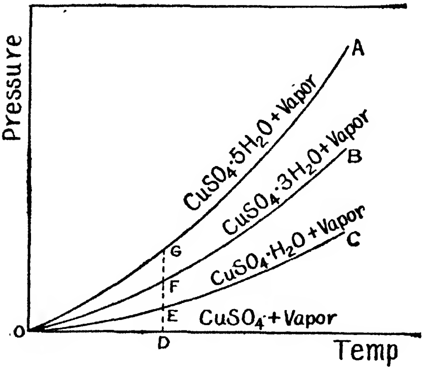

FIG. 11.27. Vapor Pressure Curves for Hydrates of Copper Sulfate

TABLE 11.8

DISSOCIATION PRESSURES OF HYDRATES OF COPPER SULFATE

Temp.	$CuSO_4.5H_2O$ $- CuSO_4.3H_2O$	$CuSO_4.3H_2O$ $- CuSO_4.H_2O$	$CuSO_4.H_2O - CuSO_4$
25°	7.8 mm.	5.6 mm.	0.8 mm.
30	11.6	—	—
35	16.5	11.8	—
40	23.2	—	—
45	32.8	22.1	—
50	45.4	30.9	4.5
80	260.1	183.1	—

A number of conclusions may be drawn from Fig. 11.27. As to dehydrating efficiency, it is apparent that $CuSO_4$, put in a moist atmosphere or into a nonreacting liquid containing water, will never remove all the water, but will combine with it at a given temperature *D* and reduce the aqueous pressure to a certain definite amount, depending on the quantity of $CuSO_4$ present; if it be so small that it is completely converted into $CuSO_4.5H_2O$, the pressure will fall to *G*; if it be larger, so that all the water possible can be taken up without the formation of any hydrate higher than $CuSO_4.H_2O$, the pressure will fall to *E*; but under no circumstances can it fall to zero. The same reasoning applies of course if other salts forming hydrates are used as desiccating agents. Further, it will be seen that, at a given temperature, all three hydrates are perfectly stable and capable of existence; there is no necessary lower limit for the existence of a hydrate in equilibrium with a vapor, although there frequently is a lower limit for its existence in contact with solution. The upper limit of a vapor-pressure curve of this character is reached where there is a congruent melting point or a transition, producing a liquid phase and therefore a new system with a new vapor-pressure curve. That this is the single limitation to the curves at high temperatures is frequently forgotten, and was not at all understood previous to the use of the phase rule; as a result, the student should be on his guard against statements emanating from the older literature to the effect that such and such a hydrate "loses water at 100°," when all that is meant is that the experimenter noticed a rapid loss of water at that temperature, and not that a transition point exists. As Fig. 11.27 indicates, a given hydrate will lose water at any temperature, if the aqueous pressure is less than that of its dissociation curve; in the terms of the phase rule, since a hydrate and its vapor constitute a bivariant system, they may exist at any pressure, if the temperature is low enough, and at any temperature if the pressure is high enough (provided only that a transition or melting point does not intervene).

A pressure-composition diagram of the same system, given in Fig. 11.28, shows the conditions at a fixed temperature, taken arbitrarily here as 50° C. If anhydrous copper sulfate be introduced into a vessel and water vapor introduced continuously, the pressure will rise continuously along *ab* from zero pressure to 4.5 mm. before any water is taken up by the salt, since up to *b* the aqueous pressure is less than the dissociation pressure of the monohydrate. At *b* the monohydrate begins to form, and since there are now two solid phases and vapor present at constant temperature the system is invariant and pressure increase is impossible as long as the three phases coexist. The water vapor continuously introduced is taken up in the formation of the monohydrate, resulting in a change of total composition of the solid phases along the line *bc*; when the conversion of $CuSO_4$ into $CuSO_4.H_2O$ is complete, at *c*, the pressure again rises without affecting the composition of the monohydrate, along *cd*, until the dissociation pressure of the trihydrate is reached at *d* (30 mm.), at which point the trihydrate begins to form. Similar changes in direction of the vapor-pressure curve occur at *e*, *f*, and *g*; the diagram as a whole shows a series of horizontal curves where two solids and vapor are present.

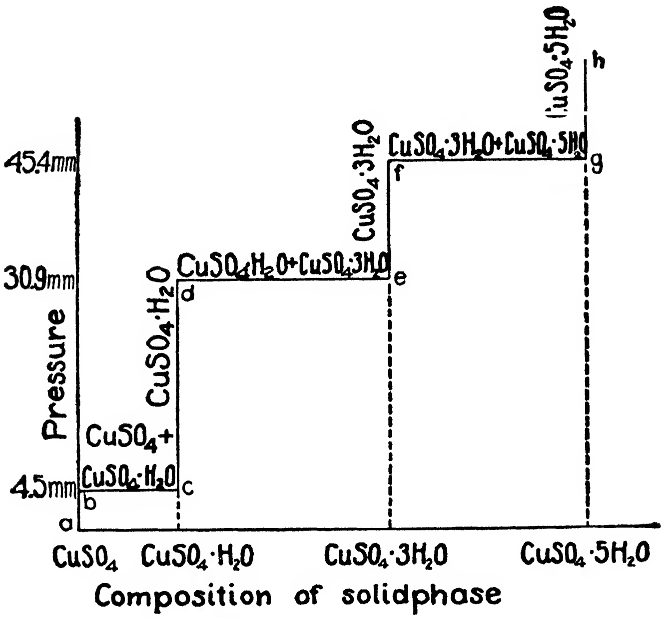

FIG. 11.28. The System, Copper Sulfate-Water. Isotherm at 50° C.

The same general conditions, described above for systems in which a hydrate is formed, are met with in any system in which the two components form a solid compound or compounds, and a vapor composed of one component. Important examples which have been studied include among others the following systems: $CaO - CO_2$; $AgCl - NH_3$, and similar ammines; $Hg - O_2$. Systems in which both components are volatile, as in the case of $NH_3 + HCl$ and $NH_3 + CO_2$, exhibit more complicated relations.

THE EQUILIBRIUM SOLID-SOLID

The methods by which the phase relations of solid alloys are studied are necessarily much more difficult than those for liquid systems, and may be found described in the texts on metallography; the commonest methods are thermal in character (i.e., use of cooling curves and warming curves) or microscopical. Details as to solid systems cannot be given here, but a brief outline of some of the work on a single such system (the iron-carbon system, important because of the use of such alloys as steel) will be given in order to illustrate equilibria of this class.

When iron and carbon (the latter in any reasonably small proportion) are considered, the system is found to give rise to a very considerable number of solid phases, which may enter into various phase equilibria with each other or with the liquid solution of carbon in iron. An enumeration of these solid phases is given below:

$$\text{Three (possibly four) allotropic modifications of iron}\begin{cases}\alpha\text{-ferrite}\\ [\beta\text{-ferrite}]\\ \gamma\text{-ferrite}\\ \delta\text{-ferrite}\end{cases}$$

A carbide of iron, Fe_3C = Cementite
Solid solution of carbon in γ-ferrite = Austenite
Solid solution of carbon in δ-ferrite = ?

$$\text{Two allotropic forms of carbon}\begin{cases}\text{graphite}\\ \text{amorphous carbon}\end{cases}$$

The relationships of these phases have been extensively studied and are embodied in a voluminous literature. There is not an agreement on all of the details, because of the difficulty of the experimental work, but that on which there is common agreement is diagrammed in Fig. 11.29. Leaving out of consideration the small area near *A* in which solid solution of carbon in δ-ferrite is found, the principal relationships will be mentioned. γ-ferrite dissolves carbon, giving rise to a solid solution called Austenite, occupying the field *AEHGF*. The dissolving of carbon in the iron brings a fall in the melting point, giving rise to a liquidus curve (*AC*) and a solidus curve (*AE*) such as always occurs when solid solution is formed. These curves fall in this case to a eutectic *C*, as previously shown in Fig. 11.22; the three phases are a liquid and two conjugate solids, Austenite (*E*) and the carbide of iron Fe_3C known as Cementite (*D*); the eutectic temperature is 1130° C., and the composition is 4.3 per cent carbon. There is of course a second area of conjugate liquid-solid phases, *CBD*, where the solid phase is Cementite. If we now follow the curves of the conjugate solids, *EH* and *DL*, an interruption occurs at the point *H*, where the curve for Austenite (*EH*) meets

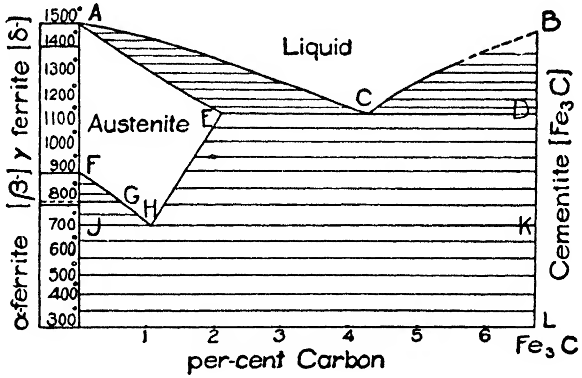

Fig. 11.29. The System, Iron-Carbon

the curve for the transition of γ-ferrite into α-ferrite (*FGH*). Regarding β-ferrite and α-ferrite as identical except for the occurrence of magnetic properties in the β-ferrite, or adopting any of the other views which have been advanced to the effect that the two varieties are not allotropic forms, we may look on the point *F* (900°) as the transition point of pure γ-ferrite into pure α-ferrite, and *FGH* as the curve showing the depression of this transition point by the presence of carbon dissolved in the one solid (Austenite). The intersection of these two curves at *H* (0.89 per cent C and 700°) gives a point of equilibrium of three solid phases, namely, α-ferrite, Austenite, and Cementite, and is called a eutectoid; it resembles a eutectic in being the point of equilibrium between two components (here α-ferrite and Cementite) and a solution (here Austenite), differing from the eutectic in that the solution is here a solid solution in place of a liquid solution. At temperatures below the eutectoid there will be two solid phases in equilibrium, namely, α-ferrite and Cementite; these will settle out on cooling in the usual form of a eutectic conglomerate, which, because of its approximation to homogeneity, is looked upon as a structural element and called Pearlite.

SYSTEMS OF THREE COMPONENTS

In systems of three components, brief study of the new relations of components, variables and degrees of freedom will be helpful. With respect to components, no new principle is involved, but it will be useful to note what general types of reacting substances fall under the heading of ternary systems. Perhaps the most frequently studied cases are those consisting of water with two salts having a common ion, such as $NaCl + KCl + H_2O$; such a system, if it includes new compounds, can have them only of a composition intermediate between that of two or more components, such as double salts or hydrates, and therefore any phase which occurs can have its composition expressed in terms of the three components. It will be noted that a system consisting of water and two salts without a common ion would not fall into the division of ternary systems, since by double decomposition new phases will be produced whose composition is not intermediate between the two salts and water; this very common type of system is a four-component system. On the other hand, two salts without common ion do form a ternary system if water or other substances be absent; although the chemical equation for the double decomposition shows four compounds present, yet any one of them can have its composition expressed in terms of the other three, as was discussed earlier for the system $CaCO_3$, CaO, CO_2, where the system was shown to be binary despite the existence of three compounds. A third common instance of a ternary system consists of a single salt and water where the salt suffers hydrolysis, forming basic or acidic salts whose composition again is not intermediate between the salt and water; in this case, the choice of the three components depends upon convenience in representing the system, and an excellent example exists in the case of bismuth nitrate and water, which is most conveniently regarded as having the three components Bi_2O_3, N_2O_5 and H_2O.

The number of independent variables in a ternary system is larger by one than for a binary system, namely, pressure, temperature and two concentration variables, since a ternary solution requires a statement of its composition with respect to two components before its total composition is fixed. The degrees of freedom for ternary systems follow directly from substitution in the phase-rule equation; five coexisting phases at a quintuple point give an invariant system, four give a univariant system, three a bivariant and so on.

29. **Graphic Representation of Ternary Systems:** Complete representation of all the variables in ternary systems is a complex matter, if at all possible. In most work that has been accomplished such a representation is unnecessary, since the systems studied have been chiefly condensed systems in which the pressure has been kept constant or is ignored. Our problem is therefore to represent the temperature as one variable and the composition as a second. Many geometrical means have been devised for this purpose, of which only one will be discussed and used here, namely, the representation of the composition by triangular coordinates and of the temperature at right angles to the triangular diagram, giving, therefore, a triangular prism as the space figure in which the two variables are represented. At any fixed temperature, the isotherm would then be a triangle, representing the composition, the properties of which will be briefly discussed.

Following the method of Gibbs, an equilateral triangle is chosen and the composition of each pure component represented by a vertex (A, B and C in Fig. 11.30); the total or unit composition is expressed by the altitude of the triangle, and the fractional part which a particular component contributes to a complex is measured by the perpendicular distance of the point representing that complex from the side opposite the vertex for that component. Thus the point m represents a complex made up of component A in amount proportional to the perpendicular ma, B in the proportion mb, and C in the proportion mc, a representation made possible by the property of an equilateral triangle that the sum of the perpendiculars from a point to the three sides is equal to the altitude

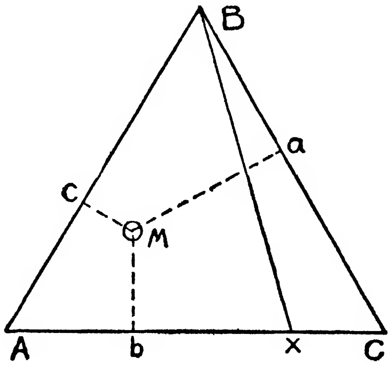

Fig. 11.30. Equilateral Triangle for Composition of a Ternary System

of the triangle. For the general properties of the equilateral triangle the reader is referred elsewhere; yet one such property is of such usefulness to our problem as to warrant explicit statement, namely, that if a complex of A and C represented by the point x is taken and increasing amounts of B added, the composition will change along the straight line xB and therefore all points on such a straight line represent the same ratio of A and C to each other.

To exemplify ternary systems we shall discuss only two examples, that of bismuth nitrate and water and a case of a ternary alloy. The former illustrates the case already mentioned of a salt suffering hydrolysis. The latter is of fundamental importance in metallurgy.

The system bismuth nitrate-water is a three-component system, which may be regarded as made up of the three components Bi_2O_3, N_2O_5 and H_2O. Fig. 11.31 shows schematically the relationships found at 20° C. The system at this temperature shows four ternary compounds which are marked I, II, III and IV in the figure. The composition of each is given below.

TABLE 11.9

SOLID PHASES IN THE TERNARY SYSTEM, $Bi_2O_3 - N_2O_5 - H_2O$

Point in Figure 11.31	Composition	Conventional Formula
I	$Bi_2O_3.N_2O_5.2H_2O$	$BiONO_3.H_2O$ (basic salt hydrate).
II	$Bi_2O_3.N_2O_5.H_2O$	$Bi_2O(NO_3)_2(OH)_2$ (basic salt hydrate).
III	$Bi_2O_3.3N_2O_5.10H_2O$	$Bi(NO_3)_3.5H_2O$ (normal salt hydrate).
IV	$Bi_2O_3.3N_2O_5.3H_2O$	$Bi(NO_3)_3.1\frac{1}{2}H_2O$ (normal salt hydrate).

It will be seen that each of these solid phases may be in equilibrium with solutions varying in composition over a limited range (*ab*, *bc*, *cd*, *de*) and that two solid phases can be in equilibrium only with a solution of fixed composition, as shown by the triangles having *b*, *c* and *d* as their angles. The composition of I, II, III and IV may be ascertained by analysis first of the solutions, which will lie respectively somewhere along the curves *ab*, *bc*, *cd* and *de*, and then of the *wet* solid phases in equilibrium with these solutions. At least two solutions and two solids wet with such solutions must be analyzed for each compound whose composition is to be ascertained. The more of such analyses made the more certainly will the composition of the solid compound be identified, since the analyses of each solution and the corresponding solid wet with the solution must lie along a line joining a point on the curve corresponding to the solution with the point representing the dry solid.

Fig. 11.32 illustrates a triangular prism constructed to show simultaneously variation in composition and temperature. The cross sections of such a prism are the triangular isotherms of the system in question.

In the diagram shown, the point *d* is the ternary eutectic, or quintuple point below which all mixtures of the components can exist only in the solid state. As already stated, for a three component system such a quintuple point gives an invariant system. That is, $F = 0$ and P is therefore equal to 5. Three solid phases, the liquid and gaseous phases are in equilibrium at this point and this point only. The points *a*, *b* and *c* are the three binary eutectics for the three two component systems and *e*, *f* and *g* are the melting points of the three pure components, *C*, *A* and *B*. The three shaded surfaces separate the region of solid phases below from the region of liquid phases above. These surfaces represent a single solid phase (*B* for *bgad*, etc.) in equilibrium with liquid. The lines *ad*, *bd*, and *cd* represent two solid phases in equilibrium with liquid, a univariant system therefore.

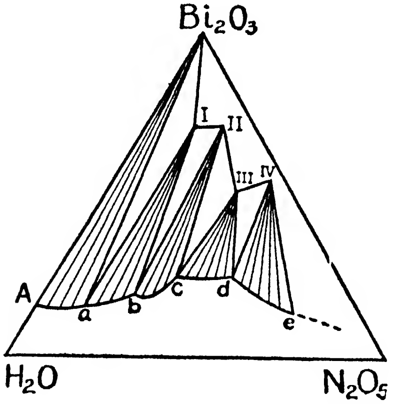

FIG. 11.31. The System $Bi_2O_3 - N_2O_5 - H_2O$ (Schematic)

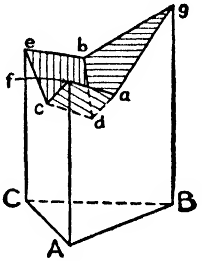

FIG. 11.32. Ternary System Showing Ternary Eutectic

If then we consider any liquid of composition above the diagram to be cooled down gradually, a single solid will separate at the corresponding composition on one of the surfaces, and, as the temperature continues to drop, the composition must continue to vary along this surface as more of the solid component settles out, until a point is reached on one of the eutectic curves *ad*, *bd*, or *cd*. Here a second solid will begin to precipitate and the composition and temperature will vary along the specific eutectic curve until, finally, at *d*, the system becomes invariant. No change in composition or temperature will then occur until the mass has completely solidified. It is clear that a knowledge of such a complete diagram will enable the metallurgist to foretell in what order the three components will solidify from a given complex taken. Further, since the ternary eutectic is necessarily lower than all the binary eutectics it becomes possible to contrive especial low melting alloys of three components. The following examples will illustrate the point.

TABLE 11.10

EUTECTICS IN TERNARY ALLOYS

Pb – Bi – Sn			Pb – Bi – Cd		
M. P. of Component	Binary Eutectic	Ternary Eutectic	M. P. of Component	Binary Eutectic	Ternary Eutectic
Pb = 325°	Pb + Bi = 127°	96°	Pb = 320°	Pb + Cd = 245°	92°
Bi = 268°	Bi + Sn = 133°		Cd = 320°	Cd + Bi = 145°	
Sn = 232°	Pb + Sn = 182°		Bi = 270°	Pb + Bi = 125°	

EXERCISES (11)

1. The following weights of bromine per 10 cc. of water and CS_2 were found at 20° C. in a distribution experiment:

H_2O	0.176	0.030	0.020	0.0011
CS_2	14.1	2.46	1.55	0.09

Calculate the distribution coefficient.

2. Show that acetic acid exists mainly as double molecules in benzene from the following distribution data between benzene and water:

Benzene	0.043	0.071	0.094	0.149
Water	0.245	0.314	0.375	0.500

3. If 100 cc. water contained 0.3 g. bromine, what fraction would be extracted (*a*) by using 100 cc. CS_2 in one extraction, (*b*) by using 50 cc. in each of two extractions? How many successive extractions using 10 cc. CS_2 would theoretically be necessary to remove 99 per cent of the bromine?

4. A mixture of 30 g. phenol and 70 g. water is kept at 30° C. What are the amounts and compositions of the phases?

5. A mixture of 80 per cent phenol and 20 per cent water is maintained at 40° C. What will be the effect of successive additions of water (*a*) on the liquid, (*b*) on the vapor phase?

6. From the data in Table 11.6 determine the constants A and B for the rectilinear diameter: $c_1 + c_2 = A + Bt$ where c_1 and c_2 are the weight per cents of phenol in the two layers at temperatures $t°$ C. Hence find the consolute temperature.

7. Determine the consolute temperature for propionic nitrile and water from the following data:

$t°$ C.	c_1	c_2
40	10.7	92.1
60	12.7	88.5
100	22.4	75.5

8. Determine the melting point of an alloy containing 70 per cent Pt and 30 per cent Au given the following:

Per cent Pt	0	10	20	30	40	50	60	100
Crystallization begins	1064°	1174	1299	1437	1503	1544	1579	1744
Crystallization ends		1079	1109	1177	1203	1253	1285	

What is the composition of the first portion of liquid from the alloy?

9. The vapor pressure of water at 95° C. is 633.78 mm. and that of naphthalene is 15.5 mm. Assuming the two substances are insoluble in each other calculate the weight of naphthalene which will be distilled from this mixture at 95° C. along with 100 cc. water.

CHAPTER 12

ELECTRICAL CONDUCTANCE AND IONIZATION

THE distinction between conductors and non-conductors of electricity was first made experimentally by Stephen Grey (1728–1736). Good conductors are metals, many sulfides such as galena and pyrites, aqueous solutions of acids, bases and salts, fused salts, and water when not perfectly pure. Bad conductors, or insulators, are dry solid salts, metallic oxides, ice, some metallic compounds, such as $SnCl_4$, $AsCl_3$, HgI_2, AsS_2, and As_2S_3, most non-metallic elements, pure water, most organic compounds, mica, and glass, all at the ordinary temperature.

1. **Classes of Conductors:** Early experimenters, such as Davy, noticed that conductors could be divided into two classes: (i) those in which the electricity moves without producing chemical changes; (ii) those in which chemical changes always accompany the passage of the current. Metals are typical of the first class, called *metallic conductors*. The second class comprises what are called, following Faraday, *electrolytes*, or *electrolytic conductors*. Davy noticed that the conductivity of metals diminishes with rise of temperature, while Ohm found that of electrolytes to increase. Carbon is the principal exception to this rule: it conducts metallically but its conductivity increases rapidly with rise of temperature. Silicon also shows this peculiarity. Hittorf noted that the conductivity of copper sulfide is increased by traces of free sulfur and the conductivity of the native sulfide depends on free copper. Silver sulfide appears to conduct metallically because of the formation of fine threads of silver. The supposed metallic conduction of fused silver halides is also due to threads of silver stretching from pole to pole.

2. **Unipolar Conduction:** A peculiar class of conductors are those known as *unipolar*, which allow electricity to pass from one electrode only. Erman noticed that if wires from a battery are introduced into a piece of dry soap no current passes. If the soap is connected to earth, current flows to earth from the negative wire only. The positive electrode becomes coated with an insulating layer of fatty acid. If the soap is moist, this is dissolved and current passes between the two wires. The same phenomenon has been noticed in solutions, and whenever electrolysis leads to the formation of a sparingly soluble, poorly conducting, substance, which adheres to one of the electrodes, unipolar conduction occurs. This is applied in the aluminum rectifier, which consists of a cell in which the anode is of aluminum and the electrolyte a solution of alkali phosphate, or borate, or a mixture of equivalent amounts of

ammonium phosphate and borate. In this way an alternating is converted into a direct current.

3. Theory of Metallic Conduction: Metallic conduction differs from electrolytic conduction in the following particulars: (1) There are no products of electrolysis; (2) there is no polarization; solid electrolytes, e.g., barium sulfate, exhibit a polarization of over one volt; (3) a substance which dissolves in water without decomposition to give a solution containing ions will probably conduct electrolytically in the solid state; (4) the resistance of a pure solid conductor has a minimum value at some temperature, while that of an electrolyte always diminishes with rise of temperature; (5) selective absorption and emission in the ultraviolet and infrared are exhibited by electrolytic conductors, while in the case of metallic conductors, absorption and emission are continuous.

On the theory of metallic conduction now accepted, free electrons are supposed to carry the current, the positive ions of the metal being immobile, or practically so. Other results lead to this theory, such as the work of Tolman and Stewart, who calculated the ratio of the effective mass of the current carriers to the quantity of electricity carried. This ratio indicates that the carriers are free negative electrons. The thermionic emission from metallic wires at high temperatures is also in good agreement with the electron theory.

In the theory of metallic conductance due to Drude the electrons in a metal are assumed to have the same mean kinetic energy as a gas molecule at the same temperature, and collisions between electrons and between electrons and metal atoms occur in the same way as those between gas molecules. The conduction is explained by the directive effect of the applied E. M. F. on the motion of the electrons, which preserve their random motion unchanged. On these assumptions, with certain simplifications, the conductivity of a metal can be shown to be given by:

$$\kappa = (e^2nl)/(2\sqrt{2\alpha Tm}), \tag{12.1}$$

where e = electronic charge; n = number of molecules per unit volume; l = path traversed by an electron between two successive collisions; T = absolute temperature; m = mass of electron; α is a constant given by the relation $\frac{1}{2}mv^2 = \alpha T$, where v is the velocity of the electron. Thus:

$$\kappa = e^2nl/2mv. \tag{12.2}$$

On the assumption of the classical kinetic theory we replace $\frac{1}{2}mv^2$ by $(\frac{3}{2})kT$, where k is Boltzmann's constant, hence:

$$\kappa = e^2nlv/4\cdot\tfrac{1}{2}mv^2 = e^2nlv/6kT. \tag{12.3}$$

By a similar calculation the coefficient of thermal conductivity is found to be given by:

$$\theta = \tfrac{1}{2}nklv, \tag{12.4}$$

hence

$$\theta/\kappa = 3k^2T/e^2 = T \times \text{const.}, \tag{12.5}$$

which is the law of Wiedemann and Franz.

Although experimental evidence on the whole supports Drude's theory, it is not free from difficulties. In the first place, the Wiedemann-Franz law is only approximate. The experiments of Onnes at very low temperatures (Sec. 12, 4) show that a state of "super-conductivity" is reached before the absolute zero, when the resistance has practically vanished, and the resistance falls off more rapidly with temperature than according to the Wiedemann-Franz law.

The simplest assumption would appear to be that the number of free electrons is equal to the number of metal atoms. This, however, would yield a concentration of the electron gas, that is, their number per cubic centimeter, which is extremely high in comparison with the concentration of gas molecules under ordinary conditions of temperature and pressure. Now, with gases, the molecular concentration may be effectively reduced by increasing the temperature. Owing to the small volume change of a metal with temperature, however, the electron gas concentration is still quite large at very high temperatures.

A method of accounting for the properties of gas molecules at low temperatures where their concentration is large has recently been suggested by Bose and Einstein and by Fermi. The application of this same treatment to the electron gas in a metal gives for the Wiedemann-Franz constant a value 7×10^{-11} at 291° K. in remarkably good agreement with observed values.

The resistance of a metallic conductor is proportional to the probability of collision between electrons and atoms. In wave mechanics such a collision involves the scattering of the wave representing the electron by the irregularity of potential representing the atom. If the lattice of the atoms is regularly spaced as in crystals at the absolute zero the electron wave will not be scattered, that is, the resistance will be zero. At higher temperatures the atoms vibrate, the lattice is no longer regular and scattering occurs, that is the resistance increases, roughly proportional to the temperature. Quantitative consideration of such scattering permits calculation of the resistance and the good agreement with experiment is one of the most important results of the wave mechanical theory of metallic conduction.

4. **Effect of Temperature on Resistance of Metals:** The relation between the specific resistance of a metal and temperature may be expressed by the formula

$$r = a + bT + cT^2. \tag{12.6}$$

For small ranges of temperature the linear relation,

$$r = a + bT, \tag{12.7}$$

is sufficient, the coefficient having the value about $(1/r)dr/dT = 0.004$ (cf. coefficient of expansion of a gas), although for magnetic metals it is higher. The coefficient increases with temperature, large changes being observed in the neighborhood of transition points and melting points. The coefficients for liquid metals are usually one fifth those for solid.

At very low temperatures the resistance diminishes very rapidly with the temperature, and, at 3° or 4° K., the resistance may be zero, i.e., the metal is a perfect conductor. Our knowledge of the resistance of metals at very low temperature is due to the work of Kamerlingh Onnes and his co-workers at Leyden. In the case of mercury, for example, at 13.9° K. the resistance is 0.034 that of solid mercury at 273° K. At 4.3° K. it is 0.0013 times, and at 3° K. less than 0.0001 times. Gold and lead behave similarly. Metals at these low temperatures are said to be in a "super-conducting" state. Some metals, such as platinum, copper, and metals which tend to form solid solutions, do not become super-conducting, but the resistance decreases to a minimum, and then rises again with further fall in temperature.

The existence of the super-conducting state at once rules out these metals for use as resistance thermometers for measuring very low temperature. For such measurements Giauque[1] has suggested the use of amorphous carbon, the temperature coefficient of resistance of which increases greatly at lower temperatures. A more interesting method lies in the dependence of magnetic susceptibility on temperature. Since the process of magnetization of paramagnetic substances involves an increase in order, it is always accompanied by a decrease in entropy ΔS. An amount of heat corresponding to $T\Delta S$ must therefore be evolved. If the magnetized substance is then thermally isolated and the magnetic field removed, demagnetization will occur adiabatically with a corresponding reduction in temperature. Thus if a paramagnetic substance at a temperature around 1.5° K., obtained by boiling liquid helium, is first isothermally magnetized, then isolated thermally from its surroundings and the magnetic field removed, the adiabatic demagnetization results in temperatures considerably below 1° K. Giauque using a gadolinium salt obtained 0.097° K. Using potassium chromium alum, de Haas and Wiersma claim to have reached 0.0044° K.

5. Conductivity of Alloys: The electrical conductivity of alloys is characteristic. Each component contributes to it, so that if an alloy is purely a mechanical mixture its conductivity is an additive property of the volume percentages of the components. Isomorphous mixtures have a conductivity which is always less than that calculated from the mixture law, and is diminished by addition of foreign substances. The formation of a solid solution is accompanied by considerable increase in

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[1] *Ind. Eng. Chem.*, 28, 743 (1936). Giauque here gives a survey of the field.

the resistance of the alloy, and this increases also with increase of concentration. When the components form a compound this possesses a peculiar and characteristic conductivity which is relatively high, and is diminished by additions of foreign substances. The temperature coefficients of intermetallic compounds differ but little from the normal value (0.004) for pure metals. In the case of solid solutions the temperature coefficients are much lower.

6. **Theory of Electrolytic Conduction:** The current flowing through an electrolytic conductor under the influence of an applied potential difference involves a transport, not of electrons as in a metallic conductor, but of charged particles called ions. These ions may be positively or negatively charged and will consequently move in opposite directions through the conductor for a given applied field. The positively charged ions, moving towards the negative electrode, the cathode, are termed cations; the negatively charged ions move towards the positive electrode, the anode, and are termed anions. The current carrying capacity of a given electrolytic conductor will thus depend on several factors, such as the numbers of anions and cations present, their charges and their velocities, the latter of course partly depending upon the magnitude of the potential drop across the conductor.

7. **Faraday's Laws of Electrolysis:** It has already been stated in Chapter 1, 10 that the relationship between the quantity of electricity passing through an electrolyte and the amount of material produced at the electrodes was discovered by Faraday and is embodied in the two laws of electrolysis. The reliability of Faraday's laws is one of the very well-established facts in experimental science and provides a means of measurement of the quantity of electricity. The amount of material deposited by a current of I amperes flowing for t secs. is $It/96500$ g. equiv., or if e is the equivalent weight of the electrolyte, $Ite/96500$ g. The experimental determination of this weight provides a means of calculating the current strength I amp. or the quantity of electricity, It coulombs.

8. **The Coulometer:** The coulometer is the apparatus used for this measurement of the quantity of electricity. The silver coulometer is probably the most reliable. Silver is deposited on a platinum dish acting as a cathode from a solution of highly purified silver nitrate. Contamination of the deposit by products formed around the anode is prevented by surrounding the latter with a porous cup. The deposit is carefully washed, dried and weighed. From the weight, the current can be calculated. For general purposes the copper coulometer is used, involving the determination of the weight of copper deposited on a copper plate from an acid solution of copper sulfate, containing a small amount of alcohol or tartaric acid to prevent oxidation of the deposit. Lead from

solutions of lead silicofluoride and electrolytic gas from water, either acid or alkaline, have also been used in rough measurements.

9. Measurement of Electrolytic Conduction: The resistance, R, of a conductor of uniform cross-section, A, is found to be directly proportional to its length, L, and inversely proportional to its cross-section:

$$R \propto L/A.$$

Thus

$$R = r \cdot L/A, \tag{12.8}$$

where r is the *specific resistance* or *resistivity*. The reciprocal of the resistance is termed the conductance and the reciprocal of the specific resistance, the *specific conductance* or *conductivity*, κ:

$$\kappa = 1/r = L/RA. \tag{12.9}$$

Now the conductivity of a solution of an electrolyte depends on its concentration. Thus, to compare results for different solutions it is necessary to take the concentration of the solutions into consideration. This may most easily be done by using the *equivalent conductance*, Λ, defined as the ratio of the conductivity, κ, to the concentration, c^*, expressed in equivalents per cubic centimeter (not per liter): $\Lambda = \kappa/c^*$. The reciprocal of this concentration, the number of cubic centimeters containing one equivalent is called the dilution and denoted, φ. Thus if a volume of solution containing one equivalent is enclosed between two parallel plates one centimeter apart, the conductance will be the equivalent conductance. This is easily seen, since the solution may be divided into φ cubical cells, each of unit volume and each having the specific conductance, κ. Hence the total conductance will be $\kappa\varphi = \kappa/c^* = \Lambda$.

An alternative unit, used by Ostwald, is the *molar conductance*, μ, defined as the ratio of the conductivity to the concentration, c, expressed in moles per cc.: $\mu = \kappa/c$.

Since the measurement of conductance is thus a measurement of resistance, the familiar Wheatstone bridge method may be employed. For solutions of electrolytes, owing to the possibility of electrolysis and subsequent polarization effects, the use of direct current is in general prohibited for highly conducting solutions. Kohlrausch[1] first showed that the most satisfactory method of eliminating polarization is by the use of alternating currents. This introduces certain difficulties in connection with the inductance and capacity of the Wheatstone bridge circuit which however can usually be taken care of by a proper arrangement of the apparatus. Fig. 12.1 illustrates the simplest essentials of the ar-

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[1] Kohlrausch and Holborn, *Leitvermögen der Electrolyte.* See also Grinnell Jones, *J. Am. Chem. Soc.*, **50**, 1049 (1928) et seq.; Shedlovsky, *ibid.*, **54**, 1411 (1932).

rangement. The added refinements can be found in the original literature to which reference is given. The bridge balance is determined by a telephone or other alternating current detector. The known resistances in the resistance box are adjusted until approximately equal to the resistance of the electrolyte. Under this condition the connection to the bridge wire will be approximately in the center of the wire. A fine adjustment of this is made until a minimum sound is heard in the telephone. With this condition the bridge is balanced and the ratio of the resistances of the box and electrolyte will be the ratio of the resistances of the two sections of the bridge wire, which, if uniform, is simply the ratio of the two lengths of the sections.

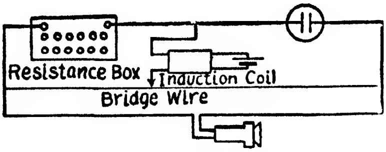
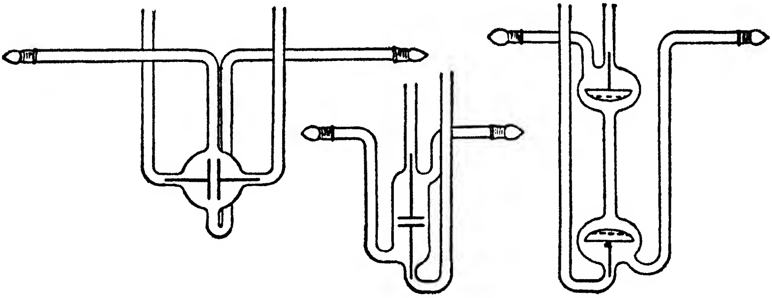


Fig. 12.1. Experimental Arrangement for Conductivity Measurements

The electrolyte solution is enclosed in a conductivity cell. Several types due to Washburn are illustrated in Fig. 12.2. The dipping electrode shown in Fig. 12.3 is often very convenient. Since polarization effects are reduced by increasing the electrode area, electrodes are frequently coated with platinum black thus reducing the surface density of deposited ions. In such cases, however, the electrodes tend to adsorb the electrolyte so that in studying a series of solutions of different concentrations of the same electrolyte, the more dilute solutions should be used first since otherwise electrolyte adsorbed on the electrodes from the more concentrated solutions would be desorbed in the more dilute solutions.



Figs. 12.2. Conductivity Cells—Washburn Types

For poorly conducting solutions a direct current method[1] may be used which amounts essentially to using a galvanometer as an ammeter

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[1] Kraus and Fuoss, *J. Am. Chem. Soc.*, 55, 23 (1933).

and computing the cell resistance by Ohm's law from the current so measured and the voltage applied.

10. **Cell Constant:** The solution to be examined when contained within a conductivity cell corresponds to a particular volume and shape controlled by the area of the electrodes and their distance apart. It has been shown that:

$$\kappa = L/RA. \tag{12.9}$$

Hence, for a particular cell L/A should be a constant, whence

$$\kappa = C/R, \tag{12.10}$$

where C is known as the cell constant. By careful construction of cells it is possible to determine C from the measured dimensions. In practice, however, it is more easily determined by using a liquid of known conductivity in the cell. The usual standard[1] is a solution of 7.47896 g. of potassium chloride in 1000 g. of water, the specific conductance of which at 25° C. is 0.012852 reciprocal ohm (usually designated mho).

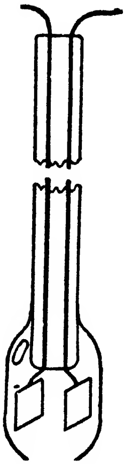

FIG. 12.3. Dipping Electrode Cell

11. **Conductivity of the Solvent:** A measurement of the conductivity of a solution may only be interpreted as a conductivity due to the solute if the solvent is a non-conductor. Few solvents are actually non-conductors but the vast majority, when pure, have such low conductivities that they may be either neglected in comparison with the total conductivity of the solution, or simply subtracted from the measured value for the solution if such a correction would involve a change greater than the experimental error of the determination.

It is essential, therefore, to use highly purified solvents since the presence of impurities, especially electrolytes, increases the conductivity enormously. Kraus and Fuoss found the following values at 25° C. for various solvents: dioxane, 5×10^{-15}; benzene, 3×10^{-15}; ethylene dichloride, 3×10^{-10} mho. In the case of water, the purest sample ever obtained was prepared by Kohlrausch and Heydweiller by repeated low temperature distillation and collection finally in a glass cell which had previously been kept filled with conductivity water for ten years to remove traces of soluble matter from the glass. The conductivity was 0.0384×10^{-6} mho at 18° C. In air the conductivity rises rapidly to 0.7×10^{-6} owing to solution of carbon dioxide.

12. **Effect of Temperature on Conductivity:** The conductivity of an aqueous solution of an electrolyte increases approximately two per cent

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[1] Parker and Parker, *J. Am. Chem. Soc.*, **46**, 332 (1924).

per degree rise in temperature. The effect is complex, however, involving a changing viscosity of the solution with change in temperature as well as the various effects of temperature on the electrolyte which will be referred to later. Suffice to point out here that very careful temperature control is necessary in experimental work.

13. **Ionic Migration. Transport Number:** It has already been pointed out that the current carrying capacity of a given electrolytic conductor will depend, among other things, on the velocities of the ions present. Since it is known that ions of different elements have different sizes it might be expected that they would experience different frictional effects on their passage through the solvent during an electrolysis and hence would travel with different velocities. It follows, therefore, that the total current carried will not be evenly divided between the anions and cations, but that the faster moving ions would carry the larger fraction. This was first established by Gmelin and later by Daniell and Miller but on account of the experimental difficulties most of the early reliable information is due to Hittorf.

The principle involved may be seen from Fig. 12.4. The trough *AB* is divided by partitions *C* and *D* into three parts. These diaphragms are permeable to the solution and their object is to prevent mixing of the liquids in the different compartments by diffusion. The trough is filled with hydrochloric acid, the ions of which move with velocities in the ratio $H^+/Cl^- = 5$. Let one faraday be passed through the solution from electrode *B* to *A*. This will cause the electrolysis of one equivalent of the electrolyte. Since the ionic velocities are in the ratio of 5 : 1, 5/6 equivalent of H^+ will pass every section of the electrolyte in one direction and 1/6 equivalent of Cl^- in the opposite direction. The following changes must therefore occur:

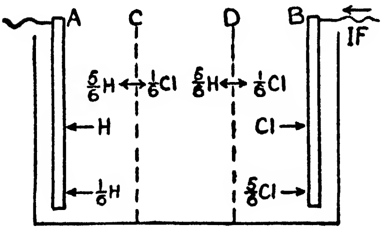

FIG. 12.4. Current Transport by H^+ and Cl^- ions.

(1) In *AC*. The total loss of H^+ is one equivalent, of which 5/6 migrated in from the rest of the system and thus 1/6 was taken directly from *AC*

(2) In *BD*. The total loss of Cl^- is one equivalent, of which 1/6 migrated in from the rest of the system and thus 5/6 was taken directly from *BD*.

Hence, so far as the neutral electrolyte HCl is concerned, the loss for *AC* was 1/6 equivalent and for compartment *BD* 5/6 equivalent HCl; that is, in the ratio of the velocities of the ions moving away from the electrodes.

This example may thus be generalized. If in an electrolysis, one equivalent of anion is deposited at the anode, a fraction t_+ is taken from the immediate vicinity of the electrode and a fraction t_- migrates into the anode compartment from the bulk of the solution, where $t_+ + t_- = 1$. Hence t_+ equivalents of cation must migrate out of the anode compartment to make up the total current of one faraday crossing each section. The current is thus carried by cations and anions in the ratio of t_+/t_-. The fraction t_+ is the Hittorf *transport* (or transference) *number* of the cation, t_- that of the anion. If the velocities of anion and cation are v and u respectively it follows that:

$$t_+/t_- = u/v. \tag{12.11}$$

Since

$$t_+ + t_- = 1,$$

therefore

$$t_+ = \frac{u}{u+v}, \quad \text{and} \quad t_- = \frac{v}{u+v}\cdot \tag{12.12}$$

14. **Determination of Transport Number. Hittorf Method:** Fig. 12.5 shows a form of apparatus used by Hittorf. The electrolyte used was sodium chloride. The anode was cadmium and the cathode, platinum. Cadmium chloride is formed at the anode and Cd^{++} ions move towards the cathode, but, being slow, never catch the Na^+ ions, the two layers of liquid remaining separate. At the cathode, all the Cl^- ions having migrated towards the anode are replaced by OH^- ions which, being fast, cause a mixing as shown. The hydrogen evolved at the cathode escapes easily and does not cause mixing. Fig. 12.6 shows alternative forms of apparatus that have been used.

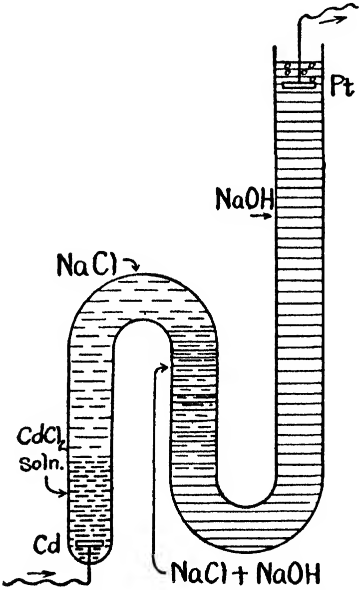

Fig. 12.5. Hittorf's Transport Number Apparatus

The calculation of transport numbers may best be illustrated by an example. The original NaCl solution contained 0.01784 per cent Cl. The weights of solution in the three compartments were: anode part, 226.99 g.; middle part, 195.24 g.; cathode part, 331.49 g. The weights of Cl before electrolysis were thus, 0.04048 g., 0.03482 g. and 0.05913 g. The weights found by analysis after the electrolysis were, 0.04671 g., 0.03483 g. and 0.05289 g. The middle part was unchanged showing that diffusion was absent, the anode gained 0.00623 g. and the cathode lost 0.00624 g. The electrolysis had been brought about by a voltage of 150 volts applied for 108 minutes, being measured in a silver coulometer wherein silver was deposited equivalent to 0.01021 g. Cl. The transport number of Cl in NaCl is thus 0.00624/0.01021 = 0.611.

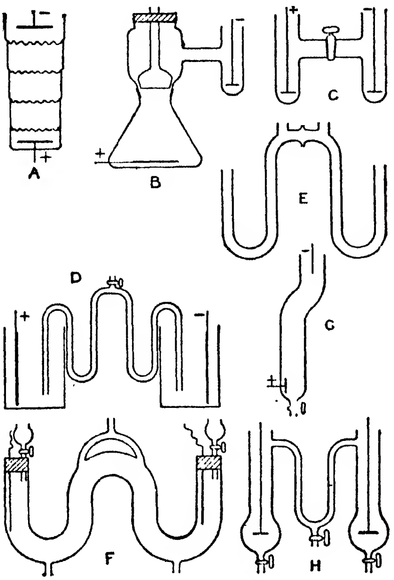

Fig. 12.6.

It must be observed that the interpretation of results is not always as simple as is indicated in the above example. The presence of a complex ion will always yield incorrect results unless an allowance is made. Thus, cadmium iodide yields the ion $CdI_4^{=}$ whence cadmium is actually transported to the anode and an apparent transport number of the anion greater than unity may be found, or a negative transport number of the cation.

15. **The Moving Boundary Method:** Lodge filled a tube with saline jelly to which phenolphthalein was added, colored red by a trace of alkali. The ends were placed in contact with dilute acid and on passing a current the color was progressively bleached. From the rate of motion of the boundary the actual velocity of H^+ could be calculated.

Lodge's method was improved by Whetham who used two solutions with a common ion, with the same concentrations and nearly the same conductances but different in color and density, stratified in a vertical tube. In one example $K_2Cr_2O_7$ and K_2CO_3 were used. The colored ion moved and the rate of motion of the boundary could be followed. From the measured current and the boundary rate the transport number may be calculated. The type of apparatus used is shown in Fig. 12.7. In Fig. 12.7(2) the use of two boundaries eliminates the necessity of measuring the current used. A solution of salt AB, to be investigated, is stratified between solutions of salts AB' and $A'B$ having the same anion and cation respectively but lighter and denser than AB, giving the boundaries a and b, which may be seen owing to the different refractive indices of the solutions, even when these are colorless. After the current has passed, the boundaries move to a' and b'. The ratio $aa'/(aa' + bb')$ then gives the transport number of one ion. For the boundaries to remain sharp it is apparent that the ions B' and A' must have smaller velocities than B and A.

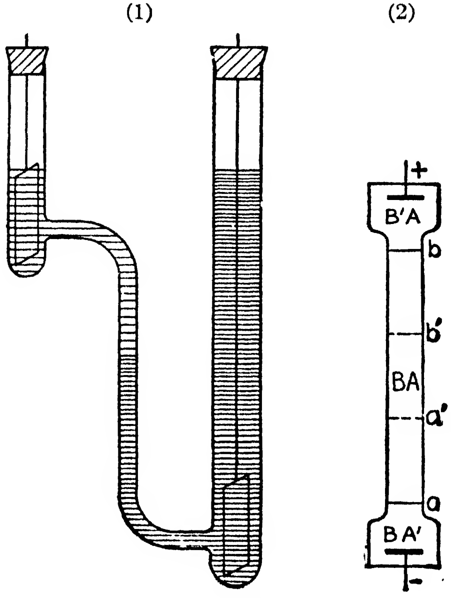

FIG. 12.7. Whetham's Apparatus for Moving Boundary Measurements

The moving boundary method has been used by MacInnes[1] and his co-workers to obtain transport data of high precision over a relatively large concentration range in aqueous solutions.

In Table 12.1 are given the values of the cation transport numbers obtained by MacInnes for 0.1 N aqueous solutions of some uni-univalent electrolytes at 25° C. Other data will be discussed later.

A third method of determining transport numbers, namely, from E. M. F. measurements of certain types of concentration cells will be discussed in a later chapter.

16. Solvent Transport: In the methods of determining transport numbers just mentioned, it has been assumed that the ions of the dissolved electrolyte alone are transported and that the solvent remains

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[1] MacInnes and Longsworth, *Chem. Rev.* **11**, 171 (1932).

TABLE 12.1

Electrolyte	t_+
HCl	0.8314
LiCl	0.3168
NaCl	0.3853
KCl	0.4898
NH_4Cl	0.4900
KBr	0.4834
KNO_3	0.5128
$AgNO_3$	0.4682

stationary. If, however, the ions themselves are solvated there will obviously be a solvent transport on that account. If A and C are the numbers of molecules of solvent bound to anion and cation respectively, then the number of molecules of solvent, x, transported per faraday passing will be given by

$$x = t_-A - t_+C, \tag{12.13}$$

where t_+ and t_- are the cation and anion transport numbers.

Two methods have been suggested to determine this in aqueous systems. The first method, due to Nernst, calls for the presence of some substance which will not move with the current and may thus be used as a reference basis for concentration changes. Such substances as various sugars or alcohols have been used. The second method involves a direct measurement by weight of the water transported through a parchment diaphragm dividing the cell into two compartments. In all cases, and especially for very dilute solutions, allowance must be made for the water transported by electro-endosmosis.

Using these methods and on the assumption that the hydrogen ion is present in water as the H_3O^+ ion, the relative hydrations of other ions have been found to be: K^+, 5; Na^+, 8; Li^+, 14; Cl^-, 4. It might at first sight be supposed that the K^+ ion being larger than the Li^+ ion could accommodate more water molecules around it and thus be more heavily hydrated. These hydrates are not, however, to be considered as compounds in the strict chemical sense but arise from the dipole nature of the water molecule. Owing to the smallness of ionic dimensions the electric fields around ions are very intense and dipoles are polarized and attracted to them. Now the charges on the alkali metal ions are all the same but since the Li^+ ion is the smallest, its field is most intense and hence the polarization greatest; the 'hydration' consequently largest.

✓ **17. Ionic Mobilities:** Consider a solution in a centimeter cube with electrodes at opposite faces as indicated in Fig. 12.8, with a potential of 1 volt between the electrodes. By definition the current through the solution is κ amps., with κ the specific conductance. If it is assumed that the electrolyte in the solution is present only as anions and cations, the current flowing may be calculated in terms of the velocities. Let u and v be the velocities in cm. per sec. per volt per cm. for cation and anion respectively. In one second all cations will have moved through a length u in a direction normal to the electrodes and similarly all anions a length v. These lengths u and v cm. will correspond to volumes of solution u and v ccs. If the concentration of the solution is c^* equivalents per cc. the volumes u and v will contain uc^* and vc^* equivalents of cation and anion respectively. Since each equivalent transports 96,500 coulombs, the total transport per second will be $96{,}500c^*(u + v)$. By definition of equivalent conductance $\kappa = \Lambda c^*$. Hence, $\kappa = \Lambda c^* = 96{,}500c^*(u + v)$, whence $\Lambda = 96{,}500(u + v)$. Writing $l_c = 96{,}500u$ and $l_a = 96{,}500v$, then

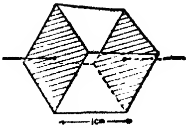

FIG. 12.8

$$\Lambda = l_a + l_c. \tag{12.14}$$

The quantities l_a and l_c were termed by Kohlrausch the *mobilities* of the anion and cation respectively and it is seen they are directly proportional to the ionic velocities. Since it has been shown that the ratio of the velocities is the ratio of the transport numbers $t_+/t_- = u/v$, then also $t_+/t_- = l_c/l_a$. Hence under the conditions specified above where the conductance is that of a solution containing only ions:

$$l_a = t_-\Lambda \qquad \text{and} \qquad l_c = t_+\Lambda, \tag{12.15}$$

whence the mobilities are frequently called the equivalent conductances of the individual ions and may be calculated from the transport numbers. Table 12.2 gives values of the mobilities of various ions at 18° C. The values of c are temperature coefficients $d \ln l/dt$ from which mobilities at other temperatures may be calculated provided the range is in the neighborhood of 18–25° C.

The mobilities of H^+ and OH^- are seen to be noticeably higher than those of other ions. The explanation lies in the peculiarity of their hydrated condition in aqueous solution. Thus the hydrogen ion is present not as a proton but in the hydrated form H_3O^+. Any one of the three hydrogen atoms in this ion has an equal chance of being transferred as a proton to a neighboring water molecule to produce a new oxonium ion, H_3O^+, which in turn can pass on a different proton to its neighboring water molecule. The transfer, therefore, though of protons, is not a transfer of the same proton through the solution. Confirmation of this is shown by the normal value that is obtained for the mobility of H_3O^+ in liquid hydrofluoric acid containing traces of water.[1] In a similar

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[1] Fredenhagen and Cadenbach, *Z. physik. Chem.*, **A146**, 258 (1930).

TABLE 12.2

MOBILITIES OF IONS AT 18° C.

	l	$c \times 10^4$		l	$c \times 10^4$		l	$c \times 10^4$
Li^+.....	33.3	265	SCN^-	56.7	221	$\frac{1}{2}Mg^{++}$	45.9	256
Na^+....	43.4	244	$C_5H_9O_2^-$	25.7	244	$\frac{1}{2}Zn^{++}$	47.0	254
F^-......	46.6	238	CHO_2^-	47*	—	$\frac{1}{2}Cu^{++}$	45.9	—
Ag^+....	54.0	229	$C_2H_3O_2^-$	35*	238	$\frac{1}{2}Cd^{++}$	46.4	245
K^+.....	64.6	217	$C_3H_5O_2^-$	31*	—	$\frac{1}{2}Sr^{++}$	51.9	247
Cl^-.....	65.5	216	IO_3^-	34.0	234	$\frac{1}{2}Ca^{++}$	51.9	247
Tl^+.....	65.9	215	ClO_3^-	55.1	215	$\frac{1}{2}Ba^{++}$	55.4	239
I^-......	66.6	213	BrO_3^-	47.6	—	$\frac{1}{2}Pb^{++}$	60.8	240
Br^-.....	67.7	215	IO_4^-	43	—	$\frac{1}{2}Ra^{++}$	58*	239
Rb^+....	67.5	214	ClO_4^-	64	—	$\frac{1}{2}C_2O_4^{=}$	63.0	231
Cs^+.....	68	212	NO_3^-	61.8	205	$\frac{1}{2}SO_4^{=}$	68.5	227
H^+.....	313.9	154	OH^-	174	180	$\frac{1}{2}CrO_4^{=}$	72*	—
NH_4^+ ..	64.7	222	$\frac{1}{2}Ni^{++}$	44	—	$\frac{1}{2}CO_3^{=}$	60*	270
$\frac{1}{2}Be^{++}$..	28	—	$\frac{1}{2}Fe^{++}$	45	—	$\frac{1}{4}Fe(CN)_6^{\equiv}$	95.0	—
$\frac{1}{2}Mn^{++}$..	44	—	$\frac{1}{3}Fe^{+++}$	61	—	$\frac{1}{3}Al^{+++}$	40	—
$\frac{1}{2}Co^{++}$..	43	—	$\frac{1}{3}Cr^{+++}$	45	—	$\frac{1}{3}La^{+++}$	61.0	—
						$\frac{1}{3}Sm^{+++}$	53.5	—
						$\frac{1}{4}Th^{++++}$	23.5	—

manner a transfer of a proton from a water molecule to a hydroxyl ion would give the appearance of a hydroxyl ion transfer in the opposite direction.

18. Effect of Concentration on Equivalent Conductance: Experiment shows that the equivalent conductance of an electrolyte varies with its concentration. The variation is apparently different for different types of electrolytes or for the same electrolyte in different solvents. One uniform observation, however, is that in dilute solutions the equivalent conductance increases with dilution and approaches a limiting value known as the equivalent conductance at zero concentration Λ_0 or at infinite dilution Λ_∞.

In Fig. 12.9 are shown values for Λ at various concentrations of potassium chloride, sodium chloride and acetic acid in water. In Fig. 12.10 similar data[1] are shown for I, HIO_3 in water, II, $NaBrO_3$ in ammonia; III, NaI in amyl alcohol; IV, $(C_6H_{11})_4N.NO_3$ in ethylene chloride; V, KNH_2 in ammonia. In the latter cases the ratio Λ/Λ_0 has been used and the ordinates for the different systems have been displaced one unit to prevent overlapping of the curves. The curves substantiate the state-

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[1] Fuoss, *Chem. Rev.*, 17, 37 (1935).

ments above relative to the apparently different variations of Λ with concentration for different electrolytes and different solvents.

It has already been shown that under such conditions that the solution of an electrolyte can be considered as made up solely of ions the equivalent conductance is the sum of the ionic mobilities. This was first shown by Kohlrausch in 1875 when he observed that for various electrolytes in water, Λ_0 is additively composed of two parts, one dependent on the anion and the other on the cation. Kohlrausch's law thus offers a means of calculating Λ_0 when the ionic mobilities are known. This is particularly important since, frequently, the direct determination of Λ_0 by experiment is impossible, owing to the slow rate of approach of Λ to its limiting value Λ_0 even in the most dilute solutions of which accurate measurements can be made. In cases such as KCl in water Kohlrausch observed that at high dilution Λ was a linear function of the square root of the concentration, thus:

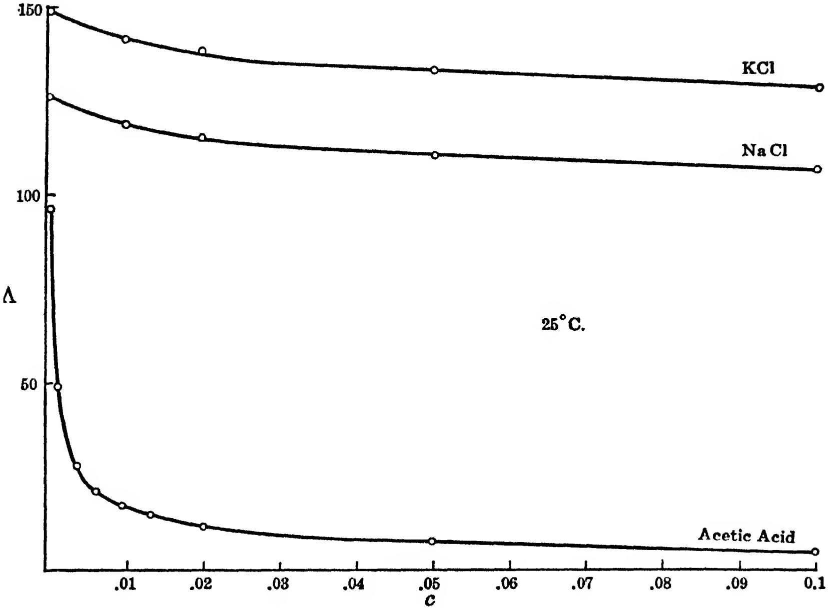

FIG. 12.9. Conductance as a Function of Concentration

$$\Lambda = \Lambda_0 - \alpha c^{1/2}. \qquad (12.16)$$

Hence a linear extrapolation of observed Λ values at low concentrations gives Λ_0 directly. This is illustrated in Fig. 12.11 for KCl and NaCl at

25° C.[1] In Fig. 12.12, similar data[2] are shown for acetic acid in water, from which it can be seen that an extrapolation to the limiting value Λ_0 is not justified and the latter value is thus best obtained from the sum of the mobilities of hydrogen and acetate ions.

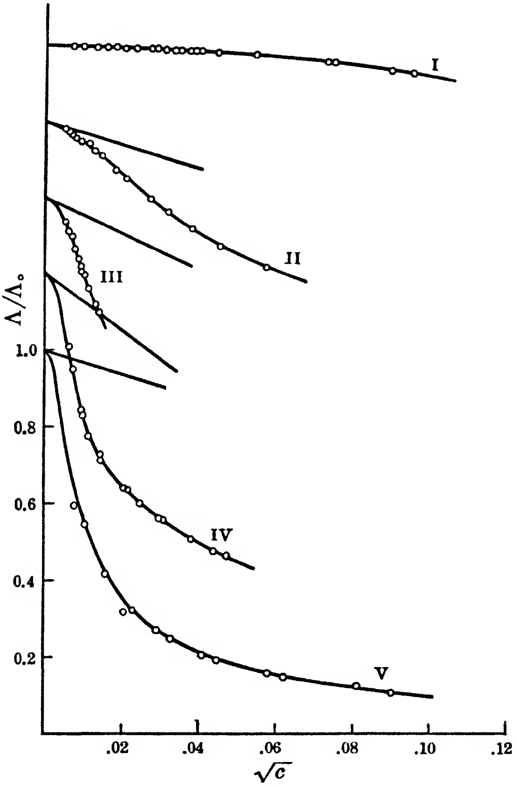

FIG. 12.10. Variation of Conductance with Concentration

On the basis of this difference, a direct or indirect determination of Λ_0, a tentative separation of electrolytes into two classes, strong or weak respectively, is possible. This separation, however, is not a hard and fast one and will depend on the solvent to some extent, that is, a particular electrolyte may be "strong" in one solvent and "weak" in another.

19. Extent of Dissociation. Arrhenius theory: The theory and experiment so far presented have assumed the presence of ions in electro-

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[1] Shedlovsky, *J. Am. Chem. Soc.*, 54, 1422 (1932).

[2] MacInnes and Shedlovsky, *J. Am. Chem. Soc.*, 54, 1435 (1932).

lytic conductors. Such an assumption had been made by Williamson in 1850 to account for the rapidity of reaction between inorganic compounds and was championed by Clausius in 1857, who pointed out that, if ions were brought into existence by the current and were not otherwise present, a definite voltage would be necessary for the decomposition of the molecule into ions, whereas the current flowing always appears to follow Ohm's law in its proportionality to the applied voltage.

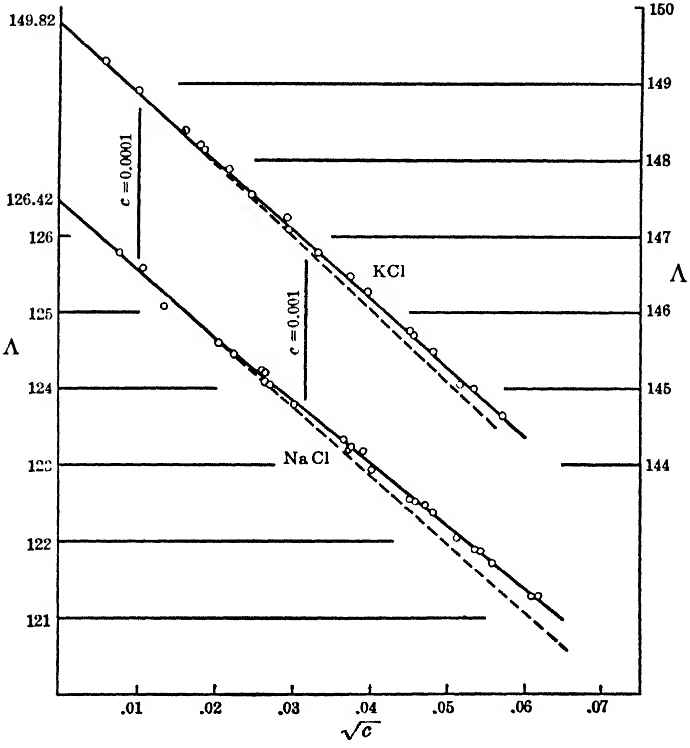

Fig. 12.11. Conductivity of KCl and NaCl at Low Concentrations

The extent of this dissociation into ions was presumed small and it was Arrhenius[1] who first suggested that electrolytes were extensively broken up into ions. He assumed that this dissociation was a function of the concentration of the solution, increasing with increasing dilution, becoming practically complete in very dilute systems. Arrhenius was thus

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[1] *Z. physik. Chem.* **1**, 831 (1887); *J. Chem. Soc.*, **105**, 1414 (1914); *J. Am. Chem. Soc.*, **34**, 353 (1912); *Trans. Faraday Soc.*, **15**, 10 (1919).

able to offer a possible explanation of the abnormal colligative properties of electrolytic solutions noted by van't Hoff, of the results of Hittorf on migration, of Kohlrausch on conductance, and of Ostwald on reaction velocity. Although the Arrhenius theory cannot be accepted as completely satisfactory at the present time it has nevertheless provided a background against which later developments could be interpreted in their true perspective.

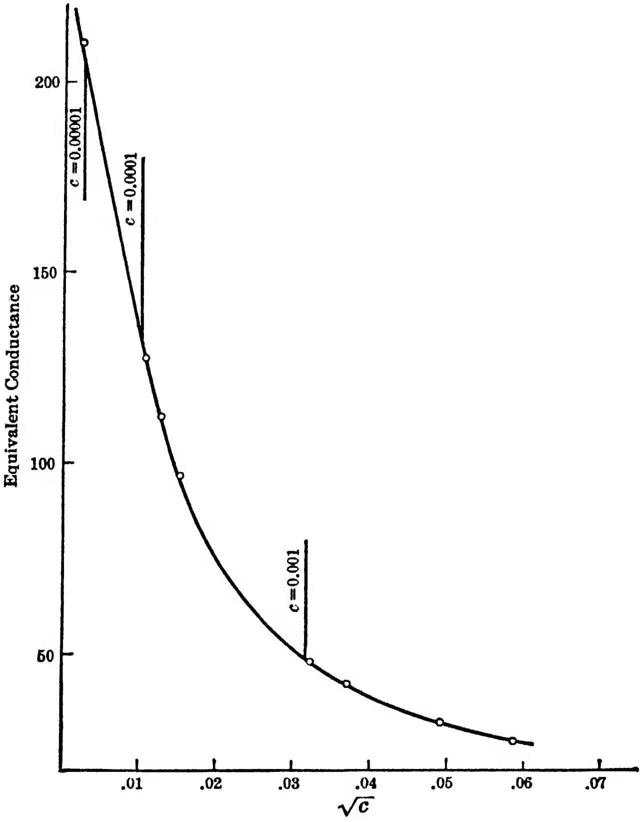

FIG. 12.12. Conductance of Acetic Acid

According to Arrhenius, the difference between strong and weak electrolytes may be traced to a difference in the extent of dissociation. Thus KCl would appear to be highly dissociated at moderately low concentrations in water, whereas acetic acid in the same concentration range would still be very far from being completely dissociated. The actual extent of dissociation, Arrhenius suggested, could be obtained from conductance measurements. Thus, by Kohlrausch's law, the limiting conductance is the sum of the mobilities:

$$\Lambda_0 = l_a + l_c. \tag{12.17}$$

That the conductance is less at higher concentrations was viewed by Arrhenius as due to the presence of some of the electrolyte in an undissociated condition, that is, fewer ions are present. If α is the fraction of each mole of electrolyte dissociated,

$$\Lambda = \alpha(l_a + l_c), \tag{12.18}$$

where Λ is the conductivity of a solution of an electrolyte dissociated to the extent α. Hence:

$$\alpha = \Lambda/\Lambda_0. \tag{12.19}$$

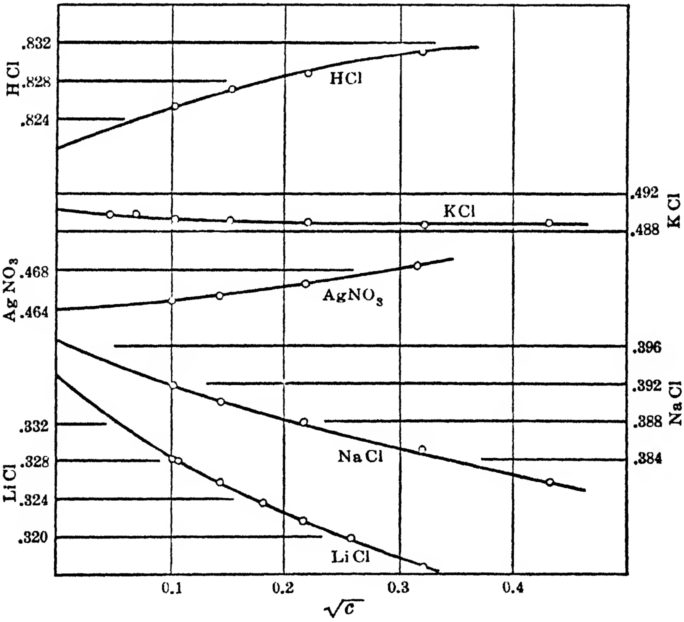

FIG. 12.13. Cation Transport Numbers

In this deduction Arrhenius assumes that the ionic mobilities are independent of concentration. Now constant ionic mobilities require constant transport numbers and there is today an ample body of evidence showing that transport numbers change considerably with a change in concentration. In Fig. 12.13 are shown data obtained by MacInnes and Longsworth[1] for the variation with concentration of the cation transport numbers of some uni-univalent electrolytes in water at 25° C. Constancy of ionic mobilities would thus appear unfounded in some cases at any rate and the changing conductance with a change in concentration must to some extent depend upon this change in mobility of the ions. Furthermore, since the examination of crystals by X-rays indicates that compounds such as KCl are made up, not of molecules of KCl nor of atoms K and Cl, but of ions K^+ and Cl^- arranged in a space lattice, it would be expected that solutions of such compounds might contain only ions and no undissociated molecules. If only ions are present, the change in conductance is due solely to a change in mobility and the equation $\Lambda = l_a + l_c$ should hold at any concentration provided the mobilities at that concentration are used. MacInnes and Cowperthwaite[2] have proved this by showing that the contribution to the equivalent conductance of a number of uni-univalent chlorides, by the chloride ion, is constant even at 0.1 N concentration. This contribution is measured as the product of the chloride ion transport number t_- and the equivalent conductance of the solution, each at 0.1 N concentration. Table 12.3 contains their data, the constancy of the values in the fourth column substantiating their claim. There are included in the table the cation con-

TABLE 12.3

	Λ	t_-	Λt_-	
HCl	390.4	0.1680	65.59	
KCl	129.0	.5080	65.53	
NaCl	106.8	.6137	65.54	
NH_4Cl	128.55	.5100	65.56	
		t_+	Λt_+	
HNO_3	385.0	.8441	325.0	
HCl	390.4	.8320	324.8	
NH_4NO_3	123.0	.5130	63.1	
NH_4Cl	128.55	.4900	63.0	
		t_-	Λt_-	α
HNO_3	385.0	.1559	60.0	—
NH_4NO_3	123.0	.4870	59.9	—
$NaNO_3$	101.26	.5903	58.77	0.996
KNO_3	120.38	.4872	58.65	.978
$AgNO_3$	109.23	.5315	58.05	.967

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[1] *Chem. Rev.*, **11**, 211 (1932).

[2] *Trans. Faraday Soc.*, **23**, 400 (1927).

tributions to the conductivity of HCl and HNO_3 as also for NH_4NO_3 and NH_4Cl from the constancy of which it may be concluded that HNO_3 and NH_4NO_3 are also completely dissociated. However, in the third section of the table similar data are presented for several other nitrates for which the nitrate contribution is less than that for HNO_3 and NH_4NO_3. This suggests that the other nitrates are incompletely dissociated and, in the fifth column, are added values for the actual degree of dissociation based on the ratio of the nitrate ion contribution for the incompletely dissociated salt to that for the completely dissociated HNO_3 or NH_4NO_3. It should be noted that these values of α are vastly different from the value which the Arrhenius conductance ratio would give for uni-univalent salts at 0.1 N concentration, which is about 0.85.

20. **Debye-Hückel-Onsager Theory:** If in completely dissociated electrolytes the change in conductivity with changing concentration is to be ascribed solely to a change in the ionic mobility it is natural to attempt to calculate this latter. Debye and Hückel[1] were the first to make such a quantitative calculation. Their results were subsequently modified by Onsager.[2]

The calculation involves the determination of the interionic forces. Owing to the electrostatic attractions there will be, in general, more ions of unlike sign than of like sign in the immediate neighborhood of every ion. Each ion thus has an "atmosphere" of other ions and the net sign of the charge on an atmosphere is opposite to that of the ion itself. For a solution under no external field the atmosphere will surround the central ion symmetrically. In presence of an external field the symmetry is destroyed, since the central ion tends to move in one direction and the atmosphere in the opposite. The resultant effect of an applied potential is fourfold.

(1) The applied field will cause the ion to move in a particular direction; anions to the anode, cations to the cathode.

(2) Opposing this motion of the ion is a frictional force exerted by the solvent, dependent on the velocity of the ion (assuming the solvent is stationary) and on the viscosity of the solvent. The frictional force is given by Stokes's law.

(3) Since the ionic atmosphere is no longer spherically symmetrical around the ion while the ion is in motion, the density of the atmospheric charge in front of the ion is less than that under symmetrical conditions while behind the ion the density will be greater. The atmosphere will of course tend to revert to the symmetrical condition but this return will require a finite time and cannot be made instantaneously. So long as the ion moves, therefore, the asymmetry will persist. Since the charge

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[1] *Physik. Z.*, **24**, 185, 305 (1923).

[2] *Ibid.*, **27**, 388 (1926); **28**, 277 (1927).

density of the atmosphere, of opposite sign to that of the ion, is greater behind the ion in the direction of its motion than in front of it, the ion is effectively retarded and to an extent which will depend on the density of the atmosphere which, in turn, is dependent on the concentration of the solution.

(4) Finally, there is also a motion of the solvent in the neighborhood of each ion. This motion is a result of collisions between the solvent molecules and the moving ions, anions causing a solvent stream in one direction, cations in the opposite direction. Since, however, there are more ions of unlike sign than of like sign in the atmosphere there will be a net solvent motion in the neighborhood of each ion in the direction opposite to that of the ion. This effect, called "electrophoresis," causes an additional frictional effect between ion and solvent to that considered under item (2) where the solvent was considered as stationary.

The combined effect of these four forces yields a value for the velocity, that is, therefore, for the mobility of an ion. The quantitative evaluation of these forces is so difficult mathematically that a complete solution is only possible for very dilute systems. Under such conditions it is found that the effect of the ionic atmosphere is dependent on the square root of the concentration. The same relation is also true for the electrophoretic effect. Hence, the mobility of an ion and therefore also the equivalent conductance of an electrolyte should so vary with concentration. This is the result which Kohlrausch found experimentally as already mentioned.

Further evidence for the correctness of the underlying ideas has been pointed out by Debye and others. If a solution is subjected to a high frequency alternating current, each ion has its motion continually reversed. This reversal of the direction of motion of an ion with each alternation will actually be aided by the asymmetry of the ionic atmosphere and hence its mobility will increase. When the frequency is great enough, the ion merely oscillates about an equilibrium position and the atmosphere is virtually symmetrical. With increasing frequency the mobility should increase to a limiting value since the electrophoretic effect is also annulled by the symmetry of the atmosphere. The conductivity of a solution at a finite concentration should therefore approach the limiting value Λ_0 as the frequency is increased. This has been substantiated in several cases by Sack[1] and his co-workers.

Alternatively, if an ion moves fast enough it may escape from its atmosphere entirely and the retardation by the atmosphere again be removed. Wien[2] had already shown that the conductance of a solution increased as the strength of the applied field was increased, approaching

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[1] *Physik. Z.*, **30**, 576 (1929); **31**, 345 (1930); **32**, 327 (1931).

[2] *Ann. Physik.*, **83**, 327 (1927); **85**, 795 (1928).

again Λ_0 as the limit. Fields of the order of one to three hundred kilovolts per cm. were used when the ion velocities were from 50 to 100 cm. per second. The observation receives a ready explanation from the Debye theory and constitutes therefore confirmation of its basic principles.

The equivalent conductance of a uni-univalent electrolyte in water at 25° C. is given, according to Onsager, by the relation:

$$\Lambda = \Lambda_0 - (0.161\Lambda_0 + 42.3)\sqrt{2c}, \qquad (12.20)$$

where c is the equivalent concentration. At 18° C. this becomes:

$$\Lambda = \Lambda_0 - (0.159\Lambda_0 + 35.7)\sqrt{2c}. \qquad (12.21)$$

The equations are limited in application to solutions whose conductivities are less than about 10 per cent different from Λ_0. For KCl and NaCl this corresponds to dilutions less than 0.001 *N*. At higher concentrations such electrolytes have higher conductivity values than those calculated from the equation. The Onsager equation should give, therefore, the limiting slope at extreme dilution of the curve for Λ plotted against $\sqrt{2c}$. The dotted lines in Fig. 12.11 are the Onsager slopes as also are the straight lines in Fig. 12.10 and are seen to be satisfactory.

It will be observed, in comparing these two figures, that in some cases the observed curve becomes asymptotic to the Onsager slope from above and sometimes from below. The Onsager equation is of course based upon the assumption of complete dissociation of the electrolyte and the effect of incomplete dissociation would be to reduce the conductivity, that is, the observed conductivity would be less than that calculated from the equation. On this basis Onsager has attempted to calculate the degree of dissociation of some 'strong' electrolytes in water whose conductivity curves approach the Onsager slope from below. Experiment shows that 0.01 *N* KCl has a conductivity about 0.5 greater than that calculated from the Onsager equation at 18° C. If potassium chloride is assumed to be completely dissociated, this difference of 0.5 is the 'error' in the Onsager approximation. Potassium nitrate on the other hand has a conductivity at 0.01 *N* which is 0.2 less than the calculated value. Hence, the actual deficit for KNO_3 as compared with a completely dissociated salt like KCl is $0.5 + 0.2 = 0.7$. From this deficit the effective ionic concentration may be calculated and, hence, the degree of dissociation. In Table 12.4 are given values so calculated for 0.01 *N* solutions at 18° C.

21. **Non-aqueous solutions:** The extension of the Debye-Onsager treatment to electrolytes in non-aqueous media involves in a much more marked manner than has just been indicated the possibility of incomplete dissociation. This is more especially so in media of low dielectric constant. The systems illustrated in Fig. 12.10 were chosen

TABLE 12.4

	KCl	KNO_3	$TlNO_3$	TlCl
Λ_0	129.9	126.3	127.5	131.1
Obs. − Calc'd $\Lambda_{0.01}$	0.5	−0.2	−1.2	−2.1
$\Lambda_{0.01}$ Deficit	0	−0.7	−1.7	−2.6
α	1	.994	.987	.980

specifically with this in mind since the dielectric constant diminishes from that of water in System I to that of ammonia in System V and as can be seen the deviation of the observed conductivities from the Onsager limiting slope increases as the dielectric constant decreases.

The dependence of the extent of dissociation of a particular electrolyte upon the medium in which it is dissolved can be illustrated by an example. Consider the case of hydrogen chloride. Measurements of the dielectric constant of the gas show it to be only slightly polar. Pure liquid hydrogen chloride is practically a non-conductor while Simon and Simon have shown that the lattice structure of the solid is atomic and not ionic. Here then is a typical weak electrolyte and in such solvents as hexane or benzene it does so behave. In water, however, as we have seen, it is a strong electrolyte and completely dissociated. That the dielectric constant of the medium is of profound importance can readily be seen from Coulomb's law wherein F, the force acting between two bodies charged, e and e', a distance, r, apart, is given by $F = ee'/Dr^2$, where D is the dielectric constant of the medium. Now since the value for D for water at 25° C. is about 79 times greater than that for air, the force acting on a pair of ions in air is 79 times greater than that for the same ions in water. Nernst and J. J. Thomson first drew attention to this aspect of the problem and Walden tested the rule that solvents of high dielectric constant should be good ionizing media by measuring the dissociation of tetraethylammonium iodide in a large number of solvents whose dielectric constants covered the range from 2 to 80. The results showed a qualitative agreement with the rule but indicated that the dielectric constant was not the sole factor involved.

Kraus and Fuoss[1] have drawn attention to the effect of ion size as well as that of dielectric constant in bringing about dissociation. They adopt a picture first used by Bjerrum that an electrolyte will be dissociated into ions by the thermal agitation of solvent molecules provided this latter is sufficient to overcome the coulomb forces holding the ions associated together. This energy of association given by Coulomb's law is $E = ee'/Dr$. The thermal energy required to separate the two ions is $2kT$. Dissociation of associated ions will thus be complete if $2kT$ is

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[1] *J. Am. Chem. Soc.*, 55, 476, 1019, 2387 (1933).

greater than E. Kraus and Fuoss therefore measured the conductivities of tetraisoamylammonium nitrate in solvents made up of mixtures of dioxane and water, in which the dielectric constant could be changed by changing the composition from that of dioxane, 2.2, to that of water, 78.6. From these determinations the energy of dissociation was calculated and shown to become equal to $2kT$ when the dielectric constant had a value 43.6. For such a solvent, as also for solvents of higher dielectric constant, this electrolyte would be completely dissociated. For solvents of lower dielectric constant the dissociation is incomplete.

Since the energy of association given by Coulomb's law depends also upon r, which for an ion pair becomes the mean effective ionic diameter, it may be seen that when r is small, the energy required for dissociation will be large and vice versa. For their particular electrolyte Kraus and Fuoss find a mean diameter of 6.4×10^{-8} cm. An electrolyte with smaller ions would require a solvent of higher dielectric constant to bring about complete dissociation. In agreement with Bjerrum they find for water at 25° C. a critical value of 3.5×10^{-8} cm. for the mean diameter so that electrolytes with ionic diameters above this value would be completely dissociated while below that value they would be only partially dissociated.

Taking the Onsager limiting equation in its general form, applicable to any solution:

$$\Lambda = \Lambda_0 - b\sqrt{c}, \tag{12.22}$$

where b is the Onsager constant, and assuming that the decreases in the conductivity values actually observed are due to partial dissociation to an extent, α, the equation becomes:

$$\Lambda = \alpha(\Lambda_0 - b\sqrt{\alpha c}). \tag{12.23}$$

In such a manner Kraus and Fuoss were able to calculate the degrees of dissociation from the conductance data. In Fig. 12.10 the circles represent observed values, the curves are calculated as above. The agreement between the two shows the correctness of the interpretation.

22. **Conductivity at Higher Concentrations:** The Onsager equation is restricted by its mode of derivation to low concentrations. The term low concentrations will be merely relative, for whereas the behavior of 0.001 N aqueous solutions is readily accounted for on the basis of complete dissociation, the same concentrations in solvents of low dielectric constant are far too complex for the same treatment to apply. In such media, for example, the equivalent conductance diminishes with increasing concentration in extremely dilute solutions but reaches a minimum value and thereafter increases again. In some cases this increase continues to a maximum value followed by a second decrease. This is

illustrated in Fig. 12.14 showing the conductivity of tetraisoamylammonium nitrate in dioxane at concentration greater than 10^{-4} N.

Fuoss has suggested that this increase in conductance may be due to an association of an ion with an already associated ion pair (Bjerrum's undissociated molecule) yielding triple ions of the type $(+ - +)$ or $(- + -)$ which would contribute to the conductivity. Evidence for such association is found in the high values that are obtained for the apparent molecular weights deduced from measurements of the colligative properties.

An alternative treatment is offered by Halpern and Gross[1] based on a suggestion by Debye concerning the interaction between ions and molecules. It is well known from electrostatics that substances of high dielectric constant accumulate in regions of a higher field of force while substances of lower dielectric constant are expelled therefrom. Hence, in the field of force surrounding an ion there will be an accumulation of dipoles. If the solvent molecules have a higher dipole moment than undissociated solute molecules, solvent will accumulate around the ions to the exclusion of the solute. This is the familiar salting-out effect. If the solute molecules have the higher dipole moments, solute will accumulate around the ions to the exclusion of solvent. This is the less familiar salting-in effect established by Gross for hydrocyanic acid in

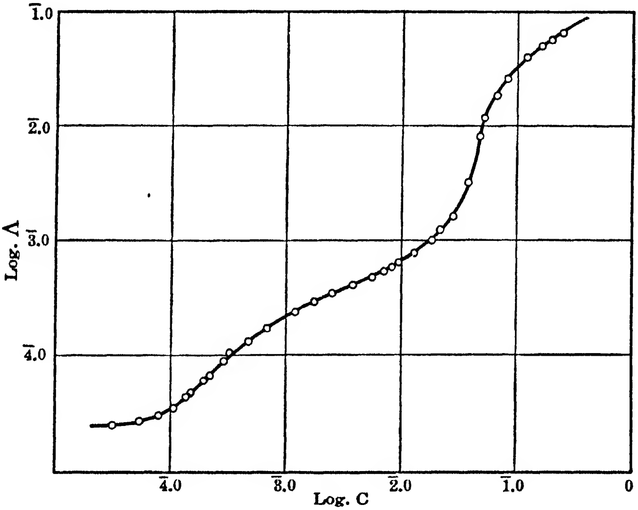

FIG. 12.14. Tetraisoamyl Ammonium Nitrate in Dioxane

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[1] *J. Chem. Phys.*, 2, 184, 188 (1934).

water. By calculating the additional free energy of the solution due to this ion-molecule interaction, Halpern and Gross show that, for solutions in media of low dielectric constant where the dissociation is small, the dissociation is given by the equation:

$$\log \alpha^2 c = A + Bc, \tag{12.24}$$

where α is the degree of dissociation at concentration, c, and A and B are constants depending on the dielectric constant and the temperature. Thus the dissociation must both decrease and increase with increasing concentration, owing to the term Bc. The concentration, c_{min}, for which the dissociation does not change with concentration is given by $d\alpha/dc = 0$, that is, $B = 1/c_{\text{min}}$ and $\log \alpha^2 c = A + c/c_{\text{min}}$, showing that the change in α as c increases is very unsymmetrical on both sides of c_{min}, α increasing very rapidly as the concentration increases once c_{min} is passed, as Kraus and Fuoss find. Furthermore, it is shown that c_{min} should increase as the dielectric constant of the solvent increases, so that, at sufficiently high values as for water, no minimum is observed, the conductivity decreasing continuously as the concentration increases.

Theoretical attempts to extend the Onsager treatment to higher concentrations have led to the prediction that the deviation of the actual limiting conductance Λ_0 from that calculated by the simple Onsager equation from measurements of conductance at higher concentrations should be of the form $Bc + Dc \log c + \cdots$. This has been verified by Shedlovsky[1] for several uni-univalent and uni-bivalent electrolytes in water.

Robinson and Davies[2] have found empirically that for uni-univalent electrolytes in water the Onsager equation, $\Lambda = \Lambda_0 - b\sqrt{c}$, is applicable up to 0.001 N. From 0.002 N to 0.02 N the equation

$$\Lambda = \Lambda_0 - b(\sqrt{c} - c + .001) \tag{12.25}$$

reproduces observed results while above 0.02 N the equation takes the form

$$\Lambda = \Lambda_0 - bf(c), \tag{12.26}$$

where $f(c)$ is an empirical function of the concentration and the same for all electrolytes. The Onsager constant here denoted by b is the same throughout the whole concentration range.

23. **Fused Salts:** Fuoss has pointed out that, for a given electrolyte in a series of solvents of low dielectric constant, the conductivities at high concentration all tend to converge to the same value. This value is

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[1] *J. Am. Chem. Soc.*, **54**, 1411 (1932); Shedlovsky and Brown, *ibid.*, **56**, 1069 (1934).

[2] *J. Chem. Soc.*, 574 (1931).

presumed to be the conductance that the fused salt would have at the temperature of the experiments.

The conductance of fused salts is mainly controlled by the temperature, increasing approximately linearly with temperature. This increase in conductance roughly parallels the decrease in viscosity of the systems as the temperature is increased. The magnitudes of the conductances of fused salts are frequently of the same order as those of their aqueous solutions at room temperature. Table 12.5 includes some typical values.

A comparison by Lowry between fused silver chloride and its aqueous solution is instructive. The specific conductance of fused silver chloride at 600° C. is 4 48 mhos. The density at this temperature is 4.715. Hence the 'normality' is $4.715 \times 1000/143.34 = 32.9\ N$ since 143.34 is the molecular weight. The equivalent conductance is thus $4.48/.0329 = 136$. Now, for the aqueous solution, $\Lambda_0 = 119$ corresponding to the completely dissociated salt. Making a proportional allowance for the increase in viscosity in going from the aqueous solution with a viscosity of 0.1056 to the fused system with a viscosity of 0.1606, Λ_0 should have the value in the fused state, if completely dissociated, of $119 \times 0.1056/0.1606 = 78$, which is only about one half the observed value. Lowry suggests this may be due to the presence of aggregates of ions carrying multiple charges, since these would increase both the viscosity and the conductivity of the melt.

TABLE 12.5

Salt	° C.	κ	Salt	° C.	κ
AgCl	600	4.48	$NaNO_3$	350	1.17
NaCl	850	3.50	KNO_3	350	0.67
KCl	850	2.28	$AlBr_3$	195	$\sim 10^{-6}$
$CaCl_2$	800	1.90	HCl	−100	2×10^{-7}

Kendall and Gross have drawn attention to the part played by association under such circumstances. The conductivities of unassociated organic liquids typified by the saturated hydrocarbons are practically zero. Increasing tendency to association is accompanied by an increase in conductivity. Thus, ethyl alcohol has a conductivity less than 10^{-10}; for water $\kappa_{18} = 0.38 \times 10^{-7}$. With fused sodium and potassium chlorides, surface tension methods indicate association factors of 9 and 7 respectively while the conductivity has risen to 3.50 and 2.28 mhos. Although a literal interpretation of such association factors is extremely doubtful, nevertheless such a condition of high association and high conductivity is precisely that found for electrolytes in media of low dielectric constant. It would seem that a logical approach to further progress might be made through further study of fused systems.

EXERCISES (12)

1. Calculate the value of the Wiedemann-Franz constant in watt degree^{-2} ohms.

2. Determine the constants a, b, c in the equation $r = a + bt + ct^2$, where r is the resistivity at a temperature t° C., from the following data for gold:

t° C. =	-253	-183	-150	-100	20	100	200	500	1000
$r \times 10^6$ =	0.018	0.68	0.997	1.40	2.44	2.97	3.83	6.62	12.52

3. The resistance of Au at 0° C. is 2.2×10^{-6} ohm cm., of Ag is 1.47×10^{-6}, of a 90 per cent Au alloy with Ag is 6.3×10^{-6}, of a 67 per cent Au alloy with Ag is 10.8×10^{-6} while the addition of a small amount of Cu to the latter raises the resistance. What conclusions can be drawn from these data on the constitution of the alloy?

4. 0.03095 g. Ag were deposited in a silver coulometer in 108 minutes under the influence of 150 volts. Calculate the resistance of the coulometer.

5. Calculate the energy necessary to dissociate a univalent electrolyte having a mean ionic diameter of 4×10^{-8} cm. (a) in water, $D = 78.6$ and (b) in dioxane, $D = 2.2$.

6. The mobilities of Cl^- and Na^+ at 18° C. are 65.5 and 43.4 respectively. Λ_0 at 18° C. for HCl is 379.4 and for sodium acetate is 78.4. Find Λ_0 for acetic acid.

7. Using the Onsager equation calculate the equivalent conductance of 0.0005 N KCl at 25° C. and compare it with the value plotted in Fig. 12.11.

8. The transport number of K^+ in KCl is 0.497 and $\Lambda_0 = 130.1$. What is the velocity of K^+ in cms. per sec. under unit potential gradient?

CHAPTER 13

IONIC EQUILIBRIA, I. WEAK ELECTROLYTES

THE term weak electrolyte covers a series of compounds, solutions of which show relatively small conductivities and which possess, therefore, only small ionic concentrations. Since the ionic concentrations are small the interionic forces discussed in the previous chapter will also be small and may, to a first approximation, be neglected. Thus, on the Arrhenius assumption of constant ionic mobilities, the equivalent conductance is given by the relation $\Lambda = \alpha\Lambda_0$, where α is the degree of dissociation and Λ_0 the limiting conductance at zero concentration. The Debye-Onsager relation corresponding to this is $\Lambda = \alpha(\Lambda_0 - b\sqrt{\alpha c})$. When α is small the last term, $b\sqrt{\alpha c}$, becomes negligible in comparison with Λ_0 and the expression reduces to the Arrhenius relation.

1. The Classical Law of Mass Action and Ionic Equilibria: Since the Arrhenius relation affords an approximate measure of the ionic concentrations in solutions of weak electrolytes, the applicability of the law of mass action may be examined. Consider the dissociation of a binary electrolyte

$$AB \rightleftarrows A^+ + B^-.$$

Let α be the fraction dissociated for a concentration of solution c moles per liter. The dissociation constant is given by

$$K = [A^+][B^-]/[AB] = c\alpha^2/(1 - \alpha). \qquad (13.1)$$

Assuming $\alpha = \Lambda/\Lambda_0$ this gives

$$K = \Lambda^2 c/\Lambda_0(\Lambda_0 - \Lambda). \qquad (13.2)$$

This equation is known as Ostwald's Dilution Law and it has been found to apply to aqueous solutions of weak organic acids and weak organic bases with a fair degree of accuracy. This is illustrated in Table 13.1

TABLE 13.1

DISSOCIATION CONSTANT OF ACETIC ACID AT 25° C.

$V =$	1000	500	250	60	30	15	7	4	2	1
$K \times 10^5 =$	1.84	1.84	1.84	1.85	1.85	1.84	1.81	1.76	1.65	1.40

for acetic acid solutions wherein V is the volume in liters containing 1 mole. The data show satisfactory constancy at dilutions from 15 to

1000 liters. It should be noted that in this range the degree of dissociation changes only from 0.5 to 10 per cent.

2. **Range of Applicability of the Dilution Law:** Experiment shows that as the value of K increases the range of concentration over which it remains constant becomes progressively smaller. Chloracetic acid with a value of $K = 15.6 \times 10^{-4}$ shows satisfactory constancy to $V = 20$. With dichloracetic acid, however, the value of K progressively increases as the data in Table 13.2 reveal. There is included in Table 13.2 the value of the fraction dissociated at each dilution based on the assumption of the validity of the Arrhenius assumption. It is at once apparent that the solutions contain such relatively high ionic concentrations that interionic effects cannot justifiably be neglected; hence the failure of the Dilution law.

TABLE 13.2

Dissociation Constant of Dichloracetic Acid at 25° C.

$V =$	256	128	64	32	16	8
$\alpha =$	0.93	0.87	0.80	0.70	0.60	0.49
$K \times 10^4 =$	495	496	511	537	565	600

3. **Dissociation Constant and Chemical Constitution:** The dissociation constant K represents a measure of the extent of dissociation of acids and bases and, as such, is a measure of the affinity existing between hydrogen ion and anion in the acid, and cation and hydroxyl ion in the case of the base. For, as in all equilibria, the free energy of the process is proportional to the equilibrium constant. From this standpoint a comprehensive study of organic acids has been made. Thus, the dissociation constant, K, of fatty acids decreases as the series is ascended, but the substitution of successive CH_3 groups does not cause a constant decrease. Substitution of H by Cl, Br or I causes a large increase of K, the magnitude decreasing in the order given. Chlorine substitution has a greater influence than iodine substitution. The substitution of a second atom of chlorine has less effect than the first, and a third less than the second. The chloracetic acids illustrate this. Acetic, $K = 0.18 \times 10^{-4}$; Chloracetic, $K = 15.6 \times 10^{-4}$; Dichloracetic, $K = 500 \times 10^{-4}$; Trichloracetic, $K =$ ca. 900×10^{-4}. Cyanogen has a much greater effect as a substituent than chlorine. Thus, cyanacetic acid has a value of $K = 37 \times 10^{-4}$ as compared with 15.6×10^{-4} for chloracetic acid. Substitution by halogen in the α-position produces a greater effect on dissociation than in the β-position, although the effect of halogen substitution is still marked even in the end carbon group of a long aliphatic acid chain. Substitution of hydroxyl for hydrogen in the hydrocarbon groupings also

increases the dissociation constant of all acids, aliphatic and aromatic, except in the case of para substitution in the benzene nucleus.

The aromatic acids show much greater regularity than the aliphatic. In the case of substitution in the nucleus, the groups $-\mathrm{CH_3}$, $-\mathrm{OH}$, $-\mathrm{NO_2}$ and $-\mathrm{Cl}$ increase K, the effect being greater in the ortho- than in the meta- and para-positions. The substitution of $-\mathrm{NH_2}$ decreases K, the greatest effect being in the ortho- and the least in the meta-position. In the case of two substituents in the same acid, the actual dissociation is less than the value computed on the assumption that each behaves independently.

Most inorganic acids are strong electrolytes in aqueous solution and do not obey Ostwald's dilution law. Carbonic acid, hydrogen sulfide and hydrogen cyanide are exceptions. Organic bases do not exhibit such regularities as do acids; secondary bases are usually stronger than primary or tertiary bases. Salts, even of weak organic acids or bases, are highly dissociated and do not obey the Ostwald dilution law. They are classed with strong electrolytes.

4. **Proton Transfer Concept of Acids and Bases:** The classical definition of acids and bases as substances capable of yielding hydrogen and hydroxyl ions respectively though fairly satisfactory in its application to aqueous solutions requires modification if it is to be used in non-aqueous media. A view, suggested by Lowry and by Brönsted, which has a more general applicability and at the same time indicates the complementary nature of acids and bases, considers an acid as a substance which can lose a hydrogen ion producing thereby a base. A base, therefore, is a substance which can accept a hydrogen ion to produce an acid. The general scheme may be indicated by the equation

$$\text{Acid} \rightleftarrows \text{Base} + \mathrm{H^+}.$$

Such an acid and base are referred to as a conjugate pair. From the generality of the definition it follows that an acid may be either neutral or electrically charged, thus

$$\begin{aligned} \mathrm{CH_3.COOH} &\rightleftarrows \mathrm{CH_3.COO^-} + \mathrm{H^+}, \\ \mathrm{NH_4^+} &\rightleftarrows \mathrm{NH_3} \qquad\quad + \mathrm{H^+}, \\ \mathrm{HSO_4^-} &\rightleftarrows \mathrm{SO_4^{=}} \qquad\quad + \mathrm{H^+}. \end{aligned}$$

Since the hydrogen ion used in the definition and the examples is the proton and since the proton rarely exists in the free state, especially in solution, the definition is to be considered as indicating the fundamental relationship without reference to the ultimate fate of the proton. In practice, naturally, this ultimate fate of the proton is important. Since the proton does not exist free it must be combined with some other molecule and since a molecule which accepts it is a base there will always be in practice a doubly conjugate relation as follows

$$\text{Acid}_1 + \text{Base}_2 \rightleftarrows \text{Acid}_2 + \text{Base}_1,$$

the subscripts referring to conjugate pairs. The reaction is known as *protolysis* or a *protolytic reaction.*

The loss of a proton by an acid in solution thus only becomes possible if the solvent has basic properties. If the solvent can also exhibit acidic properties a proton transfer to a base is possible. Water behaves in such a manner showing acidic and basic functions

$$H_2O \rightleftarrows OH^- + H^+,$$
$$H_2O + H^+ \rightleftarrows H_3O^+.$$

A solution of acetic acid in water exhibits an electrical conductivity due to the protolytic reaction

$$\underset{(\text{Acid}_1)}{CH_3.COOH} + \underset{(\text{Base}_2)}{H_2O} \rightleftarrows \underset{(\text{Base}_1)}{CH_3.COO^-} + \underset{(\text{Acid}_2)}{H_3O^+}$$

and similarly for ammonia

$$\underset{(\text{Acid}_1)}{H_2O} + \underset{(\text{Base}_2)}{NH_3} \rightleftarrows \underset{(\text{Acid}_2)}{NH_4^+} + \underset{(\text{Base}_1)}{OH^-}.$$

It appears, then, that electrolytic dissociation in the classical sense becomes a special case of protolysis.

If the acid or base in solution is not an electrically neutral molecule, as in the above examples, but is an ion, an analogous relation holds

$$\underset{(\text{Base}_1)}{CN^-} + \underset{(\text{Acid}_2)}{H_2O} \rightleftarrows \underset{(\text{Acid}_1)}{HCN} + \underset{(\text{Base}_2)}{OH^-}$$
$$\underset{(\text{Acid}_1)}{NH_4^+} + \underset{(\text{Base}_2)}{H_2O} \rightleftarrows \underset{(\text{Base}_1)}{NH_3} + \underset{(\text{Acid}_2)}{H_3O^+}.$$

These are the familiar reactions of hydrolysis of the salts potassium cyanide and ammonium chloride in water. The reverse of the above reactions represents the neutralizations of hydrocyanic acid by a strong base which is completely dissociated into ions and of ammonia by a strong acid also completely dissociated.

It is evident that the double acid-base reaction furnishes a generalization for a number of apparently different phenomena and the quantitative aspects of these described by dissociation constants, hydrolysis constants, indicator constants and so forth, become special cases of a protolysis constant.

5. **Acidity Constant and Protolysis Constant:** In view of the conjugate relationship between acid and base it is sufficient in order to characterize a given system quantitatively, to specify a single quantity such as the

acidity. This may most easily be done in terms of proton concentration. It will be seen, however, in the next chapter, that this statement is rigorously true only for weak electrolytes and must be modified for strong electrolytes. Applying the law of mass action to the acid-base equilibrium gives the equation

$$K_{\mathrm{A}} = c_{\mathrm{B}}c_{\mathrm{H}^+}/c_{\mathrm{A}}, \tag{13.3}$$

where K_{A} is called the acidity constant. It will be a constant, however, only in a particular medium but may be used to express relative acidities in a given medium. The acidity of a given solution is given by $c_{\mathrm{H}^+} = K_{\mathrm{A}}c_{\mathrm{A}}/c_{\mathrm{B}}$ and is seen to depend on the ratio of acid to base present. In a similar manner it is possible, though obviously unnecessary, to develop a basicity constant $K_{\mathrm{B}} = c_{\mathrm{A}}/c_{\mathrm{B}}c_{\mathrm{H}^+}$, since this latter is related to the acidity constant by the relation $K_{\mathrm{A}}K_{\mathrm{B}} = 1$.

If two acid-base systems $A_1 - B_1$, $A_2 - B_2$ are present in the same solution, the ratio of the two acidity constants will be:

$$\frac{K_{\mathrm{A}_1}}{K_{\mathrm{A}_2}} = \frac{c_{\mathrm{B}_1}c_{\mathrm{A}_2}}{c_{\mathrm{A}_1}c_{\mathrm{B}_2}} \tag{12.4}$$

or, since $K_{\mathrm{A}_2} = 1/K_{\mathrm{B}_2}$,

$$K_{\mathrm{A}_1}K_{\mathrm{B}_2} = \frac{c_{\mathrm{B}_1}c_{\mathrm{A}_2}}{c_{\mathrm{A}_1}c_{\mathrm{B}_2}}. \tag{12.5}$$

This latter is the mass action product for the protolytic reaction

$$A_1 + B_2 \rightleftarrows A_2 + B_1.$$

Hence the protolysis constant $K_{\mathrm{A}_1\mathrm{B}_2}$ is identical with the product of the acidity constant of the acid and the basicity constant of the base which are reacting, that is,

$$K_{\mathrm{A}_1\mathrm{B}_2} = K_{\mathrm{A}_1}K_{\mathrm{B}_2}. \tag{12.6}$$

6. **The Role of Solvent:** Since a substance can only show acidic or basic properties provided a proton acceptor or donor respectively is present, the importance of the solvent is evident. Solvents may be classified as (1) proton acceptors, that is, basic or protophilic, (2) proton donors, that is, acidic or protogenic, or (3) aprotic, that is, neither acceptors nor donors. It is also possible of course that a substance may be both protophilic and protogenic and is then termed amphiprotic.

The protolysis constant has been shown to depend on the strengths of the reacting acid and base. The extent to which a protolysis will proceed must therefore depend upon the solvent. Taking water as a typical protophilic solvent, its ready acceptance of protons to produce oxonium ions H_3O^+ would permit the protolytic reaction with any fairly strong acid to go almost to completion and only with a weak acid would the reaction be incomplete. It follows that, in water, the strengths of strong acids, for example, hydrochloric and nitric, cannot be distinguished. Such distinction would require a weakly protophilic solvent, for example, acetic acid. The protolysis with an acid HA would be

$$HA + CH_3COOH \rightleftarrows CH_3COOH_2^+ + A^-.$$

Owing to the weakly basic properties of acetic acid, the $CH_3COOH_2^+$ cannot form to a large extent and the reaction is far from complete. It is actually found that perchloric acid, the strongest acid known, is only a poor conductor in acetic acid, indicating the small extent to which the protolysis has proceeded. Weaker acids as solutes in acetic acid would give a still smaller extent of reaction and thus the strengths of all acids could be distinguished.

In a similar manner, in a protogenic solvent the strengths of bases can be distinguished only when the solvent has weak protogenic properties, such, for example, as liquid ammonia. In strongly protogenic solvents, practically all bases would react to completion. In fact, substances which normally show weakly acidic properties may behave as bases in such solvents; acetic acid is a relatively strong base in hydrogen fluoride solution and even nitric acid shows some basic properties in the same solvent.

In an aprotic solvent a substance can evidence neither acidic nor basic properties. Such a solvent, nevertheless, could act as a medium for a protolytic reaction between added acid and base. Since the equilibrium produced depends solely on the acid-base system added, the range of acidity possible in an aprotic solvent should be great. The equilibrium constant for the protolysis would measure the product of the acidity and basicity constants.

7. **Dissociation Constant of Water:** A solvent such as water, which has both acidic and basic properties, will permit within itself a protolytic reaction:

$$\underset{(\text{Acid}_1)}{H_2O} + \underset{(\text{Base}_2)}{H_2O} \rightleftarrows \underset{(\text{Acid}_2)}{H_3O^+} + \underset{(\text{Base}_1)}{OH^-}.$$

This is termed autoprotolysis and is responsible for the electrolytic dissociation observed. The protolysis constant will be given by:

$$K_{H_2O,\,H_2O} = c_{H_3O^+}c_{OH^-}/c_{H_2O}^2, \qquad (13.7)$$

which, since the extent of the reaction is small and hence c_{H_2O} is constant, reduces to:

$$K_w = c_{H_3O^+}c_{OH^-}. \qquad (13.8)$$

K_w is the dissociation constant of water. In pure water $c_{H_3O^+}$ and c_{OH^-} are equal and may be estimated from the data of Kohlrausch and Heydweiller on the conductance of pure water. They found a specific conductance at 18° C. of 0.0384×10^{-6} mho. Now $\kappa = c^*(l_a + l_c)$, where c^*

is the concentration of ions in equivalents per cc. and l_a and l_c are the mobilities of the ions OH^- and H_3O^+, namely 174 and 318 respectively. Hence,

$$0.0384 \times 10^{-6} = c^*(318 + 174)$$

or

$$c^* = 0.78 \times 10^{-10}, \tag{13.9}$$

whence c the concentration per liter is 0.78×10^{-7}, and $K_w = c^2 = 0.61 \times 10^{-14}$. This value has been checked by other methods. It has been found to increase quite rapidly with a rise of temperature. Thus, at 0° C., the value is 0.11×10^{-14}; at 10° C., 0.29×10^{-14}; at 25° C., 1.01×10^{-14}, and at 100° C., about 56×10^{-14}.

Since the product of the concentrations of hydrogen and hydroxyl ions in aqueous solutions is 10^{-14} (approx.) a solution of 1 M HCl will have a hydrogen ion concentration of 1 and OH^- concentration of 10^{-14}. A solution of 1 M NaOH will have a hydrogen ion concentration of 10^{-14}. For convenience in referring to a particular hydrogen ion concentration Sörensen suggested the pH scale defined by:

$$\text{pH} = \log (1/c_{H_3O^+}) \qquad \text{or} \qquad c_{H_3O^+} = 10^{-\text{pH}}. \tag{13.10}$$

From the negative sign to the pH exponent it is seen that the scale is an inverse one, the higher the pH, the less acid is the solution. In an analogous manner the strength of an acid may be represented by the negative exponent of the logarithm, written pK.

$$\text{p}K = -\log K. \tag{13.11}$$

For example, in the case of acetic acid, $K = 1.84 \times 10^{-5}$. Hence,

$$\text{p}K = -0.265 + 5 = 4.735.$$

The distinction between the acidity and the strength of an acid must be noted. They bear the same relation to each other as pH and pK. Thus a 1 N CH_3COOH solution in water has a certain acidity, pH, but the strength of acetic acid relative to other acids in the same medium is given by pK.

8. Effect of Temperature on Dissociation: Solutions of weak electrolytes in general show a variation of dissociation with temperature similar to that of water. Applying the van't Hoff relation, equation (10.50)

$$d \ln K/dT = \Delta H/RT^2,$$

the change in heat content ΔH accompanying the dissociation process may be calculated. From the data for water given previously a value of $\Delta H = +13{,}690$ cals. at 20° C. may be calculated. This is in excellent agreement with the value found by Richards for the heat of neutralization of a strong acid by a strong base, namely, $\Delta H = -13{,}693$ cals., the essential reaction in this neutralization being the reverse of the autoprotolysis of water.

$$H_3O^+ + OH^- \rightleftarrows H_2O + H_2O.$$

9. **Buffer Solutions:** It has been shown that the acidity of protolytic systems of weak electrolytes is given by:

$$c_{H^+} = K_A c_A / c_B. \qquad (13.12)$$

A solution of an acid and its conjugate base constitutes a buffer solution, that is, a solution whose acidity changes only slightly when small amounts of acid or base are added. It is obvious from the previous relation that the acidity of such a system could only be changed by an alteration in the ratio c_A/c_B. The greater the actual values of c_A and c_B the greater will be the resistance to a change in acidity or, alternatively stated, the smaller will be the effect of added acid or base. The system acetic acid-acetate ion, the latter generally from a source other than acetic acid, is thus a typical buffer system and the acidity will depend on the acidity constant and the concentrations of acid and base. The buffer action is explained by the fact that added acid or base is neutralized by the buffer base and acid respectively. Thus, in the aqueous acetic acid-acetate buffer, hydrogen ions would react with the base, acetate

$$H_3O^+ + A^- \rightarrow HA + H_2O,$$

while hydroxyl ions (or other base) react with the acetic acid

$$OH^- + HA \rightarrow H_2O + A^-.$$

Since a change in c_{H^+} will be least when c_A and c_B are equal, the buffer action is greatest at this point and the pH of the buffer is then fixed by the pK of the protolytic system. Several such systems are given in Table 13.3 together with the pH range of each.

TABLE 13.3

Buffer System	pH Range	Buffer System	pH Range
Phthalic acid Potassium acid phthalate	2.2–3.8	Boric acid Borax	6.8–9.2
Phenylacetic acid Sodium phenylacetate	3.2–4.9	Diethylbarbituric acid Sodium salt	7.0–9.2
Potassium acid phthalate Dipotassium phthalate	4.0–6.2	Borax Sodium hydroxide	9.2–11.0
Sodium dihydrogen phosphate Disodium hydrogen phosphate	5.9–8.0	Disodium hydrogen phosphate Trisodium phosphate	11.0–12.0

10. **Indicators:** The term indicator is applied to a substance which undergoes a change of color when the pH of its solution changes beyond a certain range. The solution, therefore, is a protolytic system in which the acid and base have different colors and the equilibrium between them follows the general scheme. Since $K_A = (c_B/c_A) \cdot c_{H^+}$, where K_A is now the so-called indicator constant, and c_B and c_A are the concentrations of base and acid forms of the indicator, the color of an indicator solution will depend partly on the total concentration of the indicator, partly on the ratio of the concentrations of the two forms and partly on the acidity. If the ratio of the concentrations of the acid and base forms is equal to unity the indicator constant becomes equal to the hydrogen ion concentration. It is in this way that colorimetric measurements may be used to determine acidity. The color change sensitivity of a given indicator to change in acidity will obviously be greater the more nearly equal the concentrations of acid and base forms. The choice of an indicator sensitive in a particular pH range is thus the choice of an indicator whose pK is close to the required pH. This is illustrated in Table 13.4 which lists a few selected indicators. The table includes the pH range within which the indicator makes its full color change. If it is assumed, for example, that when less than 9 per cent of the indicator is in the acid or base form the color change is virtually complete visibly, there results for the hydrogen ion concentrations

TABLE 13.4

Indicator	Acid Color	Base Color	pH range	pK
Thymol blue (acid)......	Red	Yellow	1.2–2.8	1.5
Methyl orange..........	Red	Yellow	3.1–4.4	3.7
Bromphenol blue........	Yellow	Blue	3.0–4.6	3.98
Methyl red.............	Red	Yellow	4.2–6.3	5.1
Chlorphenol red........	Yellow	Red	4.8–6.4	5.98
Bromcresol purple.......	Yellow	Purple	5.2–6.8	6.3
Bromthymol blue.......	Yellow	Blue	6.0–7.6	7.0
Phenol red.............	Yellow	Red	6.8–8.4	7.9
Cresol red..............	Yellow	Red	7.2–8.8	8.3
Thymol blue (base).....	Yellow	Blue	8.0–9.6	8.9
Phenolphthalein........	Colorless	Red	8.0–9.8	9.7

$$c_{H^+} = K_A c_A/c_B = K_A 0.91/0.09 = 10K_A \qquad (13.13)$$

or

$$c_{H^+} = K_A 0.09/0.91 = 0.1K_A. \qquad (13.14)$$

Hence pH = pK_A − 1, or pH = pK_A + 1. Thus the pH range for this assumption is approximately one unit on each side of the particular p*K* of the indicator.

In titrations using an indicator to determine the equivalence point, the indicator chosen must show a color change at an acidity corresponding to that of the conjugate base or acid formed in the protolytic reaction occurring when an acid or base respectively is titrated. For example, a weak base, B, titrated with a strong acid undergoes reaction producing the conjugate acid, HB:

$$B + H_3O^+ \rightarrow H_2O + HB.$$

When equivalent amounts of base and acid have been mixed, if the reaction goes practically to completion, the resulting solution is one of HB in pure water. The indicator must therefore change color at the acidity of HB in pure water. Thus, in titrating ammonia with hydrochloric acid, the indicator should change color at the pH of the ammonium salt in water, which may be calculated from the acidity constant of ammonia. It is found to be in the neighborhood of $pH = 5$ so that methyl red would be an effective indicator. Similarly, in titrating a weak acid such as acetic acid with a strong base, the indicator should change color at an acidity corresponding to that of the acetate ion produced. Phenolphthalein will be found effective. Finally, it should be observed that these conclusions assume that the protolysis goes almost to completion. The titration will only be efficient when this occurs. If, for example, a weak acid is being titrated with a base which has exactly the same p*K* as the conjugate base of the weak acid, then, at the equivalence point, the protolytic reaction will only have gone halfway towards completion. This would mean that to drive the protolysis to completion a very large excess of base would have to be added and the "end point" of the titration would have been considerably overstepped. In a titration, therefore, at least one constituent should be 'strong.'

11. **Hydrolysis:** It has been seen that the constant of a protolytic reaction depends on the strengths of the acid and base reacting and also on the solvent. If the solvent is amphiprotic like water, reaction with both the conjugate acid and base from the protolysis is possible. Thus, for a protolysis

$$\underset{\text{Acid}}{HA} + \underset{\text{Base}}{B} \rightleftarrows \underset{\text{Acid}}{BH^+} + \underset{\text{Base}}{A^-},$$

the following reactions with the solvent water are possible

$$\underset{\text{Acid}}{BH^+} + \underset{\text{Base}}{H_2O} \rightleftarrows \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{B},$$

or

$$\underset{\text{Base}}{A^-} + \underset{\text{Acid}}{H_2O} \rightleftarrows \underset{\text{Base}}{OH^-} + \underset{\text{Acid}}{HA}.$$

Such reactions would tend to reverse the protolysis by producing the original acid and base and, for water as the solvent, the phenomenon is referred to as hydrolysis; solvolysis or lyolysis is the general term for any solvent.

The acidity constant of an acid has been shown to be the reciprocal of the basicity constant of the conjugate base. A protolysis between a strong acid and a strong base will therefore go practically to completion, since the conjugate base and acid produced will both be weak and will consequently show no tendency to react with the solvent. Hydrolysis is thus to be expected only when one or both of the reactants in a protolysis are weak. Three cases present themselves for discussion: (1) weak base, (2) weak acid, (3) both weak.

(1) *Strong Acid and Weak Base.* From the above it is seen that the hydrolysis occurring in this case is

$$BH^+ + H_2O \rightleftarrows B + H_3O^+,$$

since, when the base B is weak, its conjugate acid BH^+ is strong and so will react with the solvent as a weak base. The protolysis constant for this reaction is given by the equation

$$K_{A_1B_2} = \frac{c_{B_1}c_{A_2}}{c_{A_1}c_{B_2}} = \frac{c_B c_{H_3O^+}}{c_{BH^+}c_{H_2O}}. \qquad (13.15)$$

In dilute solution c_{H_2O} is constant, hence

$$K_h = c_{H_2O}K_{A_1B_2} = c_B c_{H_3O^+}/c_{BH^+},$$

where K_h is called the hydrolysis constant. If x is the degree of hydrolysis for a concentration of salt c, c_B and $c_{H_3O^+}$ will each be cx and c_{BH^+} will be $c(1 - x)$. Hence

$$K_h = cx^2/(1 - x) \quad \text{or} \quad x = (-K_h/2c) + [(K_h^2/4c^2) + K_h/c]^{\frac{1}{2}}, \qquad (13.16)$$

which, when x is small, reduces to $x = (K_h/c)^{\frac{1}{2}}$. The degree of hydrolysis is approximately proportional to the square root of the hydrolysis constant and inversely proportional to the square root of the concentration. Since $K_{A_1B_2} = K_{A_1}K_{B_2}$ and $K_{A_1}K_{B_1} = 1$, $K_{A_1B_2} = K_{B_2}/K_{B_1}$. Hence $K_h = K_w/K_B$ and the hydrolysis constant may be calculated from the dissociation constant of water and that of the weak base.

(2) *Weak Acid and Strong Base.* In this case the hydrolytic reaction will be

$$A^- + H_2O \rightleftarrows HA + OH^-,$$

since the conjugate base A^- of the weak acid will now be strong. By analogy with the previous case it is seen that the dependence of K_h on the degree of hydrolysis and on the dilution is exactly the same. Furthermore, since in general $K_{A_1B_2} = K_{B_2}/K_{B_1} = K_{A_1}/K_{A_2}$, in this case $K_h = K_w/K_{HA}$, the hydrolysis depending on the constant of the weak acid.

(3) *Weak Acid and Weak Base.* When both reactants are weak, both hydrolytic reactions pictured above may proceed and, in addition, there will also be the reverse of the autoprotolysis of water:

$$H_3O^+ + OH^- \rightleftarrows H_2O + H_2O.$$

Owing to this reaction the extent of hydrolysis is considerably greater than for those cases in which only one component is weak. The net resulting reaction is

$$BH^+ + A^- \rightleftarrows HA + B.$$

The equilibrium constant of this reaction is given by

$$K_h = c_{HA}c_B/c_{BH^+}c_{A^-}. \tag{13.17}$$

It has been shown above that $K_w/K_B = c_Bc_{H_3O^+}/c_{BH^+}$ and $K_w/K_{HA} = c_{HA}c_{OH^-}/c_{A^-}$. Hence,

$$K_h = K_w/K_{HA}K_B.$$

If x is the degree of hydrolysis for a concentration c, $K_h = x^2/(1 - x)^2$ or, for small values of x,

$$x = \sqrt{K_h} = \sqrt{K_w/K_{HA}K_B} \tag{13.18}$$

and the degree of hydrolysis is independent of the concentration. This will only strictly be true when, as here assumed, $c_{HA} = c_B$, that is when $K_{HA} = K_B$. It is found however, that, except for very large differences between acid and base strengths, a dependence of the hydrolysis on dilution is only noticeable at high dilution.

12. **Amphiprotic Substances:** It has already been seen that water is a substance showing both acidic and basic properties. In more complex molecules the acidic and basic property may be shown by a different portion of the molecule and a proton transfer within a given molecule is possible. The amino-acids constitute an important group which exemplify this possibility. Thus, glycine behaves as an acid

$$NH_2CH_2COOH \rightleftarrows NH_2CH_2COO^- + H^+,$$

or as a base

$$NH_2CH_2COOH + H^+ \rightleftarrows {}^+NH_3CH_2COOH,$$

while a proton transfer within the molecule,

$$NH_2CH_2COOH \rightleftarrows {}^+NH_3CH_2COO^-,$$

produces a molecule having no net charge but which has a positive and a negative charge at different locations in it. It is thus a dipole and has been termed a "dipole ion" or ampho-ion. In aqueous solutions the acid strength of the carboxyl group is higher than that of the NH_3^+ group; hence, the amino-acids will exist practically entirely in the ampho-ion form. In an aprotic solvent, the protolytic reaction will necessitate equal concentrations of the acid and base ions:

$$\underset{(\text{Acid}_1)}{NH_2CH_2COOH} + \underset{(\text{Base}_2)}{NH_2CH_2COOH} \rightleftarrows \underset{(\text{Acid}_2)}{{}^+NH_3CH_2COOH} + \underset{(\text{Base}_1)}{NH_2CH_2COO^-}.$$

If the solvent is not inert, protolysis with the solvent can occur in addition to the above and the concentrations of the acid and base ions will depend on the acidity of the solution. Thus,

$$NH_2CH_2COOH + H_3O^+ \rightleftarrows {}^+NH_3CH_2COOH + H_2O,$$
$$NH_2CH_2COOH + H_2O \rightleftarrows NH_2CH_2COO^- + H_3O^+,$$

or, in terms of the ampho-ion,

$${}^+NH_3CH_2COO^- + H_3O^+ = {}^+NH_3CH_2COOH + H_2O,$$
$${}^+NH_3CH_2COO^- + H_2O = NH_2CH_2COO^- + H_3O^+.$$

At a particular acidity for a given solvent the concentrations of acid and base forms will be equal. This is known as the *iso-electric point.* Since the ions are large they will have approximately the same speeds under the influence of an electric current and equal amounts will migrate in opposite directions giving the appearance of no migration. It can be shown that, at the iso-electric point where the ionization is a minimum, the solubility is also a minimum. The precipitation of electrolytic colloids such as proteins is brought about by adjusting the pH to the iso-electric point.

EXERCISES (13)

1. The dissociation constant of boric acid at 25° C. is 6.4×10^{-10}. Calculate the hydrogen ion concentration at dilutions (*a*) 1, (*b*) 10, (*c*) 100 liters.

2. The specific conductance of 0.1 *N* NH_4OH is 3.598×10^{-4}. Λ_0 is 238.7. Calculate the dissociation constant.

3. The dissociation constants of acetic and benzoic acids at 25° C. are respectively 1.86×10^{-5} and 6.6×10^{-5}. What concentration of benzoic acid would have the same pH as 0.1 *N* acetic acid?

4. Calculate the pH of 0.1 *N* nicotine given that the basic dissociation constant is 1×10^{-6}.

5. How much crystalline sodium acetate ($3H_2O$) must be added to one liter of 0.1 *N* acetic acid to give a solution with a pH of 4? The salt may be considered completely dissociated.

6. A salt of a weak base and a strong acid is 61.8 per cent hydrolyzed in 0.01 *N* solution and 91.6 per cent in 0.001 *N* solution. Calculate the hydrolysis constant.

7. K_w has the following values at the temperatures indicated:

$K_w \times 10^{14}$	0.11	0.29	0.68	1.00	5.48	52	550
$T°$ C.	0	10	20	25	50	100	200

Calculate the heat of dissociation of water.

8. 0.1 molal H_3PO_4 is titrated with NaOH using methyl orange as indicator. Calculate the fractions of acid converted to NaH_2PO_4 and to Na_2HPO_4 if the end point corresponds to pH of 4.3. The dissociation constants of H_3PO_4 are 7.5×10^{-3}, 6×10^{-8} and 3.6×10^{-13}.

CHAPTER 14

IONIC EQUILIBRIA II. STRONG ELECTROLYTES

It has already been shown that the concept of Arrhenius, that the conductance ratio Λ_v/Λ_0 is a measure of the degree of dissociation of electrolytes, cannot be applied without modification to a large class of electrolytes, inorganic acids and bases and most salts. These substances are classified as *strong electrolytes.* The equilibria in solutions of such electrolytes cannot be expressed by the Ostwald dilution law.

The anomaly thus presented by strong electrolytes has been continuously a matter of concern since the formulation of the dissociation theory and various essays at the solution of the problem have been undertaken. The earliest efforts were directed to a modification of the mass action equation in an effort to obtain a formula with which a constant 'dissociation constant' could be obtained. These formulas were, in reality, merely empirical equations, which, in the final issue, could only be used for interpolation purposes. None of them ever gave a satisfactory constant and, at the same time, an equation of theoretical significance. As such equations have only historical interest they may be omitted.

The formula of Arrhenius, $\alpha = \Lambda_v/\Lambda_0$, implies a constancy of ionic mobilities over the range of concentrations involved. In concentrated solutions there is experimental evidence that the mobilities are not independent of concentration. In fairly dilute solutions, however, the ratio of the mobilities may be regarded as constant; yet, even here, the conductance ratio does not yield a satisfactory measure of equilibrium to which the laws of equilibrium will apply.

Attempts to explain the anomaly by ionic hydration and complex ion formation did not succeed. The formation of ionic hydrates should not change the form of the dilution law in dilute solution but only the numerical value of the constant. The formation of complex ions would cause modification, but there is no evidence of the presence of such ions in solutions of salts such as potassium chloride, even though probable in more complex electrolytes such as copper sulfate.

Evidence has been presented that such electrolytes are completely or practically completely dissociated in solution and, owing to the relatively high ionic concentrations, interionic effects are important and cannot be neglected. Much of the information concerning strong electrolytes has been derived from a study of galvanic cells. It will be necessary therefore to consider the galvanic cell in some detail.

1. Galvanic Cells: Whenever two different phases are brought into contact, if either phase contains a substance which is electrically charged, for example ions or electrons, and which is soluble in both, the establishment of equilibrium between the phases will cause the phases to become oppositely charged and a potential difference will be manifested. The potentials between metals in contact, for example, are used in thermocouples. Potentials likewise exist between metals and gases or metals and solutions, between solutions of different electrolytes or of the same electrolyte at two different concentrations. Combinations of such contact potential differences are designated galvanic cells.

Two classes of galvanic cell may be differentiated, the first, in which chemical reaction proceeds even when no current is being drawn from the cell, the second, in which chemical change takes place only when the external circuit is closed. The original voltaic cell consisting of zinc and copper electrodes in dilute sulfuric acid evolves hydrogen continuously so long as zinc and acid remain. The Weston cell already considered, on the other hand, remains in stable equilibrium when there is no flow of electricity through it. Unless this equilibrium is disturbed by electrolyzing or discharging, and thus producing chemical reactions, the electromotive force of such a cell remains constant. It is this second class of galvanic cell that has most value in the more exact development of the subject.

2. **Reversible Cells:** The Weston cell may under certain conditions be a reversible cell, using the word reversible in the thermodynamic sense already discussed in detail in Chapter 8. Imagine the electromotive force of the Weston cell exactly balanced by some outside electromotive force so that no chemical change is produced in it. Then let this outside electromotive force be increased an infinitesimal amount. Reaction will be started in the Weston cell corresponding to some chemical change, and this reaction will be reversed if the outside electromotive force be diminished an infinitesimal amount. This would be an ideal condition of reversibility and the exactly balanced state would require an infinitely sensitive galvanometer in the Weston cell circuit for its measurement. From these considerations it is clear that any condition involving the passage of a finite current through the cell would be irreversible. In practice, the electromotive force of a cell is always measured by the method of balanced electromotive forces, or the potentiometer method, and the ideal condition, corresponding to reversibility, may be approached as more and more sensitive galvanometers are employed.

3. **Reversible Cells and Chemical Reaction:** It is important at this juncture to adopt a number of conventions for the designation of cells and the sign of electromotive force. The Weston cell will serve as an illustration, and will be written

$$\text{Cd (12.5 per cent amalg.)} \mid \text{CdSO}_4 \cdot \tfrac{8}{3}\text{H}_2\text{O}$$
$$\mid \text{CdSO}_4\,\text{(sat)} \mid \text{Hg}_2\text{SO}_4 \mid \text{Hg};\ E_{25} = 1.01810,$$

where E_{25} denotes its electromotive force at 25° C. The vertical lines serve to divide the phases. When not evident, the nature of the phase, whether solid or liquid, will be denoted by (*s*) and (*l*), respectively. A gas and its pressure will be represented thus: H_2 (1 atm.), Cl_2 (1 atm.). When the phase is a solution, the molal concentration of the solution, expressed in moles (formula weight) in 1,000 grams of solvent, will be given in brackets, and the saturated solution will be designated by (sat). The positive flow of electricity within this cell tends to take place from left to right. The chemical process corresponding to the cell is given by the equation

$$\begin{aligned} \text{Cd (12.5 per cent amalg.)} + Hg_2SO_4 + \tfrac{8}{3}H_2O \\ = CdSO_4 . \tfrac{8}{3}H_2O\ (s) + 2Hg;\ E_{25} = 1.01810. \end{aligned}$$

That is, the cell does electrical work when the reaction proceeds from left to right. The electromotive force, expressed in volts, will be taken as positive in the direction of the flow of positive current within the cell, or when negative flow is from right to left. The above electromotive force of the Weston cell will be employed as the standard.

When the electromotive force, E, is expressed in volts, it equals the electrical work in joules corresponding to the passage of one coulomb through the cell. If, in the cell reaction, n gram equivalents are changed, the total electrical work, corresponding to the passage of nF coulombs, will be nEF, where F is the faraday, or 96,494 coulombs. Since the electromotive force of such a cell is measured under conditions which approach very closely true equilibrium states, nEF will be the reversible electrical work of the cell reaction in joules. In the above cell reaction, the value of n is 2.

Now, it is possible, by constructing different combinations, to obtain the reversible electrical work corresponding to the various types of chemical reactions. The common general classes are combination, displacement, oxidation, metathesis, and neutralization, and their corresponding reverse reactions.

The reaction of the cell

$$Pt \mid H_2\ (1\ atm.) \mid HCl\ (0.1) \mid Cl_2\ (1\ atm.) \mid Pt;\ E_{25} = 1.4885$$

is

$$\tfrac{1}{2}H_2\ (g) + \tfrac{1}{2}Cl_2\ (g) = HCl\ (0.1),$$

which is illustrative of combination.

Many cells have been measured in which the chemical process is a displacement. These may be of various types, of which the Weston cell is a rather complicated example. A simpler cell is

$$Pt \mid H_2\ (1\ atm.) \mid HCl\ (0.1) \mid AgCl \mid Ag;\ E_{25} = 0.3522$$

and the corresponding cell reaction is

$$\tfrac{1}{2}H_2\ (1\ \text{atm.}) + AgCl\ (s) = Ag + HCl\ (0.1).$$

If we had written, for the cell reaction,

$$H_2\ (1\ \text{atm.}) + 2AgCl = 2Ag + 2HCl\ (0.1),$$

which would correspond to the passage of two faradays through the cell, the reversible electrical work would have been 2 × 0.3522 × 96,494 or 67,972 joules.

Another important type of cell representing a displacement reaction is the Daniell cell, or

$$Zn \mid ZnSO_4\ (1.0) \mid\mid CuSO_4\ (1.0) \mid Cu.$$

The cell reaction in this case is

$$Zn + CuSO_4\ (1.0) = ZnSO_4\ (1.0) + Cu.$$

Actually, in this cell, there will be a junction between the zinc and copper sulfate solutions, and, at this boundary, there will be a potential difference which must be eliminated by some method before the potential of the cell reaction can be known. The elimination of this "liquid junction potential" from the total electromotive force of a cell will be indicated as above by introducing two vertical lines.

The following is a good example of a cell without a liquid junction in which the cell reaction is an oxidation. The reaction of the cell

$$Hg \mid HgCl \mid KCl\ (0.05),\ K_4Fe(CN)_6\ (0.0005),\ K_3Fe(CN)_6\ (0.0005) \mid Pt;\ E = 0.0609$$

is

$$Hg + KCl\ (0.05) + K_3Fe(CN)_6\ (0.0005) = K_4Fe(CN)_6\ (0.0005) + HgCl\ (s).$$

In this cell, the solution is a mixture of three electrolytes. Commas are used merely for differentiating the electrolytes present. The cell

$$Pt \mid SnCl_2\ (0.1),\quad SnCl_4\ (0.1) \mid\mid FeCl_2\ (0.1),\quad FeCl_3\ (0.1) \mid Pt$$

would correspond to the reaction

$$2FeCl_2\ (0.1) + SnCl_4\ (0.1) = SnCl_2\ (0.1) + 2FeCl_3\ (0.1).$$

There is no example of a single cell without a liquid junction in which the reaction is a metathesis or double decomposition. However, Brönsted, by combining four cells, was able to determine the reversible electrical work of the reactions

$$NaCl\ (s) + KBr.2H_2O = KCl\ (s) + NaBr.2H_2O,$$
$$KCl\ (s) + NaClO_3\ (s) = KClO_3\ (s) + NaCl\ (s),$$

where the compounds are all in the solid state.

The cell

$$\text{Tl (amalg.)} \mid \text{TlCNS } (s) \mid \text{KCNS} \mid\mid \text{KCl} \mid \text{TlCl } (s) \mid \text{Tl (amalg.)}$$

which contains a liquid junction has been employed to measure the reversible electrical work of the reaction,

$$\text{TlCl } (s) + \text{KCNS} = \text{TlCNS } (s) + \text{KCl}.$$

Neutralization may be represented by the cell

$$\text{Pt} \mid \text{H}_2 \mid \text{OH}^- (1.0) \mid\mid \text{H}^+ (1.0) \mid \text{H}_2 \mid \text{Pt};\ \text{E}_{25} = 0.8280,$$

which corresponds to the reaction of the neutralization of strong acids and bases or

$$\text{H}^+ (1.0) + \text{OH}^- (1.0) = \text{H}_2\text{O } (l).$$

These examples are sufficient to show that the electromotive forces corresponding to all the common types of reactions involving strong electrolytes may be obtained from suitable cells, or by combining the electromotive forces of suitable cells. Since we shall find that the reversible electrical work is a very important chemical quantity, the measurement of electromotive force of reversible cells is a powerful means for investigation of reactions.

It should be emphasized that by far the most important consideration in dealing with galvanic cells is the exact knowledge of the cell reactions. Many errors have been made and many false conclusions drawn from measurements of electromotive forces without this knowledge.

4. The Calculation of Free Energy and Heat Content Increments of Cell Reactions: We have already seen (Chapter 8) that the free energy increment, ΔF, is measured in reversible cells by the quantity $-n\text{EF}$ where these symbols have the significance already assigned to them. From the variation of this magnitude with temperature it is obvious that we also obtain the change in the free energy increment with temperature and, hence, from the Gibbs-Helmholtz equation,

$$\Delta F = \Delta H + T\left(\frac{\partial(\Delta F)}{\partial T}\right)_p \tag{8.88}$$

we can derive values for the heat content increment (ΔH) with temperature. Thus, we may express the heat content increment by the equation

$$-\Delta H = n\text{EF} - n\text{F}T\frac{d\text{E}}{dT}\cdot \tag{8.91}$$

$$\Delta H = -n\text{F}\left(\text{E} - T\cdot\frac{d\text{E}}{dT}\right)$$

A comparison of values of $-\Delta H$ of a few cell reactions determined by measurement of electromotive force and by calorimetric measurement is given in the last two columns of Table 14.1. The column headings make the table self-explanatory.

TABLE 14.1

COMPARISON OF HEAT CONTENT DECREASES OF CELL REACTIONS IN CALORIES DETERMINED BY MEASUREMENTS OF ELECTROMOTIVE FORCE AND BY THERMOCHEMICAL MEASUREMENTS

Cell Reaction	E	$\frac{dE}{dT}$	$(-\Delta H)$ E.M.F.	$(-\Delta H)$ Thermochemical
(1) $Zn + 2AgCl = ZnCl_2$ (0.555M) $+ 2Ag$ (0° C.)	1.015	−0.000402	51,989	52,046
(2) $Pb + 2AgI = PbI_2 + 2Ag$ (25° C.)	0.21069	−0.000138	11,610	11,650
(3) $Cd + 2AgCl + 2.5H_2O = CdCl_2.2.5H_2O + 2Ag$ (25° C.)	0.67531	−0.00065	40,030	39,530
(4) $Cd + PbCl_2 + 2.5H_2O = CdCl_2.2.5H_2O + Pb$ (25° C.)	0.18801	−0.00048	15,250	14,650

In order to compute the heat content decrease accurately by means of the electromotive force method, the temperature coefficients of electromotive force must be obtained with great precision. Indeed, in the reactions in the above table, an error of 0.01 of a millivolt in the determination of E will cause an error of approximately 130 calories.

The above equation may be employed for the calculation of a change in heat content from free energy data. The method is well illustrated by a calculation performed by Ellis from electromotive force data of the cell

$$H_2 \text{ (1 atm.)} \mid HCl\ (c) \mid HgCl \mid Hg,$$

which corresponds to the cell reaction

$$H_2 \text{ (1 atm.)} + 2HgCl = 2Hg + 2HCl\ (c).$$

Table 14.2 contains some of his electromotive force data.

TABLE 14.2

ELECTROMOTIVE FORCE DATA OF THE CELL: H_2 (1 ATM.) | HCl (*c*) | HgCl | Hg

c	E.M.F.			$10^6\,\alpha$
	18°	25°	35°	
0.1004	0.39764	0.39884	0.40013	+ 386
0.3376	0.33845	0.33836	0.33794	− 75
0.7714	0.29654	0.29571	0.29411	− 460
4.484	0.15759	0.15506	0.15124	−2384

The electromotive force E at different temperatures may be computed for each temperature by the equation

$$\mathrm{E} = \mathrm{E}_{25}(1 + \alpha(t - 25)), \tag{14.1}$$

where the values of α are given in the last column of the table. The free energy decrease of the cell reaction as written will equal 2 × 23,074 × E calories, and also

$$(-\Delta F) = (-\Delta F)_{298}\,(1 + \alpha(T - 298)). \tag{14.2}$$

Now, if this value for $(-\Delta F)$ be substituted in the Gibbs-Helmholtz equation in the form

$$\frac{d}{dT}\left(\frac{\Delta F}{T}\right) = -\frac{\Delta H}{T^2} \tag{14.3}$$

and the differentiation performed,

$$(-\Delta H)_{298} = (-\Delta F)_{298}\,(1 - 298\alpha) \tag{14.4}$$

is obtained. In Table 14.3, are given values of $(-\Delta F)$ in calories computed from the electromotive forces, and $(-\Delta H)_{298}$ calculated by this last equation.

TABLE 14.3

$(-\Delta F)$ AND $(-\Delta H)_{298}$ OF THE CELL REACTION IN CALORIES

c	$(-\Delta F)_{291}$	$(-\Delta F)_{298}$	$(-\Delta F)_{308}$	$(-\Delta H)_{298}$
0.1004	18,351	18,407	18,466	16,290
0.3376	15,620	15,616	15,596	15,965
0.7714	13,685	13,647	13,593	15,528
4.484	7,273	7,156	6,980	12,240

This method of calculation should be employed when it is possible to express the electromotive forces as a function of the temperatures by a simple equation.

5. The Concentration Cell without Liquid Junction: Up to the present, only the free energy and heat content changes of cell reactions, which are complete chemical reactions and which do not involve changes in composition of any of the phases, have been discussed. We have now to consider free energy and heat content changes of quite a different nature, and processes in which the compositions of the phases play a predominant rôle.

The electromotive forces of cells, corresponding to the following cell reactions, will serve as an illustration:

$$\tfrac{1}{2}H_2\,(1\text{ atm.}) + AgCl = Ag + HCl\,(0.001);\quad E_{25} = 0.5785;\ (-\Delta F)_{298} = 55{,}822\text{ joules}$$

and

$$\tfrac{1}{2}H_2\,(1\text{ atm.}) + AgCl = Ag + HCl\,(0.0483);\quad E_{25} = 0.3870;\ (-\Delta F)_{298} = 37{,}343\text{ joules.}$$

If the second reaction be subtracted from the first, the result will be

$$HCl\,(0.0483) = HCl\,(0.001);\ E_{25} = 0.1915;\ (-\Delta\bar{F})_{298} = 18{,}479\text{ joules.}$$

This equation means that the net effect of the two cell reactions is the transfer of a mole of hydrochloric acid from a solution of 0.0483 molal concentration to a solution of 0.001 molal concentration, and that the free energy decrease of such a change is 18,479 joules. In other words, $(-\Delta\bar{F})$ is the free energy decrease when a mole of hydrochloric acid disappears at 0.0483 molal concentration and appears at 0.001 molal concentration. The most important point is that $(-\Delta\bar{F})$ may be regarded as the difference of two quantities, which are the change in free energy, $\bar{F}_2$, when a mole of hydrochloric acid is added to an infinitely large quantity of 0.0483 molal concentration, and the change in free energy, $\bar{F}_1$, when a mole is added to an infinitely large quantity of solution containing 0.001 molal hydrochloric acid. $\bar{F}_2$ and $\bar{F}_1$ will be denoted the partial molal free energies of the hydrochloric acid in the two solutions respectively.[1] It is always the case that the partial free energy is greater in the more concentrated solution, or $\bar{F}_2$ is greater than $\bar{F}_1$. Consider the transfer of a mole from the more concentrated to the more dilute solution. The *removal* of this mole from the concentrated solution will be accompanied by a change in free energy equal to $-\bar{F}_2$, and the addition of this mole to the more dilute solution will be accompanied by a change in free energy $+\bar{F}_1$. The total free energy increment of transfer will be the sum of these quantities $(\bar{F}_1 - \bar{F}_2)$ or $-(\bar{F}_2 - \bar{F}_1)$, which equals a decrease in free energy $(-\Delta\bar{F})$, and which in turn equals nEF.

In a similar manner, by subtracting the values of the heat content changes of the cell reactions computed by the Gibbs-Helmholtz equation (Table 14.3) at two different concentrations, the difference in partial molal heat contents of the acid at the two concentrations may be obtained. From the nature of these processes we are led to the consideration of a whole series of quantities which will prove to be of great importance in the application of thermodynamics to solutions.

These changes in partial molal free energy and heat content could

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[1] A partial quantity or a change in a partial quantity will always be represented by a dash over the symbol.

have been obtained directly from measurements of cells of the type

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(c_2) \mid \mathrm{H_2} \mid \mathrm{HCl}(c_1) \mid \mathrm{AgCl} \mid \mathrm{Ag},$$

where the net result of the cell reaction would be the change

$$\mathrm{HCl}(c_2) = \mathrm{HCl}(c_1).$$

This type of cell will be denoted the concentration cell without liquid junction. Such a cell is obtained whenever two simple cells containing solutions of different concentrations are connected in opposition. The alternative mode of connection gives the cell

$$\mathrm{H_2} \mid \mathrm{HCl}(c_2) \mid \mathrm{AgCl} \mid \mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(c_1) \mid \mathrm{H_2},$$

which has the same numerical electromotive force though the direction of current flow would be the opposite and, to adhere to convention, the acid concentrations must be reversed giving

$$\mathrm{H_2} \mid \mathrm{HCl}(c_1) \mid \mathrm{AgCl} \mid \mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(c_2) \mid \mathrm{H_2}.$$

For the measurement of partial free energy changes of electrolytes containing a metal which readily reacts with water, there are available cells in which the metal electrode is a very dilute amalgam. For example, the cell

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{KCl}(c_2) \mid \mathrm{K}\ (\text{dil. amalg.}) \mid \mathrm{KCl}(c_1) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

affords measurement of the partial free energy change corresponding to the transfer

$$\mathrm{KCl}(c_2) = \mathrm{KCl}(c_1).$$

6. **Amalgam Cells:** The determination of partial free energy and heat content changes by the electromotive force method may also be applied to the study of solutions of electrolytes in metallic solvents. The electromotive force of the cell at constant pressure and temperature

$$\mathrm{Me}(c_2)\ (\text{amalg.}) \mid \mathrm{MeX}\ (\text{solution}) \mid \mathrm{Me}(c_1)\ (\text{amalg.}),$$

consisting of two amalgam electrodes at different concentrations connected by a solution of a salt of the metal, MeX, is independent of the concentration of this salt solution and depends only on the composition of the amalgam. The net effect of the cell reaction is the disappearance of the metal from the amalgam of the higher concentration, and its appearance in an amalgam of lower concentration. This process is accompanied by a decrease in free energy equal to the difference in partial free energies of the metal in the amalgams of the two concentrations, or $-(\bar{F}_2 - \bar{F}_1)$ if c_2 is greater than c_1. A most exhaustive study of the cell

$$\mathrm{Tl}(c_2)\ (\text{amalg.}) \mid \mathrm{Tl_2SO_4} \mid \mathrm{Tl}(c_1)\ (\text{amalg.})$$

has been carried out by Richards and Daniels, as a result of which the partial free energy and heat content changes of both the thallium and mercury are accurately known. Indeed, the stability of the amalgams permitted measurements of solutions as concentrated as 40 per cent of thallium. Some of the results are presented in Table 14.4.

TABLE 14.4

E.M.F.'s of Thallium Amalgam Cells

Amalgam Concentrations		E.M.F. in Millivolts at		$E_{25} = 0.05915 \log \frac{c_2}{c_1} \times 10^3$ millivolts
c_1	c_2	20° C.	30° C.	
0.3315	1.704	45.550	46.937	42.1
1.704	3.788	26.395	27.050	20.5
4.930	10.019	29.480	29.971	18.8
10.019	17.049	24.342	24.660	13.65
20.970	27.362	11.572	11.741	6.83
20.780	34.029	20.341	20.678	12.68

7. The Free Energy Change Accompanying Concentration Changes: We saw in Chapter 8 that the free energy change accompanying the transfer of one mole of a gas from a pressure P to a pressure P' was given by the expression $\Delta F = RT \ln (P'/P)$. In section 10, 4 it was pointed out that for dilute solutions obeying Henry's law and the ideal gas laws an identical procedure would yield for a concentration change from c_2 to c_1 the expression $\Delta F = RT \ln (c_1/c_2)$. The above amalgam cells constitute a method of securing such a concentration change under circumstances such that the free energy change is simultaneously measurable, since this is given by the expression $-\Delta F = n\mathrm{EF}$. Combining these two expressions for ΔF, we obtain $n\mathrm{EF} = RT \ln (c_2/c_1)$, whence

$$\mathrm{E} = \frac{RT}{n\mathrm{F}} \ln \frac{c_2}{c_1} \cdot \tag{14.5}$$

This expression for the electromotive force of a concentration cell of any type was first derived by Nernst from a different standpoint. It is, however, a direct consequence of fundamental thermodynamics when applied to ideal solutions. We may utilize this equation to determine how far the above solutions of thallium in mercury approximate to the ideal state. Accordingly, in the final column of the preceding table are to be found the corresponding values of E calculated from this equation for a temperature of $T = 298°$ K. It is apparent, from a comparison between the calculated and experimental results, that, at low concentrations of amalgam, the agreement is fair, but that, in the more concentrated solutions, there is a very great discrepancy between experiment and the requirements of theory based on the laws of ideal solutions. It is evident therefore that for a general treatment of solutions some alternative method of theoretical approach is required. This need has been met in the use of the *activity function* introduced into thermodynamic chemistry by G. N. Lewis, as previously mentioned.

8. **Activity and Ionic Equilibria:** We may apply this general method of treatment to ionic equilibria, for example to equilibrium in a solution of a uni-univalent electrolyte,

$$\mathrm{CA} = \mathrm{C^+} + \mathrm{A^-}.$$

Let a_+ and a_- be the activities of the cation and anion respectively and let a_2 be the activity of the undissociated molecule. Then the equilibrium constant is given by

$$K_a = a_+a_-/a_2. \tag{14.6}$$

We are unaware of the concentration of the undissociated molecule in the case of strong electrolytes, so we may assume an arbitrary value for K_a. If we set it equal to 1, it follows that

$$a_2 = a_+a_- \tag{14.7}$$

and we thus can get a *definition of the activity of the electrolyte.*

It will be seen later that the activity of an individual ion cannot be determined experimentally. It is possible however to determine the mean value for a pair of ions. Thus the *mean activity of the electrolyte* is defined as

$$a_\pm = (a_+a_-)^{1/2}. \tag{14.8}$$

We shall utilize, however, a quantity, f, *the activity coefficient* of an electrolyte, which, for the present case of a uni-univalent electrolyte, is defined as the mean activity divided by the molal concentration of the electrolyte, or

$$f = \frac{a_\pm}{c} = \frac{(a_+a_-)^{1/2}}{c} = \left(\frac{a_+a_-}{c^2}\right)^{1/2}. \tag{14.9}$$

It can be seen that the activity coefficient of the electrolyte is in this case the square root of the product of the activity coefficients of the ions. The expression for f changes with the valence of the ions. Thus, with a bi-univalent electrolyte, $\mathrm{CA_2}$, we have

$$a_2 = a_+a_-^2 \tag{14.10}$$

and

$$a_\pm = (a_+a_-^2)^{1/3}, \tag{14.11}$$

since there are three ions formed on ionization. In this case

$$f = \left(\frac{a_+}{c} \times \frac{a_-{}^2}{4c^2} \right)^{1/3}. \tag{14.12}$$

In general, for an electrolyte, $C_{\nu^+}A_{\nu^-}$

$$f = \left(\frac{a_+{}^{\nu^+}}{(\nu^+c)^{\nu^+}} \cdot \frac{a_-{}^{\nu^-}}{(\nu^-c)^{\nu^-}} \right)^{1/\nu}, \tag{14.13}$$

where

$$\nu = \nu^+ + \nu^-.$$

It must be realized from the general definition that the activity of a solute in a solution becomes equal to the concentration of the solute as the concentration approaches zero. It follows that the activity coefficient approaches unity as the concentration approaches zero. The evaluation of activities or activity coefficients must involve therefore an extrapolation, directly or indirectly, to zero concentration. Since concentration is usually expressed as mole fraction, molality or molarity, an activity coefficient and hence also an activity may be defined to correspond to each concentration unit. At infinite dilution each activity coefficient will be unity, but with increasing concentration the three values will diverge from each other. We shall use in general the molality activity coefficient as defined above. It is sometimes represented by the symbol, γ.

9. **Activity from Electromotive Force:** Consider the simple reaction,

$$\text{HCl}(c') = \text{HCl}(c)$$

data for which can be obtained from a study of the cells

$$\text{H}_2 \text{ (1 atm.)} \mid \text{HCl}(c') \mid \text{AgCl} \mid \text{Ag},$$
$$\text{H}_2 \text{ (1 atm.)} \mid \text{HCl}(c) \mid \text{AgCl} \mid \text{Ag}.$$

Let the electromotive forces be E′ and E. The change in free energy of the reaction will be related to the difference of these electromotive forces:

$$\Delta\bar{F} = -n\text{F}(\text{E} - \text{E}'), \tag{14.14}$$

as also to the activities of the acid:

$$\Delta\bar{F} = \bar{F} - \bar{F}' = RT \ln (a_2/a_2'), \tag{14.15}$$

where the prime refers to the concentration c'. Hence

$$-n\text{F}(\text{E} - \text{E}') = RT \ln (a_2/a_2'). \tag{14.16}$$

If now c' could be so chosen that a_2' is unity and the corresponding electromotive force of the cell be denoted E_0, it follows that

$$-n\text{F}(\text{E} - \text{E}_0) = RT \ln a_2$$

or

$$-(\mathrm{E} - \mathrm{E}_0) = (RT/n\mathrm{F}) \ln a_2 \tag{14.17}$$

or in terms of the mean activity at 25° C,

$$-(\mathrm{E} - \mathrm{E}_0) = (2RT/n\mathrm{F}) \ln a_{\pm} = 0.1183 \log a_{\pm}. \tag{14.18}$$

Subtracting 0.1183 log c from each side gives

$$\mathrm{E}_0 - (\mathrm{E} + 0.1183 \log c) = 0.1183 \log (a_{\pm}/c) = 0.1183 \log f. \tag{14.19}$$

The value of E_0 can obviously be found from this equation since it will be equal to the value of E + 0.1183 log c when $f = 1$ and the activity coefficient is unity at zero concentration. If therefore the electromotive force of the above cell is measured at a series of decreasing concentrations of HCl and the quantity E + 0.1183 log c is plotted against some convenient function of the concentration such as c or $c^{1/2}$ an extrapolation to $c = 0$ will give the value of E_0.

In this manner, Linhart measured the cell

$$\mathrm{H_2} \mid \mathrm{HCl}_{(c)} \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

at various concentrations of (c) and found graphically a value for E_0 of 0.2234 volt. Using this value in the above expression for log f the following values for f were obtained.

TABLE 14.5

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID AT 25° C.

From Measurements of $\mathrm{H_2} \mid \mathrm{HCl}_{(c)} \mid \mathrm{AgCl} \mid \mathrm{Ag}$ and $\mathrm{H_2} \mid \mathrm{HCl}_{(c)} \mid \mathrm{HgCl} \mid \mathrm{Hg}$.

c = 0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1.0	2.0	3.0
f = 0.991	0.984	0.947	0.924	0.860	0.814	0.762	0.823	1.032	1.35

There are very few electromotive force data that are sufficiently accurate for such extrapolation purposes but the electromotive force method is very useful for more concentrated solutions, provided a value for f in dilute solutions is obtainable. We shall approach this problem from another standpoint.

10. **Freezing Point Lowering and Activity:** We saw, in discussing ideal solutions, that van't Hoff formulated the relationship between osmotic pressure and concentration by the equation

$$PV = RT$$

and pointed out that for electrolytic solutions the abnormal freezing point lowering as well as osmotic pressure required a factor, i, in the equation

$$PV = iRT.$$

Arrhenius recognized that only those solutions which possessed an i factor greater than unity conducted an electric current. As a result, he suggested that electrolytes were dissociated into ions and that i was a measure of the number of gram ions and molecules resulting from the dissociation of a mole of electrolyte under the given conditions. Arrhenius, also, associated this value of i with the degree of dissociation as determined from the conductance ratio. Thus, for an electrolyte yielding ν ions and of which a fraction α is dissociated into ions, the number of gram ions is $\nu\alpha$ and of undissociated molecules is $1 - \alpha$, a total of $1 + (\nu - 1)\alpha$ and this is equal to i. Hence, on the Arrhenius hypothesis,

$$\alpha = \Lambda_v/\Lambda_0 = (i - 1)/(\nu - 1). \tag{14.20}$$

In dilute solutions this relationship is approximately obeyed, but there are deviations in the more concentrated solutions which are far greater than the experimental error would warrant. It is therefore desirable to distinguish between the conductance ratio $\alpha = \Lambda_v/\Lambda_0$ and the van't Hoff coefficient $\gamma_0 = (i - 1)/(\nu - 1)$. Table 14.6 gives the values found for such a simple salt as potassium chloride; the activity coefficient is included for comparison. It can be seen that α decreases continuously while γ_0 and f pass through a minimum and increase again. The discrepancy between α and γ_0 at concentrations above 0.1 M is quite outside the limits of experimental error. Furthermore, that no relation exists between α and f is obvious from the fact that α as a "degree of dissociation" must always be less than one, whereas f may increase indefinitely; the activity coefficient of 16 M HCl is 43.2.

TABLE 14.6

KCl AT 25° C.

Conc.	α	γ_0	
0.01	0.941	0.940	0.903
0.05	0.889	0.892	0.821
0.1	0.860	0.863	0.779
0.5	0.779	0.791	0.659
1.0	0.742	0.780	0.613
2.0	0.697	0.820	0.566
3.0	0.665	0.894	0.575

The general trend of the values of γ_0 and f is much more similar, suggesting that a possible relationship between them could be found. To do this it is desirable to utilize in place of i, a quantity, j, defined by Bjerrum as equal to $1 - (i/\nu)$, where ν is the number of ions produced by the ionization of one molecule of the electrolyte. For uni-univalent electrolytes at low concentrations it can be shown experimentally that j

is proportional to the square root of the concentration, or

$$j = B\sqrt{c}, \tag{14.21}$$

where B is an experimentally determinable constant. Also, it can be shown thermodynamically that the expression $(-\ln f)$ is also proportional to the square root of the concentration and that the constant of proportionality is equal to $3B$. Hence

$$-\ln f = 3B\sqrt{c} = 3j. \tag{14.22}$$

Given this relationship, the values of the activity coefficient of uni-univalent electrolytes are obtainable from all measurements which are sufficiently exact to yield trustworthy values of i. This is most nearly true of freezing point data and a few vapor pressure measurements; consequently, such measurements have been utilized for the determination of activities in dilute solutions.

TABLE 14.7

ACTIVITY COEFFICIENTS IN VERY DILUTE SOLUTIONS FROM FREEZING POINT DATA

Electrolyte $c =$	0.0001	0.0005	0.001	0.005	0.01	0.05	0.1
KCl	0.982	0.970	0.961	0.926	0.903	0.821	0.779
NaCl	0.985	0.972	0.963	0.928	0.906	0.834	0.792

11. **The Theory of Debye and Hückel:** The incompatibility between the postulates of Arrhenius concerning the degree of dissociation of strong electrolytes and the evidence for complete ionization of such electrolytes has led to a number of efforts which, starting from the assumption of complete ionization, would give expressions in agreement with the results of experimental measurement of the thermodynamic properties of such solutions. Of these efforts the most notably successful is that of Debye and Hückel. These authors assume that, in dilute solution, the departure from validity of the laws of dilute solutions found with strong electrolytes, is to be ascribed to the ionization. In a solution of a non-electrolyte they point out that the relation between the partial free energy and the concentration is given by the expression

$$\bar{F} = RT \ln c + \text{Const.}$$

while for an electrolyte the equation becomes

$$\bar{F} = RT \ln a + \text{Const.}$$

or, writing the activity as the product of the concentration and activity coefficient,

$$\bar{F} = RT \ln c + RT \ln f + \text{Const.}$$

The difference between a solution of a non-electrolyte and one of an electrolyte lies in the presence of ions in the latter. The difference, therefore, between the partial free energies of an electrolyte and a non-electrolyte must lie in what may be termed an electrical free energy $\bar{F}_e$ associated with the electrical forces existing between the ions. Since the difference between the right hand sides of the above equations is $RT \ln f$ this may be written

$$\bar{F}_e = RT \ln f \qquad (14.23)$$

and a calculation of the activity coefficient necessitates a knowledge of the electrical free energy.

Debye and Hückel, assuming complete dissociation of strong electrolytes in solution, and assuming also that the forces acting between ions are simply electrostatic forces governed by Coulomb's law, that is, varying inversely as the square of the distance of separation, show that, on the average, in the neighborhood of any ion there will be more ions of unlike sign than of like sign. There is, therefore, a net attraction between a particular ion and those in its immediate neighborhood constituting its atmosphere. A dilution of the solution, consequently, involves an expenditure of energy in the separation of the ions against this attraction. It is this which constitutes the electrical free energy.

By a combination of kinetic theory in the form of the Boltzmann distribution law and the theory of electrostatic potential due to Poisson based on Coulomb's law, it is possible to calculate[1] the electrical contribution to the partial free energy of an ion and from it the activity coefficient of an ion and hence of an electrolyte. The mathematical approach becomes simple only in the case of dilute solutions yielding what is termed the limiting law:

$$-\log f = 0.507 z_1 z_2 \sqrt{\mu}, \qquad (14.24)$$

where f is the activity coefficient of an electrolyte yielding two ions of valence z_1 and z_2; 0.507 is the numerical value at 25° C. of a function involving the charge on the electron, the gas constant, the dielectric constant of the medium and the temperature. The symbol μ, the ionic strength, is a concentration function, first used by Lewis and Randall and defined by the relation $\mu = \frac{1}{2}\Sigma(c_i z_i^2)$ where c_i is the molal concentration and z_i the valence of a particular ion and where the summation is for each kind of ion in the solution. For uni-univalent electrolytes the ionic strength is identical with the molal concentration.

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[1] See Appendix 3.

This conclusion, reached by Debye and Hückel, is in conformity with one conclusion which we have already stated, namely, that j and also $\log f$ are proportional to the square root of the concentration. This was reached from an examination of the available freezing point data. To subject the theory to a further more rigorous test it is necessary first to consider the relationship between activity and solubility.

12. **Activity and Solubility:** When a solid salt is in equilibrium with its saturated solution, the activity of the solid salt is equal to that of the salt in the saturated solution. At constant temperature and pressure the activity of the solid is a constant, k. Hence, for a uni-univalent electrolyte,

$$k = a_2 = a_+a_- \tag{14.25}$$

or

$$k = f_+c_+ \cdot f_-c_- = f_+f_-c_+c_-, \tag{14.26}$$

where c_+ and c_- are the stoichiometrical concentrations of the ions, f_+ and f_- their respective activity coefficients. For a given salt $c_+ = c_- = S$, where S is the solubility; the activity coefficient, f, for the salt is $f = (f_+f_-)^{1/2}$. It follows that f is inversely proportional to the solubility

$$f \propto 1/S. \tag{14.27}$$

This is true not only for an aqueous solution of the salt but also for solutions of the salt in salt solutions which do not have an ion in common with that of the salt under study. Such salt solutions are termed by Brönsted hetero-ionic solvents.

Solutions of electrolytes having an ion in common with that whose solubility is under investigation are known as homo-ionic solvents. In these cases either c_+ or c_- may equal S and the other ion concentration equals the sum of its stoichiometrical concentration for both electrolytes. If the anion is common to both electrolytes

$$k = f_+f_-Sc_- \tag{14.28}$$

and, therefore,

$$f \propto (1/Sc_-)^{1/2}. \tag{14.29}$$

With a common cation,

$$f \propto (1/Sc_+)^{1/2}. \tag{14.30}$$

In either of these cases it is possible to determine the activity coefficient of a salt in a mixture if the activity of the pure salt is known and its solubility in the mixture is measurable.

If the mixture behaved as an ideal solution it is evident that f would be equal to 1 and the well known *law of the solubility product* would result

$$c_+c_- = k. \tag{14.31}$$

It is the *approximate* truth of this relationship, or what is the same thing, the fact that, in dilute solution, f differs only slightly from unity, which has given to the law of the solubility product its wide applicability, especially in analytical chemistry. It is evident that, so long as f does not vary widely from unity, the addition of a salt with a common ion will repress the solubility of a sparingly soluble electrolyte.

That the activity coefficient both varies in value and differs from unity is evident from the data of Bray and Winninghoff on the solubility of thallous chloride in various salt solutions, the data having been computed for f, the activity coefficient, by Lewis and Randall with the following results.

TABLE 14.8

ACTIVITY COEFFICIENTS OF THALLOUS CHLORIDE IN SALT SOLUTIONS AT 25° C.

c (Equivalents per Liter of Added Salt)	f						
	KNO_3	KCl	HCl	$TlNO_3$	$BaCl_2$	Tl_2SO_4	K_2SO_4
0	0.885	0.885	0.885	0.885	0.885	0.885	0.885
0.02	0.829	(0.843)	(0.844)	(0.836)	(0.829)	0.803	0.800
0.025	(0.819)	0.831	0.833	0.825	0.814	(0.789)	(0.787)
0.05	0.779	0.784	0.788	0.759	0.763	0.726	0.733
0.1	0.725	0.701	0.713	0.678	0.683	0.643	0.666
0.2	(0.655)	0.610	0.628	—	0.595	—	(0.588)
0.3	0.615	—	—	—	—	—	0.547
1	0.463	—	—	—	—	—	0.417

(The values in parentheses were obtained by graphical interpolations.)

The decrease in the activity coefficient signifies an increase in the solubility of thallous chloride in the absence of a common ion. Thus, in presence of 1N KNO_3 the solubility of thallous chloride has increased from 0.016, its value in pure water, to 0.031 equiv. per liter and a similar increase is found in presence of potassium sulfate. In all the other cases the presence of the common ion more than counterbalances this increased solubility due to the activity coefficient, and the solubility decreases. For higher valence electrolytes the decrease in the activity coefficient is so large that the common ion effect is obliterated and the solubility increases; the solubility of $La(IO_3)_3$ is increased fifty per cent by the addition of 0.1 M $La(NO_3)_3$. Again, Brönsted found an increase in the solubility of a sparingly soluble tri-trivalent electrolyte on addition of 1 M $MgSO_4$ of 27,700 per cent.

13. **Solubility and the Limiting Law:** For a hetero-ionic system the activity coefficient is inversely proportional to the solubility. If s_0 and s represent the solubilities of a salt in pure water and in another salt solution respectively and the corresponding activity coefficients of the

saturating salt are f_0 and f_1 it follows that

$$f_0 s_0 = f_1 s \tag{14.32}$$

or

$$-\log f_1 = \log (s/s_0) - \log f_0. \tag{14.33}$$

The value of f_0 is of course practically unity and log f_0 therefore almost zero. When f_0 is accurately known, f_1 can be calculated in the solutions of various ionic strengths.

The accurate value of f_0 can best be determined by plotting log (s/s_0) against some function of the concentration which will yield a reliable extrapolation to zero concentration. The square root of the total ionic strength of the solution is very satisfactory for this purpose since, in the dilute solution, it gives a straight line.

Brönsted and La Mer have measured the solubilities of a number of very slightly soluble cobaltammine compounds making use of the many ammonia groups to increase the accuracy of the determination of such low concentrations. The solubilities in pure water ranged from 0.0005 to 0.00005 M and were determined with an accuracy of 0.2 per cent. Calculation by the above method gave values for the activity coefficient. Fig. 14.1 shows the results obtained for $(-\log f)$ as a function of $\sqrt{\mu}$.

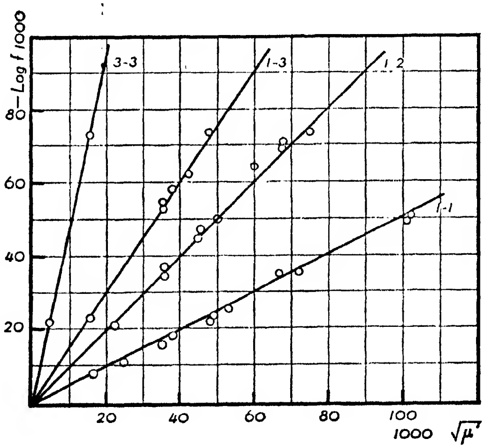

FIG. 14.1. Activity Coefficients at High Dilution

The straight lines indicate the theoretical slopes to be expected from the limiting law for, uni-uni, uni-bi and uni-trivalent salts. Later La Mer, King and Mason studied a tri-trivalent salt in a similar manner. The solvent salts included NaCl, KNO_3, $MgSO_4$, $K_3Co(CN)_6$, K_2SO_4 and $BaCl_2$.

The agreement between the experimental points and the theoretical lines verifies the limiting law in three respects, (1) the ionic strength, since a straight line is obtained, (2) the valence factor z_1z_2, since the slopes of the lines are in the ratios 1 : 2 : 3 : 9 and (3) the constant 0.507.

14. Activity Coefficients at High Concentrations: Accurate data are now available on the electromotive forces of such cells as

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{MeX}_{(c_1)} \mid \mathrm{Me(Hg)}_x \mid \mathrm{MeX}_{(c_2)} \mid \mathrm{AgCl} \mid \mathrm{Ag},$$

where $\mathrm{Me(Hg)}_x$ is a metal amalgam and MeX is an alkali halide. Potassium, sodium and lithium chlorides and potassium bromide have thus been studied. Potassium hydroxide has been studied with the aid of the cells,

$$\mathrm{Hg} \mid \mathrm{HgO} \mid \mathrm{KOH}_{(c_1)} \mid \mathrm{K(Hg)}_x \mid \mathrm{KOH}_{(c_2)} \mid \mathrm{HgO} \mid \mathrm{Hg}$$

and

$$\mathrm{H}_2 \mid \mathrm{KOH}_{(c_1)} \mid \mathrm{K(Hg)}_x \mid \mathrm{KOH}_{(c_2)} \mid \mathrm{H}_2.$$

If we consider the reaction

$$\mathrm{C^+A^-}(c_1) = \mathrm{C^+A^-}(c_2)$$

we have

$$\Delta\bar{F} = \bar{F}_2 - \bar{F}_1 = -n\mathrm{EF} = RT \ln (a_+''a_-''/a_+'a_-'). \qquad (14.34)$$

E is positive when c_1 is greater than c_2. Since $a_\pm = (a_+a_-)^{1/2} = fc$, we obtain

$$-n\mathrm{EF} = 2RT \ln (f_2c_2/f_1c_1)$$

or, at 25° C.,

$$\mathrm{E} = 0.1183 \log (f_1c_1/f_2c_2) \qquad (14.35)$$

If f is known at one concentration its value can be computed at any other concentration. At concentrations above 0.03 molal, the E.M.F. data show excellent agreement with the freezing point data. Hence, using the freezing point data for reference values for f, the E.M.F. data can be used to higher concentrations. Thus, the values for f at 0.1 molal concentrations for KCl, KBr, and NaCl were taken as 0.779, 0.766 and 0.792 respectively. For LiCl the value used was 0.804. The results obtained from the E.M.F. data using the preceding expression are shown in Fig. 14.2. It is evident that the activity coefficients of these electrolytes pass through minimum values at different salt concentrations.

15. Activity Coefficients in Mixtures by E.M.F. Measurements: By measuring the electromotive forces of cells of the type

$$\mathrm{H}_2 \mid \mathrm{HCl}(c_1) \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

and

$$\mathrm{H}_2 \mid \mathrm{HCl}(c_1), \mathrm{MeCl}_x(c) \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

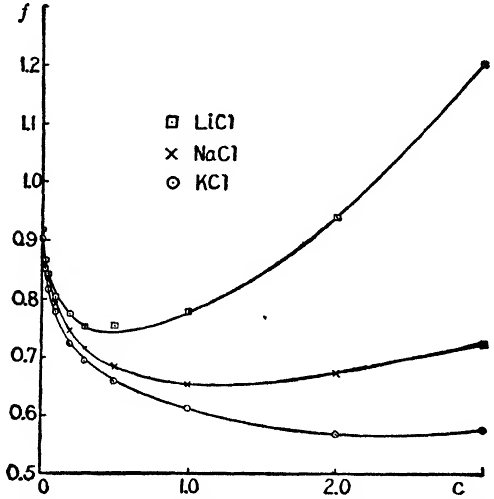

Fig. 14.2 Activity Coefficients of Uni-univalent Halides

the free energy decrease attending the reaction

$$\mathrm{HCl}(c_1),\ \mathrm{MeCl}_x(c) = \mathrm{HCl}(c_1)$$

may be computed. This decrease in free energy is equal to the difference in partial molal free energies of the acid in pure acid solution and the salt solution. We have thus,

$$-\Delta\bar{F} = -(\bar{F}_2 - \bar{F}_{2(s)}) = RT\ln\frac{a_{\mathrm{H}(s)}a_{\mathrm{Cl}(c+c_1)}}{a_{\mathrm{H}(c_1)}a_{\mathrm{Cl}(c_1)}}\,. \qquad (14.36)$$

Now, since $a_{\mathrm{H}(c_1)}\cdot a_{\mathrm{Cl}(c_1)}$ for the pure acid is known at a concentration c_1 the activity product of the hydrogen and chloride ions in the mixed solutions may be calculated. Further, the activity coefficient of the acid in the solution is given by the expression

$$f = \sqrt{\frac{a_{\mathrm{H}(s)}\cdot a_{\mathrm{Cl}(c+c_1)}}{c_1(c+c_1)}}\,. \qquad (14.37)$$

In Fig. 14.3 the activity coefficient of 0.1 molal hydrochloric acid has been plotted against the total molal concentration (curve No. 1), and also the activity coefficient of 0.1 molal acid in calcium chloride solutions against both the total molal (curve No. 2) and weight equivalent (curve No. 3) concentrations. There is a wide departure from uniformity between these curves. This is caused in part, at least, by the fact that the concentrations have been expressed in units which do not eliminate the change in properties of the solution when a unibivalent chloride is substituted for a uni-univalent chloride. For the purposes of calculation, it would be a great convenience to eliminate any differences caused by a difference in electrostatic field intensity in going from the uni-univalent to a unibivalent solution. One way by means of which this may be done is by expressing the concentration in a unit such that, at equal values of this unit, all electrolytes are subject to the same electrostatic forces. Lewis and Randall suggested for this purpose the unit which they called the "ionic strength" which has already been defined.

If now, the activities of the 0.1 molal acid in the salt solutions be plotted against μ, as shown in Fig. 14.4, the curves are all uniform and approach the 0.1 molal value uniformly. It is important to note that each of these curves has a minimum, and possesses a form similar to a similarly drawn curve for pure hydrochloric acid. Further, the activity coefficient of the acid is greater in solutions of the electrolytes which, when alone in aqueous solutions, have the higher activity coefficients.

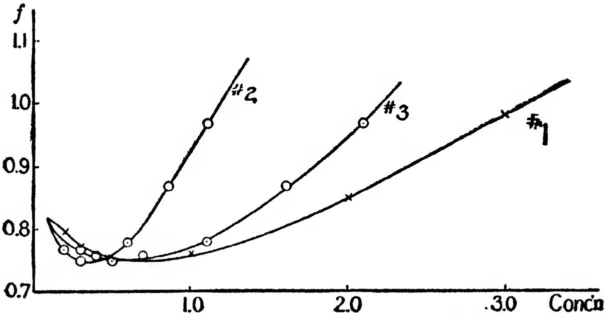

Fig. 14.3. Concentration Plot of Activity Coefficients of Hydrochloric Acid in Halide Solutions

The dependence of the activity coefficient on the ionic strength of the solution is further confirmation of the Debye-Hückel theory which assumes that the deviations from ideal behavior are to be attributed to the electrical environment; the activity coefficient of an ion depends on all the ions present as also on its valence.

16. **Cells with Liquid Junctions:** The cell without liquid junction is the only type which has been considered, and it has been shown that from measurements of such cells the activity products and mean activity coefficients may be computed with exactness. We have yet to consider the very difficult and important problems of the cell with a liquid junction. Consider the cell

$$H_2(1 \text{ atm.}) \mid HCl(c_1) \mid HCl(c_2) \mid H_2(1 \text{ atm.})$$

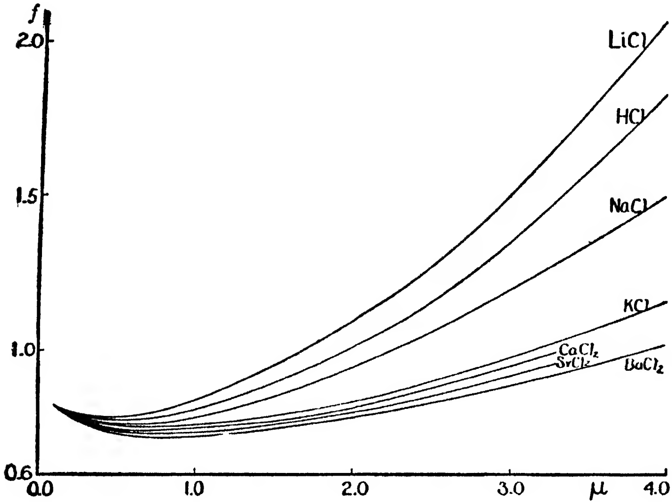

FIG. 14.4. Ionic Strength Plot of Activity Coefficients of Hydrochloric Acid in Halide Solutions

which is the concentration cell without a liquid junction previously considered from which the intermediate electrode AgCl | Ag | AgCl has been omitted and in which therefore there is now a direct contact between the two acid solutions. The possibility at once arises of a direct transfer of acid by diffusion from the more concentrated to the more dilute solution. Such a cell is known as a concentration cell with a liquid junction.

The passage of one faraday through the cell involves the following changes: (1) one equivalent of hydrogen dissolves at the left-hand electrode to produce hydrogen ions in the solution of concentration c_1, (2) a transport number, t_+, equivalent of hydrogen ions migrate across the liquid junction from left to right and t_- equivalent of chloride ion from right to left, (3) one equivalent of hydrogen ions is discharged at the right hand electrode. The net effect is a gain of $1 - t_+ = t_-$ equivalent of hydrogen ions and t_- equivalent of chloride ion by the solution at concentration c_1. This transfer of acid from c_2 to c_1 indicates that $c_2 > c_1$ when the electromotive force of the cell as written is positive. The change in free energy accompanying the transfer of t_- equivalents of each ion is given by

$$-\Delta F = t_-RT \ln (a_+'a_-'/a_+''a_-'') \tag{14.38}$$

and since the electromotive force E_T is $-\Delta F/\text{F}$, then

$$\text{E}_\text{T} = t_-(RT/\text{F}) \ln (a_+'a_-'/a_+''a_-''), \tag{14.39}$$

where the primes refer to the concentration subscripts. The electromotive force of the corresponding concentration cell without the liquid junction has been shown to be

$$\mathrm{E} = (RT/\mathrm{F}) \ln (a_+'a_-'/a_+''a_-''). \tag{14.40}$$

The two expressions differ only by the transport number term in Eq. (14.39). Thus,

$$\mathrm{E_T} = t_-\mathrm{E}. \tag{14.41}$$

It should be noted that, in the cell considered, the electrodes are reversible with respect to hydrogen whereas it is the transport number of the chloride ion that appears in $\mathrm{E_T}$. The electrodes may however be made reversible with respect to the chloride ion in the cell

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(c_2) \mid \mathrm{HCl}(c_1) \mid \mathrm{AgCl} \mid \mathrm{Ag}.$$

Analysis of the changes occurring in this form of the cell will show that the net effect is a transfer of t_+ equivalents of hydrogen and of chloride ions.

17. Liquid Junction Potentials: Liquid junction potentials are produced by the process of diffusion. Consider the boundary

$$\mathrm{HCl\ (conc.)} \mid \mathrm{HCl\ (dil.)}.$$

There will be a tendency for the acid to diffuse from the concentrated to the dilute solution, and, since the hydrogen ion has a higher mobility than the chloride ion, an excess of hydrogen ions will diffuse into the dilute solution until a sufficient potential difference is set up to retard enough hydrogen ions and accelerate enough chloride ions to equalize the diffusion rates. The net result will be an electromotive force from the more concentrated to the more dilute solution.

In the cell previously considered it was seen that the passage of one faraday involved, so far as the liquid junction alone was concerned, the transfer of t_+ equivalents of hydrogen ion from c_1 to c_2 and t_- equivalents of chloride ion from c_2 to c_1. The total change in free energy is thus

$$\Delta F = t_+RT \ln (a_+''/a_+') + t_-RT \ln (a_-'/a_-''). \tag{14.42}$$

The electrical work corresponding to a liquid junction potential E_l is $\mathrm{E}_l\mathrm{F}$ which is equal to $-\Delta F$. Thus

$$\mathrm{E}_l = t_+(RT/\mathrm{F}) \ln (a_+'/a_+'') + t_-(RT/\mathrm{F}) \ln (a_-''/a_-') \tag{14.43}$$

or

$$\mathrm{E}_l = t_+(RT/\mathrm{F}) \ln (a_+'/a_+'') - t_-(RT/\mathrm{F}) \ln (a_-'/a_-''). \tag{14.44}$$

If it is assumed that anion and cation activities are equal, then

$$\mathrm{E}_l = (t_+ - t_-)(RT/\mathrm{F}) \ln (a_+'/a_+''), \tag{14.45}$$

which, in dilute solution, becomes

$$E_l = (t_+ - t_-)(RT/F) \ln (c_1/c_2). \qquad (14.46)$$

This last equation due to Nernst is seen to be valid only as a limiting law in very dilute solutions.

It has been assumed in the foregoing treatment that a sharp boundary exists between the two solutions in contact, at which interface the concentration changed sharply from c_1 to c_2 and further that the transport numbers of the ions are independent of the concentration. This is not the condition found in practice in general. Rather will the boundary be diffuse, the concentration changing gradually from c_1 through a finite layer to c_2. In this layer the junction potential, ion activities and transport numbers will continually vary. The overall potential for the junction must thus be obtained by an integration through this layer of a function of both ion activities and transport numbers. Owing to the dependence of these quantities on the total ionic strength of the solution rather than on the individual ion concentration it appears theoretically improbable to obtain individual ion activities from measurements of liquid junction potentials.

In practice, where too high a precision is not required, it is usual to use a salt bridge to connect the liquids which would otherwise be in direct contact. Such a salt bridge consists of a saturated solution of either potassium chloride or ammonium nitrate. Since the ionic concentrations in these solutions are high, most of the current is transported by these ions. Furthermore, the transport numbers of K^+ and Cl^- are almost equal so that the liquid junction potential will be very small and, relative to the total electromotive force of the cell being measured, may be neglected.

18. **The Determination of Transference Numbers from Electromotive Force Measurements:** These results may be used to obtain the mean transference numbers between two concentrations from measurements of concentration cells with and without liquid junctions. The method has been employed with considerable success by MacInnes and Parker in the case of potassium chloride solutions, MacInnes and Beattie for lithium chloride solutions, and Pearce and Hart for potassium bromide solutions. However, since the transference numbers of most ions vary considerably with change in concentration, it is more desirable to obtain the transference number at a given concentration. To accomplish this, the differential form of equation 14.41 may be used

$$dE_T = t_+ dE.$$

If E_T be plotted against corresponding values of E, of concentration cells of which one concentration is fixed and the other varied, the slope of the curve obtained will be the cation transference number. By employing a similar method, MacInnes and Beattie determined the transference numbers of lithium ion from measurements of the cells

$$Ag \mid AgCl \mid LiCl(c_1) \mid LiCl(c_2) \mid AgCl \mid Ag$$

and

$$Ag \mid AgCl \mid LiCl(c_1) \mid Li_xHg \mid LiCl(c_2) \mid AgCl \mid Ag.$$

In Table 14.9 are given their values, which are compared with values obtained by the Hittorf method.

The agreement is very striking. It seems probable from this and other similar results that the electromotive force method, when applicable, is the most accurate for the determination of transference numbers.

TABLE 14.9

TRANSFERENCE NUMBERS OF THE LITHIUM ION IN SOLUTIONS OF LITHIUM CHLORIDE

c	t_+ (E.M.F.)	t_+ (Hittorf)
0.001	0.359	—
0.005	0.341	—
0.01	0.334	0.332
0.02	0.327	0.328
0.05	0.318	0.320
0.1	0.311	0.313
0.2	0.304	0.304
0.3	0.299	0.299
0.5	0.293	—
1	0.286	—
2	0.276	—
3	0.268	—

19. **Oxidation-Reduction Cells:** Since, from the electrical point of view, oxidation corresponds to a loss of electrons and reduction a gain of electrons the two processes must occur simultaneously; the electron lost by one atom must be gained by another. An equilibrium is thus established, in a system containing both oxidized and reduced forms, between them and the electrons. If an inert electrode such as platinum is introduced, the state of the equilibrium will manifest itself, if oxidizing, by taking up electrons from the platinum leaving it positively charged and if reducing by giving up electrons. The potential thus set up measures the oxidizing or reducing power of the system. A combination of two such potentials furnishes an oxidation-reduction cell. An example involving the stannous-stannic, ferrous-ferric systems has already been given in section 3. The electromotive force of this cell relates to the free energy change and thus to the equilibrium constant of the reaction

$$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++}.$$

An oxidation-reduction electrode which has proved most useful is the quinhydrone electrode which consists of an equimolecular mixture of quinone and hydroquinone in water. The electrode reaction is

$$C_6H_4(OH)_2 = C_6H_4O_2 + 2H^+ + 2\Theta,$$

where Θ represents a faraday of electrons. The potential acquired by a platinum wire in such a system will depend on the activities of the unionized organic molecules which will be approximately equal and on the activity of the hydrogen ions. The quinhydrone electrode thus behaves virtually as a hydrogen electrode and may be used to measure pH values.

20. **Standard Electrode Potentials:** Any cell reaction may be broken up into two parts, and the electromotive force of the corresponding cell may be divided into two electrode potentials. For example, the reaction

$$\tfrac{1}{2}Zn + H^+(1M) = \tfrac{1}{2}Zn^{++}(1M) + \tfrac{1}{2}H_2$$

may be split up into

$$(a)\ \tfrac{1}{2}Zn = \tfrac{1}{2}Zn^{++} + \Theta; \qquad (b)\ H^+ + \Theta = \tfrac{1}{2}H_2$$

or

$$(a)\ \tfrac{1}{2}Zn = \tfrac{1}{2}Zn^{++} + \Theta; \qquad (c)\ \tfrac{1}{2}H_2 = H^+ + \Theta,$$

where Θ represents one faraday of electrons. The same convention is adopted for the single electrode potentials as for the cells, namely, that its electromotive force is positive when positive current flows from left to right. For the above electrode processes, then, we obtain

$$\left.\begin{array}{l} (a)\ E = E_0 - (RT/F)\ln a_{Zn^{++}}^{\frac{1}{2}} \\ (b)\ E = E_0 - (RT/F)\ln (p^{1/2}/a_{H^+}) \\ (c)\ E = E_0 - (RT/F)\ln (a_{H^+}/p^{1/2}) \end{array}\right\} \qquad (14.47)$$

where p is the hydrogen pressure.

No method is known for the evaluation of the absolute potential of an electrode, since this would involve a knowledge of individual ion activities. For this reason an arbitrary zero of potential must be chosen. It is customary at the present time to refer all electrodes to the hydrogen electrode at one atmosphere pressure in a solution of hydrogen ions of unit activity. Thus, for the hydrogen electrode, $E_0 = 0$, at all temperatures. By referring all electrodes to the hydrogen electrode, either by direct or indirect comparison, tables of standard electrode potentials at 25° have been compiled.

To take a single example by way of illustration. For the cell:

$$H_2(1\text{ atm.})\ |\ HCl(c)\ |\ AgCl\ |\ Ag$$

it has been shown that E_0 can be obtained by suitable extrapolation of measured electromotive forces to $c = 0$. The best value for this extrapolation is $E_0 = 0.2222$. Dividing the cell into its two electrodes:

$$(1)\ H_2 \mid H^+ \quad \text{and} \quad (2)\ Ag \mid AgCl \mid Cl^-,$$

E_0 for the cell will equal $E_{0_1} - E_{0_2} = 0 - E_{0_2}$, or

$$Ag \mid AgCl \mid Cl^-; \qquad E_0 = -0.2222.$$

In Table 14.10 are given the values of the standard potentials for a number of electrodes at 25° C. taken from International Critical Tables. The electrode reactions are so arranged that the values of the free energies are equal simply to $(-E_0F)$.

TABLE 14.10

STANDARD ELECTRODE POTENTIALS AT 25°

Electrode	Electrode Reaction	E_0
$Li \mid Li^+$	$Li = Li^+ + \Theta$	2.9595
$Rb \mid Rb^+$	$Rb = Rb^+ + \Theta$	2.9259
$K \mid K^+$	$K = K^+ + \Theta$	2.9241
$Ca \mid Ca^{++}$	$\frac{1}{2}Ca = \frac{1}{2}Ca^{++} + \Theta$	2.763
$Na \mid Na^+$	$Na = Na^+ + \Theta$	2.7146
$Pt \mid H_2 \mid OH^-$	$\frac{1}{2}H_2 + OH^- = H_2O(l) + \Theta$	0.8295
$Zn \mid Zn^{++}$	$\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + \Theta$	0.7618
$Cr \mid Cr^{++}$	$\frac{1}{2}Cr = \frac{1}{2}Cr^{++} + \Theta$	0.557
$Fe \mid Fe^{++}$	$\frac{1}{2}Fe = \frac{1}{2}Fe^{++} + \Theta$	0.441
$Cd \mid Cd^{++}$	$\frac{1}{2}Cd = \frac{1}{2}Cd^{++} + \Theta$	0.4013
$Tl \mid Tl^+$	$Tl = Tl^+ + \Theta$	0.3360
$Ni \mid Ni^{++}$	$\frac{1}{2}Ni = \frac{1}{2}Ni^{++} + \Theta$	0.231
$Sn \mid Sn^{++}$	$\frac{1}{2}Sn = \frac{1}{2}Sn^{++} + \Theta$	0.136
$Pb \mid Pb^{++}$	$\frac{1}{2}Pb = \frac{1}{2}Pb^{++} + \Theta$	0.122
$Pt \mid H_2 \mid H^+$	$\frac{1}{2}H_2 = H^+ + \Theta$	0.0000
$Pt \mid Sn^{++}, Sn^{++++}$	$\frac{1}{2}Sn^{++} = \frac{1}{2}Sn^{++++} + \Theta$	−0.14
$Ag \mid AgCl \mid Cl^-$	$Ag + Cl^- = AgCl + \Theta$	−0.2222
$Hg \mid HgCl \mid Cl^-$	$Hg + Cl^- = HgCl + \Theta$	−0.2676
$Cu \mid Cu^{++}$	$\frac{1}{2}Cu = \frac{1}{2}Cu^{++} + \Theta$	−0.3441
$Pt \mid OH^- \mid O_2$	$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + \Theta$	−0.3961
$Pt \mid I^- \mid I_2(s)$	$I^- = \frac{1}{2}I_2(s) + \Theta$	−0.5345
$Hg \mid Hg_2SO_4 \mid SO_4^{=}$	$Hg + \frac{1}{2}SO_4^{=} = \frac{1}{2}Hg_2SO_4 + \Theta$	−0.6213
$Pt \mid Fe^{++}, Fe^{+++}$	$Fe^{++} = Fe^{+++} + \Theta$	−0.7477
$Ag \mid Ag^+$	$Ag = Ag^+ + \Theta$	−0.7978
$Hg \mid Hg_2^{++}$	$Hg = \frac{1}{2}Hg_2^{++} + \Theta$	−0.7986
$Pt \mid Br^- \mid Br_2(l)$	$Br^- = \frac{1}{2}Br_2(l) + \Theta$	−1.0648
$Pt \mid Cl^- \mid Cl_2(g)$	$Cl^- = \frac{1}{2}Cl_2(g) + \Theta$	−1.3583
$Pt \mid Ce^{+++}, Ce^{++++}$	$Ce^{+++} = Ce^{++++} + \Theta$	−1.55
$Pt \mid Co^{++}, Co^{+++}$	$Co^{++} = Co^{+++} + \Theta$	−1.817
$Pt \mid F^- \mid F_2$	$F^- = \frac{1}{2}F_2 + \Theta$	−1.9

21. **Weak Electrolytes. Salt Effects:** The foregoing treatment of strong electrolytes leads to an accurate treatment of the dissociation of weak electrolytes and to a method of calculating true dissociation constants.

The equilibrium constant for a weak uni-univalent electrolyte is given by the equation

$$K_a = a_+a_-/a_2 = K_cf_+f_-/f_2 = [\alpha^2c/(1 - \alpha)][f_+f_-/f_2], \qquad (14.48)$$

where K_c is the classical dissociation constant, α being the true degree of dissociation. As already pointed out in Chapter 12 for the case where a change in dissociation as well as a change in ionic mobility is to be ex-expected, the measured equivalent conductance is given by the relation $\Lambda_v = \alpha(l_a + l_k)$ where l_a and l_k are the anion and cation mobilities at the particular concentration. The sum of these may be obtained indirectly from conductance measurements of strong electrolytes. Thus, the algebraic sum of the conductances of hydrochloric acid, sodium acetate and sodium chloride each at a dilution v would give the conductance of completely dissociated acetic acid at that dilution, that is, the sum of the mobilities of the ions:

$$\Lambda_{\text{HCl}} + \Lambda_{\text{NaAc}} - \Lambda_{\text{NaCl}} = \Lambda'_{\text{HAc}} = l_{\text{H}^+} + l_{\text{Ac}^-}.$$

Knowing this and the measured equivalent conductance, the true degree of dissociation can be calculated. With this value and a knowledge of the activity coefficients, the true dissociation constant may be found. Table 14.11 contains the data obtained by MacInnes for cyanacetic acid.

TABLE 14.11

Conc.	$K_c \cdot 10^4$	$K_a \cdot 10^4$
0.05946	43.39	34.9
.02972	42.64	34.9
.01487	40.61	34.9
.00744	39.53	34.9
.00372	38.68	35.0
.00186	38.12	35.2
.00046	36.25	34.7

The second column gives the classical Ostwald constant calculated from degrees of dissociation obtained from the Arrhenius conductance ratio. The constant shows a steadily falling value whereas excellent constancy is obtained for K_a. The actual value of K_c at high dilution is the same as K_a.

In discussing acidity constants in the previous chapter, hydrogen ion concentration was used as the basis. It must now be realized that hydrogen ion activity is the correct factor. Thus, in the general acid-base scheme,

$$A \rightleftarrows B + H^+,$$

the acidity should be measured by $a_{H^+} = K_a a_A/a_B$, K_a being the activity constant for the acid. The acidity constant previously used, namely K_A, is related to the activity constant by the equation $K_A = K_a \cdot f_A/f_B$. K_A is thus constant only in dilute solutions since at least one of the species A and B is always an ion and the ratio f_A/f_B varies consequently with the concentration. If the ionic concentrations are low as in solutions of weak electrically neutral acids this variation may be neglected. This is equivalent to accepting the hydrogen ion concentration rather than its activity as a basis for an acidity scale. Acidity scales defined in an analogous way in different protolytic media are thus not comparable one with the other.

When salts are added to such weak acid solutions the ratio f_A/f_B may be markedly changed. The extent to which the change occurs will depend on the charge type of acid and base involved. It is clear from the previous relation $K_a = K_c \cdot f_+ f_-/f_2$ that, for an acid such as acetic acid in water, f_2 will be almost unaffected by a change in the ionic strength while f_+ and f_- will decrease. Hence K_c must increase with increase in the ionic strength to maintain K_a constant. In a similar manner the so-called salt effects may be analyzed for any weak electrolyte.

EXERCISES (14)

1. From the data in Table 14.1 calculate the free energy change and heat of reaction for $Zn + CdCl_2.2.5H_2O = Cd + ZnCl_2 + 2.5H_2O$ at 25° C.

2. From the data in Table 14.3 determine the change in heat capacity for the reaction $\frac{1}{2}H_2$ (1 atm.) + HgCl = HCl(0.1004) + Hg at 25° C. If the molal heat capacities of Hg, H_2, and HgCl are 6.7, 6.8 and 11.5 cals. respectively, calculate the partial molal heat capacity for HCl(0.1004).

3. The activity coefficient of 0.01 *M* KCl is 0.903. Calculate the freezing point of the solution.

4. From the data in Table 14.8 calculate the solubility of thallous chloride in 0.02 *N* K_2SO_4 given that the solubility in water is 0.386 g. per 100 g. solution at 25° C.

5. The activity coefficients of 0.001 *M* HCl and 0.1 *M* HCl are 0.965 and 0.796 respectively. Calculate the E.M.F. at 25° C. of the cell Hg | HgCl | HCl(0.1) | H_2 | HCl(0.001) | HgCl | Hg.

6. The E.M.F. of the cell H_2 | HCl(0.1) | HgCl | Hg at 25° C. is 0.3989 volt. The activity coefficient of 0.1 *M* HCl is 0.795. The E.M.F. of the cell H_2 | HCl(0.1), $BaCl_2$(.05) | HgCl | Hg at 25° C. is 0.3842 volt. Calculate the activity coefficient of 0.1 *M* HCl in 0.05 *M* $BaCl_2$.

7. The E.M.F. of the cell Ag | AgCl | LiCl(0.01) | LiCl(0.001) | AgCl | Ag is 39.06 millivolts at 25° C. The E.M.F. of the same cell without a liquid junction

is 113.90 millivolts. Find the mean transference number of the Li^+ ion in this concentation range.

8. Using the data in problem 6 calculate the standard E.M.F. of the cell $H_2 \mid HCl(0.1) \mid HgCl \mid Hg$. What is the standard potential of the calomel electrode?

9. The solubility of a tri-trivalent salt in water at 25° C. was 2.9×10^{-5} moles per liter. The solubility in 0.0005 *M* KNO_3 was 3.3×10^{-5}. Show that these results are in agreement with the Debye-Hückel limiting law.

10. The equivalent conductance at 0.0001 *N* concentration for HCl is 424.49, for NaCl is 125.54 and for sodium acetate is 90.17. The conductance of acetic acid at the same ion concentration is 133.0. Assuming that the activity coefficients of the ions are given by the Debye-Hückel limiting law and that of undissociated acetic acid is unity, calculate the dissociation constant of acetic acid.

CHAPTER 15

CHEMICAL KINETICS

THE study of the rates at which chemical processes occur and of the factors that may influence the velocity of reaction comprises the field of chemical kinetics. The introduction of the time factor into such studies provides an important method for the elucidation of mechanism in chemical reactions. Chemical equations such as, for example,

$$2H_2 + O_2 = 2H_2O,$$
$$2NO + O_2 = 2NO_2,$$

describe the initial reactants, the final products and the molecular quantities involved. They imply nothing concerning the mode of conduct of the process nor do they indicate, in any way, the speed with which reaction may be achieved. In the two examples cited, the former is very slow indeed at ordinary temperatures while the latter is very rapid. Chemical kinetics is concerned with the factors of mechanism that are responsible for such divergencies in rate between reactions that, overall, are so similar molecularly. The hydrogen-oxygen reaction can, however, be made to occur rapidly at room temperatures by activating agents such as ultra-violet light, ionization agents such as α-particles and electrons, as well as by catalytic materials such as platinum. These agencies provide alternative reaction mechanisms which are fast at room temperatures and these mechanisms do not occur in their absence when the thermal environment, or temperature, provides the sole source of activation.

1. **Order of Reaction:** Our knowledge of mechanism is greatly increased by a determination of the order of a reaction, that is to say, the number and kinds of atoms or molecules that determine, by their concentrations, the velocity or kinetics of the reaction. Chemical equations teach us nothing concerning order of reaction. The oxidation of nitric oxide is said to be third order because the rate of reaction depends on the square of the nitric oxide concentration and on the first power of the oxygen concentration. The oxidation of hydrogen is not a third order reaction. The reaction of hydrogen and iodine to form hydrogen iodide, $H_2 + I_2 = 2HI$, is a second order reaction since it involves the first power of the concentration of hydrogen and of iodine. The reverse reaction of decomposition is second order because it involves the square of the hydrogen iodide concentration. This is not true, however, of the molecularly similar reaction, $H_2 + D_2 = 2HD$. This occurs by a mecha-

nism involving hydrogen atoms and the order of reaction is fractional, proportional to the 1.5 power of the concentration, for reasons given in subsequent sections.

At the outset, we shall limit our attention to reactions in gaseous systems, since, in such systems, owing to their approximate ideality and to the applicability of the kinetic theory, it is possible to survey the factors which enter into the determination of reaction velocity and, hence, the reaction mechanism.

THE KINETICS OF GAS REACTIONS

2. **Second Order Collision Reactions:** Second order reactions, involving the collision of two molecules to give two or more reaction products, are the simplest kinetic processes. They may be generalized by the equations,

$$2\text{A} = \text{C} + \text{D} + \text{etc.}, \qquad \text{and} \qquad \text{A} + \text{B} = \text{C} + \text{D} + \text{etc.}$$

The simplest assumption that can be made concerning such a process is that the velocity of reaction is equal to or proportional to the number of collisions between the reacting molecules. It has been shown in the discussion of kinetic theory that the number of collisions Z_{11} between like molecules is given by the expression

$$Z_{11} = \tfrac{1}{2}\sqrt{2}\pi\sigma^2 u_a n^2 = 2n^2\sigma^2\sqrt{\pi kT/m}, \tag{15.1}$$

where σ is the effective diameter, n is the number of atoms or molecules per cc. and u_a, the average velocity, has the value $(8kT/\pi m)^{1/2}$. If the colliding molecules are unlike, the equation for the number of collisions has the form

$$Z_{12} = 2\sqrt{2\pi} n_1 n_2 \sigma_{12}^2 \sqrt{kT/\mu}, \tag{15.2}$$

where n_1 and n_2 are the numbers of each species per cc., σ_{12} is the effective diameter of the collision $(= (\sigma_1 + \sigma_2)/2)$ and μ is the reduced mass $(= m_1m_2/(m_1 + m_2))$. It will be found that the expression for the collision number between like molecules Z_{11} is exactly $\frac{1}{2}$ of the value to which Z_{12} reduces when $n_1 = n_2$, $\sigma_{12} = \sigma$ and $m_1 = m_2$. The factor of $\frac{1}{2}$ in Z_{11}, in collisions with like molecules, is introduced since otherwise each collision would be counted twice, each molecule being counted once as the colliding particle and again as the receiving particle in the same process.

The numerical magnitudes of such collision numbers may be illustrated with reference to hydrogen gas. The number of collisions experienced by a hydrogen molecule per second at 0° C. and 1 atm. is about 1.4×10^{10}, the total number per cc. being 1.9×10^{29}. At a pressure of 0.009 mm., where the mean free path is about 1 cm., there are still 2.6×10^{19} collisions per second per cc. The number of collisions increases with the square root of the temperature since u_a so varies. Other gases will not show large variations from these values since the large controlling magnitudes are n which is, under standard conditions, 2.7×10^{19} per cc., σ which does not vary largely from a few Ångstrom units, 10^{-8} cm., and u_a which is equal to $14{,}500 \sqrt{T/M}$ cm. per sec.

We shall discuss first of all some bimolecular reactions in which measurements of reaction velocity indicate that reaction may indeed occur at every collision. As an example, we shall choose one of a group of reactions that have been studied by Polanyi and his co-workers during the last decade. With von Hartel, Polanyi has studied the reactions between sodium vapor and halogen-containing compounds. We shall consider the reaction,

$$CH_3I + Na = NaI + CH_3.$$

We shall be concerned with the rate of formation of sodium iodide and can ignore the ultimate fate of the radical CH_3.

Special methods are needed to study fast reactions of this type since, from the collision data already given, we can compute that, at atmospheric pressure, reactions occurring at every collision are complete in times of the order of 10^{-10} second. One method devised by Polanyi to study such a reaction is indicated in the accompanying diagram Fig. 15.1.

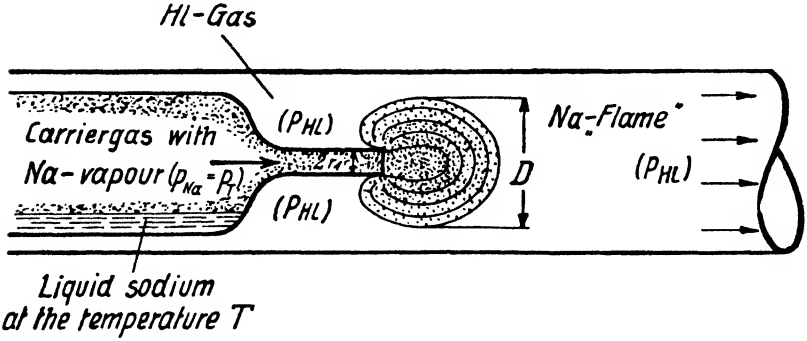

FIG. 15.1. Polanyi's Apparatus for Low Pressure "Dilute Flame" Reaction

Sodium vapor at a partial pressure of about 2×10^{-3} mm. is conveyed in a stream of carrier-gas, such as N_2 or H_2, at a pressure of 2–10 mm., through a nozzle into a reaction space where the halogen-containing compound is present under a pressure of 0.01–0.5 mm. Reaction occurs in a spherical volume where the two reactants interpenetrate, the zone of reaction being determined by measuring the diameter of the zone beyond which no detectable quantity of sodium atoms can be found. Polanyi measured this zone by illuminating the sodium vapor with the D-sodium lines from a resonance lamp (Chap. 4, Section 9), thus exciting the sodium atoms to yellow fluorescence. The limit of the fluorescence zone gives the limit of penetration of sodium vapor into the reacting gas. Polanyi showed that the velocity of reaction varies *inversely* as the square of the experimentally observed diameter of the fluorescence zone.

3. **Efficiency of Collisions:** The velocity of reaction between sodium vapor and methyl iodide vapor at 240° C. was, in this manner, found to be equal to the value given by the expression for Z_{12} when the entirely reasonable value for the collision diameter, $\sigma_{12} = 4.5$ Å, was chosen. We therefore conclude that these two gases react at practically every collision. The same conclusion was reached when ethyl iodide or phenyl iodide were substituted for methyl iodide.

With the corresponding bromides, CH_3Br, C_2H_5Br, C_6H_5Br, the experiments indicate that only one in 50 of the collisions calculated from Z_{12} leads to reaction. With the corresponding chlorides at 500° C. the efficiency of reaction falls still further: only 1 in $\sim 10^4$ collisions leads to reaction. With methyl fluoride, CH_3F, even at a pressure of 10 mm. of the gas, the whole tube filled with sodium vapor so that one can compute that less than 1 collision in 10^6 leads to reaction, even at 500° C.

By suitable modifications of this low pressure technique Polanyi discovered a number of other reactions which occur practically at every collision. Among these we may cite

$$Na + X_2 = NaX + X,$$

where $X_2 = Cl_2$, Br_2 or I_2,

$$\begin{aligned} Na + HgCl_2 &= NaCl + HgCl, \\ Na + HgCl &= NaCl + Hg, \\ Na + HI &= NaI + H, \end{aligned}$$

together with corresponding reactions of potassium vapor as well as reactions of halogen atoms, X = Cl, Br, I, with sodium molecules

$$X + Na_2 = NaX + Na.$$

4. **Collision Efficiency and Temperature:** It was at first thought that such reactions, between atoms and molecules, called by Polanyi "elementary reactions," would always occur at every collision. The cases of methyl fluoride and the chlorides showed, however, that this is not necessarily true. An important example in which reaction does not occur at every collision was then found in the interaction of hydrogen atoms and hydrogen molecules, a reaction which may be written

$$H + H_2 = H_2 + H.$$

The study of the velocity of this reaction became possible when the technique of producing hydrogen atoms in a high tension discharge tube was developed by Wood, and when the existence of two forms of molecular hydrogen, ortho- and para-hydrogen, with different specific heats (Chap. 5, Sect. 2) and different thermal conductivities, was demonstrated by Bonhoeffer and Harteck. The velocity of this reaction was studied by Geib and Harteck at 10, 57 and 100° C. by introducing hydrogen atoms at pressures of about 0.5 mm. into para-rich hydrogen mixtures and measuring by thermal conductivity methods the extent to which the para-hydrogen was converted to ortho-hydrogen by the reaction

$$H + H_{2(p)} = H_{2(o)} + H.$$

Typical results are shown in the following table:

TABLE 15.1

PARA-HYDROGEN REACTION WITH ATOMIC HYDROGEN

Temp., °C.	% Para-H_2	% Atomic H	% Reaction	Press. in mm.	k
10	100	18.8	34.8	0.56	0.548
57	100	18.8	65.3	0.56	3.17
100	100	18.8	84.0	0.56	11.7

Geib and Harteck calculated Z_{12} and by comparison with the observed conversion showed that the collision efficiency was 1 in 3×10^6 at 10° C. At the higher temperatures this efficiency increased to 1 in 5×10^5 at 57° and 1 in 1.4×10^5 at 100° C. The increased efficiency of collisions with increased temperature can be combined with the kinetic theory value for the total number of collisions to yield an expression for the observed velocity of reaction over a range of temperature. We may write the expression in the form

$$k' = Z_{12}e^{-E/RT}, \tag{15.3}$$

where k' is the number of molecules reacting per cc. per sec., Z_{12} is the total number of collisions per cc. per sec. and the term $e^{-E/RT}$ represents the efficiency of those collisions in producing reaction. Since the number of collisions Z_{12} is itself dependent on the square root of the absolute temperature we may rearrange the expression to the form

$$k' = C\sqrt{T}e^{-E/RT}, \tag{15.4}$$

where C now includes all the temperature independent terms in Z_{12}, namely, $2\sqrt{2\pi}n_1n_2\sigma_{12}^2\sqrt{k/\mu}$. That an equation of such a form correctly expressed the results is evident from a numerical recalculation of Geib and Harteck's results by Kassel which leads to the equation

$$k = 2.2 \times 10^{12}\sqrt{T}e^{-7250/RT}, \tag{15.5}$$

where the velocity constant k is now expressed in cc. per mole per sec.

Less exactly, but sufficiently accurately for data over a short temperature range, we may ignore the influence of the $\sqrt{T}$ term in the collision number. In this particular case, this approximation neglects a $\sqrt{373}/\sqrt{283} = 1.15$ fold variation due to $\sqrt{T}$ in comparison with a 22 fold variation in the collision efficiency, $e^{-E/RT}$. We may therefore write the expression for velocity in the approximate form

$$k = C'e^{-E/RT}. \tag{15.6}$$

Such an equation can be tested most conveniently in its logarithmic form

$$\ln k = const. - E/RT. \tag{15.7}$$

If such an equation is obeyed, it is obvious that, by plotting log k against $1/T$, a straight line should be obtained. The data of Geib and Harteck obey such an expression and from the slope of the line the value of $E = 7250$ calories was obtained. Fig. 15.2 shows a plot of log collision yield against $1/T$.

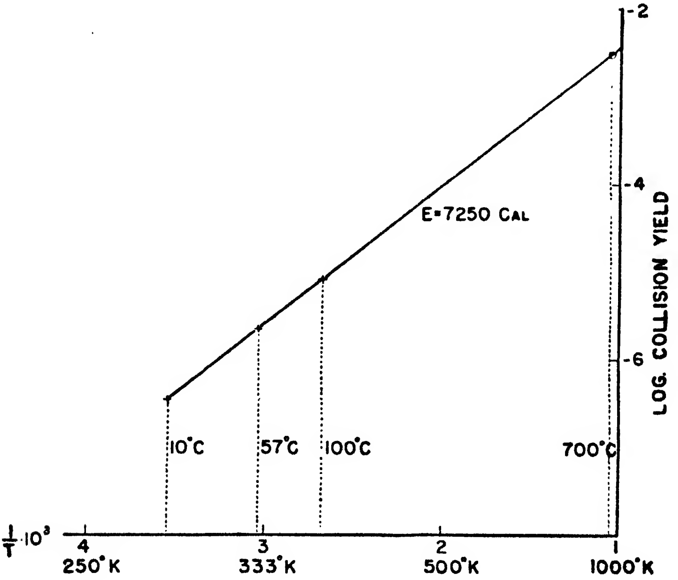

FIG. 15.2. Geib and Harteck's Data, Log. Collision Yield vs. $1/T$

Such an expression for the variation of reaction velocity with temperature, which is to be associated with an efficiency of collisions increasing with temperature, was first found empirically by Arrhenius for a large variety of reaction velocity measurements, principally in solution. He indicated that such measurements could be expressed by the equation

$$\frac{d \ln k}{dT} = \frac{A}{RT^2} \tag{15.8}$$

or its equivalent form

$$\ln k = C - A/RT \tag{15.9}$$

in which both C and A are constants.

5. **Energy of Activation:** Since all collisions do not result in reaction we may make the assumption that only those collisions in which the joint energy of the colliding molecules exceeds a certain quantity, E, give rise to reaction. From the kinetic theory, we know that the fraction of the molecules which possess an energy greater than E_1 is equal, approximately, to $e^{-E_1/RT}$. The fraction having a minimum energy, E_2, is $e^{-E_2/RT}$. The chance therefore that the two colliding molecules will have respectively minimum energies E_1 and E_2 is proportional to the product, $e^{-E_1/RT} \times e^{-E_2/RT} = e^{-(E_1+E_2)/RT}$. If now we set $E_1 + E_2 = E$ we see that the chance that, in a collision, the joint energy of the colliding molecules has a minimum value E is given by the expression $e^{-(E_1+E_2)/RT} = e^{-E/RT}$. If the assumption that such collisions result in reaction is correct it follows that

$$\frac{\text{Effective collisions}}{\text{Total collisions}} = e^{-E/RT}. \tag{15.10}$$

6. **The Rate Equation for a Second Order Reaction:** Thus far we have seen that, at constant temperature, the velocity of reaction is equal to the number of collisions multiplied by a factor expressing the efficiency of collisions at that temperature. At a given temperature, the number of collisions between like molecules is proportional to the square of their number per cc., $Z_{11} \propto n^2$, and, with unlike molecules, $Z_{12} \propto n_1n_2$. The number of molecules per cc. is directly proportional to the concentration expressed in any convenient units, so that we may set the velocity proportional to the square of the concentration c for reaction between like molecules, and to the product c_1c_2 for reaction between different molecules.

Considering the expression $v = kc^2$, as the reaction occurs the number of reacting molecules decreases, likewise the concentration, until, at the completion of reaction, since c is zero, the velocity must also be zero. We may follow this varying velocity with time by the following mathematical method. Let a be the initial concentration of the reacting molecules and let x be the concentration which has reacted in time, t. The concentration at time, t, will therefore be $a - x$ and the rate of reaction will be proportional to the square of this quantity for a second order process, in accordance with our conclusion that $v = kc^2$. We may express the velocity at time, t, in the form of an equation

$$dx/dt = k(a - x)^2, \tag{15.11}$$

which, by transposition, gives $dx/(a - x)^2 = kdt$. To perform this integration, let $(a - x) = y$. Then $dx = -dy$, and $-dy/dt = ky^2$. Therefore $-\int(1/y^2)dy = \int kdt$, or $1/y = kt +$ const. Hence, $1/(a - x) = kt +$ const. and the integration constant must be $1/a$ since this is the value of $1/(a - x)$ when $t = 0$. Therefore $1/(a - x) - 1/a = kt$. Hence,

$$\frac{x}{a(a - x)} = kt \qquad \text{or} \qquad k = \frac{1}{t}\frac{x}{a(a - x)}\cdot \tag{15.12}$$

This expression should give a constant value of k when the appropriate values of x, $a - x$, a and t are inserted in the equation. This is the form in which the velocity constant of a second order process involving like molecules is normally expressed. It is evident that the numerical value of k is dependent on the units in which a, $a - x$ and t are expressed so that these units should always be stated in an expression for k. The units which can most advantageously be employed will vary with the reaction under study. The reaction constant will however always have the dimensions of a reciprocal concentration multiplied by a reciprocal time. The velocity constant in the para-hydrogen conversion, page 400, expressed as cc. per mole per sec., conforms to this conclusion.

7. **The Half Life:** Let us examine the velocity equation (15.12) when half of the initial reactants have changed to products, that is, when $x = a/2$. Let the value of t under these circumstances be τ, which may be termed the time of half change. At time τ, $x = a - x$, and the equation becomes

$$k = 1/\tau a \qquad \text{or} \qquad \tau = 1/ka. \tag{15.13}$$

It follows that, in a second order process between like molecules, the time of half life is inversely proportional to the initial concentration. If the initial pressure or concentration be halved, the time of half life should be doubled. This is frequently a most useful criterion of second order change.

8. **General Equation for Second Order Reactions:** The more general case of second order reactions involving two different species may be similarly treated. If a and b are initial concentrations and $(a - x)$ and $(b - x)$ are concentrations after time, t, then

$$dx/dt = k(a - x)(b - x). \tag{15.14}$$

This can be transposed thus:

$$\frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\left(\frac{1}{a-x} - \frac{1}{b-x}\right) dx = kdt. \quad (15.15)$$

Integrating this expression between the limits $t = 0$ and $t = t$ we obtain

$$kt = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \quad (15.16)$$

or

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}. \quad (15.17)$$

9. **Opposing Reactions:** Bodenstein showed that both the decomposition of hydrogen iodide and the union of hydrogen and iodine were second order gaseous reactions to which, therefore, the preceding discussion is applicable. It is evident, however, that neither the decomposition of the iodide nor its synthesis can be a complete reaction. The one will always be opposed by the other. Thus, in the decomposition process, if we let $(a - x)$ represent the concentration of hydrogen iodide after time, t, there will be present in the system a concentration equal to $x/2$ of both hydrogen and iodine, since

$$2HI = H_2 + I_2.$$

The rate of decomposition of hydrogen iodide will therefore be given by the equation

$$\frac{dx}{dt} = k_1(a-x)^2 - k_2\left(\frac{x}{2}\right)^2. \quad (15.18)$$

The second term on the right-hand side of the equation takes account of the second order synthesis from the elements which reduces the rate of decomposition. It is evident that, at a certain value of x, or t, dependent on the numerical values of k_1 and k_2, there will arise a condition in which the rate of decomposition will equal the rate of synthesis, dx/dt will become equal to zero. This condition is *the condition of equilibrium* as defined kinetically. At the equilibrium point,

$$k_1(a-x_e)^2 = k_2\left(\frac{x_e}{2}\right)^2, \quad (15.19)$$

whence, also,

$$\frac{(a-x_e)^2}{(x_e/2)^2} = \frac{k_2}{k_1} = K, \quad (15.20)$$

where x_e is the value of x at the equilibrium point. This equation may be recognized at once as the *Law of Mass Action* when written in the form,

$[c_{HI}]^2/[c_{H_2}][c_{I_2}] = K$. The kinetic equation becomes therefore

$$\frac{dx}{dt} = k_1(a - x)^2 - k_1K\left(\frac{x}{2}\right)^2, \tag{15.21}$$

whence, if the value of K be known, the value of the specific reaction constant for the decomposition can be ascertained. Knowing this, the corresponding value of k_2 can be found since $k_2 = Kk_1$. Bodenstein tested these several points by measurement of the rates of decomposition and synthesis of hydrogen iodide and of the equilibrium position, at various temperatures. In each case he showed that k_1 and k_2 were constant at constant temperature; in the synthesis, with varying concentrations of hydrogen and iodine. The measured values of k_1 and k_2 were in agreement with the experimentally determined values of K. As the following table of the values of k_1 and k_2 at different temperatures shows,

TABLE 15.2

VELOCITY CONSTANTS OF HYDROGEN IODIDE DECOMPOSITION AND SYNTHESIS
Time in minutes; Concentration in gram molecules per 22.4 liters

$t°$ K.	k_1 (Decomposition)	k_2 (Synthesis)
781	0.1059	3.58
700	0.0031	0.172
647	0.00023	0.014
575	0.00000326	0.000353
556	0.000000942	0.000119

the rates of both reactions increase rapidly with temperature. When $\log k$ was plotted against the reciprocal of the absolute temperature, excellent straight lines were obtained from which the Arrhenius constants, A, equal to 44 kcal. for the decomposition process and 40 kcal. for the synthesis were obtained. Hinshelwood has calculated also that the experimental velocity constant at 556° K. for decomposition is given by the expression $k = Z_{11}e^{-E/RT}$ if the value for σ be that obtained from gas viscosity data, 3.5×10^{-8} cm. per sec., and the value of E is 44 kcal. in agreement with the data from the Arrhenius equation.

It is evident therefore that, both in reactions between atoms and molecules, which are relatively rapid, and in reactions between molecules which are much slower in general, a satisfactory interpretation of the rate of reaction can be obtained on the basis of total number of collisions and the efficiency of such collisions. The efficiency is measured in terms of an energy quantity, E, which we have called the activation energy and which we have regarded as a minimum energy of collision necessary for reaction. We shall now proceed to examine the problem of interpreting such an energy of activation in terms of the forces which are known to operate between approaching atoms and molecules. The problem is, in essentials, the problem of chemical valence and the saturation of valences of atoms in molecules. From this point of view a chemical process is a substitution of a new set of valence bonds for the set which is disappearing. With the development of quantum mechanics and the concept of a bond as a shared electron-pair, this concept of valence and of reactivity can be defined in terms of the potential energies of the system of atoms considered as a whole.

10. The Potential Energies of a System of Three Atoms: It was shown in Chapter 4, Section 12, that the potential energy of a diatomic molecule could be represented as a function of the distance separating the nuclei and that the curve showed a potential energy minimum at a distance r_e, the equilibrium distance between nuclei in the stable molecule. In Section 13 of the same chapter it was indicated that the potential energy V in such a system could be approximately expressed by an empirical equation due to Morse of the form

$$V = D_e(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}), \tag{15.22}$$

where D_e is the energy difference between the free atoms and the molecule at the potential energy minimum, a a constant related to the frequency of vibration and r the nuclear distance. The minimum in the curve corresponds to the binding energy of the two atoms in the molecule and the values of the potential energy at any nuclear distances, in terms of $V = 0$ and $r = \infty$, are equal to the binding energies of the two atoms at these distances with the sign reversed. Negative potential energy is equal to positive binding energy.

The quantum mechanics represents the binding energy P of a system of two atoms as the sum or difference of two quantities, the classical coulombic interactions of the electric charges in the system, more briefly the coulomb energy A and a quantum mechanical interchange or exchange energy α

$$P = A \pm \alpha. \tag{15.23}$$

The exchange energies are so called because they represent energy quantities which may be interpreted in terms of an electron exchange between one atom and the other, or a "sharing" of an electron. According to Heitler and London, these exchange energies represent the valence forces and account for saturation of a single valence in terms of two shared electrons. In the case, say, of hydrogen, the equation $P = A + \alpha$ represents the binding energy of two atoms to form a molecule. The term $P = A - \alpha$ represents the repulsive state of two hydrogen atoms (Chap. 4, 12). Actual calculations in the case of the hydrogen molecule indicate that the coulomb energy is about 10 per cent of the total binding energy *P*, the exchange energy representing the remainder as shown in Fig. 15.3.

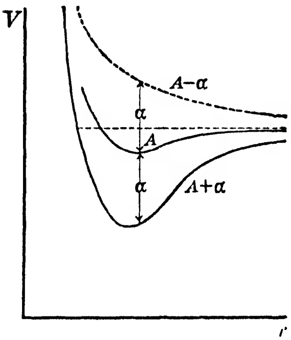

Fig. 15.3. Binding Energies of Two-Atom System XY

A system of three univalent atoms, XYZ, cannot form two molecules. The system must consist, in its lowest energy state, of one atom and one molecule. Chemical reaction in such a system means a change of the valence bond from one pair of atoms to another as in the equations

$$X + YZ = XY + Z$$

or

$$X + ZY = XZ + Y.$$

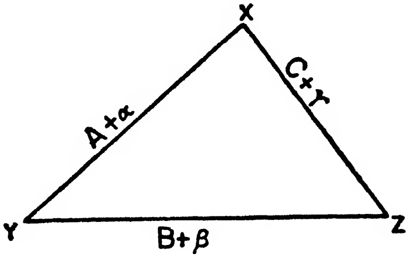

Fig. 15.4. Binding Energies of Three-Atom System XYZ

The energy of such a system of three atoms again consists of coulomb energy and exchange energy. The energy will be determined by the configuration of the three atoms in space. In any such arrangement, as for example that in Fig. 15.4, we can think of the binding energies of the three pairs of atoms XY, YZ and ZX at various internuclear distances as those of a two-atom system when the third is at a very large distance. Each of these pairs will have binding energies with coulomb and exchange portions which we may designate as $A + \alpha$, $B + \beta$ and $C + \gamma$, respectively. London has considered the energy of a three-atom system in terms of the energies of the atom pairs. He concludes that the general law of additivity applies only to the coulombic portion but that the exchange energy adds in such a way that it leads to the phenomenon of valence saturation that we imply when we say that the three univalent atom system forms one atom and one molecule. The London equation for the binding energy of such a system is

$$P_{XYZ} = A + B + C + \sqrt{\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \beta\gamma - \gamma\alpha}. \quad (15.24)$$

The first three terms are the additive coulombic portion. The complex exchange portion represents a method of addition which can be represented quite easily graphically. Thus, if we represent the individual values of α, β and γ by lines, of length proportional to the energies in question, then the total value of the exchange binding is obtained by setting off the three distances α, β and γ successively at 60° angles to each other, as in Fig. 15.5. The line joining the two extremities represents the value of the exchange binding energy of the system of three atoms. This theorem can easily be proved from the properties of 60° triangles. The energy therefore of a system of three univalent atoms can therefore be determined from the coulomb and exchange energies of the three successive atom pairs by linear addition of the coulombic portions and 60° addition of the exchange energies. To the accuracy with which such a procedure represents the energy of a system of three atoms

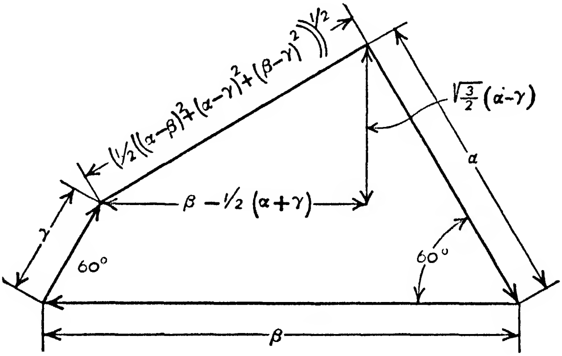

FIG. 15.5. Vector Addition of α, β and γ

we are therefore in a position to determine the energy of such a system in any configuration, the three atoms necessarily occupying a single plane.

11. **The Energy of Three Hydrogen Atoms:** Hirschfelder, Eyring and Topley have thus examined the potential energy of a system in which a hydrogen atom approaches a hydrogen molecule held at its normal internuclear distance. The potential energy of any pair of atoms was taken from a Morse curve for H_2. The potential energy at any distance, r, was divided into two fractions, 14 per cent representing the magnitude A and 86 per cent the exchange portion α. This is an arbitrary division but does not deviate markedly from exact quantum mechanical calculations. By the method just detailed the binding energies of the various three-atom systems were then determined and the resulting potential surface shown in Fig. 15.6 was obtained. Only one half of the surface is reproduced, the other half being symmetrically placed to the half shown. The diagram is in essence a contour map of the energies of the

system. It shows that, in the approach from east or west, the approaching hydrogen atom must surmount a potential energy barrier which reaches to more than 15 kcal. in either direction. The approach along the line of centers of the hydrogen molecule can, however, be achieved much more readily. A kinetic energy of little more than 7 kcal. will bring the approaching hydrogen atom to the top of a potential energy barrier in which the system is in a position to undergo chemical reaction. One of two events may occur. If the hydrogen atom returns by its path of approach we can regard the event as an unsuccessful collision. If, alternatively, as a result of the approach, the valence bond between the hydrogen atoms in the original molecule is destroyed and is reestablished between the approaching atom and its nearest neighbor, the more remote hydrogen of the original molecule will now be free and will leave by the path, on the undrawn portion of the potential surface, which corresponds to that shown for the approaching hydrogen atom. The reaction

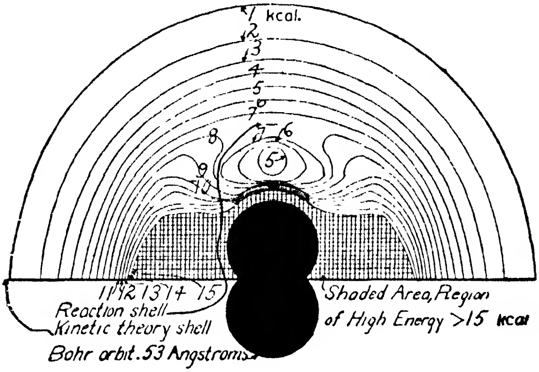

FIG. 15.6

$$H + H_2 = H_2 + H$$

will have been achieved. The diagram teaches us therefore that the approach of an atom along the line of centers of the nuclei of the molecule is the method of approach involving the least expenditure of energy.

The mean kinetic energy of an atom or molecule is equal to $\frac{1}{2}RT$ for a uni-directional approach or 300 cal. at $T = 300°$ K. This average kinetic energy of an approaching atom will be exhausted by conversion to potential energy even before the 1 kcal. contour line is reached. This line represents the limiting kinetic theory shell for the average collision. The 7 kcal. line at the top of the potential energy barrier represents the reaction shell. The reactants must approach quite closely before interaction occurs. This comparison of kinetic theory diameters and reaction diameters indicates that the choice of kinetic theory diameters for σ in preceding calculations of this chapter is somewhat arbitrary. The true choice of reaction diameters should come from correct potential energy surfaces. It is significant that the height of the potential barrier established by the surface described above is quite closely equal to the activation energy found by Geib and Harteck for the reaction $H + H_{2(p)} = H_{2(o)} + H$.

Actually a system composed of a hydrogen atom approaching a hydrogen molecule does not behave in the manner indicated in the preceding contour map. The internuclear distance of the hydrogen molecule does not remain constant as the atom approaches. On the contrary, the nearer the atom approaches, the more do the nuclei of the molecule tend to separate. This can be easily seen by determining with our equation for P_{XYZ} the potential energies of a *linear* arrangement of three atoms at *all* distances between XY and YZ. We choose the linear configuration because, as was seen from the preceding contour map, this represents the method of approach with the minimum energy expenditure, which is the approach we measure by experimental methods in slow reactions. Using as before the same Morse potential function for two hydrogen atoms and our equation for P_{XYZ} the results of such computations for the linear configuration can be represented by a contour map shown in Fig. 15.7. The map plots the equipotential lines of the linear arrangement of the three atoms with r_1 the distance between two particular atoms as one axis and r_2 that between the other pair as the second axis. The two axes are inclined at an angle of 60° to one another so that a surface constructed from such a map would represent, by a ball rolling mechanically on the surface, the behavior of the three-atom system. A potential energy surface of such a system of three hydrogen atoms with, however, the axes at an angle of 90° is shown in the accompanying plate from a photograph by Goodeve, who has described methods of constructing such models. In this model can be seen directly what must be inferred from the energy contour map. At the extremities of the two axes, where either r_1 or r_2 is large, the system is virtually a hydrogen molecule with an atom at a very great distance. We therefore obtain at each of these positions the potential energy curve of a diatomic molecule H_2, the general form of which can readily be seen on the front face of the model. The minimum in the potential curve comes at 0.75 Å, which is the equilibrium distance of the atoms in the hydrogen molecule. The hydrogen molecule would occupy, normally, the lowest vibrational state in this potential energy curve, and have the zero-point energy of the molecule.

12. The Reaction $H + H_2 = H_2 + H$: The process of interaction between a hydrogen atom and a hydrogen molecule can best be followed on the energy contour map, Fig. 15.6. The initial state is represented in the right-hand bottom valley of the diagram with $r_2 = 0.75$ Å and r_1 a

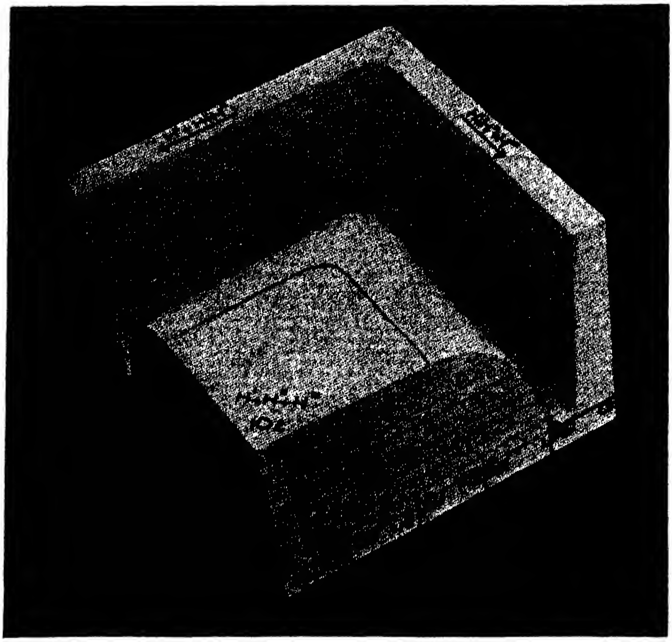

Plate from Goodeve, Trans. Faraday Society, **30,** 60 (1934.)

relatively large distance. The final state is the similar position at the top left-hand corner where $r_1 = 0.75$ Å and r_2 a relatively large distance. As the atom approaches the molecule, that is, as r_1 decreases in value, the energy of the three-atom system can be visualized as a point on the contour map passing from the initial to the final state. Elementary acquaintance with such contour maps will indicate that the reaction path, the *easiest* method of transit from initial to final state, is along the bed of the horizontally located energy valley, between the steeply rising

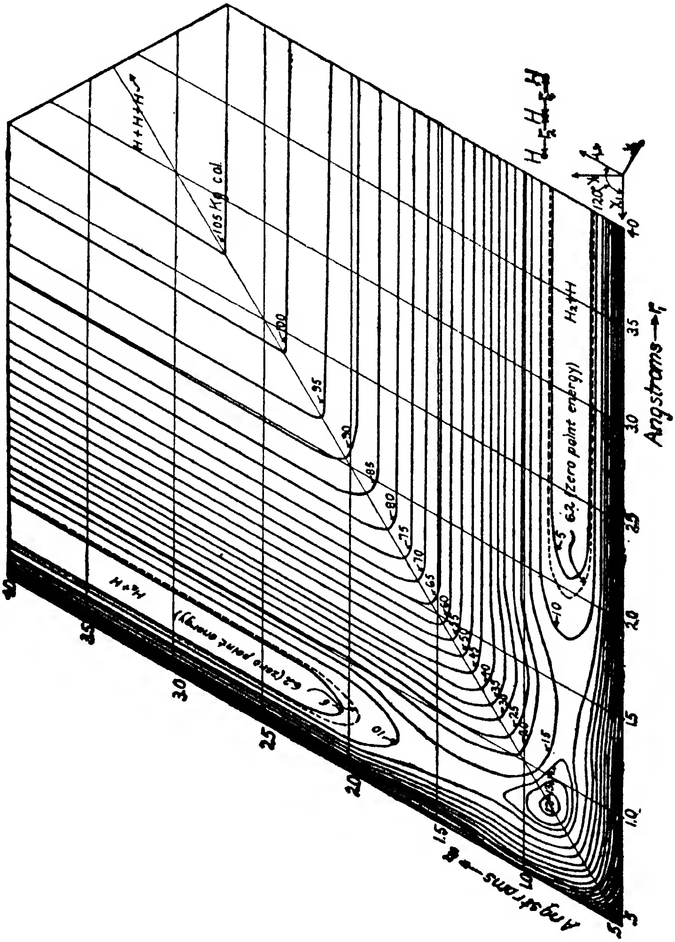

Fig. 15.7

energy hills on each side, over the saddle located at $r_1 = r_2 = 0.9$ Å in the left angle of the map at the bisector line, and then along the bed of the second energy valley to the final state. The highest point in the "mountain-pass" or saddle separating the two energy valleys represents an energy of about 14 kcal. which is 7.8 kcal. greater than the zero-point energy of the hydrogen molecule before the approach of the atom, namely 6.2 kcal. (Chap. 5, 5). The saddle-point represents the activated state of the three-hydrogen atom system, a linear configuration of three atoms, the two exterior ones each equidistant from the central atom at 0.9 Å. As the third atom has approached, the distance between the two atoms of the molecule has extended under the influence of the field of force of the approaching atom until, at the activated state, there exists an assembly of three atoms. Whether reaction occurs or not depends on which energy valley is entered by the system after leaving the activated state. We may, therefore, represent the stages of the total process in the form of an equation:

$$\underset{\text{Initial State}}{H + H_2} \rightleftarrows \underset{\text{Activated Complex}}{H - H - H} \rightleftarrows \underset{\text{Final State}}{H_2 + H.}$$

Eyring has designated the intermediate state at the top of the potential energy saddle as the activated complex. He has shown that it is possible to calculate the absolute velocity of many chemical reactions in terms of (*a*) the concentration of the activated complex, (*b*) the rate of passage over the saddle, and (*c*) a transmission factor which is a measure of the efficiency with which a system passes over the energy saddle, this latter in many cases being not markedly different from unity. (See Section 42.) The activated complex is a system of higher potential energy than the initial and final states of the reaction. It is produced by the conversion of the kinetic energy of collision into the potential energy of the complex.

13. **Recombination of Hydrogen Atoms:** Two other observations as to the contour map may be made. The high plateau in the top right hand of the diagram represents the potential energy of the three separate atoms relative to the energy of the hydrogen molecule valley at its deepest point as zero. The recombination of three hydrogen atoms is represented, on such a map, by a ball rolling off the plateau in such a way that eventually it will be found on the "floor" of one or other valley. The reaction occurring would be

$$H + H + H = H_2 + H.$$

Eyring and his co-workers have shown that the potential energy surface may be used to calculate the velocity of such a process. We return to this subject later (Section 42).

14. **The Stability of H_3:** The region in the neighborhood of the saddle-point reveals a slight energy depression or bowl where the 12 kcal. contour line is located. This represents the equilibrium position of the triatomic

molecule, H_3. It is evident from the contour map that such a molecule has no stability, since if it suffers an activating collision of only two kcal. the system may pass over its potential energy barrier (at 14 kcal.) to the more stable system $H + H_2$. In general, however, a stable triatomic molecule occupies at equilibrium an energy level at a low region of a potential energy surface, crater-like in configuration. The decomposition of such a molecule is interpreted on the potential energy surface as a passage of the system over the lip of the crater, normally at the low energy point of the crater.

15. **Activation Energies of Atom-Molecule Reactions:** Eyring and his co-workers have explored the potential energy surfaces of a number of three-atom systems. The results of such study can best be expressed in terms of the activation energies of the reactions which occur. A comparison of some of these calculations with conclusions from experimental observations is contained in the following table compiled by Morris and Pease. While the agreement is not complete the calculations show that, in the approach to the problem of the velocity of chemical reactions, the use of potential energy surfaces is a most important advance in the understanding of the important problem of inertia in chemical systems, supplying a concept of activation energy hitherto entirely lacking in physical chemistry. The table shows that many atom-molecule reactions are processes of low activation energy. The high values of the last two examples, $Br + H_2$ and $I + H_2$, are due for the most part to the endothermic nature of the total process.

TABLE 15.3

ACTIVATION ENERGIES OF ATOM-MOLECULE REACTIONS

Reaction	E (experimental)	E (theoretical)
$H + Cl_2$	3	2.4
$H + Br_2$	1	2.2
$H + I_2$	0	1.4
$H + HCl$	5	11.8
$H + HBr$	1	6.6
$H + HI$	1	7.6
$Cl + H_2$	6	12.8
$Br + H_2$	17.7	24.0
$I + H_2$	33	40

16. **Activation Energy and Heat of Reaction:** We may trace the relationship between activation energy and heat of reaction in a reversible process by reference to the reaction

$$H + HBr \underset{E_2}{\overset{E_1}{\rightleftarrows}} H_2 + Br.$$

The best calorimetric data at present available for this reaction give $H + HBr \rightarrow H_2 + Br$; $\Delta H = -16.7$ kcal. This agrees with the values which have been assigned in the previous table to the experimental energies of activation, namely, $E_1 = 1$ and $E_2 = 17.7$. The relationship

$$E_1 - E_2 = \Delta H \tag{15.25}$$

obtains for all such reactions. The reason is obvious if we consider the potential energy surface, since E_1 and E_2 are the heights of the potential energy barrier above the lowest energy levels of the reactants and resultants in their respective energy valleys. In the system $H + H_2 = H_2 + H$, as the contour map, symmetrical about the diagonal axis shows, $E_1 = E_2$ and $\Delta H = 0$. We may represent the relation graphically by the following schematic diagram, Fig. 15.8, for the reaction

$$A + BC \underset{E_2}{\overset{E_1}{\rightleftharpoons}} AB + C.$$

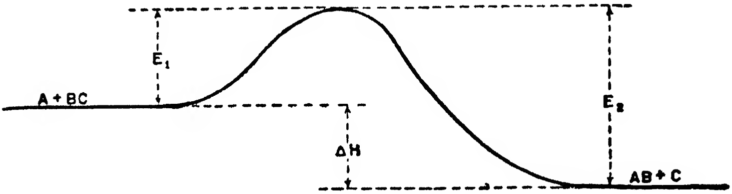

FIG. 15.8. The Relation between Activation Energies and ΔH

17. Reaction Velocity in Systems of Four Atoms: The extension of the method developed for three-atom systems to reactions involving four atoms was shown by Eyring to permit the study of reaction velocity between two diatomic molecules, reactions which may be generalized by the equation

$$WX + YZ = WY + XZ.$$

The London expression for the energy of a system of four atoms takes the form

$$\begin{aligned} P_{WXYZ} = {} & A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + [(\alpha_1 + \alpha_2)^2 \\ & + (\beta_1 + \beta_2)^2 + (\gamma_1 + \gamma_2)^2 - (\alpha_1 + \alpha_2)(\beta_1 + \beta_2) \\ & - (\alpha_1 + \alpha_2)(\gamma_1 + \gamma_2) - (\beta_1 + \beta_2)(\gamma_1 + \gamma_2)]^{1/2}. \end{aligned} \tag{15.26}$$

With the system of four atoms we trace the possibility of six separate bonds between the atoms, the bonds having binding energies $(A_1 + \alpha_1)$,

$(A_2 + \alpha_2)$, $(B_1 + \beta_1)$, etc., when the other *two* atoms are far away. These six bonds are indicated in the diagram, Figure 15.9.

The same 60° graphical method of addition of the exchange energies in the above expression gives the value for any configuration of the four atoms to which must be added the six coulombic energy terms to yield the total binding energy of a four-atom system in a given configuration. It is found that the approach of two molecules in a single plane is the most favorable method of approach from the activation energy standpoint. The representation of the potential surface obtained in such studies is more complex since an additional axis is required for the third distance involved.

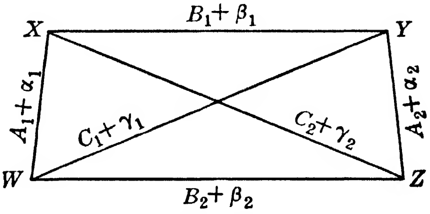

FIG. 15.9. Binding Energies of Four Atom (Two Molecule) System WXYZ

Eyring applied this method of calculation to the molecule reactions $H_2 + I_2$, $H_2 + Br_2$, $H_2 + Cl_2$ and $H_2 + F_2$ and came to the conclusion that only in the first case, that of $H_2 + I_2$, is the reaction between two molecules a process with lower activation energy than the alternative path through atoms. For example, we shall see later that the hydrogen bromide synthesis does not occur as a bimolecular reaction, but by a sequence: $Br_2 = 2Br$; $Br + H_2 = HBr + H$; $H + Br_2 = HBr + Br$; $H + HBr = H_2 + Br$; $Br + Br = Br_2$. Eyring also reached, from these calculations, the very surprising conclusion that the reaction $H_2 + F_2$ was a quite slow process, contrary to the current opinion concerning this reaction which was supposed to occur with explosive violence. Experimental work by von Wartenburg, concurrently with Eyring's calculations, showed that the purified gases react only slowly.

The bimolecular reaction, $H_2 + H_2 = H_2 + H_2$, was calculated by Eyring to have an activation energy of more than 100 kcal. A. Farkas could study the possibility of such a bimolecular change by following the homogeneous para-hydrogen conversion to ortho-hydrogen at 700–800 °C. Had the reaction been bimolecular, we know that the half life τ would have been inversely proportional to the pressure of the gas. Instead, he found that it was inversely proportional to the square root of the pressure

$$\tau \propto P^{-1/2}. \tag{15.27}$$

This is characteristic of a reaction which is of the 3/2's order. This indicates that the rate of reaction is not bimolecular but involves atomic hydrogen, which must result from a thermal dissociation of hydrogen, $H_2 = 2H$, followed by the process already studied, $H + H_{2(p)} = H_{2(o)} + H$. The activation energy of the overall process was approximately 58 kcal. of which 51 kcal. can be assigned to the thermal dissociation to atoms leaving approximately 7 kcal. for the three-atom reaction in agreement with the Geib-Harteck determinations already discussed. The bimolecular reaction between hydrogen molecules is therefore analogous to the $H_2 + Br_2$, $H_2 + Cl_2$ and $H_2 + F_2$ reactions already mentioned. A mechanism via atoms is one of lower activation energy and, therefore, the preferred process.

18. **Zero Point Energy and Reaction Velocity:** The potential energy surface, Fig. 15.7, indicates that the initial state in the reaction $H + H_2 = H_2 + H$ is the molecule in its lowest vibrational state, i.e., with its zero point energy, $\frac{1}{2}h\nu_0$, the atom being far away. The activation energy of this reaction is equal to the difference in potential energies between this state and the top of the potential energy saddle separating the two valleys. Now we have already observed (Chap. 5, 5) that there is a distinct difference in zero point energies between hydrogen and its isotope, deuterium, while the potential energy curves are substantially alike. Thus, for H_2 the zero point energy is at 6.18 kcal. and for D_2 at 4.39 kcal. The difference $6.18 - 4.39 = 1.79$ kcal. represents the increase in activation energy for the reaction $H + D_2 \rightarrow HD + D$ as compared with $H + H_2 \rightarrow H_2 + H$ arising from this zero point energy difference. We have seen that the reaction with hydrogen can be represented by an equation

$$k_{H_2} = C_{H_2}\sqrt{T}e^{-7250/RT}. \tag{15.28}$$

We would therefore expect for the deuterium process an equation

$$k_{D_2} = C_{D_2}\sqrt{T}e^{-(7250+1790)/RT} \tag{15.29}$$

and consequently a slower process in the ratio $e^{-1790/RT}$, neglecting the effect of velocity differences in C_{H_2} and C_{D_2}. At a temperature of 1000° K. this would amount to $e^{-1790/2000} = e^{-0.895} = 0.41$, the reaction velocity should be less than one half of the hydrogen reaction. This is approximately true, according to recent measurements of Farkas and Farkas, who found velocity constants $k \times 10^{-9} = 2.2$ and 1.2 liters per mole per sec. at 1000° K. A more exact treatment of zero point energy influence in such systems must take into account not only the differences in zero point energies of the initial reactants but also the zero point energies of the activated complex. This has been done by Hirschfelder, Eyring and Topley and we give in Table 15.4 the reaction rates of the various hydrogen atom isotope reactions together with the experimental data of Farkas and Farkas.

Rollefson found that chlorine atoms react with hydrogen molecules about 13.4 times more rapidly than with deuterium at 0° C. and 9.75 times more rapidly at 32° C. We can interpret this as due to a factor

$e^{-1630/RT}$ to take account of the zero point energy differences in the two three-atom systems. The velocities of hydrogen and deuterium also affect the ratio. The very much greater effect of the zero point energy on the rate of reaction is due to the temperature being much lower than in the hydrogen isotope reactions just discussed. At 30° C., $e^{-1630/RT} = e^{-1630/606} = e^{-2.75} = 0.064$ or a ratio of 15.6. The velocity factor in the two cases will vary as $\sqrt{1/\mu}$ varies or approximately as $\sqrt{2} = 1.414$ for $k_{H_2} : k_{D_2}$. Similarly Bonhoeffer and Bach showed that bromine atoms react five times faster with hydrogen molecules than with deuterium molecules at 581° K. which corresponds to a difference in activation energy of about 1500 cal. due largely to the zero point energy differences of the two isotopes.

TABLE 15.4

REACTION RATES OF HYDROGEN ATOM ISOTOPES WITH HYDROGEN ISOTOPE MOLECULES AT 1000° K.

Reaction	Reaction Rates in liter mole^{-1} sec.$^{-1}$ $\times 10^{-9}$	
	$k_{\text{exp.}}$ (F and F)	$k_{\text{calc.}}$ (H, E and T)
$H + H_2 \rightarrow H_2 + H$	2.2	1.5
$D + D_2 \rightarrow D_2 + D$	1.2	0.76
$H + DH \rightarrow HD + H$	0.68	0.52
$D + HD \rightarrow HD + D$	1.0	0.44
$H + HD \rightarrow H_2 + D$	0.95	0.45
$D + H_2 \rightarrow HD + H$	2.5	1.2
$D + DH \rightarrow D_2 + H$	0.79	0.5
$H + D_2 \rightarrow HD + D$	1.2	0.74

As an illustration of the influence of zero point energy on the velocity of reaction between two molecules we may cite the work of A. H. Taylor and Crist[1] on the decomposition and synthesis of hydrogen and deuterium iodides. These authors found that, at 700° K., the ratio of the rates of decomposition, k_{1HI}/k_{1DI}, was 1.60 while the ratio of the rates of synthesis, k_{2HI}/k_{2DI}, was 1.93. These ratios are lower than those calculated by Wheeler, Topley and Eyring from potential energy surfaces which can only yield, as yet, approximate values for the ratios. The calculated ratios were 1.92 and 2.34 for decomposition and synthesis respectively.

These differences in the rates of reaction of isotopic species and the corresponding differences in equilibrium positions have been utilized, as already indicated in Chapter 1, Section 35, by Urey and his co-workers

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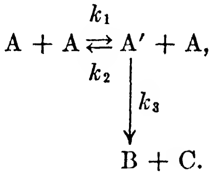
[1] *J. Am. Chem. Soc.*, **63**, 1377 (1941).

to effect important separations of isotopes. We owe to this method of separation the present available isotopes, ^{13}C and ^{15}N.

19. First Order Collision Reactions: In our discussion hitherto we have assumed that a collision with the necessary activation energy to yield an activated complex leads inevitably to reaction products. We may now examine the reaction kinetics of a system which may yield an activated complex capable of existence for a period of time without forming the reaction products, during which time it may suffer de-activation by collision. We can describe this state of affairs by the scheme



$$\begin{tikzcd} A + A \arrow[r, shift left, "k_1"] & A' + A, \arrow[l, shift left, "k_2"] \arrow[d, "k_3"] \\ & B + C. \end{tikzcd}$$

The collisions of a reaction species A give rise to an energy-rich molecule, A′, at a reaction velocity, k_1. The energy-rich A′ may suffer deactivating collisions with velocity k_2, or may undergo decomposition at velocity k_3 to yield the products, B + C. The kinetics of the process may be understood from the following. The rates of formation and disappearance of A′ are given by the expressions

$$+\frac{d[A']}{dt} = k_1[A]^2, \tag{15.30}$$

$$-\frac{d[A']}{dt} = k_2[A'][A] + k_3[A']. \tag{15.31}$$

After a brief interval, these rates become equal giving a stationary state in which the concentration of A′ is constant,

$$k_1[A]^2 = k_2[A'][A] + k_3[A']. \tag{15.32}$$

Hence

$$[A'] = \frac{k_1[A]^2}{k_2[A] + k_3}. \tag{15.33}$$

The rate of formation of products, B + C, is given by the expression

$$+\frac{d[B + C]}{dt} = k_3[A'] = \frac{k_3k_1[A]^2}{k_2[A] + k_3}. \tag{15.34}$$

In second order reactions the value of k_3 is very large compared with $k_2[A]$ so that this latter may be neglected and we derive the usual equation

$$+\frac{d[B + C]}{dt} = k_1[A]^2. \tag{15.35}$$

If, however, the decomposition to yield products is small compared with the deactivating collisions, $k_3 < k_2[\mathrm{A}]$, the kinetic expression becomes

$$+\frac{d[\mathrm{B}+\mathrm{C}]}{dt} = \frac{k_3k_1[\mathrm{A}]^2}{k_2[\mathrm{A}]} = \frac{k_3k_1}{k_2}[\mathrm{A}]. \tag{15.36}$$

The collision process now appears as though the reaction were first order

$$+\frac{d[\mathrm{B}+\mathrm{C}]}{dt} = k[\mathrm{A}]. \tag{15.37}$$

The best investigated case of such a first order process is the decomposition of nitrogen pentoxide first studied by Daniels. In such reactions if a be the initial concentration and $(a - x)$ the concentration at time t, then the rate of reaction is given by the expression

$$dx/dt = k(a - x), \qquad \text{or} \qquad dx/(a - x) = kdt, \tag{15.38}$$

which upon integration and setting the limit $a - x = a$ when $t = 0$ gives

$$\ln\frac{a}{a - x} = kt, \qquad \text{or} \qquad k = \frac{1}{t}\ln\frac{a}{a - x}\cdot \tag{15.39}$$

From this equation it follows that, in such reactions, the time of half change τ is independent of the initial concentration since

$$\tau = \frac{1}{k}\ln\frac{a}{a/2} = \frac{1}{k}\ln 2. \tag{15.40}$$

This is the distinguishing characteristic of first order processes. Both the 'half-life' and the reaction constant, k, are independent of the initial concentration or the units in which the concentration is expressed. Hunt and Daniels have shown this to be true for nitrogen pentoxide over a range of initial pressures from 278 mm. to 0.0185 mm. The following table demonstrates the correctness of this.

TABLE 15.5

Decomposition of Nitrogen Pentoxide at 45°

p.....	278	114	49.5	9.6	0.0264	0.0185 mm.
k......	0.027	0.026	0.027	0.026	0.020	0.021

In calculating these values of k, corrections must be applied to the pressure readings to take account of the fact that the N_2O_4 formed changes its degree of dissociation as its concentration increases due to reaction. The dissociation of the tetroxide causes an additional pressure increase since the equation of the dissociation is $N_2O_4 = 2NO_2$. The dissociation is greatest when the concentration of N_2O_4 is least.

The excellent constancy of the values of k is proof of the first order or unimolecular nature of the decomposition of the pentoxide and this conclusion is further supported by the observation that approximately the same rate of decomposition occurs in solutions of nitrogen pentoxide. That the reaction is homogeneous and not caused by the walls of the containing vessel was shown by adding glass wool to the reaction system. No change in speed was observed.

The persistence of the reaction velocity unchanged down to quite low values of the pressure, as shown in Table 15.5, indicates that throughout this range of pressure the condition holds that $k_2[A]$, the deactivation process, is large compared with k_3, the decomposition of activated molecules. Decrease of pressure steadily decreases the value of $k_2[A]$ relative to k_3 since the velocity constant $k_2 \propto n^2$ where n is the number of molecules per cc. In the case of nitrogen pentoxide, the best experiments indicate that somewhere between 0.05 and 0.005 mm. pressure, the transition from an apparent unimolecular towards a second order process occurs.

The reaction rate increases with increasing temperature and, at moderate pressures, between 0 and 65° C., the rate of reaction is represented by the equation

$$k = 10^{13.579}e^{-24590/RT}. \tag{15.41}$$

A large number of processes, including the decompositions of many organic molecules, appear to belong to this group of first order or quasi-unimolecular reactions. There is at present divergence of opinion as to their unimolecular character and, in many cases, it has already been shown that the mechanism is one involving the breaking of bonds and a sequence of reactions in which the fragments take part. We shall return to some examples of these later. Kistiakowsky and his co-workers have studied a number of cis-trans isomerizations, racemizations and decompositions of tertiary alkyl compounds which appear to be kinetically simple and do not involve complicating secondary reactions. Thus, the cis-trans isomerization of stilbene, $C_6H_5.CH=CH.C_6H_5$ behaves unimolecularly with a rate constant, $k = 6.10^{12}\cdot e^{-42800/RT}$; cis methyl cinnamate is slower with $k = 3.5 \times 10^{10}\cdot e^{-41600/RT}$. Dimethyl maleate gives the constant $k = 6.8 \times 10^{5}\cdot e^{-26500/RT}$. In the case of β-cyano styrene the accuracy of the velocity measurements is given by $k = 10^{11.6\pm0.4}$ $e^{-48000\pm1000/RT}$ sec.$^{-1}$. The isomerization of cyclo-propane to propylene has also the characteristics of a unimolecular process.

Tuttle and Rollefson find that the thermal decomposition of oxalyl bromide, $(COBr)_2$, occurs unimolecularly at about 200° to form carbon monoxide and bromophosgene as an intermediate, this latter then decomposing, by a wall reaction, to carbon monoxide and bromine. The activation energy of the first order reaction to form bromophosgene is found to be 32 kcal. which appears to be insufficient to break any bond in the molecule. No evidence for bromine atoms or radicals was found in this case although, in the photo-decomposition, radicals, — COBr, or bromine atoms are certainly produced.

20. **Third Order or Termolecular Reactions:** The simplest system in which a termolecular reaction has been studied kinetically is the recombination of hydrogen atoms. Two atoms of hydrogen will not, of themselves, recombine to form a stable molecule since there is no method whereby an association of two atoms can divest itself of the energy of recombination which, as we have seen, is as high as 102 kcal. Instead therefore of the reaction $2H = H_2$ we find the recombination proceeds by a termolecular mechanism

$$H + H + M = H_2 + M$$

where M is an available third body, e.g., a third hydrogen atom or a hydrogen molecule. In the absence of third bodies the atoms may migrate to the wall and there recombine

$$H + H \xrightarrow{\text{Wall}} H_2,$$

by a heterogeneous surface reaction.

For the homogeneous atom recombinations the velocity equations, when atom and molecule are respectively the third body, become

$$-\frac{d[H]}{dt} = k[H]^3 \qquad \text{and} \qquad -\frac{d[H]}{dt} = k[H]^2[H_2]. \qquad (15.42)$$

If the concentrations are expressed as moles per cc. it follows that, in each case, the dimensions of the reaction constant are cc.^{2} per mole^2 per sec., or cm.^{6} mole^{-2} sec.$^{-1}$. The velocity of reaction is measured by determining the hydrogen atom concentration in a stream of atomic and molecular hydrogen flowing through a tube at a known speed. From a determination of the respective concentrations at points along the tube the velocity data can be obtained. The kinetic treatment of such flow systems is difficult and the problem is further complicated by the simultaneous presence of a wall recombination. This may however be minimized by poisoning the walls with materials such as phosphoric acid, which is less efficient than glass in the recombination process. The best estimate of Steiner for the velocity of reaction with molecular hydrogen as the third body is

$$k = 11 \pm 2 \times 10^{15} \text{ cm.}^6 \text{ mole}^{-2} \text{ sec.}^{-1} \text{ at } 20^\circ \text{ C.} \qquad (15.43)$$

Steiner concludes that the atom is only about 1/10th as efficient as the third colliding particle. Amdur, also using a flow system, suggests that the atom is more efficient.

Smallwood attempted to avoid the difficulties of the flow system by a static method of study. He concludes that the average value of the termolecular constant is

$$k = 17 \pm 3 \times 10^{15} \text{ cm.}^6 \text{ mole}^{-2} \text{ sec.}^{-1} \text{ at } 20° \text{ C.}, \tag{15.44}$$

with a very small influence of temperature. He concludes that the atom is more than 50 times as efficient as the molecule. Eyring and his co-workers reach the conclusion from theoretical analysis based on potential energy surfaces that the molecule should be at best one sixth as efficient as the atom as third particle. In general they conclude that the efficiency to transfer energy which is involved in such termolecular collisions is intimately connected with reactivity. They cite, in this regard, qualitative data of Bonhoeffer on relative efficiencies of third bodies for atomic hydrogen recombination. The order he finds agrees well with the order of reactivities.

Four gas reactions, all involving nitric oxide, appear to be reactions requiring a collision between three molecules. The reactions are

$$\begin{aligned} 2NO + O_2 &= 2NO_2, \\ 2NO + Cl_2 &= 2NOCl, \\ 2NO + Br_2 &= 2NOBr, \\ 2NO + 2H_2 &= N_2 + 2H_2O.^1 \end{aligned}$$

The kinetic equation for such third order reactions will be, for reasons indicated in the discussion of second order reactions,

$$dx/dt = k(a - x)^2(b - x) \tag{15.45}$$

where a is the initial concentration of the nitric oxide, b the concentration of the other reactant. If b is actually maintained equal to $\frac{1}{2}$ of a this equation becomes

$$dx/dt = k(a - x)^3, \tag{15.46}$$

and, in this form, the integration gives

$$k = \frac{1}{t} \cdot \frac{1}{2} \left\{ \frac{1}{(a - x)^2} - \frac{1}{a^2} \right\}. \tag{15.47}$$

The first three termolecular gas reactions have been found to have velocities on which the influence of temperature is very small. Indeed the first named decreases in velocity with increase of temperature. This

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[1] The reaction rate is found to be proportional to the square of the nitric oxide concentration and to the first power of the hydrogen concentration, is, therefore, termolecular.

really means that the measured process is composite of at least two effects varying with temperature in opposite directions. The actual rate of any reaction should increase proportionally to the square root of the absolute temperature even though there were no activation energy, that is, every collision efficient for reaction. Recently, Bodenstein has put forward an explanation of the three reactions with oxygen, chlorine and bromine which follows along lines originally suggested by Trautz. His proposal in the oxygen reaction is that the oxidation which is measurable in rate succeeds a very rapid establishment of an equilibrium between nitric oxide and its dimer. The process then becomes a succession of two bimolecular reactions

$$(1) \quad 2NO \rightleftarrows N_2O_2,$$
$$(2) \quad N_2O_2 + O_2 = 2NO_2.$$

If the equilibrium constant in reaction (1) is

$$K = [NO]^2/[N_2O_2] \tag{15.48}$$

the velocity of reaction (2) becomes

$$\frac{d[NO_2]}{dt} = k_2[N_2O_2][O_2] = \frac{k_2}{K}[NO]^2[O_2]. \tag{15.49}$$

The measured velocity constant of the supposedly termolecular process becomes on this basis the velocity constant of the bimolecular process divided by the equilibrium constant of (1).

$$k_{obs} = k_2/K. \tag{15.50}$$

The observed decrease in the value of k_{obs} with temperature would, on this basis, be accounted for by a bimolecular constant k_2, rising with temperature, corresponding to a small activation energy and an equilibrium constant with an even larger increase with temperature. Bodenstein shows that a variation of K with temperature corresponding to a heat of reaction of 4000 cals. and a bimolecular reaction (2) with an activation energy of 2000 cals. gives agreement with experimental observations. Fig. 15.10 shows the observed variation of log k_{obs} against $1/T$ as the continuous curve A. The dotted curve gives the calculated curve on the above assumptions as to variation of constituent factors with temperature. Naturally, the assumption as to the variation of K with temperature must also apply to the reactions with chlorine and bromine. Curves B and C, full line and dotted, show the agreement obtained. Curve D in the same diagram shows a normal variation with temperature for a bimolecular reaction. The temperature coefficients of all three processes are thus neatly exhibited. The possibility of the initial reaction being one between NO and O_2 must not be overlooked as is seen from the following reactions involving hydrogen and deuterium.

A recent study by Hinshelwood and Mitchell of the reaction of nitric oxide with hydrogen and also with deuterium leads to a similar conclusion that the reaction though essentially termolecular involves binary collision complexes. In addition to the collision between N_2O_2 and H_2 analogous to those just considered, Hinshelwood and Mitchell also consider the binary collisions between $(NO.H_2)$ and NO and find that the relative importance of such binary collisions depends in part on the nitric oxide-hydrogen ratio. With excess nitric oxide, the $N_2O_2 - H_2$ collision is the important factor. In this reaction, the temperature coefficient is much higher than in the reactions with oxygen, chlorine and bromine. For a mixture of 400 mm. NO and 200 mm. H_2 the activation energy is 47 kcal. The reaction with deuterium is slower than that with hydrogen, the constants being in the ratio 0.7 to 1, for collisions with the N_2O_2 complex.

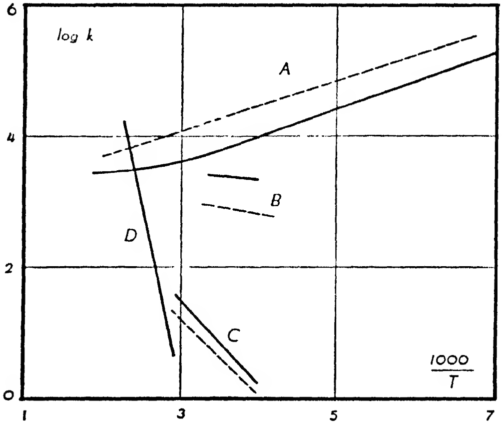

FIG. 15.10. Bodenstein's Data for log k_{obs} against $1/T$. Curve A, $2NO + O_2$. Curve B, $2NO + Cl_2$, Curve C, $2NO + Br_2$. Curve D, Normal Bimolecular Reaction

21. Consecutive Reactions: In a succession of reactions a preponderatingly slow reaction will govern the rate of the whole process. Under such circumstances the equation representing the reaction velocity would not necessarily be that expected from the reaction equation representing the whole process. We may illustrate this by the thermal reaction of hydrogen and bromine molecules studied by Bodenstein and Lind. They found, empirically, a complex reaction velocity equation of the form

$$\frac{d[2HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{m + \frac{2[HBr]}{[Br_2]}},$$

where the square brackets indicate concentrations of the reactants and products. We shall show that such a kinetic equation follows from a sequence of reactions which may be written

1. $Br_2 = 2Br;$ $\Delta H = +\ 45.2$ kcal. (k_1)
2. $Br + H_2 = HBr + H;$ $\Delta H = +\ 16.7$ kcal. (k_2)
3. $H + Br_2 = HBr + Br;$ $\Delta H = -\ 40.5$ kcal. (k_3)
4. $H + HBr = H_2 + Br;$ $\Delta H = -\ 16.7$ kcal. (k_4)
5. $Br + Br = Br_2;$ $\Delta H = -\ 45.2$ kcal. (k_5)

To derive the kinetic expression use is made of a stationary state principle, enunciated by Bodenstein, according to which it is assumed that, after the operating conditions for the reaction have been established for a brief interval, no change occurs in the concentrations of the intermediate atomic species. In a number of cases such an assumption has been justified by experimental observations. Applied to the present case, it assumes that the production of bromine atoms through reactions 1, 3 and 4 is equal at the stationary state to their disappearance by reactions 2 and 5. Similarly, with hydrogen atoms, formation in reaction 2 will equal disappearance through reactions 3 and 4. Hence, two equations result relating to bromine and hydrogen atoms respectively:

$$(a)\quad 2k_1[Br_2] + k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2] + 2k_5[Br]^2 \tag{15.51}$$

and

$$(b)\quad k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2]. \tag{15.52}$$

Subtracting equation (*b*) from (*a*) we obtain

$$2k_1[Br_2] = 2k_5[Br]^2 \tag{15.53}$$

whence the bromine atom stationary state concentration is

$$(c)\quad [Br] = \sqrt{k_1[Br_2]/k_5} \tag{15.54}$$

and similarly the hydrogen atom concentration from equation (*b*) is

$$(d)\quad [H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} \tag{15.55}$$

or substituting the value for [Br] in (*c*) we obtain

$$(d')\quad [H] = \frac{k_2[H_2]\sqrt{k_1[Br_2]/k_5}}{k_3[Br_2] + k_4[HBr]}. \tag{15.56}$$

Inspecting equations 1 to 5 we find that the velocity of hydrogen bromide formation is given by the expression

$$+\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr]. \tag{15.57}$$

Inserting (*c*) and (*d′*) for the bromine and hydrogen atom concentrations we obtain

$$+\frac{d[\mathrm{HBr}]}{dt} = k_2[\mathrm{H_2}]\sqrt{\frac{k_1}{k_5}[\mathrm{Br_2}]} + \frac{k_3[\mathrm{Br_2}]k_2[\mathrm{H_2}]\sqrt{k_1[\mathrm{Br_2}]/k_5}}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} - \frac{k_4[\mathrm{HBr}]k_2[\mathrm{H_2}]\sqrt{k_1[\mathrm{Br_2}]/k_5}}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]}. \qquad (15.58)$$

Collecting all terms, this expression reduces to

$$+\frac{d[\mathrm{HBr}]}{dt} = \frac{k_2[\mathrm{H_2}]\sqrt{k_1[\mathrm{Br_2}]/k_5}}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} \cdot 2k_3[\mathrm{Br_2}]$$

$$= \frac{2k_2[\mathrm{H_2}]\sqrt{k_1[\mathrm{Br_2}]/k_5}}{1 + \frac{k_4}{k_3}\frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}} = \frac{2k_2\sqrt{k_1/k_5}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + \frac{k_4}{k_3}\frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}}. \qquad (15.59)$$

It will be seen that this equation is identical in form with the empirical equation of Bodenstein and Lind and that the constants of their equation are determined by the individual steps in the process, and their respective rate constants.

Bodenstein and his co-workers have investigated this mechanism by studies of the photochemical process which is kinetically identical, except that the bromine atoms are produced by absorption of light. Over a range of temperature, these workers found that k_4/k_3, the competition of HBr and $\mathrm{Br_2}$ for hydrogen atoms, was independent of temperature. This means that these reactions have identical activation energies. The assignment of $E = 1$ kcal. in Table 15.3 fulfills this condition. The reaction velocity increases rapidly with temperature corresponding to an activation energy $E = 17.7$ kcal. The influence of temperature is attributed to the increase in velocity of the rate-determining reaction (2) with $E_2 = 17.7$ kcal. Reaction (4) which is the reverse of (2) with an energy of activation $E_4 = 1$ kcal. brings these energy data into line with the observed ΔH for the process, $+ 16.7$ kcal.

If we consider reactions (1) and (5) alone,

$$\mathrm{Br_2} = 2\mathrm{Br}\ (k_1) \qquad \text{and} \qquad 2\mathrm{Br} = \mathrm{Br_2}\ (k_5),$$

the rates of formation of bromine atoms and their disappearance are given respectively by $2k_1[\mathrm{Br_2}]$ and $2k_5[\mathrm{Br}]^2$. The thermal equilibrium between bromine molecules and bromine atoms occurs when these two are identical, i.e., when $2k_1[\mathrm{Br_2}] = 2k_5[\mathrm{Br}]^2$ or $[\mathrm{Br}] = \sqrt{k_1[\mathrm{Br_2}]/k_5}$. This expression gives, therefore, the equilibrium concentration of bromine atoms at a given temperature. This term is present in the rate expression for hydrogen bromide formation because the other bromine atom consuming process is a slow process compared with (5) even though this latter involves a bimolecular process between a reactant, Br, present only in small concentration. We now proceed to examine the analogous reaction involving chlorine where k_2 is now a rapid process.

22. **Chain Reactions:** The hydrogen-chlorine combination proceeds by a sequence of reactions similar to those just discussed. We shall consider the following

$$\begin{aligned} &(1) &\quad Cl_2 &= 2Cl \\ &(2) &\quad Cl + H_2 &= HCl + H \\ &(3) &\quad H + Cl_2 &= HCl + Cl \end{aligned}$$

and note that the reaction (2) proceeds much more rapidly than the corresponding reaction with bromine atoms. The activation energy is about 6 kcal. and hence collision with hydrogen molecules as in equation (2) to yield hydrogen chloride is a much more frequent process than the collision with another chlorine atom to form the molecule. The activation energy of reaction (3) is also small, about 3 kcal., so that this process also is one of high collision yield. Since, in reaction (3), a chlorine atom is produced which may again react with a hydrogen molecule giving a hydrogen atom according to (2) a whole sequence, or *chain,* of reactions may succeed an initial production of chlorine atoms either thermally or by other suitable means. This deduction can be confirmed in two ways. Polanyi and Beutler produced chlorine atoms in a hydrogen-chlorine mixture by means of sodium vapor according to the reaction

$$Na + Cl_2 = NaCl + Cl.$$

They found that as many as 10^4 molecules of hydrogen chloride were produced per sodium atom introduced. Quanta of light energy dissociate chlorine molecules to atoms,

$$Cl_2 + h\nu = 2Cl.$$

Bodenstein showed that as many as 10^6 molecules of hydrogen chloride were produced per quantum of light energy absorbed by the chlorine. Chlorine atoms produced by thermal dissociation will likewise lead to a chain of the reactions (2) and (3). Morris and Pease concluded that the thermal hydrogen-chlorine combination proceeds by the above chain, starting on the walls by a dissociation of chlorine molecules and ending by a reversal of that process. At 200° the chain length was calculated to be 10^4.

A chain of reactions will continue until one or other of the links in the chain is stopped. This may occur, for example, by a recombination of atoms, thus $H + Cl = HCl$, $H + H = H_2$, $Cl + Cl = Cl_2$. Such atom recombination processes occur readily at the walls of the containing vessel. It is significant that, at low working pressures, the yield of hydrogen chloride is relatively low, largely owing to diffusion of the atoms to the walls there to recombine with other atoms. At low pressures we therefore expect shorter chains.

23. **Inhibitor Action:** Chains may be broken by removal of the atoms by reactions, other than (2) or (3), which do not lead to a reaction chain or sequence. Oxygen has long been known as an inhibitor of reaction between hydrogen and chlorine; it is probable that oxygen removes hydrogen atoms from the system by a sequence of reactions which is not certain but which probably involves, with M as a third body,

$$\begin{aligned} H + O_2 + M &= HO_2 + M, \\ HO_2 + HO_2 &= H_2O_2 + O_2. \end{aligned}$$

Nitrogen-containing materials such as ammonia, albumen and the like readily remove chlorine atoms, being themselves chlorinated. Since the activation energy of the reaction $Cl + H_2$ is the larger of the chain reactions, removal of chlorine atoms has a much more striking retarding action than hydrogen atom removal, since more collisions are necessary with chlorine atoms to continue the chain. The more efficient the collisions between atom and inhibitor, the greater the inhibitor efficiency. This latter may reach very striking proportions. A few tenths of one per cent of oxygen is sufficient to reduce to negligible proportions the reaction of hydrogen and chlorine initiated at room temperatures by light. The longer the sequence or chain of reactions succeeding the initial reaction, the greater the possible effect of an inhibitor. Thus, in a reaction in which 10^4 chains succeed the initial process the reaction rate may be diminished by the presence of an inhibitor to 10^{-4} of its normal value. In this case the inhibitor would prevent all chains propagating. Inhibitor action by materials present in small amounts is therefore an important criterion of chain reactions. Inhibitors are now used technically to prevent undesired chain reactions. Hydroquinone inhibits the chain oxidation of sodium sulfite solutions; acetanilide is used to inhibit the decomposition of hydrogen peroxide solutions; inhibitors are added to rubber, gasoline, artificial leather, etc., to minimize chain reactions of oxidation which result in deterioration. Bäckström has shown that as many as 50,000 molecules of sodium sulfite may be oxidized in solution by a chain mechanism succeeding an initial activation either by light or catalysts. He showed that the velocity of reaction could be expressed by an equation

$$V = \frac{k_1}{kc + k_2}, \tag{15.60}$$

where k_1, k and k_2 are constants and c is the concentration of added inhibitor. The constant k_2 appears in the denominator to take account either of accidental inhibitors present in constant concentration or a normal termination of reaction chains. The constant k_1 depends on the method of starting the chains. It is probable that atoms or free radicals are involved even in the reactions in solution and that inhibitors act on these. In the chain decomposition of hydrogen peroxide solutions the radicals OH and HO_2 play an important rôle.

$$\begin{aligned} OH + H_2O_2 &= H_2O + HO_2, \\ HO_2 + H_2O_2 &= O_2 + H_2O + OH. \end{aligned}$$

24. **Chain Mechanisms in Decompositions of Organic Molecules:** Hinshelwood and his co-workers demonstrated the quasi-unimolecular nature of many decompositions of organic molecules including acetaldehyde, acetone, and various ethers. Other workers extended the survey to azo-compounds, saturated hydrocarbons, nitrous oxide and other substances. F. O. Rice, however, pointed out that such processes might occur, not by intramolecular rearrangement to the final products, but by breaking of bonds with the production of free radicals, followed by a chain of radical reactions. Rice and Herzfeld showed that a chain mechanism might give first, second or 1.5 order processes depending on the nature of the chain and the chain-breaking steps. As an example of a *postulated* chain mechanism we may cite the decomposition of ethane.

$$\begin{array}{lrl} \text{P.} & C_2H_6 &= CH_3 + CH_3, \\ \text{C.S.} & CH_3 + C_2H_6 &= CH_4 + C_2H_5, \\ \text{C.} & C_2H_5 &= C_2H_4 + H, \\ \text{C.} & H + C_2H_6 &= C_2H_5 + H_2. \end{array}$$

The letters refer to primary rupture (P), chain starting (C.S.) and the chain reactions (C).

There is as yet no large body of agreement among the experts in this field as to whether a chain mechanism is present or absent in certain of these decompositions. Hinshelwood[1] regards acetone decomposition as probably a unimolecular reaction in which chains play very little part. The thermal decompositions of the ethers appear to contain chain and non-chain reactions. Nitrous oxide and acetaldehyde decompositions are in Hinshelwood's view possibly non-chain, but have different modes of activation with differing transformation probabilities contributed in varying proportions in different pressure ranges. In Pease's view there is definite evidence of chains in most of these reactions and a close approach in most cases to a 1.5 order kinetics.

The effect of nitric oxide as an inhibitor is definite evidence for the existence of radical chains in some of these reactions. Presence of 2 mm.

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[1] Compare, for example, Hinshelwood, Kinetics of Chemical Change, Oxford Univ. Press, 1940, and Pease, Equilibrium and Kinetics of Gas Reactions, Princeton Univ. Press, 1942. See also *Proc. Roy. Soc.*, 180, 237 (1942).

NO reduces the velocity of decomposition of di-ethyl ether to less than 30 per cent of the uninhibited rate. The proportion of chain reaction, as measured by the nitric oxide method, falls steadily as the number of carbon atoms in the ether increases. With ethane the relative rate of the chain reaction falls below 5 per cent with 4 mm. NO in 57 mm. ethane. Pease and his colleagues have shown inhibitory effects of nitric oxide in other decompositions of saturated hydrocarbons and in the hydrogenation and polymerization of olefines. The nitric oxide is assumed to act by formation of a complex which in the case of methyl radicals may be CH_3NO or its isomer, formaldoxime, CH_2NOH. This latter has been shown by H. A. Taylor and H. Bender to yield hydrogen cyanide and water on decomposition in agreement with observations of the presence of cyanides in inhibited chain decompositions.

25. **Induced Decompositions:** The chain mechanism of decomposition postulated by F. O. Rice suggests the possibility of induced decomposition of organic compounds at temperatures below their normal decomposition temperatures by the introduction into the system of one of the radicals assumed to produce a reaction chain. Allen and Sickman achieved the induced decomposition of acetaldehyde at temperatures around 300° C. by decomposing azomethane in the presence of acetaldehyde. In this temperature range acetaldehyde alone is stable. Azomethane decomposes and it is assumed that free methyl groups are formed. The kinetics of the induced decomposition was studied and found to agree with the Rice-Herzfeld postulates. The chain length determined by the ratio of aldehyde molecules decomposed to azomethane molecules decomposed was found to increase with increase in the ratio $P_{ald}/P_{azo}^{\frac{1}{2}}$. Chain lengths between 22 and 500 were thus found. The chain length decreased with rise of temperature. This is to be ascribed to a breaking of reaction chains by recombination of radicals becoming increasingly important, with increase of radical concentration, as the reaction temperature rises.

Additional evidence of chain mechanism in such systems is obtained from photochemical studies of decomposition in which increasing yields per unit of light energy absorbed are obtained with increase of temperature. Leermakers in this way found that the chain length in the photodecomposition of acetaldehyde was as high as 200 at 300° C.

26. **Explosions:** The rapid reactions leading to explosions in many cases involve chain reactions. A rapid development of reaction may of course be due to the heat liberated by reaction and failure to dissipate it rapidly enough, leading therefore to ever faster reaction and a consequent thermal explosion. A number of explosive reactions have been studied where this is not an adequate explanation of the whole phenomenon and a chain of reactions is postulated to account for the facts. Explosive reactions entirely independent of the thermal conditions may arise when a chain branches. Thus, if the velocity of reaction V is equal to n_0, the

number of primary activated molecules produced per second, plus the number of activated molecules produced by each link, αV, then

$$V = n_0 + \alpha V \tag{15.61}$$

where α is the probability that a link in the chain will produce another activated molecule. It follows therefore that

$$V = \frac{n_0}{1 - \alpha}\cdot \tag{15.62}$$

This equation is of such a form that when α becomes unity or greater the velocity becomes infinite. The probability α is dependent on the shape and size of the vessel, and on the pressure, since chains may be terminated at reaction walls. If the average chain length $1/(1 - \alpha)$ is large, that is, when α is nearly one, a slight increase in the pressure may make α equal to or greater than one, changing the reaction from a steady reaction to an explosion. We thus understand the existence of a low pressure explosion limit for such reactions. There also exists a high pressure limit for many explosive reactions, since, at sufficiently high gas pressures, the chains may be broken in the gas phase before reaching the reaction walls. Upper and lower explosion limits in many gas mixtures have been studied by Hinshelwood and his co-workers in England and by Semenoff and his colleagues in Russia. Haber and Alyea showed that, in hydrogen-oxygen mixtures, which show upper and lower explosion limits, the low pressure process is probably initiated at the reaction walls, since crossed streams of gas at reaction temperature did not ignite before a suitable surface such as a silica rod was introduced into the gas stream.

The mechanism of such reactions is difficult to establish but the following processes may be regarded as reactions consistent with the observations on the hydrogen-oxygen reaction as to upper and lower explosion limits, and the initiation of reaction produced by hydrogen atoms with agents such as excited mercury and from the photo-decomposition of hydrogen iodide and ammonia. They are also consistent with the data on the inhibitory reaction of oxygen in the hydrogen-chlorine chain. In the following, M is either a third body or wall.

$$\begin{aligned}
H + O_2 + M &= HO_2 + M,\\
H + O_2 + H_2 &= H_2O_2 + H,\\
HO_2 + HO_2 &= H_2O_2 + O_2,\\
H + O_2 &= OH + O \text{ (Chain branching)},\\
O + H_2 &= OH + H \text{ (Chain branching)},\\
OH + H_2 &= H_2O + H.
\end{aligned}$$

Atomic hydrogen, oxygen and hydroxyl radical are all destroyed at the wall by surface action. Chains are initiated at the surface and, in the thermal reaction, HO_2 is destroyed at the surface. At high temperatures and pressures it can undergo reactions

$$HO_2 + H_2 = H_2O_2 + H,$$
$$HO_2 + H_2 = H_2O + OH.$$

Similar detailed analyses of explosive reactions in hydrocarbon, carbon monoxide, carbon disulfide and oxygen systems have been studied.

THE KINETICS OF REACTIONS IN LIQUID SYSTEMS

Many reactions, notably the reactions of organic chemistry, occur in solution at measurable rates. The same methods of chemical kinetics are applicable as in the case of gas reactions. Indeed, from the classic researches of Wilhelmy in 1850 on the inversion of cane sugar solutions, accelerated by acids, in which he laid down the broad principles governing reaction kinetics, much of the work in this field has been performed with reactions in solution. In the early days of the theory of electrolytic dissociation, after the observation of Ostwald that, in acid hydrolyses, the catalytic activity was proportional to the conductivity of the acid, Arrhenius concluded in 1889 that the active catalytic agent was the hydrogen ion and the catalytic activity proportional to its concentration. Modern research has revealed the limitations of this concept, applicable indeed only to weak acids. The range of kinetic studies has broadened to a wide variety of reactions and an intimate knowledge of mechanism of reaction in liquid systems. It will only be possible to indicate some of the more important features and accomplishments.

27. **First Order Reactions in Liquid Systems:** The decomposition of nitrogen pentoxide occurs in a variety of solvents according to a first order kinetics at approximately the same rate as in the gaseous phase (Eyring and Daniels, 1930). In nitric acid, possibly due to compound formation, the reaction is slower and the activation energy is higher. The isomerization of pinene to dipentene occurs at the same rate in the gaseous and liquid states. Other examples also show that there is no fundamental difference between the two states as far as the factors influencing rate processes are concerned. Nevertheless, in many first order reactions, the solvent may effect a change of even one thousandfold in velocity. The decomposition of 2.4.6 trinitrobenzoic acid into carbon dioxide and trinitrobenzene is such a case. In water at 60° the rate constant is 3.33×10^{-6} while in nitrobenzene it is 4.07×10^{-9}. These effects are to be attributed to mutual interactions between solvent and solute the nature of which the study of reaction kinetics may assist in revealing.

Many first order reactions in solutions involve both solute and solvent kinetically but the first order observed is due to the normally large excess of solvent and to its relatively small concentration change on completion of reaction. Thus, in the inversion of cane sugar,

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6,$$

whereby dextrose and laevulose are formed, and in which we may assume with Arrhenius that the hydrogen ion is involved as a catalyst, the kinetic expression may have the form

$$dx/dt = k[C_{12}H_{22}O_{11}][H_2O][H^+]. \qquad (15.63)$$

Such an equation, termolecular in form, is actually first order, or *pseudo-unimolecular*, since, in dilute sugar solutions, both the water concentration and the hydrogen ion concentration remain substantially constant. We can therefore apply the first order rate equation, $dx/dt = k(a - x)$, where $(a - x)$ represents the concentration of sugar at time t. Actually, in place of concentrations in the integrated expression, $k = 1/t(\ln a/a - x)$, we may substitute the rotatory power in degrees for the solution, the initial value for a at $t = 0$, and the value at $t = t$ for $a - x$. In this way, with a 20 per cent solution of cane sugar at 25° C., 0.5 N with respect to lactic acid the following data were obtained.

TABLE 15.6

VELOCITY OF INVERSION OF CANE SUGAR

t (mins.)	$a - x$	$\frac{1}{t}\log\frac{a}{a-x}$
0	34.50°	—
1,435	31.10	0.2348
7,070	20.16	0.2343
14,170	10.61	0.2301
19,815	5.08	0.2291
29,925	−1.65	0.2330
∞	−10.77	—

The proportionality to the hydrogen ion concentration can be shown strikingly by comparison of the catalytic activity of a weak acid in presence and absence of a salt having a common ion. If α_1 represents the degree of dissociation of the weak acid in concentration c_1 and the concentration of the salt with common anion is c_2, then, assuming complete dissociation of the salt, the degree of dissociation α in presence of the salt is given, by application of the law of mass action, by the expression

$$(\alpha_1 c_1)(\alpha_1 c_1) = \alpha c_1(\alpha c_1 + c_2). \qquad (15.64)$$

The degree of dissociation α is thus calculable in terms of the value of α_1 for the weak acid, and this is deducible from conductivity measurements. In this manner, Arrhenius obtained the following observed and calculated data for the catalytic activity of mixtures of acetic acid and sodium acetate in the inversion of cane sugar.

TABLE 15.7

INVERSION OF CANE SUGAR BY 0.25 N ACETIC ACID-SODIUM ACETATE MIXTURES

	Concentration of Sodium Acetate					
	0	0.0125	0.025	0.05	0.125	0.250
$k_{\text{obs.}} \times 10^3$	0.75	0.122	0.070	0.040	0.019	0.010
$k_{\text{calc.}} \times 10^3$	0.74	0.129	0.070	0.038	0.017	0.010

The hydrolysis of esters in acid solutions is analogous to the inversion of cane sugar as far as proportionality to hydrogen ion concentration in weak acid is concerned. With mixtures of strong acids and neutral salts with a common ion, in both reactions, a similar treatment is not possible. Such mixtures show an increased rate of reaction on addition of salt. The phenomenon has been termed *neutral salt action* and will be discussed in its generalized aspects in Section 30.

28. **Second Order Reactions in Liquid Systems:** The saponification of esters by alkali is the classical example of a second-order, bimolecular reaction. The reaction may be expressed in terms of hydroxyl ion and ester as reactants

$$CH_3COOC_2H_5 + OH^- = CH_3COO^- + C_2H_5OH,$$

yielding the kinetic equation, $dx/dt = k(a - x)(b - x)$ with a as the ester and b as the hydroxyl concentration. The integrated form of this equation (15.17) yields good constants for k. All strong bases show approximately the same reaction rate irrespective of cation, pointing to the hydroxyl ion as the essential reactant. Weak bases on the contrary show low reaction constants due to incomplete dissociation and low hydroxyl concentration, responsive also to the effect of added salts with a common cation.

Comparison of the velocity of hydrolysis of the same ester with hydrogen and hydroxyl ions under the same conditions showed that the rate due to the latter is some 1400 times greater than that due to hydrogen ions. This result was utilized by Wijs to determine the dissociation constant of water. The initial rate of hydrolysis of methyl acetate in pure water may be expressed by the equation

$$dx/dt = k_1[OH^-] + k_2[H^+], \qquad (15.65)$$

where $k_1 : k_2 = 1400 : 1$. The OH^- and H^+ are derived from the dissociation of water where

$$[H^+][OH^-] = K_w. \tag{15.66}$$

Differentiation of this gives

$$[OH^-]\frac{d[H^+]}{dt} + [H^+]\frac{d[OH^-]}{dt} = 0. \tag{15.67}$$

By differentiating (15.65) with respect to t and equating it to zero, we obtain the position of minimum velocity, i.e.,

$$\frac{d^2x}{dt^2} = k_1\frac{d[OH^-]}{dt} + k_2\frac{d[H^+]}{dt} = 0. \tag{15.68}$$

Comparison of (15.67) and (15.68) reveals that the latter equation is satisfied when

$$[H^+] : [OH^-] = k_1 : k_2. \tag{15.69}$$

Since $k_1 : k_2 = 1400$ it follows that the velocity of hydrolysis of methyl acetate in initially pure water must be a minimum when the hydrogen ion concentration is 1400 times that of the hydroxyl ion. Wijs determined this minimum experimentally and, hence, the concentrations of hydrogen and hydroxyl ions. These concentrations satisfy the equation $[H^+][OH^-] = K_w$ which can therefore be determined. His experimental result was $K_w = 1.44 \times 10^{-14}$ at 25° C. in good agreement with the value of Kohlrausch and Heydweiller from conductance measurements in pure water.

Hudson used a similar method of determining K_w from the rate of muta-rotation of glucose in acid and alkaline media. His results are less reliable but yield a value for K_w of the same order of magnitude, 1.0×10^{-14}.

29. **Quaternary Ammonium Salt Formation:** The reaction between amines and alkyl halides in various solvents, first studied by Menschutkin in 1887 using triethylamine and ethyl iodide, may be cited as a further example of second order reactions in solution with important aspects in the recent development of the theory of chemical kinetics. Menschutkin found wide variations in velocity in various solvents from $k = 0.00018$ in hexane to $k = 0.133$ in benzyl alcohol at 100° C. The influence of solvent is not the same in different reactions. The solvent influence in the Menschutkin reaction is practically the reverse of that operative in the esterification of acetic anhydride by ethyl alcohol. Soper has pointed out a relation to the internal pressure of the solvent. If the reaction products have a higher internal pressure than the reactants the rate of reaction is accelerated by solvents of high internal pressure, and vice versa. Another generalization is that polar solvents tend to accelerate

a reaction in which a polar substance is the product. This is qualitatively in agreement with the comparative data for the Menschutkin reaction and the esterification reaction with acetic anhydride.

The kinetics of quaternary ammonium salt formation has a further interest. Reactions in solution can be analyzed from the standpoint of the collision mechanism in the same manner as holds for gas reactions. Thus, if we analyze the rate of isomeric conversion of ammonium cyanate to urea in aqueous solution (J. Walker, 1895) by following the change of conductance with time, it is found that the reaction is second order involving reaction of two ions,

$$NH_4^+ + CNO^- = CO(NH_2)_2.$$

If such a reaction is examined from the standpoint of collision theory over a range of temperatures it is found that the rate constant is well expressed by the equation $k = Ze^{-E/RT}$ where Z is the collision number and E the activation energy. In the Menschutkin reaction, on the contrary, this equation does not apply. The reaction appears to proceed much more slowly. In the reaction of dimethyl aniline and methyl iodide the rate is $0.5 \times 10^{-7}Ze^{-E/RT}$. The recognition of these 'slow' reactions has led to a modification of the collision equation, by the introduction of a factor P, the 'probability' or 'steric' factor, giving

$$k = PZe^{-E/RT}. \tag{15.70}$$

Values of P of the order of $0.1 - 1.0$ are readily understandable on the basis of the necessity for a suitable steric arrangement of the two colliding molecules. Thus, in the very simple collision of H and HBr, the direction of approach will determine in part whether reaction to $H_2 + Br$ occurs. This should readily result from a linear approach H — HBr but not from one of the type H — BrH. Values of P of the order of 10^{-8}, such as occur in the Menschutkin reactions, are difficult to account for sterically. Newer ideas are necessary which will be later reviewed (Section 43).

TABLE 15.8

ACTIVATION ENERGIES FOR QUATERNARY SALT FORMATION

Amine	Iodide	E, kcal
Triethylamine	Methyl	9.7
	Ethyl	11.4
	Isopropyl	17.1
Pyridine	Methyl	14.3
	Ethyl	15.8
	Isopropyl	18.0

Quaternary ammonium salt formation also provides examples illustrating the effect of substituents on reaction velocity. Table 15.8 shows the effect of increasing substituent on the activation energy of salt formation. As the alkyl radical becomes more complex the charge on the carbon atom which attracts the approaching base is made more negative or less positive. This change should be accompanied by an increase in activation energy.

30. **Activity and Reaction Velocity:** The lack of co-ordination between reaction velocity and catalyst concentration, for example in the case of reactions catalyzed by strong acids and added salts, prompted efforts to correlate activity and reaction velocity. A general theory involving such a relation has been developed by Brönsted. If we assume that a bimolecular reaction between A and B proceeds by formation of an unstable intermediate complex, AB, which undergoes further decomposition to yield the reaction products,

$$A + B \rightarrow AB \rightarrow \text{Products},$$

we can formulate a kinetic equation in terms of the rate of decomposition of the complex as the rate-controlling step,

$$dx/dt = kc_{AB}. \qquad (15.71)$$

The quantity c_{AB} can be obtained from the equilibrium constant K_a of its formation, thus:

$$K_a = \frac{a_{AB}}{a_A a_B} = \frac{c_{AB}}{c_A c_B} \cdot \frac{f_{AB}}{f_A \cdot f_B} \qquad (15.72)$$

or

$$c_{AB} = K_a c_A c_B \cdot \frac{f_A f_B}{f_{AB}}, \qquad (15.73)$$

whence

$$dx/dt = k' c_A c_B . f_A . f_B / f_{AB}, \qquad (15.74)$$

where the f values are the activity coefficients of the respective species and k' includes both the reaction constant k and the equilibrium constant K_a. It differs from the expression in terms of concentration by the *kinetic factor*, $F = f_A f_B / f_{AB}$.

The magnitude of the kinetic factor in very dilute solutions may easily be estimated by means of the Debye-Hückel limiting law. According to this, the activity coefficient of an ion is given by:

$$-\log f = 0.5\, z^2 \sqrt{\mu}. \qquad (15.75)$$

Now

$$\begin{aligned} \log F &= \log f_A + \log f_B - \log f_{AB} \\ &= -0.5\,(z_A^2 + z_B^2 - z_{AB}^2)\sqrt{\mu}. \end{aligned} \qquad (15.76)$$

Remembering that the valence of the complex must necessarily be equal to the sum of the valences of the reactants which form it, then

$z_A + z_B = z_{AB}$ and $z_A^2 + z_B^2 - z_{AB}^2 = -2z_Az_B$. Therefore,

$$\log F = z_Az_B\sqrt{\mu} \qquad \text{or} \qquad F = 10^{z_Az_B\sqrt{\mu}}. \tag{15.77}$$

The Brönsted equation may thus be written:

$$\frac{dx}{dt} = kc_Ac_B 10^{z_Az_B\sqrt{\mu}}. \tag{15.78}$$

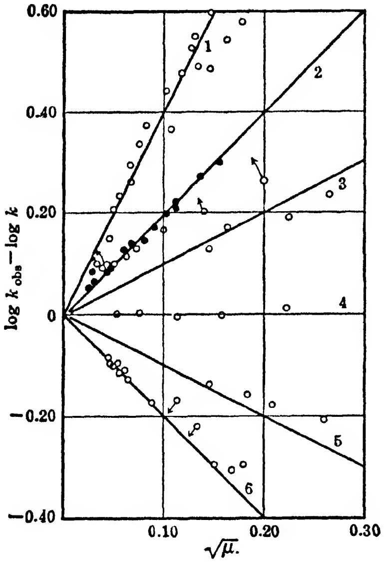

Fig. 15.11. Dependence of Reaction Rates on Ionic Strength (La Mer)

Rate Determining Reaction	z_Az_B
1. $Co(NH_3)_5Br^{++} + Hg^{++}$	$+4$
2. Circles. $CH_2BrCOO^- + S_2O_3^=$	$+2$
Dots. $S_2O_8^= + I^-$	$+2$
3. $NO_2:N.CO_2C_2H_5^- + OH^-$	$+1$
4. $C_{12}H_{22}O_{11} + OH^-$	0
5. $H_2O_2 + H^+ + Br^-$	-1
6. $Co(NH_3)_5Br^{++} + OH^-$	-2

Three cases may be considered: (1) A and B are two ions of the same sign. The valence product z_Az_B is therefore positive. Hence, if the ionic strength of the reaction system is increased, the velocity dx/dt must increase to maintain the constancy of k. (2) A and B are two ions of opposite sign. The valence product z_Az_B will be negative and the velocity of reaction must decrease with increase in the ionic strength. (3) Either A or B is a neutral molecule. The valence product z_Az_B is then zero and the velocity will be unchanged by a salt addition.

If for such reactions an observed velocity constant k_{obs} is calculated by means of the equation, $dx/dt = k_{obs}c_Ac_B$, it follows by comparison with the Brönsted equation that

$$k_{obs} = k \cdot 10^{z_Az_B\sqrt{\mu}} \tag{15.79}$$

or

$$\log k_{obs} = \log k + z_Az_B\sqrt{\mu}. \tag{15.80}$$

If $\log k_{obs} - \log k$ is plotted against $\sqrt{\mu}$ a straight line should be obtained. In Fig. 15.11 are shown typical results, collected by LaMer, illustrative of such effects.

If such reactions are carried out in solutions of higher ionic strengths than those to which the limiting law is applicable, the above relations will give the limiting slopes of the exponential increase and decrease of cases 1, 2, 3, 5 and 6. For case 4, the zero type, since the activity of a neutral molecule may increase or decrease with increasing ionic strength of the medium, but always linearly with the ionic strength, a small linear salt effect, positive or negative, may be observed. Such a linear positive effect is observed with acid hydrolyses of esters and inversion of cane sugar in presence of salts with a common ion, as illustrated in Table 15.9.

TABLE 15.9

VELOCITY OF HYDROLYSIS OF ETHYL ACETATE AT 25° C.

c.HCl =	0.25	0.10	0.05	0.025	0.01 *N*.
$k(c.\text{HCl}) \times 10^5$	71.6	28.3	13.8	7.0	2.9
$k(c.\text{HCl} + 1.0\,N.\text{KCl}) \times 10^5$	85.7	34.45	16.9	8.7	3.6

The effect so far dicussed, termed the primary kinetic effect, has dealt with the variation of the activity coefficients of the reactants alone and not with any change in concentration due to addition of a neutral salt. If the ionic reactants come from strong electrolytes, no such change in concentration can occur. However, if the ions come from weak electrolytes, a change in concentration is to be expected.

The dissociation of acetic acid may be represented:

$$CH_3COOH = H^+ + CH_3COO^-.$$

The equilibrium in an aqueous solution will be given by the equation, $K_a = a_+a_-/a_2$, or in terms of concentration

$$K_a = \frac{c_+c_-}{c_2} \cdot \frac{f_+f_-}{f_2} = K_c \cdot \frac{f_+f_-}{f_2} \cdot \qquad (15.81)$$

Upon addition of a neutral salt such as sodium chloride to acetic acid, the activity coefficient factor will diminish and, in order to maintain K_a constant, K_c must increase, that is, the hydrogen ion concentration of the acetic acid will increase. The effect of addition of neutral salt to a reaction catalyzed by hydrogen ions derived from acetic acid will be to cause an increased rate of reaction.

HETEROGENEOUS REACTIONS INVOLVING GASES

A large number of gas reactions do not occur homogeneously. They may be readily shown to occur at the surface of the containing vessel or at the surface of some material present in the reaction system. These reactions are known as 'wall' or 'surface' or contact reactions. They may be classed quite generally as contact catalytic gas reactions. The wall or surface is the catalyst or accelerator of the given reaction. This effect of wall surface on the speed of reaction can very readily be demonstrated in the reaction between ethylene and bromine

$$C_2H_4 + Br_2 = C_2H_4Br_2.$$

In a glass vessel, the reaction is rapid but the process occurs practically exclusively on the glass walls of the containing vessel. If the interior of the glass vessel be coated with paraffin wax, the reaction proceeds extremely slowly, probably only at imperfections in the wax covering. By using various surfaces, varying rates of reaction were obtained at a given temperature. Stearic acid surfaces were more active than glass, which, in its turn, was more active than cetyl alcohol, which was much more active than paraffin wax.

Surfaces are, therefore, obviously specific in their action. This specificity may also be illustrated by the varying nature of the products which may result from association of a given molecule with a surface. Thus, formic acid, $HCOOH$, decomposes exclusively into hydrogen and carbon dioxide in contact with metal surfaces at various temperatures,

$$HCOOH = H_2 + CO_2.$$

At the surfaces of oxides, however, in addition to this dehydrogenation process, there also occurs a dehydration process,

$$HCOOH = H_2O + CO.$$

The relative amounts of the two processes which occur vary with the nature of the surface and, indeed, with the method of preparation of the surface. Thus, with alumina the process is mainly one of dehydration. With zinc oxide it is mainly dehydrogenation. But, varying methods of preparing these contact agents vary the ratio of the two alternative reactions. The same is true of the decomposition of alcohols to yield olefine and water or aldehyde and hydrogen as exemplified in the equations

$$CH_3CH_2OH = CH_2 : CH_2 + H_2O,$$
$$CH_3CH_2OH = CH_3.CHO + H_2.$$

31. **Adsorption:** This specific influence of the surface is assumed to be exerted on the molecules of reactant in contact with or *adsorbed* on the contact agent. According to Langmuir, the adsorbed molecules are held to the surface of the contact agent by the forces of attraction of such surfaces, the forces which, under suitable circumstances, lead to crystal growth or, in the case of liquids, lead to the phenomena of surface tension. Langmuir assumes such adsorbed molecules to form, generally, a unimolecular layer at most on the surface. The adsorbed molecules are also assumed to be oriented at the surface. An extremely interesting piece of evidence in support of this idea of orientation is the observation of Palmer and Constable that the activity of copper in the dehydrogenation of primary alcohols was such that the rates of reaction of five primary alcohols were all equal at a given operating temperature. This points to an adsorption with the $-CH_2OH$ group next to the catalyst and the

hydrocarbon chain away from the surface, with little or no influence on the reaction rate. The surface, moreover, is not necessarily uniform and, hence, adsorption and also catalytic action may vary in amount over given areas of surface. Scratched glass surfaces are known to be frequently very much more active than plane or fused surfaces. Catalysts generally confirm this behavior and the inhomogeneity of the surface is of great importance in the characteristics of a given surface, as emphasized by H. S. Taylor. It may result in a catalyst adsorbing a reactant and causing it to react on only a small fraction of the total surface. Such areas of activity are known as "active centers."

32. **Activated Adsorption or Chemisorption:** Adsorption which leads to chemical activity has been found to occur at characteristic velocities which involve activation energy. The activation energy required is dependent not only on the gas to be adsorbed but also on the surface which adsorbs. In some cases, as, for example, the adsorption of hydrogen on metal surfaces, the velocity of adsorption may be too rapid to be conveniently measurable. On oxide surfaces, notably those which are used for effecting catalytic hydrogenation reactions, the activation energies, save on the most active centers of the surface, are sufficiently large so that the rates of adsorption are readily measurable. As an illustration, we cite the data of Burwell and Taylor on the velocity of adsorption of hydrogen on chromic oxide gel surfaces in the temperature range, 184–218° C., the surface covered being fairly uniform and the velocity of adsorption involving an activation energy of 21.7 kcal. per mole. The amounts of gas adsorbed by a given sample at successive intervals of time are shown in Table 15.10 at the two temperatures. Tangents to the curves constructed from such data give the velocities of adsorption v for equal quantities of gas adsorbed at the two temperatures. The activation energy is then calculated from the equation

$$\log \frac{v_{T2}}{v_{T1}} = \frac{E}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right). \tag{15.82}$$

TABLE 15.10

VELOCITY OF ADSORPTION OF HYDROGEN ON CHROMIC OXIDE GEL

	Volume Adsorbed in ccs. at N.T.P. after t mins.						
Temp. ° C.	$t = 1$	2	4	8	20	40	60 mins.
184	2.25	3.15	4.65	6.95	12.05	17.8	22.05
218	4.5	6.85	10.7	16.3	27.5	38.6	44.75

The velocity of adsorption of a gas may be the slowest process in a whole sequence of reactions at a surface. This appears to be true in the industrially important synthesis of ammonia from nitrogen and hydrogen. The work of Emmett and Brunauer indicates that the slow step in the whole sequence of processes is the adsorption of the nitrogen on the active iron catalyst surface. The activated adsorption of such diatomic gases on the surface probably involves the complete rupture of the molecule and the formation of surface-atom linkages such as Me-N and Me-H. All available evidence indicates that the association of nitrogen and hydrogen atoms on the surface to yield successively NH, NH_2 and, finally, NH_3, which then evaporates, are faster processes than the transition from gaseous N_2 molecules to the surface complex. In agreement with this view, Emmett and Brunauer point out that the activation energy of nitrogen adsorption, 16 kcal., is the same as that for the total synthesis on the same catalyst. In many surface reactions, however, the velocity of adsorption is more rapid than the subsequent formation on the surface of reaction products.

33. **van der Waals Adsorption:** Gases are also adsorbed on materials with extended surfaces by forces which are akin to those operative in gases which cause the deviations from the ideal gas equation. Such attractive forces may be termed van der Waals forces and the corresponding adsorption van der Waals adsorption. These adsorptions are nonspecific in character and occur on porous surfaces which are not chemically active or on catalytic surfaces at such low temperatures that the process of activated adsorption is too slow. Charcoal and silica gel are examples of surfaces which show adsorption by van der Waals forces, though even in these cases exceptions are to be noted. At liquid air temperatures on charcoal, oxygen and hydrogen are adsorbed by van der Waals forces, and the process of adsorption is readily reversible by evacuation. At room temperatures, oxygen is adsorbed with an activation energy at measurable velocities and the association is so powerful that it cannot be reversed by evacuation. Instead, on heating the mass, the oxygen leaves the surface mainly in association with carbon atoms as carbon monoxide or carbon dioxide. A similar behavior is shown by hydrogen but at higher temperatures. Water vapor is also held by silica gel by specific forces.

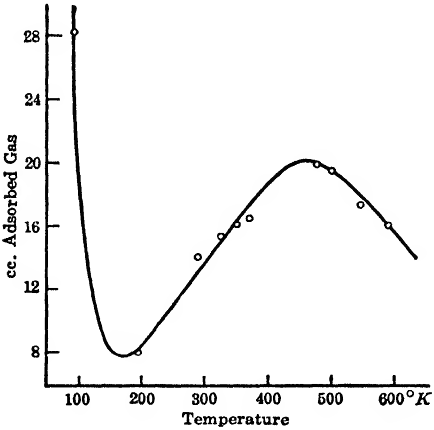

Fig. 15.12. Adsorption of Hydrogen by Zinc Chromite (12.5 g.) after 1000 min. at 1 atm. Pressure.

Adsorption by van der Waals forces is akin to liquefaction and the heats of adsorption are not markedly greater than heats of liquefaction. Activated adsorption, on the contrary, frequently involves heats of activated adsorption of the magnitude of heats of chemical reaction. The heat of adsorption of hydrogen on charcoal or on zinc oxide at liquid air temperatures is about 1000 calories and in each case is a van der Waals adsorption. On zinc oxide at higher temperatures the heat of adsorption is much higher, 11 kcal.; on nickel it amounts to 15 kcal. and on chromic oxide gel at 300° C. the heat of activated adsorption is about 28 kcal. On zinc chromite the heat of activated adsorption is 23 kcal. Fig. 15.12 shows both van der Waals adsorption at low temperatures and activated adsorption at high temperatures on zinc chromite. It is the activated adsorption, or chemisorption, not the physical or van der Waals adsorption, which is important in surface reactions.

34. **Adsorption and Pressure:** Assuming a unimolecular adsorption layer or a saturation limit to the surface, Langmuir showed that it was easy to find the relation between extent of adsorption and the gaseous pressure, p, in contact with the surface assumed to be uniform.

Let θ be the fraction of the surface occupied by adsorbed atoms, then $(1 - \theta)$ is the fraction not occupied. Let us assume a plane surface in which all atoms in the surface are capable of adsorbing the gas molecules. If the surface is not homogeneous, a definite portion only may be capable of adsorbing the gas. The case would be parallel to that we are discussing but the portion capable of adsorption would then be the 'available surface.' The rate of condensation of gas molecules will be proportional to the gas pressure p (Chap. 3, 15), and to the surface which is not covered. Hence,

$$\text{Rate of condensation} = k_1p(1 - \theta). \tag{15.83}$$

The adsorbed molecules will, from time to time, evaporate from the surface, as in the case of evaporation of liquids, and the rate of evaporation will be directly proportional to the amount of gas on the surface, that is, to the extent of surface covered,

$$\text{Rate of evaporation} = k_2\theta. \tag{15.84}$$

These two opposing processes will, in the steady state, equal one another. Hence

$$k_1p(1 - \theta) = k_2\theta, \tag{15.85}$$

from which we can solve for θ, the fraction of the surface covered,

$$\theta = \frac{k_1p}{k_2 + k_1p}. \tag{15.86}$$

This expression for the fraction of the surface covered leads to three important cases relating θ and p.

(*a*) *Surface nearly bare:* When θ is small the equation (15.85) reduces to

$$k_1 p = k_2 \theta, \tag{15.87}$$

since θ is negligible compared with 1. In such case we find that

$$\theta = k_1 p / k_2 = kp, \tag{15.88}$$

or, the fraction of the surface covered is directly proportional to the gas pressure.

(*b*) *Surface nearly covered:* Here θ is nearly unity so that the percentage variation in θ is small and the corresponding variation in $(1 - \theta)$ is very greatly magnified. Hence, we obtain the approximation

$$k_1 p(1 - \theta) = k_2 \tag{15.89}$$

or

$$1 - \theta = k_2 / k_1 p. \tag{15.90}$$

This equation means that, when adsorption is nearly complete, the extent of free surface is inversely proportional to the pressure. In this case, also, the surface covered is practically independent of the pressure.

(*c*) *Surface partially covered:* This intermediate state to the two extremes already discussed is intermediate also in the variation of θ with pressure. In case (*a*), θ varies directly as p. In case (*b*), θ is independent of the pressure, i.e., it varies as p^0. In the intermediate case (*c*) it is found that θ varies as some power of p between 0 and 1. We may express this relation by the equation

$$\theta = kp^n, \tag{15.91}$$

where n is a fraction less than unity. This is a well-known relation verified for a large number of cases of adsorption not only of gases but also of substances from solutions. Sometimes known as the Freundlich 'adsorption-isotherm' it is a valid expression for adsorptions at constant temperature over a restricted range of pressures or concentrations.

35. **The Kinetics of Heterogeneous Reactions:** These relationships between gas pressure and the concentration of adsorbed molecules govern the rate of chemical reaction in heterogeneous reactions. Such surface actions differ from homogeneous processes in that, the reaction being localized at the surface, only that portion of the gas present at the surface is potentially reactive. The reaction velocity, negligible in the gas phase, is therefore proportional to the amount of gas adsorbed. We may, therefore, examine what kinetic equations of reaction will result from the three cases of adsorption just considered. For simplicity, we shall first consider reactions involving one molecular species only.

Case a: With the surface nearly bare it was shown that the amount adsorbed varies directly as the gas pressure. Consequently, in such cases, the reaction velocity being proportional to the adsorbed gas will likewise be proportional to the pressure, and, thus, we derive

$$v = -dp/dt = k_1 p \tag{15.92}$$

where k_1 is a proportionality factor connecting rate with pressure. This equation is none other than a first order velocity equation identical with that we have already considered in homogeneous systems $dx/dt = k(a - x)$. It should show the characteristics of a first order reaction, a rate constant independent of the units in which the concentration is expressed and a half-life independent of the initial concentration.

There are many examples of such a behavior. The classical example is due to van't Hoff and Kooij who showed that the decomposition of phosphine on glass obeyed such an equation. The decomposition at glass surfaces apparently occurs with single molecules and the reaction whose rate is measured is the surface action

$$PH_3 \rightarrow P + 3H.$$

Naturally, this is followed by association of both phosphorus and hydrogen atoms to give the molecular species, P_4 and H_2.

Hinshelwood and his co-workers have supplied other good examples of this type of decomposition in the case of nitrous oxide on gold and hydrogen iodide on the surface of platinum. The latter case illustrates the change in order of reaction that may result from surface catalysis. The bimolecular homogeneous decomposition becomes a unimolecular decomposition on platinum. Formic acid decomposes unimolecularly on various surfaces as shown by Hinshelwood and Topley.

Case b: With the surface practically covered, the adsorption is practically constant and independent of the pressure. The rate of reaction should therefore also be constant and independent of the pressure. This situation is new in our study of reaction kinetics. The equation is

$$dx/dt = k. \tag{15.93}$$

The gas pressure or concentration does not enter into the equation, or, alternatively, it enters in the form $p^0(= 1)$. Such reactions are spoken of as *'zero order' reactions.* They are independent of gas concentration or pressure.

A convenient example of this is to be found also in the decomposition of hydrogen iodide, in this case in contact with a surface of gold. Evidently the hydrogen iodide, over the pressure range studied, practically covers the active portion of the gold surface, so that, as fast as decomposition occurs, the adsorbed layer of hydrogen iodide is maintained without appreciable change in extent. The same is practically true for the decomposition of ammonia on tungsten filaments.

Case c: With the surface partially covered, an adsorption equation of the form, $\theta = kp^n$, was derived. The corresponding velocity equation is

$$dx/dt = kp^n. \tag{15.94}$$

Such an expression was found by Stock and Bodenstein to fit the experimental data in the decomposition of antimony hydride, n having a value of 0.6. The reaction only occurs extremely slowly on glass but it is rapid, even at 25° C., on the antimony deposited by the reaction

$$SbH_3 \rightarrow Sb + 3H.$$

In a clean glass vessel the reaction is initially slow and accelerates as the antimony becomes deposited on the surface. Such cases are known as auto-acceleration or *auto-catalysis*, catalysis by the reactants themselves or by their products.

36. **Autoretardation and Poisoning:** In the example just considered it was pointed out that the product, antimony, accelerated the reaction. The rate of decomposition was faster on antimony than on glass. The reverse case is possible and is actually found in a number of cases. One of the products remains on the initial surface and slows down the subsequent change. A simple case of this kind is to be found in the decomposition of ammonia on platinum surfaces. Evidently, the hydrogen produced in the decomposition is strongly adsorbed by the platinum and further decomposition of the ammonia is hindered. With strong adsorption we saw that the free surface is inversely proportional to the pressure, in this case the pressure of the strongly adsorbed gas, hydrogen. The rate of reaction will be determined by the rate at which ammonia strikes such free surfaces; that is, it will be proportional to the ammonia pressure and the free surface,

$$dx/dt = k_1 \cdot p_{NH_3} \cdot (1 - \theta) \tag{15.95}$$

and, since, with hydrogen strongly adsorbed, $(1 - \theta) = k_2/p_{H_2}$ the velocity equation becomes

$$dx/dt = kp_{NH_3}/p_{H_2}, \tag{15.96}$$

which is the equation approximately found by Hinshelwood and Burk.

In industrial catalytic processes there are frequently present in technical gases small amounts of impurities which are tenaciously held by the catalyst. Such impurities are known as *poisons*. They have exactly the same effect as the hydrogen in the reaction just considered. They cover the surface and restrict the area over which reaction may occur. The velocity equation will be modified correspondingly. Thus, an equation

$$dx/dt = k[A], \tag{15.97}$$

involving a single reactant, A, will be changed to one of the form

$$dx/dt = k[A]/[\text{Poison}]. \tag{15.98}$$

Water vapor is a poison in ammonia synthesis. It acts by converting the iron catalyst surface into iron oxide, on which no ammonia synthesis occurs. With a given water vapor concentration, at a given temperature, a definite fraction of the surface is rendered inactive so long as the water concentration is maintained. Oxygen acts similarly. On removal of the poison from the incoming gas stream the oxide is reduced by the hydrogen of the gas mixture and the activity of the catalyst is restored. Such cases are known as reversible or temporary poisoning. In many cases, however, irreversible or permanent poisoning occurs. Thus, hydrogen sulfide gives, with many catalysts, metallic sulfides, inert catalytically, which are not readily reduced when gases free from sulfur content are employed. Such cases of permanent poisoning require complete regeneration of the catalyst and are serious problems in technical work.

The general investigation of poisons is of great theoretical importance. The small amounts of poison which annihilate a catalyst surface lead to the conclusion that, in many reactions, only a fraction of the total surface has catalytic activity.

37. **Heterogeneous Reactions Involving Several Gases:** The case of autoretardation just considered is paralleled by many cases of reaction between two constituents. Thus, in the combination of ethylene and hydrogen on metallic copper at 0° C., the ethylene is strongly held by the surface and hence hinders the reaction. The rate is governed mainly by the rate at which the hydrogen strikes the surface. This was established by Pease. The velocity equation for the reaction

$$C_2H_4 + H_2 = C_2H_6$$

would not, under such circumstances, have the bimolecular form, but would approximate to the expression,

$$dx/dt = k[H_2]/[C_2H_4]. \qquad (15.99)$$

At 200° C., however, the copper surface is relatively bare of both gases so that the rate of reaction will then be determined by the rate at which hydrogen and ethylene strike the surface within reaction distance of each other. This may be on adjacent spaces on the surface. With such bare surfaces, a bimolecular equation will therefore result,

$$dx/dt = k[H_2][C_2H_4], \qquad (15.100)$$

as was found by Grassi and by Pease.

In none of these cases does the reaction product, ethane, appear to influence the velocity. This is not so in the classical example of such multimolecular reactions. Bodenstein and Fink showed that, in the oxidation of sulfur dioxide at a platinum surface, the sulfur trioxide formed played a predominant part in the reaction. They showed that it was strongly adsorbed by platinum. It thus appears in the denominator of the kinetic equation, the velocity is inversely proportional to the concentration of sulfur trioxide, actually to its concentration to the power 0.5. Evidently, under the experimental conditions chosen, the surface covered by the trioxide is proportional to the square root of the trioxide pressure. Bodenstein and Fink found that, in the main, the velocity was also directly proportional to the sulfur dioxide concentration and independent of the oxygen concentration.

$$dx/dt = k[SO_2]/[SO_3]^{1/2}. \tag{15.101}$$

This points to a platinum surface covered by sulfur trioxide to an extent proportional to the square root of its pressure, oxidation of sulfur dioxide occurring when a molecule of sulfur dioxide strikes that portion of the residual platinum surface on which an oxygen atom is already present.

It was on the basis of this investigation that Bodenstein and Fink offered a general theory of heterogeneous reaction velocities which, for a long time, was generally accepted. The retarding action of the reacting constituents of a process was attributed to the formation of an adsorbed layer of the retarding agent over the surface of the catalyst, the thickness of the adsorbed layer being assumed to vary with the pressure according to some relationship suggested by the experimental result. Thus, in the case just considered, the thickness of the layer of sulfur trioxide was assumed to be proportional to the square root of the pressure. On this theory, the rate of reaction was determined by *the rate of diffusion* through such an adsorbed layer, this physical process being assumed to be slow; the chemical reaction occurring when the reactants had passed through the presumed diffusion layer was supposed to be extremely rapid compared with the diffusion process. This diffusion theory of heterogeneous gas reactions has been practically abandoned. There is no experimental evidence for thick diffusion layers in these catalyzed reactions. There is evidence that, in many cases, the surfaces are relatively bare and have very considerably less than a unimolecular layer of adsorbed gas on the surface. A further strong argument against the theory is that the influence of temperature on the process is not that characteristic of diffusion processes but that normal to chemical reactions. Some examples of this may now be considered.

38. Influence of Temperature in Heterogeneous Reactions Involving Gases: The reactions of gases at surfaces show the same exponential increase of velocity with temperature that is shown by the homogeneous reactions. For these reactions, also, the Arrhenius equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \tag{15.102}$$

may be used to represent the variation with temperature. In general, the value of E so obtained is less than the value of E for the corresponding homogeneous reaction. Thus, whereas, from thermal data, the energy of activation for the *unimolecular* decomposition of hydrogen iodide must be at least 68 kg. cals., the corresponding value for E in the heterogeneous reaction on platinum is 14 kcal. and on gold 25 kcal. This latter is probably a true energy of activation since the reaction is of zero order. In the case of platinum, however, the value is probably not the true energy of activation of the process for this latter is unimolecular and the quantity of reacting constituent on the surface varies both with temperature and pressure. In such cases the apparent heat of activation found by applying the above Arrhenius equation is related to the true heat of activation by a relation pointed out by Hinshelwood

$$E_{\text{app.}} = E_{\text{true}} + \lambda' - \lambda, \tag{15.103}$$

where λ' is the heat of desorption of one mole of the reaction product, λ is the heat required to desorb one mole of the reactant. Recent experiments on these latter quantities have shown that they may be quite large, comparable in size with the value of E_{true}. This is indicated in the decomposition of ammonia. On tungsten, the process is of zero order and unretarded, in which case λ' and λ do not enter into the value of $E_{\text{app.}}$ which therefore equals E_{true}. A value of 39 kcal. is obtained. On platinum, however, in which case the hydrogen formed acts as a retardant, a value of 140 kcal. is obtained. This can be ascribed in part to the large energy required to desorb hydrogen atoms from the platinum surface, a value for λ' as high as 50 kcal. per atom of hydrogen being found in this case.

39. **Promoters:** If the catalytic effect produced by a given substance in a reaction is materially enhanced by the addition of a small amount of substance, itself not markedly catalytic, the catalyst is said to have been promoted and the substance so employed is termed the promoter. The term is usually restricted to cases where the amount of substance so employed is small. With more or less equal amounts of two materials the product is normally called a mixed catalyst; if the non-catalytic material is in large excess, it is usually termed a catalyst support.

The phenomenon of promoter action was discovered during the technical development of catalytic processes of hydrogenation and ammonia synthesis. It was a logical consequence of a research conducted by Baxter at a very much earlier date, for a very different purpose, on the occlusive power of nickel and cobalt for hydrogen, when these metals were prepared by reduction of the oxide in hydrogen. Baxter found that cobalt of atomic weight purity occluded negligible amounts of hydrogen. When the ordinary minute quantities of impurities, e.g., silica, were present, marked amounts of gas were occluded, the metal product being less compact, sintering being prevented.

The quantitative examination of a few promoted catalysts has been made. Wyckoff and Crittenden showed by X-ray studies that iron catalysts for ammonia synthesis were of a smaller crystal unit when promoted with $K_2O - Al_2O_3$ than when pure, the promoter effect being in part at least, therefore, an extension of surface. Russell and Taylor showed, however, that, in the synthesis of methane over nickel, an extension of surface equal to 20 per cent produced a ten-fold increase in reaction velocity. This indicated a qualitative improvement of the surface rather than a quantitative extension as the principal cause of the observed effect. Almquist and Black in their poisoning studies showed that whereas in ordinary iron only about one atom in 2000 had ammonia synthetic activity, this ratio increased to one in 200 for the good promoted catalyst. It was pointed out by Taylor that the increase of crystal faces, edges and corners would increase the unsaturated catalyst atoms and that the enhanced activity of such unsaturated atoms would account in part for the quantitative data. More recent research has indicated that promoters cause the activated adsorption of reactants to occur more rapidly or at lower temperatures than is possible on unpromoted catalysts.

Promoter action will be most advantageously employed in those reactions which are most difficult to achieve, that is to say reactions which only occur on small fractions of an unpromoted catalyst surface. Such reactions are also the most sensitive to catalyst poisons. Reactions which occur readily on whole areas of surface will not normally be considerably aided by the addition of promoters.

40. Isotopic Molecules and Surface Mechanisms: The interaction of hydrogen and deuterium, $H_2 + D_2 = 2HD$ occurring on surfaces such as nickel, tungsten and chromium oxide at temperatures as low as that of liquid air indicates that activation of hydrogen is occurring even at such low temperatures. The activation of hydrogen cannot therefore be rate-determining in a number of surface reactions employing hydrogen. Similarly, the exchange reaction between ammonia and deuterium occurs on synthetic ammonia catalysts at room temperature. Hence, in ammonia synthesis, which only occurs at much higher temperatures, the rate-controlling mechanism would not appear to involve either the $N-H$ or $H-H$ bond formation or rupture. By elimination, this leaves the activation of the $N-N$ bond in nitrogen molecules as the rate-determining step in best accord with the correlation of velocity of activated adsorption of nitrogen and velocity of ammonia decomposition. On synthetic-ammonia iron catalysts the exchange reaction between $^{28}N_2$ and $^{30}N_2$ to yield two molecules of $^{29}N_2$ is even slower than ammonia synthesis and hydrogen accelerates the exchange. On osmium catalysts the exchange reaction between light and heavy nitrogen is faster than ammonia synthesis and occurs at lower temperatures; hydrogen retards the exchange presumably by preferential adsorption on the catalyst surface.

Exchange reactions occur on nickel catalysts between deuterium and both saturated and unsaturated hydrocarbons. In the latter case, this may occur by formation of intermediate half-hydrogenated states which revert to the unsaturated species; thus,

$$C_2H_4 + D \xrightarrow{Ni} C_2H_4D \xrightarrow{Ni} C_2H_3D + H.$$

With the saturated hydrocarbons, adsorption and exchange must involve breaking of C—H bonds.

$$D + CH_4 \xrightarrow{Ni} D + CH_3 + H \xrightarrow{Ni} CH_3D + H.$$

With hydrocarbons containing two or more carbon atoms two types of bond can be involved in the surface reaction, C—H bonds in an exchange reaction, C—C bonds in a hydrogenation decomposition. Thus,

$$\begin{aligned} C_2H_6 + D_2 &\xrightarrow{Ni} C_2H_5D + HD, \\ C_2H_6 + D_2 &\rightarrow 2CH_3D. \end{aligned}$$

Experiment shows that the exchange occurs the more readily; with ethane it occurs at 100–130° whereas the reaction to form methane requires temperatures from 160–300° C. The activation energy in this latter case may be 15 kcal. higher than the exchange reaction.

41. **Wall Reactions:** The importance of walls of the containing vessel in the recombination of atoms and radicals has already been discussed in treating chain reactions and in the kinetic studies of hydrogen atom recombination. In such processes the wall reaction is competitive with recombination in the gas phase and the combining species must diffuse from the interior of the gas to the wall surface. This diffusion process depends on the distance, l, to be traversed and the mean free path of the particle, λ, according to a formula developed by Smoluchowski for the number of collisions, n, suffered in traversing the distance,

$$n = 3\pi l^2/4\lambda^2. \tag{15.104}$$

In any reaction system the atoms or radicals may be generated uniformly over the whole volume. If, for simplicity, we consider the containing vessel as having parallel faces a distance, d, apart then the average number of collisions suffered by a particle in reaching the wall is

$$\bar{n} = \pi d^2/16\lambda^2. \tag{15.105}$$

The wall effect therefore decreases in importance as the square of the distance between walls. It increases in importance the lower the pressure because of the increase in mean free path, λ. If, as in the hydrogen-chlorine reaction, each stage in the process generates a new chain carrier,

$$\mathrm{Cl} + \mathrm{H_2} = \mathrm{HCl} + \mathrm{H},$$
$$\mathrm{H} + \mathrm{Cl_2} = \mathrm{HCl} + \mathrm{Cl},$$

and if, on the average, g collisions are necessary for the atom to react, the chain length is

$$\nu = \pi d^2/16g\lambda^2. \tag{15.106}$$

For this reason, we expect, and it is actually found, that long chains are absent when the hydrogen-chlorine reaction is studied either in narrow capillary tubes or at very low pressures. The packing of spaces in which explosions may occur to prevent explosions is to be ascribed to the operation of the same factors. Semenoff showed, also, that the chain oxidation of phosphorus was dependent on the square of the diameter of the reaction vessel, on the square of the mean free path and also on the pressure of inert gas p_I present, his expression, for a cylindrical vessel, being

$$\nu = \frac{6\pi d^2}{4\lambda^2}\, p_{\mathrm{P_4}} p_{\mathrm{O_2}} \left(1 + \frac{p_\mathrm{I}}{p_{\mathrm{P_4}} + p_{\mathrm{O_2}}}\right). \tag{15.107}$$

When the chains terminate in the gas phase as well as on the walls the problem is more complex. Qualitatively it can be seen that the amount of wall reaction depends on the nature of the homogeneous chain breaking process and on the concentration of the atoms or radical chain carriers. We can illustrate the general principle by reference to a specific example of the recombination of atomic hydrogen, in presence of a third body, M, or at the wall. Since the velocity of homogeneous recombination is proportional to $[\mathrm{H}]^2$, the homogeneous reaction decreases in importance relative to the wall reaction with the square of the atom concentration. Hence, in a system where the original recombination of atomic hydrogen is predominantly homogeneous, the disappearance of the atoms finally produces such a low concentration that the probability of gas phase reaction is negligible and only wall reaction is important.

THE STATISTICAL TREATMENT OF REACTION RATES

It has been shown in Sections 10 to 12 that the activation energy of a reaction can be interpreted in terms of the passage of the system over a potential energy barrier separating the initial and final states of the reaction. At the top of the energy barrier the system may be regarded as the activated complex. Consideration will show that such a complex is to be regarded as an ordinary molecule, with all the usual thermodynamic properties, save in one respect. In the complex, one degree of freedom which in a normal molecule would be a vibrational degree of freedom consists, in this case, of a motion in the direction of the reaction co-ordinate and leads to a decomposition of the complex at a definite rate to yield the products. This point of view has already been touched upon briefly in Section 12 for the case of three hydrogen atoms.

42. **The Statistical Theory of Reaction Rates:** Consider the generalized reaction between two reactants, A and B, which proceed through an activated complex $M^{\ddagger}$ to form the reaction products

$$A + B \rightarrow M^{\ddagger} \rightarrow \text{products.}$$

The rate of reaction must obviously be given by the concentration of activated complexes at the top of the potential barrier multiplied by the frequency of crossing the barrier.

$$\text{Rate of reaction} = \bar{c}^{\ddagger}\bar{u}/\delta, \tag{15.108}$$

where $\bar{c}^{\ddagger}$ is the number of complexes per unit volume in a length δ representing the activated state at the top of the barrier and $\bar{u}$ is the mean velocity of crossing. Remembering that activated complexes differ from normal molecules in the manner already indicated, we can treat them statistically (Chapter 8, Sect. 28–33) as normal molecules replacing however one degree of freedom of vibration by translational motion along the reaction co-ordinate. Thus,

$$\bar{c}^{\ddagger} = c^{\ddagger}\frac{(2\pi m'kT)^{1/2}\delta}{h}. \tag{15.109}$$

We recognize the expression $(2\pi m'kT)^{1/2}\delta/h$ as the partition function for one degree of freedom of translation, m' being the mass of the activated complex. Eyring has shown that the mean velocity $\bar{u}$ is given by the expression

$$\bar{u} = \frac{\displaystyle\int_0^{\infty} ue^{-mu^2/2kT}du}{\displaystyle\int_{-\infty}^{\infty} e^{-mu^2/2kT}du} = \left(\frac{kT}{2\pi m}\right)^{1/2}. \tag{15.110}$$

Equation (15.108) then becomes

$$\begin{aligned}\text{Rate of reaction} &= c^{\ddagger}\frac{(2\pi m'kT)^{1/2}\delta}{h}\cdot\left(\frac{kT}{2\pi m'}\right)^{1/2}\cdot\frac{1}{\delta}\\ &= c^{\ddagger}\frac{kT}{h}.\end{aligned} \tag{15.111}$$

This equation indicates that the effective velocity of crossing the energy barrier is the universal frequency, kT/h, dependent on temperature and independent of the nature of the reactants and the type of reaction.

If the specific reaction rate is k', and the velocity of reaction is given by the usual expression,

$$\text{Rate of reaction} = k'c_Ac_B,$$

it follows that

$$k' = \frac{kT}{h}\frac{c^{\ddagger}}{c_Ac_B} = \frac{kT}{h}K^{\ddagger}, \tag{15.112}$$

where $K^{\ddagger}$ is the equilibrium constant in the process

$$A + B \rightleftharpoons M.$$

The assumption is here made that equilibrium exists between reactants and activated complex. The Brönsted theory (Section 30) involves the same assumption. Such an equilibrium can be treated thermodynamically and statistically as in the case of normal equilibria. Hence we may write

$$k' = (kT/h)e^{-\Delta F/RT}, \tag{15.113}$$

$$k' = (kT/h)e^{-\Delta H/RT}e^{\Delta S/R}, \tag{15.114}$$

where ΔF, ΔH and ΔS are the free energy, heat content and entropy of activation with reactants and activated complex in their standard states and the thermodynamic relations $\Delta F^o = -RT\ln K$ and $\Delta F = \Delta H - T\Delta S$ are applied, the conventional zero superscript indicating the standard states having been omitted.

The equilibrium constant $K^{\ddagger}$ can be treated statistically making use of appropriate partition functions for the respective species. Thus,

$$k' = \frac{kT}{h}K^{\ddagger} = \frac{kT}{h}\cdot\frac{F^{\ddagger}}{F_AF_B}e^{-E_0/RT}, \tag{15.115}$$

where F_A, F_B and $F^{\ddagger}$ are the respective partition functions per unit volume and E_0 is the difference between the zero-point energy of the complex and that of the sum of the reactants.

43. Comparison of Collision and Statistical Theories: A comparison of the two methods of approach to reaction rate theory which, at the same time, yields a definition of the limitations under which the collision theory operates, can be made by considering a reaction between two *atoms*, A and B, of masses m_A and m_B and collision diameters σ_A and σ_B. The activated complex AB will resemble a diatomic molecule AB, will have its three normal degrees of freedom of translation and two of rotation, its normal vibrational degree of freedom being replaced by translation in the co-ordinate of decomposition. The partition function F will therefore be

$$F^{\ddagger} = \frac{[2\pi(m_A + m_B)kT]^{3/2}}{h^3}\cdot\frac{8\pi^2IkT}{h^2}. \tag{15.116}$$

The moment of inertia I of the complex is given by definition (Chapter 4, Section 11) as

$$I = \sigma_{AB}^2 m_A m_B/(m_A + m_B). \tag{15.117}$$

The atoms A and B have each only translational degrees of freedom of the form $F_A = (2\pi m_A kT)^{3/2}/h^3$ and $F_B = (2\pi m_B kT)^{3/2}/h^3$. Hence, the rate of reaction is given by substitution of these three expressions for $F^{\ddagger}$, F_A and F_B in Equation (15.115), yielding

$$k' = \sigma_{AB}^2 \left[8\pi kT \left(\frac{m_A + m_B}{m_A m_B} \right) \right]^{1/2} e^{-E_0/RT}, \tag{15.118}$$

which is at once recognizable as $Z_{AB}e^{-E_0/RT}$ (compare Section 2). The statistical approach yields therefore the collision number Z_{AB} with, at the same time, a much clearer definition of the quantity σ_{AB}, i.e., the atom-atom distance at the top of the potential barrier, rather than the kinetic theory diameter originally employed. The possible variations in these distances have already been indicated in Section 11 dealing with three hydrogen atoms.

When the statistical method is applied to molecules rather than atoms the expression $F^{\ddagger}/F_A F_B$ becomes correspondingly more complicated and the collision number Z_{AB} no longer emerges. This is equivalent to saying that the unmodified collision theory is actually only applicable to hard spherical atoms with only translational degrees of freedom and can never be more than the grossest approximation when complex molecules, with degrees of freedom of rotation and of vibration in addition to those of translation, are the colliding species. It is this grossness of approximation that emerges in reactions between complex molecules in both gaseous and liquid systems. It is to be concluded that the modification of the collision equation by substitution of $PZe^{-E/RT}$ in place of $Ze^{-E/RT}$ is an attempt empirically to correct for the implicit approximation in the calculation of Z.

The problem may be approached also from the standpoint of equation (15.114) in which the entropy of activation enters into the rate expression. A negative value of $\Delta S^{\ddagger}$ implies a small probability of formation of the activated complex. This implies alternatively that not every collision with the necessary energy leads to complex formation, and the probability of this formation is an essential element in the determination of rate. There should therefore be a parallelism between the 'steric' factor P and the entropy of activation $\Delta S^{\ddagger}$. When this latter is not greatly different from the total entropy change ΔS for the reaction, which means that the activated state closely resembles the final state, there should be a parallelism between the over-all entropy change and the probability or steric factor P. It is this parallelism that Soper detected between the P factor and the over-all entropy change in several reactions. For the reaction of dimethyl aniline and methyl iodide $P = 0.5 \times 10^{-7}$ while $e^{\Delta S/R} = 0.9 \times 10^{-8}$, whereas in the isomerization of ammonium cyanate in solution $P = 1$ and $e^{\Delta S/R} = 0.1$ (See Section 29). In gas reactions the same principles hold. Thus, in the dimerization of ethylene to form butylene there is an entropy decrease of -30.1 cal./degree. Since the activated complex should be very similar to the butylene molecule we might expect, as Pease found, that the bimolecular association was 2000 times slower than the value found from the simple collision theory. The reaction is slow in spite of the fact that Pease and Burnham found it to be inhibited by nitric oxide, the process involving therefore, at least in part, a chain mechanism, which would increase the observed reaction rate. Qualitatively also, one can predict that the formation of cyclohexane from the hexamethylene diradical, $-(CH_2)_6^-$, will be a slow process since it involves an entropy decrease, and alternatively reactions breaking a ring, accompanied by large increases in entropy, will probably be correspondingly fast.

The statistical treatment of reaction rates opens up, therefore, new avenues of approach to a more intimate understanding of the problems of reaction kinetics. The treatment of more complex systems by statistical methods is beyond the scope of this text but attention may be directed to a detailed presentation of the whole subject by Glasstone, Laidler and Eyring.[1] At the present level of presentation, however, it is possible to show how this statistical treatment permits an analysis of physical processes such as viscosity and diffusion which previously were not within the scope of reaction rate theories.

RATE THEORY FOR PHYSICAL PROCESSES[2]

44. **Viscosity:** The viscous flow of a liquid is representable by Fig. 15.13. Under the influence of a shearing force, f, applied across two layers of molecules, flow occurs when one molecule passes by one of its neighbors and drops into a vacant equilibrium position (a hole) at a distance, λ, from its original position. Fluidity, ϕ, the reciprocal of the viscosity, η, is defined as the difference in velocity per unit shear

$$\phi = \frac{1}{\eta} = \frac{\Delta u}{\lambda_1 f}\cdot \qquad (15.119)$$

The difference in velocity is given by the distance a molecule moves in one jump multiplied by the net rate of jumping, or

$$\Delta u = \lambda(k'_f - k'_b), \qquad (15.120)$$

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[1] *The Theory of Rate Processes,* McGraw Hill Book Co., New York, 1941.

[2] This section is based on Powell, Roseveare and Eyring, *Ind. Eng. Chem.,* **33,** 430 (1941).

where k'_f and k'_b are the rates of forward and backward motion. If the free energy of activation for a molecule jumping under no external force is $\Delta F^{\ddagger}$, the forward process is helped due to the force f acting on an area $\lambda_2\lambda_3$ through a distance $\lambda/2$, and the reverse process is hindered by the same amount. Hence, using Equation (15.113)

$$k'_f = \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT} e^{+f\lambda\lambda_2\lambda_3/2kT} \tag{15.121}$$

and

$$k'_b = \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT} e^{-f\lambda\lambda_2\lambda_3/2kT}. \tag{15.122}$$

Combining Equations (15.119), (15.121) and (15.122) and expanding the two exponentials * involving $f\lambda\lambda_2\lambda_3/2kT$ and omitting higher terms, the viscosity equation becomes:

$$\phi = \frac{1}{\eta} = \frac{\lambda^2\lambda_2\lambda_3}{\lambda_1 h} \times e^{-\Delta F^{\ddagger}/RT}. \tag{15.123}$$

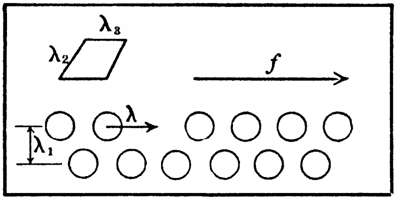

FIG. 15.13. Model Illustrating Fluid Flow

To a close approximation the factor $\lambda^2\lambda_2\lambda_3/\lambda_1$ is equal to the volume of the molecule and so the expression may be transformed, using the molecular volume V and the Avogadro number N, to

$$\phi = \frac{V}{Nh} e^{-\Delta F^{\ddagger}/RT} \tag{15.124}$$

or to its alternative form,

$$\phi = \frac{V}{Nh} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}. \tag{15.125}$$

This last equation shows that the viscosity should vary exponentially with the reciprocal of the temperature and this is in excellent agreement with experimental result. The heat of activation $\Delta H^{\ddagger}$ is from one-fourth to one-third the heat of vaporization for typical organic liquids but is more for associated liquids which in general require the breaking of hydrogen bonds. Fig. 15.14 shows the relation between $\Delta H^{\ddagger}$ for viscosity and ΔE for vaporization for most of the now available data.

In the flow process, bonds are broken as in vaporization, but the flowing molecule does not gain the entropy of expansion into the vapor

* $e^x = 1 + x + \frac{1}{2}x^2 + \cdots; e^{-x} = 1 - x + \frac{1}{2}x^2 - \cdots.$

nor does it perform the external work RT per mole of expansion against the atmosphere. Hence

$$\Delta F_{\text{vap}} + T\Delta S_{\text{vap}} - RT = \Delta E_{\text{vap}}. \qquad (15.126)$$

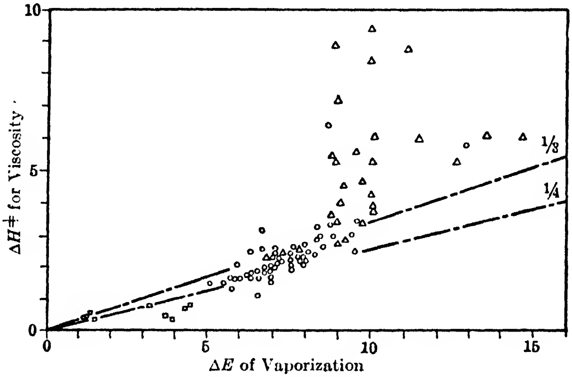

FIG. 15.14. Relation between $\Delta H^{\ddagger}$ and ΔE_{vap}.

In Fig. 15.15 are shown the values of $\Delta F^{\ddagger}$ for viscosity plotted against ΔE_{vap} for liquefied gases such as nitrogen, oxygen and argon at the lower left, through typical organic liquids in the central portion to the triangles for water and the alcohols with a viscous material such as glycerine at the top right. From the slope of the median line we may rewrite equation (15.124) in the form of an approximate empirical equation for viscosity

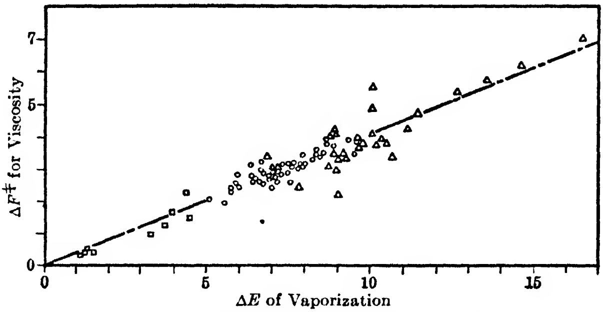

FIG. 15.15. Relation between $\Delta F^{\ddagger}$ and ΔE_{vap}.

$$\eta = \frac{Nh}{V} e^{\Delta E_{\text{vap}}/2.45RT}. \qquad (15.127)$$

From a study of the heat of activation $\Delta H^{\ddagger}$ at constant volume, i.e., no change in the volume of holes, the importance of this factor can be studied. It is found that for typical organic liquids the heat of activation at constant volume is small so that holes control the flow in these liquids. For associated liquids the heat of activation at constant volume is almost all the total heat of activation so that in such cases the breaking of hydrogen bonds is the important factor. In acetone and water the heat of activation at constant volume is negative and this is to be interpreted as due to a change in liquid structure with increase of pressure. At high pressures, using the thermodynamic relation that $(\partial \Delta F^{\ddagger}/\partial p)_T = \Delta V^{\ddagger}$, the activation volume, and writing the viscosity expression in the form,

$$\ln \frac{1}{\phi} = \ln \eta = \ln \frac{Nh}{V} \cdot \frac{\Delta F^{\ddagger}}{RT} \tag{15.128}$$

it follows that a plot of $RT \ln \eta V/Nh$ against the pressure p should give the activation volume $\Delta V^{\ddagger}$. This is found to be about one-sixth of the molecular volume in ordinary liquids and one-twentieth of the molecular volume for liquid metals. This latter result indicates that it is the smaller metal ion which flows in this case, not the metallic atom.

In mixtures of normal liquids, involving hole-formation, the ability of a particular molecule to flow is determined not so much by its own properties as by the readiness of the solvent to contribute holes in which it can flow. The explicit expression is

$$\eta = \frac{Nh}{V} e^{(N_1 \Delta F_1{}^{\ddagger} + N_2 \Delta F_2{}^{\ddagger} - \Delta F_{ex}{}^{\ddagger}/2.5)/RT}, \tag{15.129}$$

where $\Delta F_{ex}{}^{\ddagger}$ is inserted to take account of the imperfect nature of the solution, if any. This reduces, for solutions which are not too imperfect, to

$$\log \eta = N_1 \log \eta_1 + N_2 \log \eta_2, \tag{15.130}$$

an equation discovered by J. Kendall as the best empirical expression for the viscosity of mixtures.

Long molecules probably flow in segments rather than as a whole. This is definitely indicated by the fact that observed heats of activation are only about 10 kcal. even for large nonvolatile molecules, and also by the observation of Flory that the heats of activation are independent of chain length for homologous polymers.

45. **Diffusion:** Diffusion is analogus to viscous flow. A molecule moves from one site to the next through the liquid. The diffusion coefficient D for unit cross section is defined by the relation

$$\text{rate of diffusion} = D \frac{dn_1}{dx}, \tag{15.131}$$

where dn_1/dx is the gradient of concentration. The gradient assists the forward diffusion and hinders the backward diffusion. Over a distance

λ from one site to the next the concentration changes by $\lambda(dn_1/dx)$; hence, on the statistical theory,

$$k'_f = \left(n_1 + \lambda \frac{dn_1}{dx}\right)\lambda \cdot \frac{kT}{h} \cdot e^{-\Delta F^{\ddagger}/RT}, \tag{15.132}$$

$$k'_b = n_1\lambda \cdot \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT}, \tag{15.133}$$

in which equations n_1 is the concentration per cc. of the diffusing molecule. The net rate $k'_f - k'_b$ is therefore

$$\lambda^2 \frac{dn_1}{dx} \cdot \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT}. \tag{15.134}$$

The diffusion coefficient thus becomes

$$D = \lambda^2 \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT}. \tag{15.135}$$

The relation with viscosity is seen by combining this expression with equation (15.123) yielding

$$D = \frac{\lambda_1 kT}{\lambda_2\lambda_3\eta} \tag{15.136}$$

or

$$D\eta = \text{const. } kT, \tag{15.137}$$

which is a well-known relation connecting diffusion and viscosity. It is obvious also that there must be a close correspondence between the influence of temperature on the diffusion and viscosity processes which is confirmed by experimental data.

Across a boundary separating two immiscible solvents a dissolved solute in equilibrium shows no net diffusion although there may be a large concentration difference. This indicates quite definitely that concentration is not the real driving force but rather it is the activity of the solute which should be considered. The correction introduced into equation (15.136) to take account of this yields the expression

$$D = \frac{\lambda_1 kT}{\lambda_2\lambda_3\eta}\left[\frac{d\log a_1}{d\log N_1}\right], \tag{15.138}$$

where a_1 is the activity of species 1 in molar concentration N_1. The activity can be computed when the vapor pressure data are known. Fig. 15.16 shows the experimentally observed values for $D\eta$ in the case of two mixtures, chloroform and ether, and chloroform and acetone and the linear relation with composition that results from computation when the activity correction is applied. Water and n-propyl alcohol do not show a linear variation but the calculated curve agrees well with the experimental values.

With large molecules diffusing through a liquid composed of small molecules the rate-determining mechanism is the passage of the small molecules around the oncoming large molecules by the same mechanism that these small molecules employ in passing other small molecules.

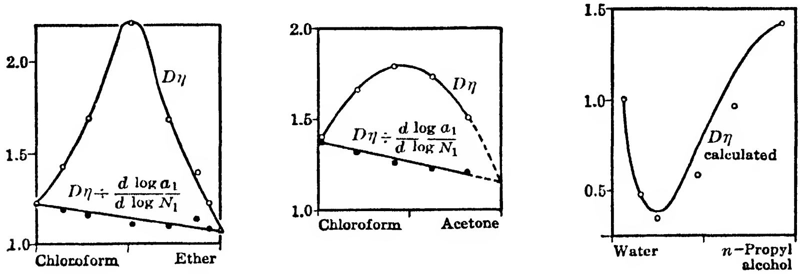

FIG. 15.16. Activity Effects in Diffusion

Because of the larger distance that the small molecules have to travel to get around the larger molecule we may expect the diffusion of the latter to be slower. If we assume that $\lambda_1 = \lambda_2 = \lambda_3 = d$, the diameter of the small molecule, the diffusion expression (15.136) for small molecules becomes $D = kT/d\eta$. For large spherical molecules such as gold sols the Stokes-Einstein diffusion equation (see Chapter 17) gives the slower rate $D = kT/3\pi d\eta$.

EXERCISES (15)

1. Calculate the number of collisions occurring per cubic centimeter per second (*a*) between two molecules of H_2, (*b*) between two molecules of I_2, and (*c*) between a molecule of H_2 and one of I_2 in a 50 per cent mixture of H_2 and I_2 at a total pressure of 1 atmosphere and at 700° K. The diameters of H_2 and I_2 may be taken as 2×10^{-8} and 3×10^{-8} cm. respectively.

2. If the collision efficiency in the reaction between sodium atoms and methyl fluoride is less than 1 in 10^6 at 500° C., calculate the minimum energy of activation.

3 The velocity constant of the reaction Na + HCl is 2.5×10^{12} cc. per mole per sec. at 600° K. If the energy of activation is 6250 cal. calculate the effective cross-sectional area of the collisions.

4. In the homogeneous para- to ortho-hydrogen conversion at 923° K. the following half lives, τ, were obtained for the initial pressures, p, indicated:

p mm.	50	100	200	400
τ sec.	648	450	318	222

Determine the order of the reaction.

5. With an initial pressure of 42.2 mm. of n-propyl iodide and 172.6 mm. of hydrogen iodide at 290° C. the following values for the pressure of iodine de-

veloped were obtained at the times indicated:

t secs.	420	600	840	1200	1680
p_{I_2} mm.	11.4	16.7	21.2	28.0	32.6

Assuming the reaction to be bimolecular calculate the velocity constant in cc. mole^{-1} sec.$^{-1}$.

6. The ratio of the velocity constants in the hydrogen-chlorine combination at 35° and 25° C. is 1.37. Calculate the energy of activation.

7. The formation of nitrosyl chloride from nitric oxide and chlorine is catalyzed by bromine by the formation of an intermediate NOBr which subsequently reacts with chlorine. Derive an expression for the total rate of reaction of the catalyzed and uncatalyzed reactions.

8. What difference in the zero point energy between an N—H and an N—D bond would be necessary to account for a decomposition ratio of 5 : 1 for NH_3 as compared with ND_3 at 25° C.

9. During the decomposition of azomethane the following pressures of azomethane were determined at the times indicated:

t min.	0	10	20	33	46	65
p mm.	430.8	371.8	313.6	251.9	205.2	155.1

Calculate the velocity constant in secs.$^{-1}$.

10. Assuming a uniform activation energy of adsorption of 6000 cals. for 10 ccs. of a gas on a particular surface, calculate the relative velocities of adsorption of this amount of gas at 127° C., 27° C. and − 73° C.

11. At − 78° C., 7 cc. of hydrogen were adsorbed by a manganese oxide catalyst at a pressure of 40 mm. At 0° C. the same volume was adsorbed at 165 mm. Calculate the heat of adsorption. Compare this with the heat of adsorption calculated at 305° and 444° C. where the pressures for comparable volumes adsorbed are 5 mm. and 140 mm. respectively.

12. In the decomposition of nitrous oxide on gold the half-life was found to be independent of the initial pressure. Show that the following data are consistent with this observation:

Time mins.	15	30	53	65	80	100	120
Per cent decomposed	16.5	32	50	57	65	73	78

13. Following the Langmuir method, derive an expression for the fraction of a catalyst surface covered by each of two gases which may be simultaneously adsorbed.

14. The rate of decomposition of ammonia on platinum under certain conditions may be expressed by the equation $dx/dt = k(a - x)/x$ where a is the initial concentration of ammonia and x is the amount decomposed in time t. Deduce a relation between the half-life and initial concentration. To what order of reaction does this relation correspond?

15. The apparent activation energy of the low temperature reaction between hydrogen and ethylene on copper (see section 30) is 10 kcal. The heats of adsorption of hydrogen and ethylene are respectively 11 and 16 kcal. Calculate the true energy of activation.

CHAPTER 16

PHOTOCHEMISTRY

Photochemical reactions are reactions which occur when a system is "illuminated," that is to say when the system receives, from an external source, radiation of a frequency which is practically non-existent in the radiation of the system itself. The science of photochemistry hitherto has been concerned more especially with the reactions caused by the light of the visible and ultraviolet spectrum. This represents but a small fraction of the electromagnetic waves now known to be emitted by vibrating particles. There has recently developed a tendency to widen the scope of the study of reactions brought about by radiations from without the reaction system to include all varieties of wave motions. Eventually, it is to be hoped, a general treatment for all such reactions will be available.

When light falls on any body the incident energy may suffer various changes. A portion is generally reflected, a further portion absorbed and the residue transmitted. The amounts of the incident light which take part in these several processes vary relatively to one another, depending on the wave length of the light and on the nature of the body upon which the light impinges. The total incident light energy must, however, by the law of conservation of energy, be equal to the sum of the energies of the light reflected, absorbed and transmitted. It is with the light which is absorbed from the incident radiation that the science of photochemistry is concerned. This fact is embodied in the first law of photochemistry.

1. **The Grotthuss-Draper Photochemical Absorption Law:** Grotthuss, in 1818, enunciated the fundamental principle underlying all process of photochemical change in the statement that: *Only the rays that are absorbed are effective in producing chemical change.* Grotthuss's statement was based upon theoretical considerations alone. Its importance became recognized when stated anew by J. W. Draper as a deduction from investigations of the photochemical reaction between hydrogen and chlorine. "This quality gained by chlorine arises from its having absorbed tithonic rays, corresponding in refrangibility to the indigo."

Not all absorbed radiation results in chemical change. The numerous investigations of spectroscopy demonstrate the occurrence of absorption of light in many cases entirely unassociated with chemical change. In such case, the light suffers a transformation into one or other forms of radiant energy or into change in the energy content of the molecules, which change, however, need not result in chemical reaction. Photochemical change is, therefore, one possible resultant of the absorption of radiation. Furthermore, as will be more fully discussed in the sections dealing with photosensitization, it is not necessary that the reacting species absorb the radiation. Photo-reactions may result from the absorption of light by one of the non-reactive constituents of the system.

The quantitative formulation of the Grotthuss-Draper principle may be derived from the quantitative laws of absorption.

2. **Fresnel's Law of Reflection:** The proportion of incident monochromatic light reflected by a surface perpendicular to the incident beam is given by the expression

$$I_r = \left(\frac{n-1}{n+1}\right)^2 I_0, \tag{16.1}$$

where I_0 is the incident light, I_r the reflected light, n the refractive index of the reflecting medium for light of the wave length employed. Since n is a constant for a given medium and given wave length, it follows that

$$I_r = RI_0, \tag{16.2}$$

where R is a proportionality factor connecting the two magnitudes. From this equation is follows that the light penetrating the medium under the above circumstances is given by the expression

$$I_0 - I_r = I = I_0(1 - R). \tag{16.3}$$

The quantity of this light, I, which is absorbed by the medium, is given by two laws of absorption, one for pure substances, one for solutions.

3. **Lambert's Absorption Law:** Equal proportions of the penetrating radiation are absorbed by layers of equal thicknesses of a homogeneous absorbing medium. In other words, if I is the penetrating radiation, and I_d the radiation transmitted by a layer of depth d, the relationship between these two magnitudes is given by the expression,

$$I_d = Ie^{-kd}. \tag{16.4}$$

The constant, k, is the absorption coefficient of the substance for the light employed and is dependent, not only on the nature of the medium, but also on the wave length of the light employed. The law obviously associates the absorptive power with the number of molecules present. In equal layers, equal numbers of molecules absorb equal fractions of the penetrating radiation. When applied to solutions of an absorbing body in a non-absorbing or diactinic solvent, it is evident that the expression must be modified to indicate the molecular concentration.

4. **Beer's Law:** The absorption of light by solutions depends upon the thickness, d, of the layer traversed and on the molecular concentration, c, in that layer,

$$I_d = I \cdot e^{-k'cd}. \tag{16.5}$$

The constant, k', is, in this case, the molecular absorption coefficient.[1] Beer's law has been tested and found to be valid in many cases. Exceptions are, however, known. It is obvious that in many solutions difficulty will arise in expressing the magnitude of the concentration of the absorbing species.

For media obeying Beer's law, it is evident that the absorbed light is given by the expression

$$I - I_d = I(1 - c^{-k'cd}). \tag{16.6}$$

The principle embodied in the Grotthuss-Draper absorption law would therefore be expressed mathematically by the equation

$$\frac{dc}{dt} = kI(1 - e^{-k'cd}), \tag{16.7}$$

where k is a proportionality factor connecting the rate of change, dc/dt, with the energy absorbed by a layer of thickness d. It must be emphasized anew that all these laws of absorption apply only to monochromatic radiation. The equation given represents the simplest possible relationship between absorbed light and photochemical reactions; it was found to be approximately obeyed by Wittwer in his researches on the photochemical interaction of dissolved chlorine with water. It will be shown that many factors may operate to produce deviations from this simple law connecting absorption and extent of reaction.

5. **Actinometry:** It is upon an assumption of such a proportionality between chemical reaction and intensity of absorbed light that all actinometers are based. The light is measured by measurement of the chemical reaction produced. Draper used the rate of hydrogen and chlorine combination as an actinometer. Bunsen and Roscoe in their classical researches on the same reaction considerably improved the technique of the measurement. They concluded that the ordinary laws of optics were obeyed, in that they found (1) that the reaction occurring was inversely proportional to the square of the distance from the source of illumination, (2) that the laws of reflection and absorption were likewise applicable. The actinometer is capricious because the reaction is a chain reaction but is, for this reason, sensitive to low light intensities. The photolysis of uranyl oxalate solutions has proved the most reliable of chemical actinometers. The reaction is

$$H_2C_2O_4 = H_2O + CO + CO_2.$$

The decomposition is measured by permanganate titration and the yield has been carefully measured at various wave lengths.

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[1] When Beer's law is expressed in the form $I_d = I \cdot 10^{-\epsilon cd}$, ϵ is frequently called the molecular extinction coefficient.

The technique of all modern photochemical investigation, correlating light energy with chemical energy produced, involves actual physical measurement of the energy of the incident radiation, of the fractions reflected and absorbed. Thermocouple-galvanometer systems are employed, calibrated against standard candle-power sources. Monochromatic radiation is employed as far as practicable, this being attained by the use of suitable light filters with arc, filament or mercury-vapor lamp sources, or by use of a monochromator which is a spectrograph modified to produce a single line or band of a given spectrum.

THE ENERGETICS OF PHOTOCHEMICAL PROCESSES

The reactions produced by the agency of light include both reactions occurring with a free energy decrease and those in which the direction of change is opposed to the normal operation of the chemical forces of the system, in which, therefore, a free energy increase occurs. In the former, the normal, "dark," or purely thermal reaction is promoted by the agency of the light, which therefore acts somewhat as does a catalyst. The hydrogen-chlorine reaction is the best known example of such a process.

Of photo-reactions in opposition to the normal chemical forces, accompanied, therefore, by a free energy increase, the most important reaction is that occurring in the plant kingdom, where carbon dioxide and water are converted, in sunlight, into complex organic molecules. In such photo-synthesis, free energy is accumulated. It is evident that, since the law of conservation of energy must be fulfilled, comparatively large amounts of light energy must be consumed in such processes. It appears that the efficiency of utilization of light energy by green leaves to produce chemical energy is high but not ideal. The ozonization of oxygen, the decomposition of ammonia and of hydrogen chloride, the polymerization of anthracene to dianthracene are also photo-reactions opposed to the normal free-energy factors of the reaction system.

The relationships existing between light energy consumption and chemical energy produced were investigated in the era of photochemistry prior to the establishment of the quantum theory by determining the number of calories absorbed by the reacting system and comparing this with the energy change accompanying the chemical process as determined from ordinary calorimetric data. With the application of quantum concepts to molecular processes a new method of approach was possible, as was indicated by Einstein in 1905, and developed by him more particularly in 1912 and 1916.

6. Einstein's Concept of Quantum Absorption: Einstein assumes that the occurrence of a photochemical reaction is to be ascribed to the absorption of quanta of radiation, each single molecule requiring one quantum, $h\nu$, of a frequency, ν, characteristic of the absorbing molecule.

The absorption of a quantum of radiation becomes, on such assumptions, the primary stage in a photochemical reaction. It is evident that this concept brings about a parallelism between the reactions of photochemistry and the phenomena of the photoelectric effect and the existence of the stationary states of the atom as involved in the Bohr theory of the atom and of spectral series. It will be realized, however, that the application of quantum concepts in the two latter phenomena will, in general, be simpler than in the case of photochemical reaction; for, with photochemical processes, it is only the primary process which will involve the simple quantum relationship. This primary process may be succeeded by further processes, initiated by the quantum process, to yield the net observed photo-reaction. The secondary processes will, in general, be entirely independent of the light action. They may be so considerable as to mask almost completely the energy change inherent in the primary quantum absorption, which alone will be governed by the nature and intensity factors of the light absorbed.

We may examine the energy, E, obtained in the absorption by a gram molecule of an absorbing reactant, when each molecule receives a quantum, $h\nu$, of frequency ν. The relationship existing is

$$E = Nh\nu, \tag{16.8}$$

where N is the Avogadro constant. The following table gives the magnitude of $h\nu$ in ergs and of E in calories for several typical wave lengths in the visible and ultraviolet spectrum.

TABLE 16.1

ENERGY CORRESPONDING TO VARIOUS WAVE LENGTHS OF LIGHT

Color of Light	Wave length in Ångströms	$h\nu$ ergs	$E = Nh\nu$ calories
Red	7500–6500	$2.62–3.02 \times 10^{-12}$	37,800–43,630
Orange	6500–5900	$3.02–3.33 \times 10^{-12}$	43,630–48,060
Yellow	5900–5750	$3.33–3.42 \times 10^{-12}$	48,060–49,320
Green	5750–4900	$3.42–4.01 \times 10^{-12}$	49,320–57,880
Blue	4900–4550	$4.01–4.32 \times 10^{-12}$	57,880–62,330
Violet	4550–3950	$4.32–4.97 \times 10^{-12}$	62,330–71,800
Ultraviolet	2000	9.9×10^{-12}	142,000

It is at once evident that the absorption of light brings to a reaction system considerable energy quantities, whereby secondary processes of change may be secured. The table shows, qualitatively at least, why, in general, photo-reactions are more frequently initiated by ultraviolet light than by visible light. Energy is accumulated in larger units with the shorter wave lengths of light. Following Bodenstein and Wagner, we may call the energy quantity, E, the energy of 6.0×10^{23} quanta, or the energy absorbed by one mole, one *Einstein*, analogous to the faraday in electrochemistry.

THE PRIMARY ABSORPTION PROCESS

Our knowledge of the primary processes of light absorption in photochemical systems is due, in large measure, to the investigations of the spectroscopist in atomic and molecular systems. From such studies, we learn what are the primary products of the absorption process. The succeeding secondary processes are determined by the chemical kinetics of the system produced in the primary process, which systems will be found often to contain free radicals and atoms. For this reason, the study of photo-processes, in the two separate stages, constitutes an important auxiliary to the general subject of chemical kinetics.

7. Absorption by Atomic Systems: It has already been pointed out (Chap. 4, 8, 9), that the absorption of light by atoms, normally present in an unilluminated system in the lowest energy state, produces either *excited atoms* by absorption of definite energy quanta, appearing in the spectra as absorption lines, or, alternatively, ionization to ion plus electron, in which case the spectrum reveals a continuous, non-discrete absorption beyond the frequency which corresponds to ionization. The excess energy in the continuum above that required for ionization is dissipated as kinetic energy of the ion and electron fragments. Hence the absence of quantization. We can illustrate this general behavior once more in reference to an atomic system of importance in photochemical reactions. Mercury in its normal atomic state absorbs light at 2536.7 Å, the first resonance line, corresponding to an energy of 4.865 e.v.[1] or 112,000 calories. The second resonance line is at 1849.6 Å corresponding to 6.674 e.v. or 153,500 calories. The ionization limit beyond which the absorption is continuous occurs at 1188 Å, the ionization energy being approximately 10.4 e.v. or 240,000 calories. Such energy quantities absorbed by mercury atoms under suitable illumination can only become available for photochemical change when they are transferred, either wholly or in part, to other reactive systems by collision processes. In the absence of such collisions the energy absorbed by the mercury atoms will be remitted as fluorescence radiation. By an analysis of this emitted fluorescence as a function of mercury concentration and pressure of admixed gas the conclusion can be reached, from ordinary collision calculations, that the excited state of the mercury atom may endure for about 10^{-8} sec. unless robbed of its energy by collision with other atoms or molecules.

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[1] e.v. = electron volt.

The extinction of mercury fluorescence by added air was observed by R. W. Wood in 1912. Other gases behave similarly though each gas has its own specific efficiency in transforming the energy of light absorption. Different gas molecules show widely varying efficiencies in the quenching of fluorescence. We can express this variation in the form of Table 16.2

TABLE 16.2

COLLISION CROSS SECTIONS IN EXTINCTION OF MERCURY FLUORESCENCE

Gas	$\sigma^2 \times 10^{16}$ in Extinction	$\sigma^2 \times 10^{16}$ Gas Kinetic	Gas	$\sigma^2 \times 10^{16}$ in Extinction	$\sigma^2 \times 10^{16}$ Gas Kinetic
O_2.........	13.9	10.7	CH_4	0.0596	11.6
H_2.........	6.01	8.87	C_2H_6	0.415	16.4
CO........	4.07	11.6	C_3H_8	1.62	
NH_3.......	2.94	10.8	C_4H_{10}	4.11	
CO_2........	2.48	11.6	He	0.00	7.83
H_2O........	1.00	10.0	Ar	0.00	10.4
N_2.........	0.19	11.2	Hg	—	13.4

which records the effective cross sections of various colliding molecules in extinguishing the fluorescence of mercury.

The table compiled from data by Stuart, Zemansky and Bates gives, for comparison, the collision cross-sections derived from kinetic theory data. The tabulation shows that both oxygen and hydrogen are efficient quenching agents for mercury fluorescence showing collision cross-sections comparable with gas kinetic values. Nitrogen, methane, helium and argon are particularly inefficient as quenching agents. Carbon monoxide, ammonia, carbon dioxide and water vapor are only moderately efficient. This pronounced specificity in the exchange of energy from electronic excitation of the mercury to energy of the colliding molecule is known to depend upon the capacity of the colliding molecule to take up the energy available in some form of quantized excitation, generally either of vibration or rotation with the minimum simultaneous production of kinetic energy. In certain cases, notably hydrogen, the whole of the energy of the excited mercury atom, 4.865 e.v., is consumed in the collision. In other cases, notably with nitrogen, only a small fraction of the energy of the mercury is consumed, 0.218 e.v., whereby the mercury atom passes from the normal excited state ($^3P_1$) to a metastable state ($^3P_0$) of lower energy. These latter atoms may have much longer lives than 10^{-8} sec. since they cannot revert to the normal state by radiation; they may, however, gain energy by collision or surrender their energy in the same way, returning to the normal state of the mercury atom (^1S).

We may summarize the possibilities of energy transfer by excited atoms in the following processes:

(a) *The energy may be utilized in exciting other atomic systems electronically.* This was indicated by Cario and Franck with mixtures of mercury and thallium vapors. The processes occurring may be represented by the reversible reaction

$$\mathrm{Hg'} + \mathrm{Tl} \rightleftarrows \mathrm{Tl'} + \mathrm{Hg} + \text{Kinetic Energy},$$

where the prime (′) indicates an excited atom.

(b) *The energy may be utilized in exciting molecular systems in either vibration or rotation or both.* For example, with ammonia

$$\mathrm{Hg'}(^3P_1) + \mathrm{NH_3} \rightarrow \mathrm{NH_3'} + \mathrm{Hg}(^3P_0).$$

The ammonia is excited to a vibrational level with an energy change roughly equal to that lost by the mercury, the excess energy being converted to kinetic energy.

(c) *The energy may be utilized in interaction with colliding systems.* For example, with hydrogen, excited mercury forms mercury hydride

$$\mathrm{Hg'} + \mathrm{H_2} = \mathrm{HgH} + \mathrm{H}.$$

This represents the simplest type of *secondary reaction* succeeding the primary absorption process.

(d) *The energy may be utilized by the colliding gas for a reaction in which the excited atom surrenders its energy but is chemically unchanged.* A simple case of this kind may be illustrated by the equation

$$\mathrm{Hg'} + \mathrm{H_2} = \mathrm{Hg} + 2\mathrm{H}.$$

The mercury is said to sensitize the dissociation of hydrogen to the wave length of light absorbed by mercury. The process is known as *photosensitization.* The sensitization of photographic emulsions to wave lengths such as green, yellow and red, by bathing the emulsion in suitable dyestuffs, is an important example of photosensitization.

8. Absorption of Light by Molecular Systems: The spectra of molecules are more complex than those of atoms because of the possibility of rotational and vibrational changes in addition to changes in electronic excitation (Chap. 4, 10). Three types of absorption, readily recognized in the spectra of molecules, are of importance in the discussion of the primary processes in photochemical absorption. They may be summarized thus:

(a) *Continuous Absorption,* which, by analogy with the continuous absorption revealed by atomic systems at and beyond the ionization energy limit, is ascribed to a dissociation of the absorbing molecule into fragments, either atoms or radicals.

(b) *Discontinuous Fine-Structure Band Absorption,* yielded by transitions from one electronic-vibrational state to a second such state, the fine structure of the band indicating that the rotational energy of the molecule is quantized.

(c) *Discontinuous Diffuse Structure Band Absorption or Predissociation Spectra,* also involving changes between two electronic-vibrational states, the diffuse structure of the band indicating that the rotational quantization of the molecule no longer obtains.

9. **Continuous Absorption:** It was pointed out by Franck in 1924 that, in the region of continuous absorption of the diatomic molecules Cl_2, Br_2, I_2, the primary process of absorption is to be interpreted as a dissociation of the molecule into atoms, one a normal, the other an electronically excited atom. The process may be written thus:

$$X_2 + E = X + X'.$$

Since the excitation energies of the halogen atoms are known, it is possible to verify this interpretation by comparing the energy of the long wave length limit of the continuous absorption (where the atoms separate with negligible kinetic energy), or, what is the same thing, the energy at the convergence limit of the fine-structure band absorption, with the heats of dissociation of the halogen molecules. These must differ by the energy of excitation of the atoms. The following Table 16.3 shows how well this interpretation expresses the facts.

TABLE 16.3

Spectroscopic Data and Heats of Dissociation of Halogens

Gas (1)	Convergence Limit (λ_c) in Å. (2)	$Nh\nu$ in kcal. for λ_c (3)	Excitation Energy of Atom $^2P_{3/2} - {}^2P_{1/2}$ (4)	Spectroscopic Heat of Dissociation (3)-(4)	Thermo-chemical Heat of Dissociation (6)
Cl_2......	4785	59.4 kcal.	2.5 kcal.	56.9 kcal.	57.0 kcal.
Br_2......	5107	55.6	10.5	45.1	46.2
I_2.......	4989.3	56.97	21.59	35.38	34.5

Actually, at the present time, the spectroscopic values for the heats of dissociation, so obtained, are more trustworthy than the thermochemical values determined from equilibrium measurements. In a similar manner hydrogen shows a convergence limit at 984 Å (= 14.53 e.v.) forming one normal and an excited atom having excitation energy equal to 10.15 e.v. Hydrogen iodide and the vapors of the silver halides dissociate similarly on illumination, the halogen atom, in each case, being the excited atom.

With other molecules a whole series of dissociation processes have been shown to occur with absorbed quanta of appropriate energy in the continuous region of absorption. Thus, for example, with sodium iodide vapor, dissociations into two normal atoms, and into one normal and one excited atom, have been located. In the latter case either the iodine atom or the sodium atom may be excited and two types of excitation have been found in the latter case. We may summarize these possibilities in the following equations:

$$\begin{aligned} \mathrm{NaI} + E_1 &= \mathrm{Na} + \mathrm{I}, \\ \mathrm{NaI} + E_2 &= \mathrm{Na} + \mathrm{I}', \\ \mathrm{NaI} + E_3 &= \mathrm{Na}' + \mathrm{I}, \\ \mathrm{NaI} + E_4 &= \mathrm{Na}'' + \mathrm{I}. \end{aligned}$$

The energies E_1, E_2, E_3 and E_4 are successively increasing quanta corresponding to progressively shorter wave lengths. E_1 occurs above 3900 Å, and differs in energy from E_2 by about 22 kcal., the excitation energy of iodine. E_3 corresponds to wave lengths of 2500 Å or shorter and the product is excited sodium yielding the D sodium line, 5897 Å (= 48 kcal.). E_4 corresponds to a wave length of 1862 Å and the excitation of the sodium is to the second resonance level at 3302 Å (= 86 kcal.). Other alkali halides show similar behavior.

10. Discontinuous Fine Structure Band Absorption: Fine structure bands in the absorption spectra of molecules indicate a transition from one electronic-vibrational-rotational discrete state to another at a higher energy level. The molecule thus becomes excited, and we may represent the process by the equation

$$AB + E = (AB)'.$$

The life time of such excited molecules is definite and brief as in the case of atoms so that, unless collisions intervene, the energy absorbed may be re-radiated as fluorescence. We may expect, and actually find, such fluorescence at low vapor pressures. The fluorescence of iodine vapor studied by Wood is of interest in that it demonstrates that molecules can accumulate, by light absorption in the fine structure region, energies very considerably greater than their dissociation energies. Thus, in the case of iodine, the fine structure region persists right up to the convergence limit, 4989.3 Å already discussed, and therefore excited molecules may be obtained with, in the limit, 21.59 kcal. of energy greater than the heat of dissociation (35.4 kcal.) without undergoing dissociation of themselves. Such energy-rich molecules will, however, readily dissociate on collision. High pressures of iodine vapor or added foreign gases suppress, therefore, the fluorescence phenomenon. Such collision processes, succeeding light absorption in the fine-structure region, produce in a two-stage process results analogous to those just discussed in the continuous region where light absorption alone, without collision, produces dissociation.

11. Discontinuous Diffuse Structure Band Absorption: Predissociation Spectra: Henri discovered a number of spectra showing the discontinuous band structure characteristic of quantized electronic-vibrational transitions, the bands, however, revealing, even under high resolution, no sharp line structure characteristic of quantized rotation of the molecule. Transitions from fine-line to diffuse structure bands can be found to occur either suddenly or gradually. In the latter case the fine-line structure becomes increasingly diffuse in successive bands, and may then gradually increase again in sharpness. Such spectra were termed predissociation spectra by Henri. Their interpretation was given by Bonhoeffer and Farkas and by Krönig, and is dependent on resonance effects in the molecule, on a coupling between the electronic jumps and the vibrations of the nuclei. If a particular electronic level of a molecule is energetically higher than the position of continuous absorption of the molecule which is lowest in energy, then there will be resonance between the two states and the molecule will pass, within a half-period of vibration, from the first electronic state to the second in which dissociation will spontaneously occur. Such a condition is indicated in the accompanying Fig. 16.1. Since the frequency of rotation is much less than that of vibration there will be absence of rotational structure in the original vibrational band. The more complex the molecule the greater the possibility of such an energy resonance. In the case of the diatomic molecule S_2 predissociation bands are, however, found. The spectra of NO_2 and NH_3 show diffuse discontinuous bands, important photochemically, and these must be interpreted in the manner just outlined. The absorption produces a molecule in a particular state of electronic excitation which passes by resonance to an unstable state in which dissociation occurs. It is to be noted that this dissociation is independent of molecular collisions as is true of continuous absorption. The total process is, however, more complex, involving three stages, absorption, resonance and consequent dissociation. With polyatomic molecules, in which such predissociation phenomena are common, the spectroscopic evidence does not define the nature of the dissociation products. Thus, with ammonia, showing

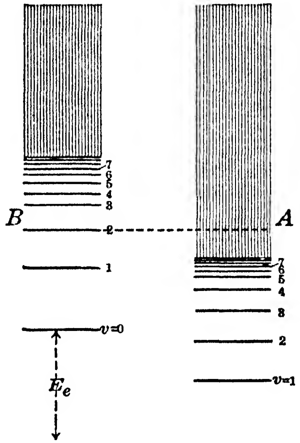

FIG. 16.1. Resonance between Electronic States Producing Diffuse Spectra.

diffuse spectra around 2200 Å, these products might be $NH + H_2$ or alternatively $NH_2 + H$. Other possibilities are ruled out on energetic grounds. The decision as to what the products are must be reached on other, generally experimental chemical, bases.

12. **The Franck-Condon Principle:** The importance in photochemistry of the nature of the absorption process whether continuous absorption or discontinuous band absorption suggests an inquiry into the factors determining which of the two types of absorption occur. The factor of greatest weight is embodied in a principle first enunciated by Franck and given a theoretical basis by Condon. The principle may best be explained in reference to a diagram, Fig. 16.2, which shows schematically the potential energy curves of two states of electronic excitation of a diatomic molecule. The lowest curve represents that of the molecule in its normal state, the lowest horizontal line representing the zero point energy of the normal molecule. The zero of the potential energy refers to the two normal atoms at infinite distance from one another as in Fig. 4.4 (Chap. 4, 12). In the upper curve the potential energy at large values of r refers to one normal and one excited atom, the vertical distance between the horizontal portions of the two curves representing the energy of electronic excitation of the one atom. The minimum in the upper curve occurs at the equilibrium distance of the molecule in its particular state of electronic excitation, the horizontal lines indicating successive vibrational states of the same molecule. Rotational states of the molecule in each vibrational state are to be understood but are not shown in the diagram.

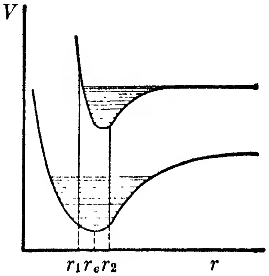

FIG. 16.2. Potential Energy Curves Illustrating the Franck-Condon Principle.

Discontinuous band absorption is represented in the diagram by transitions from rotational-vibrational levels in the lower curve to rotational-vibrational levels in the upper curve. Transitions from levels in the lower curve to positions on the upper curve at energy levels higher than the horizontal portion of the curve represent continuous absorption. The reason for this is clear. A molecule in such a position on the upper curve will during the next half-period of vibration pass down through the minimum and out to infinity; dissociation into the two atomic products will have occurred. The kinetic energy with which the atoms separate is measured by the height above the horizontal portion of the curve from which the molecule starts on its dissociative process.

The Franck-Condon principle states that the time occupied in the electronic transition involved is so brief, compared with the period of vibration, that it occurs without marked change in the distance separating the nuclei in the molecule. Such transitions must therefore be represented in the majority of cases by vertical lines. Since the kinetic energy of the molecule is zero at the distances r_1 and r_2 at the extremities of a vibrational level, these are the positions in which a molecule will exist for the longest intervals of time and are therefore the most probable positions from which the vertical transitions will occur.

The question, therefore, whether a transition leads to dissociation or not depends upon the position of the upper curve relative to the lower curve. Also, since, in absorption at ordinary temperatures, the majority of the molecules are in the lowest vibrational state the occurrence of continuous absorption or discontinuous band absorption depends upon whether the verticals from the extremities of this level cut the upper curve above or below the horizontal portion of the upper curve. If above, continuous absorption results; if below, discontinuous. Each state of electronic excitation will have its own characteristic curve. Not all of these may be stable with potential energy minima. Some may be repulsive as in the case shown in Fig. 4.4 (Chap. 4, 12). All transitions from stable states to such repulsive states result in dissociation. The energy level at large distances determines the nature of the dissociation products. If this is identical with that of the stable molecule the products are the unexcited atoms, of which we have discussed one example in the case of sodium iodide.

13. **Light Absorption by Liquids and Solids:** The preceding discussion has referred essentially to matter in the gaseous condition since the phenomena are relatively simpler due to the small intermolecular effects. With liquids and solids the influence of neighboring molecules becomes very important and the absorption phenomena consequently more complex. These effects may be expected to be least with liquids and solids having high vapor pressures, indicative of small intermolecular attractions. In such cases similarities between the spectra of the gaseous and the condensed phases have been established. The spectral lines in condensed systems are however less sharp than in gaseous systems. Even the latter at high pressures show the broadening effects due to intermolecular attractions.

Dissociation and solvation of ions are further complexities in solutions of electrolytes. In a few cases, notably some of the rare earth ions investigated by Freed and Spedding, the absorption spectra show a fine line structure both in solution and in the solid state. This is to be attributed to electronic transitions within the ion. Transitions of electrons on the outside of ions generally give diffuse absorption. The more polar the solvent the greater the influence on the absorption of the solute.

Discrete and continuous regions of absorption have the same significance as with gases. The subsequent consequences of such absorption are, however, modified by the presence of the condensed phase. Thus, a continuous absorption leads to dissociation in one act, but the opportunity for immediate recombination of the fragments in condensed phases, especially liquids, is so very much greater than in gaseous systems, since such recombinations are often three-body processes, relatively rare in gases; in liquids a very much larger proportion of all collisions can be regarded as three-body collisions. Such a factor will have the effect of decreasing the efficiency of the primary process of absorption and hence the net photochemical yield in liquid systems. Such net yield will however, in condensed phase as in gaseous, depend on the chemistry of the system produced by the process of light absorption.

THE SECONDARY CHEMICAL PROCESSES

We shall illustrate the dependence of net yield of the photochemical process on the chemistry of the system produced by the primary process of light absorption by considering three photo-reactions: (a) the decomposition of hydrogen bromide and iodide, (b) the hydrogen-bromine reaction, (c) the hydrogen-chlorine combination. In each case the primary process is the same, the production of one normal and one excited atom by the light-absorbing diatomic molecule. In reaction (a) few steps succeed the primary process, and there is a close correlation between light absorbed and molecules reacting. In reaction (b) the secondary processes are temperature sensitive and so the yield per unit of absorbed light is determined by the temperature. In reaction (c) the products of the primary absorption process can initiate a prolonged chain of secondary processes so that an enormous yield of reaction products can be secured per unit of absorbed light.

14. The Decomposition of Hydrogen Bromide and Hydrogen Iodide: The primary process can be represented thus:

$$\mathrm{HX} + E = \mathrm{H} + \mathrm{X}'. \qquad (1)$$

The possible secondary processes are:

$$\mathrm{H} + \mathrm{HX} = \mathrm{H_2} + \mathrm{X}, \qquad (2)$$

$$\mathrm{X} + \mathrm{HX} = \mathrm{X_2} + \mathrm{H}, \qquad (3)$$

$$\mathrm{H} + \mathrm{H} = \mathrm{H_2}, \qquad (4)$$

$$\mathrm{X} + \mathrm{X} = \mathrm{X_2}, \qquad (5)$$

$$\mathrm{H} + \mathrm{X} = \mathrm{HX}. \qquad (6)$$

Of these, (2) occurs practically at every collision and is therefore much more important than (4) and (6), which are three-body processes, as the method of removing atomic hydrogen from the system, owing to the relatively high concentration of HX compared with H and X. Reaction

(3) is so strongly endothermic that it does not occur either with bromide or iodide at ordinary temperatures. Halogen atoms disappear therefore by reaction (5) probably mainly as a wall-reaction, in part also as a three-body process depending on the halogen atom concentration. On this basis the total process is

$$\begin{aligned} HX + E &= H + X' \quad \text{(Primary Absorption Process)},\\ H + HX &= H_2 + X \quad \text{(Secondary Chemical Process)},\\ X + X &= X_2 \qquad\quad \text{(Secondary Chemical Process)}. \end{aligned}$$

One einstein of light energy should thus effect the decomposition of two moles of the halide.

Warburg established this experimentally by his studies of hydrogen bromide decomposition in a stream of hydrogen or nitrogen at the two wave lengths 2090 Å and 2530 Å and of hydrogen iodide at 2090, 2530 and 2820 Å. The results obtained were decisive from the standpoint of quantum theory. Thus, for hydrogen iodide, we may express the results in terms of the number of gram atoms of iodine produced per gram calorie of light energy employed. We thus obtain the data in the following table.

TABLE 16.4

PHOTOCHEMICAL YIELD OF IODINE FROM HYDROGEN IODIDE

Wave length in Å	2070	2530	2820
Mole ($\frac{1}{2}I_2$) × 10^5 per gram cal	1.44	1.85	2.09

These results show that, per gram calorie of light energy, the extreme ultra-violet is less efficient than the longer wave-length light. This surprising result, completely inexplicable without quantum theory, becomes immediately understandable when the quantum relationship is introduced. The calculation then shows that, at each wave length, two moles of hydrogen iodide are decomposed per einstein absorbed, with a maximum deviation in all experiments of not more than 5 per cent, a deviation well within the experimental error. This ratio is also obtained by Bodenstein and Lieneweg for liquid hydrogen iodide at room temperature, for the gas at 150–175° C. and by Lewis for the gas at 0.1 mm. pressure. These and similar studies with hydrogen bromide exhibit strikingly the importance of the quantum relationship in photochemical reactions when the succeeding reactions are few.

15. The Hydrogen-Bromine Combination: The primary process in the region of continuous absorption by bromine is

$$Br_2 + E = Br + Br'.$$

Bromine atoms so produced can undergo the same sequence of secondary processes as we have already discussed in the treatment of the thermal reaction (15, 17). In this photo-reaction the bromine atom concentration is determined by the number of light quanta, n, absorbed by bromine per cc. per sec. (since each quantum yields two atoms) and the constant k_5 expressing the rate of recombination of the atoms. The bromine atom concentration in light becomes (Chap. 15, 21)

$$[\mathrm{Br}] = \sqrt{n/k_5} \tag{16.9}$$

and the rate of hydrogen bromide formation, analogous to the thermal kinetics, becomes

$$+\frac{d[\mathrm{HBr}]}{dt} = \frac{2k_2[\mathrm{H_2}]\sqrt{n/k_5}}{1 + \dfrac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]}}, \tag{16.10}$$

an equation which indicates a rate proportional to the square root of the intensity of absorbed light, $I_{\mathrm{abs}}^{0.5}$. This was verified in a detailed experimental study, by Bodenstein and Lütkemeyer, of the reaction in the temperature interval 160–218° C. The equation shows that the yield per unit of light absorbed is mainly dependent on k_2, the constant of the reaction (2)

$$\mathrm{Br} + \mathrm{H_2} = \mathrm{HBr} + \mathrm{H},$$

which steadily increases with temperature, since k_3 and k_4 are relatively independent of temperature. Jost has studied the reaction in the fine-structure band absorption region around 5650 Å. He found that in this region the reaction velocity was practically identical per unit quantum of light absorbed with that obtaining in the region of continuous absorption. It is evident, therefore, that the excited molecule produced by the primary absorption process at 5650 Å must, by collision, decompose into atoms without further energy increment and set up the same chain of secondary reactions already discussed.

16. **The Hydrogen-Chlorine Combination:** At wave lengths shorter than 4785 Å chlorine shows a continuous absorption. Hence the primary absorption process yields one normal and one excited atom

$$\mathrm{Cl_2} + E = \mathrm{Cl'} + \mathrm{Cl}.$$

Two secondary reactions are possible in hydrogen-chlorine mixtures,

$$\mathrm{Cl} + \mathrm{H_2} = \mathrm{HCl} + \mathrm{H},$$
$$\mathrm{H} + \mathrm{Cl_2} = \mathrm{HCl} + \mathrm{Cl}.$$

Theoretically, then, one might anticipate a long chain of secondary processes succeeding the primary absorption. This is confirmed by the measurements of Bodenstein and Dux who found that, in highly purified mixtures of the moist gases, at atmospheric pressure, yields of the order of 10^6 moles per einstein were recorded. Both stages in the proposed chain are known to be possible. Taylor and Marshall showed that hydrogen atoms would produce a chain of reactions in a hydrogen-chlorine mixture. Polanyi and Bogdandy have shown that chlorine atoms from the interaction of chlorine and sodium vapor would behave similarly.

As has long been known, the sensitivity of the gas mixture is very dependent on its purity. The induction period, the slow attainment of a maximum velocity some time after the initial moment of illumination, was elucidated by Chapman, Burgess and MacMahon. This period of retarded action was always conditioned by the presence of foreign substances in the containing liquid or on the walls of the glass vessel or introduced with the gases into the reaction vessel. Various nitrogen compounds, including ammonia and albumens, were especially efficient in this induction period. They were removed by chlorination. Elimination of such impurities eliminated the induction period. Oxygen, however, retards the rate of reaction even in the absence of such impurities, and to an extent approximately proportional to its concentration. The enormous effect of oxygen in reducing the rate of reaction, even when it is present in small concentrations, is consistent with the high yield of the secondary processes. The removal of a hydrogen or chlorine atom by reaction with oxygen would eliminate all the subsequent reaction steps that would follow in absence of the oxygen. If every chain were stopped after the first stage, the velocity would be reduced $\sim 10^6$ fold.

Atom chains of the type postulated would be broken by removal of the atoms at the walls of the containing vessel owing to recombination. The influence of the walls on yield might therefore be anticipated and is actually found at low pressures or in vessels of small dimensions. Marshall and later Trifonoff showed reduced yields per einstein absorbed at pressures below 60 mm. and Chapman and Grigg have shown the same for capillary tubes. This effect of capillaries on atom recombination accounts for the failure of Bodenstein and Taylor and later of Marshall to obtain reaction by illuminating the chlorine alone and passing it directly (but, owing to the experimental demands, through capillaries) to unilluminated hydrogen. No reaction was observed under these circumstances even 10^{-4} sec. after illumination. The efficiency of glass in causing the recombination of chlorine atoms has been independently demonstrated by Polanyi and Schay, in their studies of chemiluminescence from the interaction of sodium vapor and chlorine.

Weigert and Kellermann have decisively demonstrated by experimental methods the existence of a chain of secondary reactions in the hydrogen-chlorine combination. The hydrogen chloride produced on illumination from a momentary intense spark is not obtained instantaneously but in an after-effect extending over 0.01 sec. after illumination. The purer the gas mixture the larger the duration of the after-effect. As already mentioned, in order to secure this effect, both gases must be illuminated simultaneously or the experimental arrangement must be such as to obviate recombination of chlorine atoms.

The velocity of combination of the moist gases is directly proportional to the intensity of absorbed light and not, as in many photo-reactions involving halogens, to the square root of the intensity. This factor in the kinetic expression indicates that chlorine atoms are removed singly in the gas phase by inhibitors and not by a triple collision of two atoms and a third body to yield the molecules; or, alternatively, recombination of chlorine atoms is a wall reaction. Recombination of chlorine atoms by triple collisions in the gas phase would yield a proportionality to $I_{abs}^{0.5}$ in the kinetic expression.

The precise mechanism of the inhibitory processes which destroy the hydrogen and chlorine atom links in the chain is still the subject of discussion.

17. **The Decomposition of Ammonia:** As an example of a photo-process produced by absorption in diffuse-structure bands we cite the case of ammonia decomposition by light of wave length 2200 Å and shorter. The bands are quite diffuse. Warburg found complete decomposition with nitrogen and hydrogen in the stoichiometric ratio as products. He found the yield at room temperatures to be 0.25 mole decomposed per einstein absorbed. Kistiakowsky and Wiig have confirmed this result, the latest measurements of Wiig, however, indicating that the yield is dependent on the pressure. It is low at pressures of a few mm., rises to a maximum at ~ 100 mm. pressure and then slowly falls as atmospheric pressure is approached. The diffuse nature of the spectrum and the ideas already expressed concerning the causes of predissociation spectra might lead one to expect a yield of one mole per einstein absorbed. The low yield has been the object of much study from which it has been learned that the primary dissociation upon light absorption is:

$$NH_3 + E = NH_2 + H.$$

The presence of atomic hydrogen has been shown by Melville to reduce considerably the overall photo-decomposition so that the low quantum yield is to be attributed in part to the reverse process of recombination

$$NH_2 + H = NH_3.$$

The variation of yield with pressure indicates that the walls assist this at low pressures. The yield at any given pressure is independent of the intensity over wide variations of this magnitude. The secondary processes do not involve either nitrogen or hydrogen molecules since these are without influence on yield. The actual yield of nitrogen and hydrogen is obtained by secondary reactions of the NH_2 and H which do not recombine to form ammonia, approximately one-fourth of the total produced in the primary process. All the various methods of disappearance of the primary products must be dependent in the same manner on concentration in order to account for the observed independence of light intensity.

PHOTOCHEMICAL REACTIONS IN LIQUID SYSTEMS

As examples of reactions in liquid systems we choose two where the yield in moles per einstein is below unity and a group of reactions in which the secondary processes effect a high yield per unit of absorbed light.

18. **Decomposition of Potassium Nitrate Solutions:** Warburg studied the photochemical yield of nitrite in solutions of potassium nitrate by the action of ultra-violet light of wave lengths 2070, 2530 and 2820 Å. The yield was in all cases less than one mole nitrite per einstein but increasing with increasing concentration, decreasing with increasing wave length. Warburg suggested that, in such condensed systems, the absorbed quantum was dissipated by 'damping' in the act of absorption, the energy being shared with solvent molecules. The broadening of absorption bands by increased pressure, about which not too much is yet known, is involved in this problem. In the meantime, we may think of the total process in terms of the formation of an excited molecule (or ion, in aqueous solution) by the primary process, its reaction or alternatively its deactivation, without reaction, by collision with solvent molecules. Warburg's data are given in Table 16.5.

TABLE 16.5

PHOTOCHEMICAL DECOMPOSITION OF POTASSIUM NITRATE SOLUTIONS (0.0033 *N* NaOH)

Wave length =	2070	2530	2820 Å.
Concentration			
0.33 *N*................	0.25	0.17	0.024
0.033 *N*................	0.19	—	—
0.0033 *N*...............	0.10	—	—

19. **Decomposition of Oxalic Acid Solutions:** Early work of Berthelot and Gaudechon on this reaction has been extended by Allmand and Reeve. They find that in the initial stages of the reaction the acid is decomposed quantitatively to formic acid and carbon dioxide, in agreement with the earlier investigators. Light of wave length longer than 3000 Å is also active photochemically, but the quantum yield decreases very rapidly with increase of wave length. At 2650 Å, a value of 0.01 was obtained; at 3650 Å, the yield had fallen to 0.00095 mole per einstein.

This reaction is sensitized by uranyl salts. Leighton and Forbes have made a most careful study of this reaction in nine monochromatic radiations, with solutions of various concentrations. The gross quantum yield at 25° C. for a solution 0.05 M in oxalic acid and 0.01 M in uranyl sulfate varies between 0.60 at 2540 Å and 0.58 at 4350 Å, with a minimum of 0.49 at 3660 Å. These values are approximately half those previously accepted, and this is important, since such solutions have been used for actinometric purposes. The velocity increases in the ratio of 1 : 1.03 per ten degrees in the range 10 to 25° C. both at 3660 and 3130 Å. The results support an earlier conclusion of Büchi that the photolyte is a complex which may be $UO_2HC_2O_4^+$ or $UO_2C_2O_4$ or some optical cluster of this type. Leighton and Forbes regard it as improbable that photolysis depends on collisions between excited UO_2^{++} and $H_2C_2O_4$. If the acidity of the solution is kept high, the products are H_2O, CO and CO_2. When the acid concentration is lower, formic acid and carbon dioxide become increasingly important products.

20. Reactions in Liquid Systems Showing High Quantum Yields: That very many secondary processes may succeed an initial absorption in liquid systems has been convincingly demonstrated by Bäckström in the case of sodium sulfite oxidation in aqueous solution. Bäckström found that as many as 50,000 molecules of sodium sulfite react per absorbed quantum of light of wave length 2536 Å.

It has long been known that the thermal oxidation of these solutions at room temperatures was susceptible to inhibition and also that the reaction was very sensitive to minute amounts of accelerating agents, notably, according to Titoff, copper salts. The association of these facts led to the Luther-Titoff theory that inhibitors act by suppression of a positive catalyst. While this is one possible mechanism of inhibition it will be seen that the phenomenon of inhibition may be expected in any reaction in which a large number of secondary processes succeed the primary activation process, whether thermal or photochemical. This point of view was first put forward by Christiansen. Any reagent which reduces or suppresses the chain of reactions succeeding the primary activation will produce inhibition.

The photochemical oxidation of sulfite solutions was found by Matthews, Dewey and Weeks to be faster than the thermal reaction and inhibited by a variety of added agents. The chain character of the process follows from Bäckström's yield measurements. A link between the thermal and photo-processes was provided by his observation that alcohols affect both rates alike, the relative rates in presence of such inhibitors being satisfactorily represented in both cases by the equation

$$V = \frac{k_1}{k_2c + k_3}, \tag{16.11}$$

where c is the concentration of inhibitor, the constants k_2 and k_3 are common to both thermal and photochemical reactions, k_1 varying according as the reaction was thermal or photochemical, being dependent on the rate of activation or formation of the initial stage in the chain process. The inhibitor constant k_2 is specific for a given inhibitor. The presence of k_3 indicates the possibility of ending chains other than by the added inhibitor.

The correctness of these general conclusions and the mechanism of inhibitor action in this particular case were established later by Alyea and Bäckström. The inhibition involves an induced oxidation of the inhibiting alcohol, two molecules of the oxidation product (aldehyde or ketone) being formed whenever a chain is broken. The experimental results which support this conclusion may be summarized. At low alcohol inhibitor concentrations the amount of alcohol oxidized increases with increasing alcohol concentration. At high inhibitor concentrations the amount of alcohol oxidized per unit time is constant independent of its concentration, in both the thermal and photochemical reactions. In this latter concentration region the number of inhibitor molecules oxidized per unit time is quantitatively the same for different alcohols of widely different inhibitory powers. Two alcohols present in a solution have an additive inhibitory effect and are oxidized in the ratio of their inhibitory powers; the total number of alcohol molecules oxidized is, however, the same as when only one alcohol is present. The number of successive secondary processes is the same in both thermal and photochemical reaction and is equal to the efficiency (moles per einstein) as determined photochemically. Copper sulfate accelerates the thermal reaction without altering the ratio of sulfite oxidized to alcohol oxidized. This means that the positive catalyst in this case initiates the chain process; the inhibitor quite independently breaks the chain of secondary reactions. This is a definite disproof of the Luther-Titoff theory in this particular case.

The autoxidations of benzaldehyde and oenanthaldehyde were shown by Bäckström to be of the chain type also. As many as 10,000 molecules of benzaldehyde were oxidized per quantum of absorbed light. Another type of reaction in liquid system showing the same abnormal yield is the decomposition of hydrogen peroxide where yields as high as 80 moles of peroxide decomposed per einstein absorbed have been obtained. This reaction also shows inhibition the details of which were studied by Anderson and Taylor. Inhibitors may show a screening action but may also break the chains involved in the high yield decomposition process. Processes of polymerization, e.g., of styrene and of vinyl acetate, are also photo-reactions which show inhibition phenomena and high yields per einstein absorbed by the liquid system. We have already cited cases of halogenation involving chains. Further examples of this type are the chlorination of toluene studied by Book and Eggert at − 80° C. with a quantum yield of 27, and the sensitized conversion of maleic ester to fumaric ester by bromine in carbon tetrachloride solutions. For this reaction Eggert and Borinski found yields as high as 300 moles per einstein.

PHOTOCHEMICAL REACTIONS IN SOLID SYSTEMS

21. **The Light Sensitivity of Silver Compounds:** The reactions already treated have been confined to gaseous and liquid systems. The energetics of photo-change has been investigated thoroughly in two solid systems. Weigert has studied the photochemistry of silver chloride in a printing out paper; Eggert and Noddack have studied specially prepared silver bromide-gelatine emulsions on plates.

Pure silver halides show little if any sensitivity to light. The blackening action of visible light is the more pronounced the more the adsorbed silver salt. Adsorption extends the spectral sensitivity of the photohalide. Photographic experience has shown that the gelatine of the emulsion and the colloidal silver produced during the "ripening" of the emulsion also increase the photosensitivity of the silver halide.

Weigert's measurements show that, with a silver chloride gelatine emulsion containing a known excess of soluble silver salts, the silver produced on exposure to light comes practically exclusively from the soluble silver salts. With increasing time of illumination, the curve for increase of silver produced is a typical S-shaped curve of the autocatalytic reaction type or what is perhaps better characterized as the type shown by reaction at the boundary of phases. The silver produced increases the spectral sensitivity of the emulsion. With monochromatic blue light, Weigert established that the photochemical yield was considerably less than the absorbed light. Assuming, however, that the metallic silver was the real photosensitive constituent of the system, Weigert showed that the ratio of reaction produced to light absorbed by metallic silver was much more nearly unity, 1 molecule per $h\nu$, and approached unity for low concentrations of metallic silver in the emulsion.

Eggert and Noddack used for their investigations silver bromide-gelatine emulsions containing respectively 0.90 mg. and 0.42 mg. silver per square cm. They measured the reflected, absorbed and transmitted light, and determined the silver produced by fixing the plates with sodium thiosulfate, estimating the residual silver in the gelatine. They conclude, from the experimental measurements, that, with weak illumination, the law of the equivalent is fulfilled for both types of plate at wave lengths of 4360, 4050 and 3650 Å. With increasing illumination the yield falls, which they attribute to recombination of the silver and bromine atoms produced in the light, when these are produced in that portion of a grain around which the surrounding gelatine, which normally acts as an acceptor for the bromine, is already brominated. When other acceptors for bromine are present in the reaction system, e.g., silver nitrate, alkalis or water, the proportionality between silver produced and light energy absorbed obtains at much higher proportions of absorbed light. This is evident from the accompanying table for dry and wet plates.

TABLE 16.6

PHOTOCHEMICAL YIELD FOR SILVER BROMIDE EMULSIONS

No. of Quanta Absorbed	Molecules per $h\nu$ Dry Plates	Molecules per $h\nu$ Wet Plates
14×10^{16}	0.50	0.89
50×10^{16}	0.22	0.43

PHOTOSENSITIZATION

It was noted in an earlier section that it is not necessary that the reacting species absorb the activating radiation in a photosensitive system. Photo-reactions may result from the absorption of light by one of the non-reactants of the system. This was shown by Vogel in 1873 in respect to the silver halides in photographic processes. The spectral region to which the photohalides are sensitive can be extended by bathing the emulsions in suitable dye-stuffs. This discovery is the basis of the production of panchromatic photographic plates, and is a most important example of photosensitization. The role of chlorophyll in the synthesis of plants seems also in part to be that of an optical sensitizer, making the reaction system, carbon dioxide and water, sensitive to the visible rays of sunlight. A variety of photosensitizations of bacteria by fluorescent substances rendering the bacteria sensitive to illumination have an importance in the study of the biology of light processes.

22. Sensitization by Halogens: Such complex systems are of little avail when mechanism of sensitization is under study. Fortunately, Weigert showed that the phenomenon is also found in gaseous systems. He showed that phosgene, which is a colorless gas absorbing in the ultraviolet only, can be decomposed photochemically by visible light when chlorine is added to the phosgene. The studies by Bodenstein and his co-workers of the thermal and photochemical formation and decomposition of phosgene have shown that both forward and backward reactions are both brought about via chlorine atoms produced by illumination.

Weigert showed that such halogen sensitizations are quite general phenomena. Among others the sensitization by chlorine of the decomposition of ozone, the combination of hydrogen and oxygen, of carbon monoxide and oxygen and of sulfur dioxide and oxygen have been studied.

Bromine sensitizes the conversion of maleic to fumaric acid as was shown by Bruner.

In solutions uranium salts and ferric salts act as sensitizers in the decomposition of oxalates and of hydrogen peroxide, and in the oxidation of benzoic to salicylic acids.

23. **Sensitization by Mercury Atoms:** The best understood case of photosensitization is the production of atomic hydrogen by collision of excited mercury atoms with hydrogen molecules, as already discussed in Section 7. Atomic hydrogen so formed has been shown to reduce metallic oxides, react with oxygen, carbon monoxide, ethylene and even saturated hydrocarbons. The action of mercury as sensitizer is not confined, however, to hydrogen; photosensitized ozonization of oxygen and the decomposition of water vapor, ammonia and numerous organic compounds have been studied.

TABLE 16.7

PHOTOCHEMICAL GAS REACTIONS

Reaction	Quantum Yield	Wave Length in Å.	Remarks
$2HI = H_2 + I_2$	2±0.1	2070–2820	Independent of inert gases to 2.5 Atm.
$2HBr = H_2 + Br_2$	2±0.1	2070–2530	Independent of inert gases to 2.5 Atm.
$3O_2 = 2O_3$	1–3	1700–2530	High pressures employed at longer wave lengths.
$2O_3 = 3O_2$	2–3.6	3130 and 6200	Short chains present.
$2NH_3 = N_2 + 3H_2$	~0.25	~2100	Varies with pressure between 0 and 1 Atm. Independent of light intensity.
$2Cl_2O = 2Cl_2 + O_2$	3.5	3130–4360	Short chains.
$H_2 + Cl_2 = 2HCl$	$\sim 10^5$	~4000	Long chains, readily inhibited.
$CH_4 + Cl_2 = CH_3Cl$	$\sim 10^4$	2536–4360	Long chains, readily inhibited.
$CO + Cl_2 = COCl_2$	$\sim 10^3$	4000–4360	Long chains at room temperature, inhibited by oxygen. Chain length shortens with increased temperature and oxygen effect decreases.

TABLE 16.7—*Continued*

Reaction	Quantum Yield	Wave Length in Å.	Remarks
$H_2+Br_2=2HBr$	—	4300	Quantum yield increasing with temperature.
$2NO_2=2NO+O_2$	0.009 0.72 1.54	4350 4050 3660	Quantum yield increases in passage from fine structure to predissociation absorption.
$CH_3CHO=CH_4+CO$	2	3130	Yield increases from 2 at room temperature to 300 at 300° C., due to secondary chain reactions.
$CH_3COCH_3=C_2H_6+CO$	2	3130	Yield independent of temperature up to 400° C.
$nC_2H_2=(C_2H_2)_n$	~9	2150	Yield increases to 250 at 250° C.
$CH_3N:NCH_3=C_2H_6+N_2$	2	3660	Yield independent of temperature to 300° C.

PHOTOCHEMICAL YIELD

Tables 16.7 to 16.10 list some of the principal results based upon a compilation by Bonhoeffer and Harteck [1] from the study of photochemical and photosensitized reactions in gaseous and condensed systems. The quantum yields are expressed as moles of reactant disappearing per einstein of light absorbed. Special remarks concerning the reactions are to be found in the last column.

THE STATIONARY STATE OR PHOTOCHEMICAL EQUILIBRIUM

Every reversible reaction, in which one or both directions of change are sensitive to light, will produce, with a given intensity of illumination, a definite "equilibrium" or stationary state. This state will be dependent, obviously, on the concentrations of the reacting substances, on the temperature, on the illumination employed both as to intensity and frequency, and on the velocity with which the two reactions occur under such conditions. It follows also, from thermodynamic considerations,

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[1] Grundlagen der Photochemie, Steinkopf, Dresden and Leipzig, 1933.

that the shift of the normal "dark" equilibrium shall never be in that direction in which a perpetuum mobile is possible; that is, the change in free energy occurring must come from the radiant energy supplied.

TABLE 16.8

SENSITIZED GAS REACTIONS

Reaction	Sensitizer	Quantum Yield	Wave Length in Å.	Remarks
$2O_3 = 3O_2$..........	Cl_2	2–30	4300	Increased yield with increase of ozone concentration.
$2CO + O_2 = 2CO_2$....	Cl_2	$\sim 10^3$	4050–4360	Dependent on temperature and concentration.
$2H_2 + O_2 = 2H_2O$....	Cl_2	$2(H_2O)$	4300	Simultaneous formation of HCl.
$H_2 + O_2 = H_2O_2$.....	Hg	$\sim 3(H_2O_2)$	2537	
$H_2 + CO = HCHO$...	Hg	$\sim 2(HCHO)$	2537	

The simplest case will be found with a reaction light sensitive in one direction only. Such a case has been well investigated and will now be discussed.

24. **The Polymerization of Anthracene:** Solutions of anthracene when exposed to ultraviolet light undergo polymerization of the anthracene to form dianthracene. The reaction

$$2C_{14}H_{10} = C_{28}H_{20}$$

is reversible, the depolymerization, which is not photosensitive to the type of radiation used, occurring spontaneously in the dark. Upon illumination, therefore, a definite stationary state is finally attained dependent, at a given temperature, on the light intensity. The reaction has been studied in detail by Luther and Weigert. The depolymerization or dark reaction was found to be pseudo-unimolecular at all temperatures, practically complete, and to have a large temperature coefficient (circa 2.8 for 10°). The polymerization or light reaction was of zero order for complete absorption, between zero order and first order for partial absorption. The reaction is, therefore, evidently determined by the amount of light absorbed. The reaction obeys approximately the law of the photochemical equivalent. The temperature coefficient for the light reaction is small and equal to about 1.1 for 10° C. Several solvents were tried, including phenetol, anisole and xylol. The solvent exercises a specific influence upon both the velocities and the equilibrium. It is evident that the reaction occurring at a given temperature can be expressed by an equation of the form

$$\frac{dx}{dt} = k_l I_{abs} - k_d x, \tag{16.12}$$

where x is the dianthracene formed, I_{abs} the light energy absorbed, k_l and k_d specific constants of the light and dark reactions. At equilibrium,

TABLE 16.9

PHOTOCHEMICAL REACTIONS IN LIQUID MEDIA

Reaction	Quantum Yield	Wave Length in Å.	Medium	Remarks
$2HI = H_2 + I_2$	1.84	3000	Liquid HI	
$2HI = H_2 + I_2$	1.52	2220	Hexane	0.8 normal solutions; not very sensitive to concentration.
	1.78	2820		
$2HI = H_2 + I_2$	0.336	2070	Water	Yield strongly dependent on concentration.
	0.078	2220		
	0.114	2820		
$2Fe^{++} + I_2 = 2Fe^{+++} + 2I^-$	1	5790	Water	
Br_2 + Maleic Ester	8.2	4360	CCl_4	
	4.1	5460		
Cl_2 + Toluene	27	4050		At −80° C.
$2KNO_3 \rightarrow 2KNO_2 + O_2$	0.25	2070	Water	Data for 0.33 N solutions. Yields decrease with increasing dilution.
	0.17	2530		
	0.024	2820		
$2H_2O_2 \rightarrow 2H_2O + O_2$	7–2500	3100	Water	Yield increases with concentration. High values deduced from action of inhibitors.
$2C_{14}H_{10} \rightarrow C_{28}H_{20}$	0.5	3130	Benzene	
		3650	Toluene	
			Xylene	
$ClCH_2COOH + HOH = OHCH_2COOH + HCl$	1.0	2537	Water	0.3 to 0.5 normal.
Fumaric → Maleic	~0.1	2070 2537 2820	Water	0.01 normal.
Maleic → Fumaric	~0.03			
$CH_3COOH \rightarrow CH_4 + CO_2$	0.5	1850–2300	Water	0.5 normal.

or the stationary state,

$$k_l I_{abs} = k_d x. \tag{16.13}$$

This equation summarizes the influence of various factors upon the equilibrium state. It is apparent that x depends on the value of the specific constants k_l and k_d and on the intensity of light absorbed. It will also vary, at constant intensity, with temperature, since, under such conditions,

TABLE 16.10

PHOTOSENSITIZED REACTIONS IN LIQUID MEDIA

Reaction	Sensitizer	Quantum Yield	Wave Length in Å.	Medium	Remarks
Maleic Ester→ Fumaric Ester...	Br_2	295 155	4360 5460	CCl_4	Large temperature coefficient.
$(COOH)_2 = CO + CO_2 + H_2O$....	UO_2^{--}	0.49–0.60	2540–4350	Water	0.05 M $(COOH)_2$ 0.01 M UO_2^{--}

$$x = I_{abs}k_l/k_d. \tag{16.14}$$

As already pointed out, k_l and k_d vary differently with temperature, k_l has a temperature-coefficient of 1.1 per 10° and k_d 2.8 per 10° C. The equilibrium concentration at a given intensity will therefore decrease in the ratio $\frac{1.1}{2.8}$ for a 10° rise in temperature. These conclusions were experimentally verified.

25. **Stationary State in Gas Reactions:** Coehn and his co-workers have investigated a number of cases of photo-equilibria in gaseous systems. The most thoroughly investigated is the photo-equilibrium in the reversible reaction

$$2SO_3 = 2SO_2 + O_2.$$

In this case, in quartz reaction vessels, neither reaction proceeds thermally at the temperatures employed. It was shown that the reaction was truly reversible in that the same stationary state was reached from both sides. The mass action law equation

$$K = \frac{[O_2][SO_2]^2}{[SO_3]^2}$$

was fulfilled in all cases with variable reactant ratios. The extent of displacement of the thermal equilibrium may be judged from the fact that at 45° C., at which temperature sulfur trioxide is practically undecomposed, as much as 35 per cent decomposition occurred under the given experimental conditions. With increasing intensity of illumination, the decomposition of the trioxide increased. With constant illumination, between reaction temperatures of 50 and 800° C., the photo-equilibrium is the same, independent of the gas temperature. This indicates that the temperature coefficient of the two photo-processes is the same, since the thermal reaction does not occur under the given conditions.

THE TEMPERATURE EFFECT IN PHOTOCHEMICAL CHANGE

The temperature coefficient of most photochemical reactions is small in comparison with coefficients of thermal reactions. Goldberg in 1903 first called attention to this fact. From the preceding analysis it can be seen that the effect of temperature may be exerted either in the primary absorption process or in the subsequent secondary chemical processes. These effects will be quite separate and distinct from one another.

26. **Temperature and the Primary Process:** In the primary absorption process the effect of rise in temperature will be exerted on the absorbing molecules. At high temperatures these will no longer necessarily be mainly in the lowest vibrational state but the higher states will be occupied by a certain fraction of the molecules. This fraction is given by the Boltzmann equation as $e^{-E/RT}$ where E is the energy of the state with reference to the lowest vibrational state as zero. These molecules in higher vibrational states can reach a given energy level in the upper electronic state by absorption of light longer in wave length than that required by molecules in the lowest vibrational state. This reveals itself therefore as a shift of the absorption spectrum to the red. The convergence limit of a band series starting from other than the lowest level may also be shifted to longer wave length. Hence, it may happen that absorption of a given wave length will produce only an excited molecule at room temperatures and dissociation in a continuum at high temperatures.

Transitions from the higher vibrational states conform to the Franck-Condon principle in the same manner as was already discussed for the normal vibrations. The electronic transitions will occur most frequently in the manner described by vertical lines on the curves of Fig. 16.2, page 474, from the extremities of a particular vibrational state. It will be obvious that there will be different transition probabilities from the various lower vibrational levels to a given upper level and this effect will also be included in the effect of temperature.

The effect of temperature on the primary absorption process must, from the considerations already advanced, be small since special spectral conditions must be present to secure the effect and since the temperature only changes the distribution of the molecules between vibrational states in the exponential manner already stated. Also, the effect of temperature will be dependent on the wave length of light employed. For some wave lengths the shift in vibrational level distribution will have negligible importance. For others it may mean the difference between activity and no activity.

27. **Temperature and the Secondary Process:** The influence of temperature on the secondary chemical processes is the normal influence of temperature in thermal processes. It can in no way be dependent on the wave length of light employed. The coefficients of such secondary processes will in general be small for one of two reasons. If they are reactions between molecules, occurring, as most photo-reactions are studied, in the neighborhood of room temperature, they must necessarily be processes of low activation energy. In photo-processes in which the primary absorption leads to dissociation the reaction constituents of the secondary processes include in general either atoms or free radicals. We have already seen (p. 413) that these react much more rapidly than molecules, with low activation energies. They will therefore show low temperature coefficients.

We have already discussed in detail one reaction, the photochemical combination of hydrogen and bromine where the temperature coefficient of one of the secondary processes $Br + H_2 = HBr + H$ is the rate-determining process. Also, in the hydrogen-chlorine reaction the secondary processes have all such small activation energies that a large number of such processes succeed the absorption act and give a very high quantum yield.

An abnormally high temperature coefficient of the photo-reaction may also be due to secondary processes which, with increase in temperature, give rise to a chain of reactions. This may be illustrated in the case of the decomposition of acetaldehyde. In the interval between room temperature and 100° C. the quantum yield does not differ markedly from 2. Between 100 and 300° C. the yield rises rapidly to 300, as found by Leermakers. This rise in yield is to be attributed to a chain reaction of decomposition of acetaldehyde, of low efficiency in the range to 0–100° C., due to the high activation energy of one or more of the steps, but becoming important in the range 100–300°. The yield below 100° C. is to be attributed to a true photo-decomposition not involving any chains.

Exercises (16)

1. Calculate the absorption coefficient of a gas which absorbs 80 per cent of the radiation traversing 10 cm. What length will be required to absorb 50 per cent?

2. Calculate the molar absorption coefficient of a solute which absorbs 20 per cent of the monochromatic radiation traversing 10 cm. of a 0.1 molar solution.

Assuming the applicability of Beer's law how much light would be absorbed in the same cell by a 0.2 molar solution?

3. Derive a relation between the einstein in kcal. per mole and wave length in Ångstrom units.

4. Determine the dependence of the rate of photolysis of an aldehyde on the intensity of the absorbed light assuming the sequence of reactions: (1) $RCHO + h\nu = R + HCO$, (2) $HCO = H + CO$, (3) $H + RCHO = H_2 + RCO$, (4) $RCO = R + CO$, (5) $R + RCHO = RH + RCO$ and (6) $2R = R_2$.

5. In the photolysis of uranyl oxalate at 2080 Å, 2.462×10^8 ergs absorbed by the solution caused the decomposition of 1.34×10^{19} molecules. Calculate the quantum yield.

6. Methyl bromide at a pressure of 67.2 mm. at 26° C. in a cell of length 2.70 cm. was exposed to 2537 Å radiation with initial intensity I_0 of 1.03×10^{18} quanta per sec. for 180 min. The bromine liberated required 0.2773 g. $Na_2S_2O_3$ solution containing 0.0091 milliequiv. per g. for titration. The extinction coefficient ϵ of methyl bromide is 1.26 where $I/I_0 = 10^{-\epsilon cl}$ where c is in moles per liter and l is in cm. Calculate the quantum yield on the basis of bromine atoms.

CHAPTER 17

COLLOID CHEMISTRY

COLLOID chemistry is a study of the physical and chemical phenomena associated with matter in a particular state or condition. Whereas chemistry is normally concerned with the behavior of individual atoms or molecules treated statistically, colloid chemistry is concerned with systems composed of aggregates of atoms or molecules in various media, gaseous, liquid or solid. Such systems are called colloidal systems. As examples we may cite: smoke, fog, gelatine solution, emulsions, gold sol and finely divided cadmium in solid cadmium chloride. The systems, it will be noted, are not restricted to liquid systems. With the broad concept of solutions outlined in Chapter 9, they may also be termed colloidal solutions.

It is impossible to distinguish sharply between true solutions and colloidal solutions unless we make use of the criterion that the former are completely stable systems while the latter are but metastable, although they may change very slowly indeed with time. The maximum and minimum size of the aggregate that determines the colloidal state cannot be given with definiteness. It depends on the nature of the aggregate. Certain complex dyes of large molecular weight exhibit many of the properties of the colloid particle although molecularly dispersed in solution. Aggregates varying in size between 1 $m\mu$ ($= 10^{-6}$ millimeter) and 200 $m\mu$ represent the normal limits in size. The aggregates in the solution are known as the *disperse phase,* while the medium in which they are dispersed is known as the *dispersion medium.* These correspond respectively to the solute and solvent in an ordinary solution.

1. **Historical:**[1] The science of colloid chemistry has developed consciously since the time of Graham's researches, 1861. Previous to this, certain colloid systems were known and their nature recognized. Gold tinctures were described in the eighteenth century and it was known that they were finely divided particles floating in the medium. Colloidal solutions of arsenic sulfide were known to Berzelius. Selmi, an Italian chemist, in 1843, studied colloidal solutions of sulfur, Prussian blue, casein and albumin. Graham, however, first defined the field by pointing out that colloids did not diffuse through membranes and only very slowly in free diffusion as contrasted with molecularly dispersed solutes, Graham's crystalloids, which diffused through membranes and relatively

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[1] Svedberg, *Colloid Chemistry,* Chemical Catalog Co., New York, 1924.

rapidly in liquid media. To the method of separation by diffusion through membranes Graham gave the name *dialysis*. He also introduced the term *sol* for a colloidal solution and *gel* for the product formed by the setting of such a solution. We now know that the properties of a gel are dependent on the structure which the aggregates assume, so that structure becomes one of the important objectives of colloid study.

Faraday showed (1857) that in a gold sol, the particles could be rendered evident by focussing the sun's rays on the fluid, the light they reflected indicating their presence, as it was gold in color. He also investigated the properties of ruby glass showing there, also, the presence of gold particles. Tyndall (1869) followed up the work of Faraday by demonstrating that the scattered light was polarized.

The English botanist, Robert Brown, had shown, in 1827, that particles visible in the microscope showed irregular motions when suspended in a fluid medium. The production of the ultramicroscope by Siedentopf and Zsigmondy (1903) permitted the observation of ultramicroscopic particles and the much livelier Brownian motion they display. The ultramicroscope is nothing more than the microscope applied to the Faraday-Tyndall cone of light in a colloid medium. A fine and intense beam of light is concentrated by a lens system on the colloidal solution, the beam being observed at right angles by a microscope. Through this the observer sees the diffraction image or the light scattered by the particle.

2. **The Formation of the Colloid Particle:** This disperse phase in a colloid system can be produced in two ways: (*a*) by subdivision of coarser material or (*b*) by aggregation of atoms or molecules. These are known respectively as dispersion and condensation methods. The use of atomizers in the spraying of paints and lacquers and in the Schoop process of sputtering molten metals are important technical examples of dispersion in gases. Quite recently, dispersion in liquid media by mechanical grinding, in specially designed high speed mills, as, for example, the Plauson mill, has attained considerable technical significance. Earlier efforts in this direction failed owing to coalescence or coagulation of the particles produced. The addition of various substances to such suspensions can be employed to prevent such coagulation. Emulsions, dispersions of one liquid in another, can also be secured by such means; the agent added to stabilize the emulsion is known as the emulsifying agent.

3. **Condensation in Gases:** Condensation methods are important in the preparation of the colloid particle. They depend on the production of supersaturation in the medium and on the presence of nuclei as starting points for the condensation. Particle size will be dependent on the degree of supersaturation and the rate of formation of the particle. Films of condensed metal vapors belong to this class and it is significant that the high-boiling metals, such as tungsten, give the finest-grained structure.

Electrons, ions, and dust particles may serve as nuclei for the condensation process as illustrated in the formation of clouds and fogs in the experiments of C. T. R. Wilson (Chapter 1, page 13). The formation of colloids by the various electric arc processes are also condensation methods. This method of preparing colloids in liquid media was devised by Bredig in 1898. It consists in producing an arc between two electrodes immersed in a suitable liquid. The method was greatly improved and extended by Svedberg who studied the relative effects of direct and alternating currents on the colloid produced. He found that a higher degree of dispersion and of purity in the sols could be attained with an oscillatory current in place of a direct current arc. With the latter there is a much greater decomposition of the medium in which the arc is struck.

4. **Condensation in Liquids:** Both physical and chemical methods are employed in the preparation of colloid systems by condensation in liquid media. Sudden cooling of saturated solutions may be employed, or the addition of a true solution in one solvent to another medium in which the solute is little soluble. Sulfur sol may thus be prepared by the addition of an alcoholic solution of sulfur to water.

The most important processes are based however on chemical reactions and they may be classified by the nature of the reaction. Reduction, oxidation, dissociation, hydrolysis, and metathesis are all used in colloid formation. The reduction of gold chloride to metallic gold by several reducing agents (hydrogen peroxide, alkaline formaldehyde, hydrazine hydrochloride, etc.) is probably the most important and most comprehensively studied. Colloidal silver and silver mirrors thus prepared rank next. As examples of oxidation we may cite the oxidation of hydrogen sulfide and selenide to form the corresponding sulfur and selenium sols. Colloidal nickel is formed by dissociation of nickel carbonyl in various organic solvents, especially benzene. The action of cathode rays and radioactive rays in producing colored salts, e.g., blue rock salt, is another method of producing colloid systems by dissociation. The production of the latent image in photographic emulsions is the most important practical example of a dissociation process. Hydrolysis of salts is a common method of production of colloidal hydrous oxides. Of metathetical processes, Linder and Picton's studies of arsenious sulfide sols are a good example. From arsenious acid solutions with the aid of hydrogen sulfide these authors were able to get sols of arsenic sulfide of varying capacity. The formation of barium sulfate sols from solutions of barium thiocyanate and ammonium sulfate constitutes another example. Polymerization processes, for example, of styrene, vinyl esters, acrylic acid esters, butadiene, chloroprene are being increasingly used in industry to produce high molecular weight particles, colloidal in nature, suitable for the preparation of artificial gums, resins, varnishes and rubber-like materials.

KINETIC THEORY AND THE COLLOID PARTICLE

The discovery, with the aid of the ultramicroscope, that colloid particles possess a very marked Brownian motion led to the application of the concepts of the molecular kinetic theory to the colloid particle as a unit in motion. In this development the initiative is due to Einstein (1905) and Smoluchowski (1906). The fundamental idea in this development is that the kinetic energy of the colloid particle suspended in a liquid or a gas is the same as that of a dissolved molecule, namely $3/2\ (RT/N)$, where N is the Avogadro Number, the number of molecules in a gram molecule and R is the gas constant. Upon this basis it is to be expected that the colloid particles should manifest the properties which we have already noted the dissolved molecules to possess. We shall examine this idea in reference to two properties: (*a*) osmotic pressure and (*b*) the diffusion of colloid particles.

5. **Osmotic Pressure of Colloidal Solutions:** For a molecularly dispersed solute van't Hoff deduced, by analogy with the equations of the kinetic theory of gases, that the osmotic pressure, P, of a dissolved solute was given by the equation

$$P = cRT, \tag{17.1}$$

where c is expressed in moles per liter.

On the same basis, in a colloidal solution, we should expect an osmotic pressure,

$$P = \frac{RT}{N} n, \tag{17.2}$$

where n is the number of particles per unit volume and $c = n/N$. It is difficult to verify such an expression for a colloid solution because the value of n is so exceedingly low as compared with the corresponding number in a molecularly dispersed solute. Thus, 1 $m\mu$ represents a lower limit of size for observation purposes, and, with a feasible concentration of colloid, for example, 0.5 per cent, the calculated value for the osmotic pressure is only 1–2 mm. of water pressure. Zsigmondy claims to have measured osmotic pressures in certain gold sols and has computed from the measurements reasonable values for the particle size; but it is difficult to be sure of the results, since small amounts of dissolved impurities would easily exercise osmotic effects of this magnitude. A much more exact technique would be needed before this deduction could be decisively established experimentally.

6. **The Donnan Theory of Membrane Equilibria:** The measurement of osmotic pressure in colloidal solutions is complicated by the fact that the stability of such solutions often depends upon the presence of suitable electrolytes and, if the colloid functions as a colloidal electrolyte, effects first examined by Donnan in 1911 arise. We can illustrate these effects

by examining the membrane equilibria in the case of a solution of two ionized uni-univalent electrolytes with a diffusible common ion separated by a membrane impermeable to one non-common ion. We may illustrate the condition thus

$$\begin{array}{ccc} \text{I} & \vdots & \text{II} \\ H_2O\ Na^+\genfrac{}{}{0pt}{}{X^-}{Cl^-} & \vdots & Cl^-Na^+H_2O \end{array}$$

At equilibrium, thermodynamics demands that the activities satisfy the equations:

$$a^{\text{I}}_{H_2O} = a^{\text{II}}_{H_2O};\ a^{\text{I}}_{NaCl} = a^{\text{II}}_{NaCl} = a^{\text{I}}_{Na^+} \times a^{\text{I}}_{Cl^-} = a^{\text{II}}_{Na^+} \times a^{\text{II}}_{Cl^-}.$$

For dilute solutions, and complete dissociation, we may use concentrations as a first approximation and obtain

$$c^{\text{I}}_{Na^+} \times c^{\text{I}}_{Cl^-} = c^{\text{II}}_{Na^+} \times c^{\text{II}}_{Cl^-}. \qquad (17.3)$$

Since the solutions must also be electrically neutral

$$c^{\text{I}}_{Na^+} = c^{\text{I}}_{Cl^-} + c^{\text{I}}_{X^-} \qquad \text{and} \qquad c^{\text{II}}_{Na^+} = c^{\text{II}}_{Cl^-}. \qquad (17.4)$$

Combining these last two equations, we obtain

$$\left(\frac{c^{\text{II}}_{NaCl}}{c^{\text{I}}_{NaCl}}\right)^2 = 1 + \frac{c^{\text{I}}_{NaX}}{c^{\text{I}}_{NaCl}}. \qquad (17.5)$$

From this equation it is seen that the presence of the non-diffusible ion X^- leads to an unequal distribution of the diffusible ions. The ratios of salt concentrations calculable from such an equation due to varying concentrations of NaX are shown in the following Table 17.1.

TABLE 17.1

DISTRIBUTION RATIO OF SALT CONCENTRATIONS IN MEMBRANE EQUILIBRIA WITH IDEAL SOLUTIONS DUE TO A NON-DIFFUSIBLE ION

Ratio of NaCl in II to that in I for

c^{I}_{NaX} / c^{I}_{NaCl}	0.001	0.01	0.1	1.0
0.001	1.42	3.32	10.05	31.64
0.01	1.05	1.42	3.32	10.05
0.1	1.005	1.05	1.42	3.32
1.0	1.0005	1.005	1.05	1.42

The different salt concentrations on each side of the membrane give rise to "membrane potentials" corresponding to those in concentration cells, the potentials of which are expressible by the equation,

$$\mathrm{E} = -\frac{RT}{\mathrm{F}} \ln \frac{c^{\mathrm{I}}_{\mathrm{Na}^+}}{c^{\mathrm{II}}_{\mathrm{Na}^+}} = -\frac{RT}{\mathrm{F}} \ln \frac{c^{\mathrm{II}}_{\mathrm{Cl}^-}}{c^{\mathrm{I}}_{\mathrm{Cl}^-}} \,. \tag{17.6}$$

There is a corresponding osmotic pressure difference in the two compartments which may be stated in terms of the anions by the expression,

$$\frac{P'}{RT} = 2c^{\mathrm{I}}_{\mathrm{Cl}^-} - 2c^{\mathrm{II}}_{\mathrm{Cl}^-} + 2c^{\mathrm{I}}_{\mathrm{X}^-} \,. \tag{17.7}$$

The osmotic pressure P_0 due to the non-diffusible electrolyte is given by

$$\frac{P_0}{RT} = 2c^{\mathrm{I}}_{\mathrm{X}^-} \,, \tag{17.8}$$

which, by combination with the preceding relations, gives

$$P_0 = P'\left(1 + \frac{c^{\mathrm{I}}_{\mathrm{NaCl}}}{c^{\mathrm{II}}_{\mathrm{NaCl}}}\right) \,. \tag{17.9}$$

The two values of the osmotic pressure thus become equal only when the salt concentration is very low relative to the colloidal salt since, as the previous table shows, the salt ratio then becomes negligible compared to unity. Since aqueous colloidal solutions often function as non-diffusible electrolytes the Donnan theory assumes considerable importance, especially in biochemical systems as emphasized by Loeb, Northrop and others. Tests by Donnan and by these investigators in relatively simple systems served to confirm the approximate validity of the theory.

Donnan effects occur in systems where permeable membranes are not present whenever diffusion of a positive or negative component is occurring in the presence of free ions in an enclosed space. The sedimentation of colloidal electrolytes in ionic media gives rise to non-uniform distribution of ions. In gels the framework may function as a colloidal ion and as a membrane. Procter and Wilson applied the Donnan theory to this latter case in their studies of the swelling of gelatine in the presence of electrolytes. The combination of specific ions with the colloid and the prevention of diffusion of the product from the gel lead to an accumulation of diffusible ions and a greater osmotic pressure within the gel. Osmosis into the gel occurs until the elasticity of the gel balances the difference in osmotic pressures. The Donnan effect is superimposed on the swelling which occurs at the iso-electric point.

7. Diffusion of Colloid Particles: The Brownian motion of the colloid particles will evidently produce diffusion, in the same manner that diffusion in gases and liquids is produced by molecular motion. As the particles are more massive and their velocity consequently smaller than that of molecules, the actual velocity of diffusion will be slow. The amount of material, D, diffusing across an imaginary boundary in the solution in unit time is,

$$D = \frac{RT}{N \cdot 6\pi\eta r}, \tag{17.10}$$

where the quantity $6\pi\eta r$ is the frictional resistance that applies to a moving particle of radius, r, in a medium of viscosity, η. This equation may also be written in the form,

$$\Delta^2 = \frac{RTt}{3N\pi\eta r}, \tag{17.11}$$

where $D = \Delta^2/2t$ and Δ is the mean horizontal displacement of a particle in the time, t. Both of these equations can be used to determine either the particle size (r) assuming a value for N, Avogadro's number, or, alternatively, the value of the Avogadro number with particles of a given size. Numerous tests of these formulas have been made. Perrin used colloidal solutions of gamboge and mastic in a test of equation (17.11). He used particle sizes varying in the ratio 1 : 15000 and observed the displacements they exhibited in solutions of varying viscosities. He concluded from his experiments that the most reliable value for N was 6.9×10^{23}. Svedberg carried out experiments on gold sols of known radius of particles. From an experimentally determined particle radius of 1.33 $m\mu$ and the observed diffusion constant, Svedberg deduced a value for $N = 5.8 \times 10^{23}$. More recently Nordlund, in Svedberg's laboratory, has studied colloidal solutions of mercury in which spherical particles are more readily obtained. His mean value was 5.91×10^{23}.

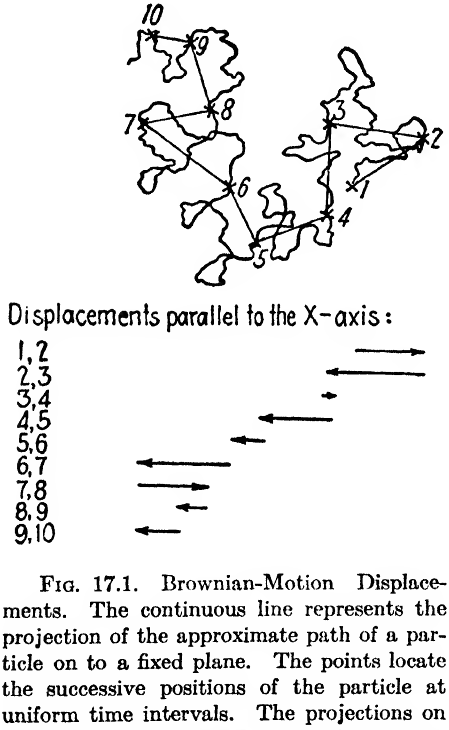


FIG. 17.1. Brownian-Motion Displacements. The continuous line represents the projection of the approximate path of a particle on to a fixed plane. The points locate the successive positions of the particle at uniform time intervals. The projections on the X-axis of the straight lines joining the successive points measure the separate displacements, indicated by Δ.

8. Sedimentation of Colloid Particles: The action of gravity on the colloid particles in a given medium, tending to draw the particles to the bottom of the medium, is opposed by the Brownian motion of the particles, tending to distribute them throughout the liquid. Eventually, these forces balance and an equilibrium is established. In this state, the concentration of particles is greatest at the bottom of the vessel and becomes less with increasing height. The phenomenon is entirely analogous to the variation in gas density or pressure at various levels in a long column of gas as a result of gravitational forces. (Cf. Chap. 3, 10.) The number of molecules n, is related to the number, n_o at a distance, h, below, by the equation,

$$h = \frac{RT}{Mg} \ln \frac{n_o}{n}, \tag{17.12}$$

where g is the gravitational attraction and M the molecular weight of the gas. This we may set equal to Nm where m is the mass of a molecule. Transposing this to the case of colloid systems we can substitute for the mass of the colloid particle, m_c,

$$m_c = 4\pi r^3(d - d_m)/3, \tag{17.13}$$

where d is the density of the particle of radius r and d_m is the density of the medium. The expression for h in the colloid system then becomes

$$h = \frac{3RT}{4\pi r^3(d - d_m)Ng} \ln \frac{n_o}{n} \cdot \tag{17.14}$$

It is evident from this equation that the greater the particle size the greater the value of n_o/n or the greater the concentration differences in a column of colloidal solution. It will be noted that the particle size enters into the expression as the cube of the radius. This spread in concentration may be illustrated by a calculation from the equation assuming particles 10 $m\mu$ in diameter in a colloidal gold solution. At a distance of 10 cm. from the bottom the solution should contain a number of particles per unit volume only one tenth of that present in the bottom layer. However, no such differences are ever observed because of the slow rate of settling of such particles, it being calculable by Stokes's law that gold particles of such size would require 290 days to settle a distance of 10 cm. (See next section.)

Perrin tested the above equation with a gamboge suspension over a height $h = 100\ \mu$ obtaining fair agreement with observations. Westgren made similar observations with gold sols over $1000\ \mu = (1$ mm.), and obtained even better agreement. The observations of n at different heights can also be used to evaluate N. Westgren's determinations gave a value of 6.05×10^{23}.

Some of Westgren's data are given in the following table.

TABLE 17.2

SEDIMENTATION EQUILIBRIUM IN A GOLD SOL ($r = 21$)

h in μ	0	100	200	300	400	600	800	1000	1100
n obs	889	692	572	426	357	217	152	108	78
n calc	886	712	572	460	369	239	154	100	80

9. **Velocity of Sedimentation and the Ultra-Centrifuge:** The velocity of sedimentation of a colloidal particle can be obtained by equating the product of the velocity u and the frictional resistance offered by the liquid medium to the moving particle assumed spherical, i.e., $6\pi\eta r$, to the force of gravity acting on the sphere, $4\pi r^3 g(\rho_p - \rho_m)/3$,

$$6\pi\eta r u = 4\pi r^3 g(\rho_p - \rho_m)/3, \qquad (17.15)$$

where ρ_p and ρ_m are the densities of particle and medium respectively, g is the acceleration of gravity, η is the viscosity of the medium. Hence,

$$u = \frac{2r^2 g(\rho_p - \rho_m)}{9\eta} \,. \qquad (17.16)$$

It is evident that the smaller is r, the slower the velocity of the sedimentation process. The following Table 17.3 gives the rate of sedimentation of gold particles and benzene spheres in water calculated with the aid of equation (17.16) for different particle sizes.

TABLE 17.3

TIME OF SEDIMENTATION PER CENTIMETER IN WATER

Radius	Gold Spheres	Benzene Spheres
0.1 mm.	2.5 sec.	6.3 min.
1μ	4.2 min.	10.6 hr. (Homogenized Emulsion)
100 $m\mu$	7 hr.	4.4 days
10 $m\mu$	29 days	12 yr.
1.5 $m\mu$	3.5 yr. (Faraday sol)	540 yr.

It is the slowness of these velocities of sedimentation which caused the sedimentation equilibrium to be the object of experiment. For a given particle size the velocity can be increased by increasing the effect of gravity and this is accomplished by the use of centrifuges, as developed recently so brilliantly by Svedberg and his co-workers. Ultra-centrifuges have now been developed in which the centrifugal forces are equivalent to 900,000 times gravity. Such machines are driven by high pressure oil turbines mounted directly on the rotor shaft. Great care is taken to eliminate vibration and temperature inequalities. Gas friction on the rotor is reduced and heat interchange is facilitated by the use of a hydrogen atmosphere in the housing at pressures of about 15 mm. for the larger centrifuges where the velocity may rise to 44,000 r.p.m.

The rotating cell and its contents can be observed continuously through the windows during the operation. In quantitative work the cell may be photographed by transmitted light, the extent of light absorption being a measure of the concentration of the disperse phase. With quartz cells and windows, ultraviolet light $\lambda = 2536.7$ Å has been used. More recently, a photographic, refractive-index method has been devised for recording concentration gradients. As example of the orders of magnitude of the observations we may cite the case of haemoglobin which, at 38,750 r.p.m. (85,000 *g.*), had a velocity of sedimentation of 1.7 mm. per hour. Sedimentation equilibrium can also be established. For example, in a 5.6 mm. column of 1.1 per cent egg albumin, sedimentation equilibrium was attained in less than 60 hours at 10,700 r.p.m. (5900 *g.*). The sedimentation-velocity method gives a more accurate estimate of the size distribution. The equation connecting velocity of sedimentation and ω, the angular velocity, is

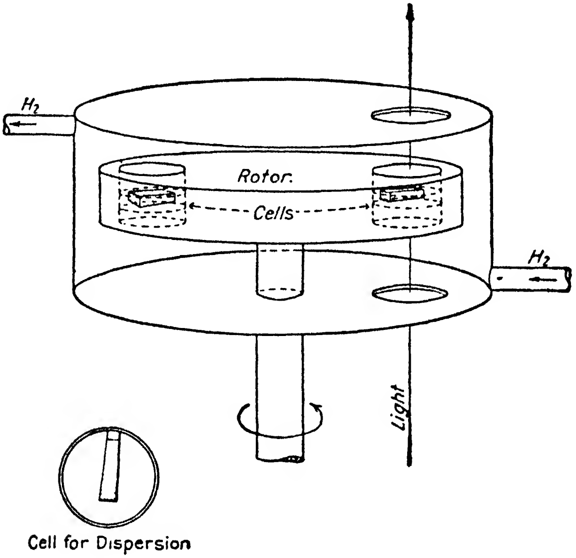


FIG. 17.2. Schematic Diagram of Ultra-centrifuge

$$\frac{\ln x_2/x_1}{t_2 - t_1} = \frac{2r^2(\rho_p - \rho_m)\omega}{9\eta}, \tag{17.17}$$

where x_2 and x_1 are the distances of the particle from the axis of rotation at times t_2 and t_1. The sedimentation equilibrium equation resembles that under the influence of gravity and has the form

$$\ln \frac{c_0}{c} = \frac{2RT}{N} \cdot \frac{1}{m\omega^2(x_0^2 - x^2)} \tag{17.18}$$

where c_0 and c represent the relative concentrations at distances x_0 and x from the axis of rotation.

Svedberg has applied these methods to the determination of particle size in a comprehensive group of proteins. Some typical results are shown in Table 17.4. The measurements reveal that many proteins, after suitable purification, are uniform in size, suggesting that they are chemically identical single molecules of high molecular weight. The accuracy of the determinations by the several methods is within 5 per cent. The data in the table suggest that several proteins are multiples of a unit with a molecular weight of 34,500.

TABLE 17.4

MOLECULAR WEIGHTS AND PARTICLE SIZES IN PROTEIN SOLUTIONS

Substance	Radius in mμ by Sedimentation	Molecular Weight by	
		Sedimentation	Sedimentation Equilibrium
Egg albumin	2.18	34,500	34,500
Bence-Jones protein	2.18	....	35,000
Haemoglobin	2.44	68,000	66,800
Serum albumin	2.39	67,000	68,000
Serum globulin	2.75	104,000	103,000
Phycocyan	2.76	105,000	106,000
Phycoerythrin	3.93	214,000	213,000
Edestin	4.16	215,000	208,000
Amandin	3.89	....	208,000
Excelsin	3.93	....	212,000
Limulus-haemocyanin	6.96	2×10^6	$0.3\text{–}1.9\times10^6$
Helix-haemocyanin	12.00	4.9×10^6	5×10^6

Different forms of centrifuges have been developed in this country notably those permitting continuous-flow concentration, due to Beams, and directly air-driven transparent small ultra-centrifuges developed by McBain. These latter have advantages on the score of expense and yet are capable of giving accurate results with proteins as small as egg albumin.

The Properties of the Colloid System

We may now consider some of the properties of the colloid particle which are dependent in part on the medium in which the particle exists. This leads to a discussion of adsorption, the electrical properties of the particle, cataphoresis and electro-endosmosis, as well as to the problems of structure involved in gels, emulsions and the like.

10. **Adsorption:** As already discussed in Chapter 15, adsorption consists in a concentration at a surface of the gaseous or dissolved material of the medium surrounding the surface. It was discovered by Scheele, in 1777, who observed that charcoal had the capacity to concentrate various gases on its surface. The same phenomenon with dissolved substances was demonstrated by Lowitz in 1791.

The phenomenon undoubtedly arises, in the case of plane surfaces, from the unsaturation which is always present at such surfaces. In the case of liquids we have already noted one of the effects of such unsaturation in the surface tension of liquids. In the case of solid surfaces, the forces operative there are the same forces which produce growth of crystals in a supersaturated solution. In the last analysis, such forces arise from the electrical nature of the atomic constituents of both the adsorbing surface and the adsorbed atoms or molecules. We may therefore expect in the first place to find attractions at surfaces similar to those which are involved in gaseous systems and which lead to deviations from the ideal gas laws, that is, effects due to van der Waals forces. Also, we may expect effects at surfaces due to forces identical with those involved in compound formation, differing only in degree. We have seen that such chemical reactions require, in general, an activation energy which may vary from low to quite considerable values and specific for each reaction. Similarly, for the adsorption processes which are akin to such chemical reactions, we may also expect characteristic activation energies. It is for this reason that H. S. Taylor suggested that such adsorption might be termed "*activated adsorption.*" It has also been termed '*chemisorption.*' The adsorption due to forces of the van der Waals type may be termed *van der Waals* or *physical adsorption.* The velocity of such is immeasurably rapid; there is little or no activation energy. The molecular identity of the adsorbed substance is not altered by van der Waals adsorption. The identity of the adsorbed substance in activated adsorption is merged in that of the surface complex which partakes of the nature of a chemical compound, with definite breaking and making of chemical bonds accompanying its formation.

In the general phenomenon of adsorption there is also included a third type of condensation on surfaces, due to capillarity. In the fine pores of a solid, gases may condense to the liquid state at pressures below those at which the gas liquefies in the free state. Porous materials such as charcoal, silica gel and the like show considerable capacity thus to concentrate gases. The phenomenon is entirely analogous to the phenomenon of condensation to the liquid state; it is not specific or dependent on the chemical characteristics of the adsorbent but is a function of pore size and pore size distribution.

11. **Adsorption of Gases by Solids:** We have already discussed in Chapter 15 the relations obtaining in the case of adsorption by plane surfaces, the theory of which has been given by Langmuir. In this case, the extent of adsorption is proportional to the gas pressure when the surface is relatively bare, and is independent of the pressure when the surface is covered (saturation). In the intermediate region, the empirical formula examined by Freundlich

$$x/m = kp^{1/n}, \tag{17.19}$$

gives x the amount adsorbed by a mass, m, at a pressure, p, where n is an integer. It will be noted that, if the surface is bare, $n = 1$; at saturation, $n = \infty$, so that $x/m = k$. On Langmuir's view, adsorption is the resultant of a time-lag occurring between the condensation of a gas molecule on the surface and its subsequent evaporation.

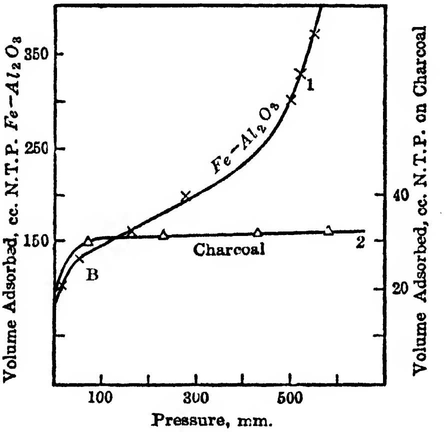


FIG. 17.3. Adsorption of N_2 at 77.2° on Charcoal and Fe-Al_2O_3 Catalysts

A method developed by Emmett and Brunauer for measuring the surface areas of catalysts and finely divided or porous materials depends on the adsorption of gases and is instructive with regard to the nature of the adsorption layer on such solid substances. The principle of the method depends on the determination of the volume of some gas, generally nitrogen, required to form a monolayer of physical adsorption over the entire surface of the material. The total area can be calculated by multiplying the cross-sectional area of each adsorbed molecule by the number of molecules in the monolayer.

The method may be illustrated by the isotherm shown in Curve 1, Fig. 17.3 for the adsorption of nitrogen on an iron synthetic-ammonia catalyst at 77° K. The S-shaped isotherm is typical for a variety of gases adsorbed near their boiling points on a variety of surfaces, including oxide and metal catalysts, finely divided salts, pigment, gels, catalyst supports, soil colloids and powdered bacteria. Only on charcoal have isotherms corresponding to the Langmuir treatment, with saturation adsorption, been obtained (Curve 2). Various lines of evidence including measurements with different gases lead to the conclusion that point B, the beginning of the approximately linear portion of the isotherm, marks the completion of the monolayer and the beginning of a second, or multilayers of adsorbed gas. Typical values of v_m, the volume in cc. per gram for a monolayer, are given in Table 17.5.

TABLE 17.5

VALUES OF v_m OBTAINED BY ADSORPTION OF NITROGEN AT 90.1° K.

Substance	v_m	Substance	v_m
Unpromoted Fe catalyst, 973.2	0.29	Fused Cu catalyst	0.05
Fe-Al_2O_3 catalyst, 954	2.86	Cr_2O_3 gel	53.3
Fe-Al_2O_3-K_2O catalyst, 931	0.81	Cr_2O_3 'glowed' gel	6.1
Fe-K_2O catalyst, 930	0.14	Silica gel	116.2

The values in Table 17.5 are calculated from an isotherm equation developed by Brunauer, Emmett and Teller to account for the experimental data on adsorption. The values agree closely with the B-point values obtained from the isotherms. The isotherm equation has the form

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \cdot \frac{p}{p_0}, \tag{17.20}$$

where v is the volume adsorbed at pressure p and absolute temperature T; p_0 is the vapor pressure of the gas at the same temperature, v_m is the volume of the adsorbed monolayer and c is approximately equal to $e^{-(E_1 - E_L)/RT}$ where E_1 is the heat of adsorption of the monolayer, E_L is the heat of liquefaction. A plot of $p/v(p_0 - p)$ against p/p_0 gives a straight line whose slope and intercept give the values of v_m and c.

If adsorption is restricted to n layers at saturation the expression has the form

$$v = \frac{v_m cx}{1 - x} \cdot \frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (c - 1)x - cx^{n+1}} \tag{17.21}$$

where $x = p/p_0$, and the capillaries are assumed to have plane parallel sides which can hold n layers of adsorbed gas. Equation (17.21) reduces to (17.20) when $n = \infty$. When $n = 1$, i.e., the condition examined in the Langmuir equation, the expression becomes

$$p/v = p_0/cv_m + p/v_m \tag{17.22}$$

identical with that deduced by Langmuir. Brunauer, Deming, Deming and Teller have shown that these equations can be extended to interpret all the five types of adsorption isotherm hitherto found with different gases and surfaces. These are shown schematically in Fig. 17.4. The abscissas represent pressures up to the saturation pressure, p_0 (dotted line). The ordinates represent amounts adsorbed. Type I is the Langmuir type (Curve 2, Fig. 17.3). Type II is that obtained with adsorption of nitrogen and many gases on surfaces (Curve 1, Fig. 17.3). Reyerson and Cameron found Type III for the adsorption of bromine and iodine on silica gel. In Type III, E_1 is equal to or somewhat less than E_L. Types IV and V suggest the almost complete filling of the pores of the adsorbent at pressures lower than the vapor pressure of the gas.

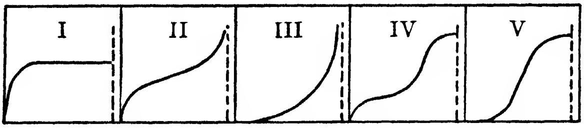


FIG. 17.4. The Five Types of van der Waals, Physical Adsorption Isotherms

The heats of adsorption in multilayers do not greatly differ from the heats of liquefaction but they may be greater (Type II and IV) or less (Types III and V). Heats of activated adsorption or chemisorption are generally much greater, of the order of magnitude of chemical reactions. Thus, the heats of activated adsorption of hydrogen and carbon monoxide on copper are respectively 10 and 30 kcal. whereas the heats of liquefaction are 0.5 and 1.8 kcal.

12. **Adsorption from Solutions:** In the case of solutions, there is the possibility of one or other or both constituents being adsorbed. If the solute alone is adsorbed the solution becomes more dilute. This is spoken of as positive adsorption. If the solvent is adsorbed and not the solute, the solution will become more concentrated. This phenomenon has received the unfortunate term, negative adsorption. When both are adsorbed it will depend on the relative extent of adsorption whether positive or negative adsorption is shown. Freundlich showed that the adsorption isotherm applied also in the case of solutions as illustrated in the following table.

TABLE 17.6

ADSORPTION OF ACETIC ACID ON CHARCOAL

$x = 2.606 \cdot c^{0.425}$.

c	0.00092	0.00259	0.00669	0.01708	0.02975
x obs	2.07	3.10	4.27	5.44	6.80
x calc	2.19	3.01	4.15	5.73	6.87

Even in these cases, however, when followed to high concentrations of acid, saturation values of x are reached, where the Freundlich equation no longer is applicable.

In solutions, there is an additional factor of interest which arises when the solute is an electrolyte and therefore present in the ionized condition. The ions may or may not be adsorbed to equal extents. The result of unequal adsorption will be that the adsorbent will acquire the electric charge of the ion most strongly adsorbed. Adsorbents composed of salts, such as silver halides, tend to adsorb the common ion most strongly. Thus, silver iodide adsorbs the iodide ion more strongly than the cation in solutions of iodides, thereby becoming negatively charged. In silver salt solutions, on the other hand, it adsorbs the silver ion more strongly and thus acquires a net positive charge. Adsorption of this type has long been familiar to analytical chemists in the retention of electrolytes by precipitates. By studying the adsorption of radioactive lead salts (thorium-B salts) on lead sulfate crystals, determining the distribution of the activity between solution and precipitate, and the number of lead ions per unit area of surface, Paneth and Vorwerk calculated the total surface area of the adsorbent, and confirmed their result by obtaining constant values of the area with different concentrations of thorium-B in the solutions. The adsorbed thorium-B ions were shown to occupy the positions of lead ions in the surface of the lattice. The determinations of surface area were checked also in several cases by measurements of the adsorption of suitable dyestuffs.

On non-ionic adsorbents such as charcoal the adsorption of electrolytes was early found to be small. Oden showed that the ash-constituents of the charcoal might be responsible for much of this. More recently, adsorption by relatively ash-free charcoals has been studied by Bartell and his co-workers and by Frumkin. The latter showed that adsorbed gas on charcoal influences its adsorptive capacity. It is now certain that ash-free, gas-free charcoal adsorbs negligible amounts of either strong acids or strong bases. It is also known that charcoal, which adsorbs oxygen by van der Waals forces at liquid air temperatures, shows activated adsorption of oxygen at room temperatures. The former is readily reversible by evacuation; the latter is a very strong union and when destroyed by heat and evacuation causes the evolution of carbon monoxide and dioxide. Charcoal saturated with oxygen at room temperatures adsorbs strong acids positively and strong bases negatively. Carbon shows activated adsorption of hydrogen at somewhat higher temperatures. A charcoal so charged with hydrogen adsorbs strong bases but not acids. Charcoals laden with gas effect hydrolysis of solutions of strong electrolytes, adsorbing the hydrolyzed acid or base dependent on the gas layer on the surface.

13. **Adsorption and Surface Tension:** We can relate the concentration in the surface layer with the interfacial tension at the surface by means of a mathematical deduction due to J. Willard Gibbs. Let the solution of surface, s, have an interfacial tension, γ, when one mole of solute in

excess of that in the solution is present in the surface and let the tension diminish by $d\gamma$ when an additional small amount of solute enters the surface. The energy change involved will be $sd\gamma$. The energy liberated is equal to the osmotic work involved in removing this solute from the solution. This latter is $-vdP$ where v is the volume of solution containing 1 mole of solute and dP is the change in osmotic pressure due to the removal of the solute. Hence,

$$sd\gamma = -vdP. \tag{17.23}$$

Assuming the laws of dilute solutions, $Pv = RT$

$$sd\gamma = -\frac{RT}{P}dP, \tag{17.24}$$

or,

$$\frac{d\gamma}{dP} = \frac{RT}{Ps}, \tag{17.25}$$

or, in terms of concentration,

$$\frac{d\gamma}{dc} = -\frac{RT}{cs}, \tag{17.26}$$

or, for unit surface, where u is the excess of solute and equal to $1/s$,

$$u = -\frac{c}{RT}\frac{d\gamma}{dc}. \tag{17.27}$$

This equation of Gibbs tells us that, if the interfacial tension increases with increasing concentration, u will be negative and the surface will contain less solute than the solution. This is negative adsorption. Positive adsorption will occur when γ decreases with increasing concentration. With $d\gamma/dc$ equal to zero the concentration in the surface will be identical with that in the bulk of the solution.

The experimental investigation of this equation was first made by Donnan and Lewis and subsequently by Donnan and Barker. The experimental results showed satisfactory agreement between observed and calculated values so far as order of magnitude is concerned. The systems studied included caffeine on mercury surfaces, nonylic acid and saponin at air-liquid interfaces.

More accurate tests of the Gibbs equation have been undertaken also by Harkins and by McBain. Two methods have been used. The one attempts to determine the concentration of dissolved solute in the surfaces of bubbles which have passed through solutions of known concentrations of solute. McBain has also attempted to shear a layer from the surface of a large trough of liquid solution and determine its concentration. The observed values are definitely greater than those theoretically deduced but parallel them. The correct explanation for the discrepancy is still a matter for discussion.

Most inorganic salts when dissolved in water increase the surface tension of water. Their concentration in the surface layer is less than that in the bulk solution (negative adsorption). A wide variety of organic solutes lowers the surface tension of water to a marked extent and the solutes therefore concentrate in the surface layer, the more the greater the lowering of surface tension, as the Gibbs equation requires.

14. **Surface Energy of Small Particles:** The relation between the vapor pressure of a small particle of liquid and that of a liquid at a plane surface is given by the equation, due to Lord Kelvin,

$$\Delta F = RT \ln \frac{p}{p_A} = \frac{2\gamma v}{r} \tag{17.28}$$

where p is the vapor pressure of the particle of radius r, p_A that of the liquid in bulk ($r = \infty$), γ is the surface tension and v the molal volume. It is here assumed that the gas laws are applicable to both vapors. This means that the vapor pressure increases rapidly as the radius of the particle diminishes and this conclusion with respect to vapor pressure is applicable alike to the free energy of the particle. It holds likewise for solids as well as liquids.

Evidence for this increase in free energy with subdivision of particle size was obtained by Hulett, who showed that fine particles of barium sulfate and gypsum possessed markedly higher solubilities than coarse particles. Changing gypsum crystals from 2 μ to 0.3 μ caused an increase in solubility of nearly 20 per cent. A coarsely crystalline barium sulfate (1.8 μ) was soluble to the extent of 2.29 mg. per liter at 25° C. At 0.1 μ the solubility had risen to 4.5 mg. per liter. Lipsett, Johnson and Maass attempted to obtain a quantitative measure of the change in surface energy. They measured the heat of solution of finely divided and coarsely crystalline sodium chloride. They find that a mole of sodium chloride having a total surface of 1.25×10^6 sq. cm. has an amount of energy equivalent to 12.3 cal. bound up in its surface, which indicates a surface energy of 400 ergs per square cm. at 25° C. This can only be regarded as an approximate result. It represents a method alternative to that of solubility for determining this important magnitude in solid surfaces.

15. **Electro-endosmosis and Electrophoresis:** If a vessel be divided into two parts by means of a porous diaphragm and a potential be established across the diaphragm by inserting electrodes in a liquid present in the two halves of the vessel it can be shown that, under the influence of the potential, liquid will move through the diaphragm. This phenomenon, observed by Reuss in 1807, is known as electro-endosmosis. The reverse of this, the production of a potential by forcing a liquid through a

membrane as the result of the application of pressure, can also be achieved and the potential difference is known as the streaming-potential.

The application of a potential to a liquid in which, instead of a diaphragm, there are present small particles, will produce migration of the particles under the influence of the electric field. This is known as cataphoresis or electrophoresis. The reverse process gives the migration potential, produced by the migration of the small particles through a stationary body of liquid. Reuss discovered these effects simultaneously with that of electro-endosmosis.

All these phenomena are closely related to the potential existing at the interface between the two phases. According to Helmholtz, the electrical charge is the result of a condenser effect with layers of oppositely charged ions at the interface forming the condenser or double layer. For example, in a capillary tube, assumed to have a negative charge located in the surface, there would be a positive charge at some distance, d, out in the liquid. Helmholtz showed, by equating the electrical force tending to move the liquid through such a capillary with the frictional force opposing the motion of a volume, v, of liquid flowing through the tube of radius r, that

$$v = \frac{r^2 \zeta E D}{4\pi\eta l} \tag{17.29}$$

where E is the externally applied potential, l the distance between the electrodes, D is the dielectric constant of the liquid, η the viscosity of the liquid and ζ is the potential difference between the two phases.

For a diaphragm of unknown cross section q,

$$v = \frac{q \zeta E D}{4\pi\eta l}, \tag{17.30}$$

or, since by Ohm's law $E = RI$ and $1/R = \kappa q/l$, where κ is the specific conductivity

$$v = \frac{\zeta I D}{4\pi\eta\kappa}. \tag{17.31}$$

This equation is in accord with the observation of Wiedemann that the mass of liquid transported is directly proportional to the current and, for a given diaphragm material and given current, independent of the length and cross-section of the diaphragm. The direction of flow of liquid will obviously depend on the charge carried by the diaphragm.

In a similar manner, for electrophoresis, it can be shown that the velocity with which a charged particle moves through a liquid in an electric field is

$$u = \frac{\zeta E D}{4\pi\eta l}. \tag{17.32}$$

Similarly the streaming potential is given by the expression

$$E' = \frac{P\zeta D}{4\pi\eta\kappa} \tag{17.33}$$

where P is the hydrostatic pressure applied to the liquid. Hence, it follows from equations (17.31) and (17.33) that

$$\frac{v}{I} = \frac{E'}{P}. \tag{17.34}$$

Equation (17.34) permits a ready test of the validity of the above formulas. The following data were obtained by Saxèn.

TABLE 17.7

COMPARISON OF ELECTRICAL ENDOSMOSE AND STREAMING POTENTIAL

Solution	v/I	E'/P
0.0174 mole $ZnSO_4$	0.360	0.352
0.0261 " "	0.382	0.379
0.0348 " "	0.346	0.344
0.0195 " $CdSO_4$	0.582	0.588
0.0390 " "	0.116	0.115
0.0400 " $CuSO_4$	0.385	0.385
0.0800 " "	0.233	0.237

The zeta-potential, ζ, is found to vary greatly with the nature and concentration of the dissolved matter, as well as with the nature of the material of the wall. Most solids are negatively charged against water; oxides, carbonates, and halides are exceptions inasmuch as they carry a positive charge under similar conditions. The above statements are only true in a limited sense, as it is possible to change the sign of the charge in most cases by the addition of extremely small quantities of certain active electrolytes to the water.

The relation between ζ and concentration of electrolytes is complicated and may best be summarized by means of a series of experimental curves. The following graphs express the value of ζ obtained from electrophoresis experiments plotted against the concentration of the electrolyte solution. The disperse phase in all cases consists of oil particles. It is to be noted that the addition of $K_4Fe(CN)_6$ increased the original negative charge between the oil and the water, while the addition of $BaCl_2$, $AlCl_3$, and $ThCl_4$ all reduced the negative charge, the latter two salts causing a positive charge between the particles and the solution. The effectiveness of the various chlorides may be well illustrated by the following figures:

TABLE 17.8

LOWERING OF ELECTROKINETIC POTENTIAL AT AN OIL-WATER INTERFACE PRODUCED BY THE ADDITION OF CHLORIDES

Electrolyte	Concentration Millimole/liter Necessary to Reduce ζ from 0.046 to 0.037
KCl	24
$BaCl_2$	0.45
$AlCl_3$	0.01
$ThCl_4$	0.005

The electrophoresis experiments are obviously more important than those of electro-endosmosis. Several methods of investigation have been worked out, principally by Burton, Michaelis and Svedberg who has utilized the fluorescence of proteins to study their migration under a potential.

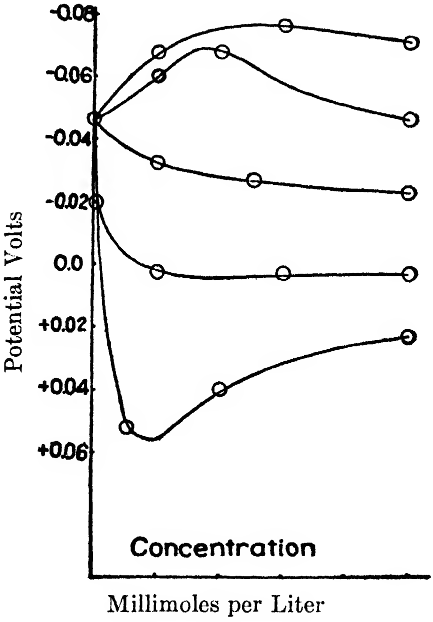
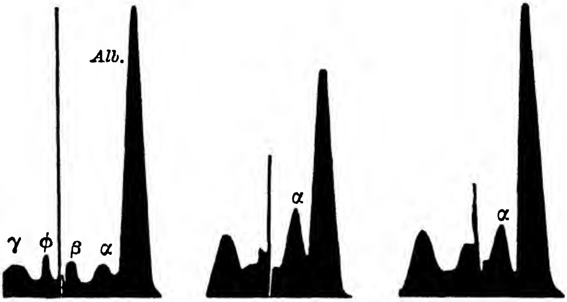
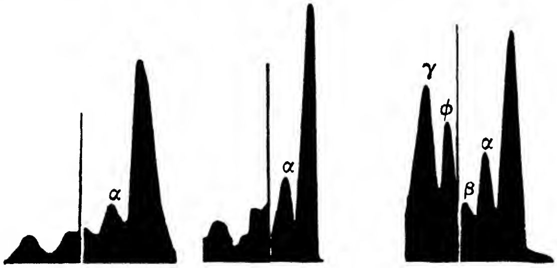


FIG. 17.5. ζ from Electrophoresis Experiments. The curves in descending order refer to the influence of $K_4Fe(CN)_6$, KCl, $BaCl_2$, $AlCl_3$ and $ThCl_4$.

In Svedberg's laboratory, Tiselius has developed, since 1930, the moving boundary method (Chap. 12, Section 15) for measurement of the electrophoretic mobility of proteins, especially at low mobilities in the neighborhood of the iso-electric points. The method consists in photographing with ultraviolet light the boundary movement, due to the applied field, in a quartz U-tube apparatus. The photographic images are registered in a microphotometer on an enlarged scale and the movement of the boundaries is obtained from measurements of the displacement of the photometric records. The method was tested with well-defined, homogeneous proteins which yield sharp boundaries. From the measurements of the mobilities in the iso-electric regions it is possible to determine the iso-electric points with good accuracy. The iso-electric point appears to depend to some extent upon the medium. By combining mobility measurements in the iso-electric region with the molar frictional coefficients determined with the ultra-centrifuge the apparent charge on the proteins can be calculated. The Tiselius electrophoresis apparatus has been found to be of great assistance in biological science since it has been shown that moving boundary electrophoresis is one criterion of the chemical uniformity of proteins. Tiselius demonstrated this with artificial mixtures of pure proteins and then applied the technique to non-uniform proteins and impure preparations. It has been shown that proteins may be uniform as to particle size and non-uniform as regards mobility and vice versa. The use of the apparatus constitutes an important adjunct to ultra-centrifugal studies. In Fig. 17.6 are shown the types of electrophoretic patterns obtained with various blood plasma.



Normal plasma   Tuberculosis



Coronary thrombosis   Lymphosarcoma
6 weeks   1 week

FIG. 17.6. Electrophoretic Patterns on Normal Human Plasma and on Plasma from Individuals with Tissue Injury from Various Causes. (Shedlovsky and Scudder)

16. **Coagulation:** Coagulation is the aggregation of particles of the disperse phase to form new particles of different size and structure. The process may be reversible or irreversible. In the first stage it is probably always reversible but frequently irreversible effects supervene. In dis-

cussing this phase of the subject it is customary to recognize two definite classes of colloids, designated by Perrin as lyophobe and lyophile sols. Sometimes the expressions suspensoid and emulsoid are used in the same sense. The lyophobe sols or suspensoids show little tendency to become hydrated or solvated; the lyophile sols or emulsoids show a marked tendency so to unite with the dispersion medium.

So far we have considered the colloidal system as if made up of a disperse phase and a dispersion medium, the former being always regarded as a pure substance. As a matter of fact, careful analysis always discloses the fact that the disperse phase is never pure, but usually has associated with it a certain amount of impurity. With arsenious sulfide, polysulfides are always found; silver oxide is always associated with colloidal silver, etc. The whole particle together with its associated "impurity" is termed the micelle. The stability of the sol is largely a matter of the composition of the micelle, it being known that it is practically impossible to prepare a stable lyophobe sol that consists of a pure substance dispersed in a pure dispersion medium. The composition of the micelle depends upon the composition of the surrounding solution. In the case of ferric oxide sols it is known that the micelle consists of Fe_2O_3 together with a certain amount of chloride. If the sol is subjected to ultra-filtration and the chloride composition of the filtrate determined, an increase in the latter concentration brings about an increase in the chloride content of the micelle. This is shown by the experiments of Maffia.

TABLE 17.9

DISTRIBUTION OF CHLORIDES BETWEEN THE MICELLE AND INTERMICELLAR LIQUID OF A FERRIC OXIDE SOL

$\alpha = 1.539, \quad 1/n = 0.268$

Cl Content of Filtrate	$a = \frac{\text{millimole Cl}}{\text{g. } Fe_2O_3}$	Calculated
.65	1.36	1.37
.82	1.47	1.46
.90	1.51	1.50
1.07	1.58	1.57
1.21	1.62	1.62
1.38	1.67	1.68
1.55	1.73	1.73

17. Coagulation of Lyophobe Sols by Electrolytes: One of the most important chapters of colloidal chemistry concerns itself with the phenomena that result from the addition of electrolytes to lyophobe sols. A perfectly stable sol when treated with a sufficiently strong solution of an electrolyte will give evidences of instability and will finally precipitate the disperse phase at the bottom of the containing vessel. This coagulation or flocculation of the sol is usually a gradual change, and may be best studied by measuring the rate of the coagulation. Unfortunately, such measurements are not easily carried out; the best method depends upon a determination of the size of particle with the ultramicroscope. This method does not lend itself to all solutions and is at best a laborious and time-consuming operation. Therefore, most investigators have studied the minimum concentration of electrolyte (threshold value) necessary to bring the sol to a certain arbitrary stage of coagulation. Instead of determining the whole course of the coagulation, they have simply selected one point on the coagulation-time curve and determined the quantity of electrolyte necessary to bring the system to that point. Such a procedure is obviously theoretically inadequate in many ways and it is only recently that more attention has been paid to the phenomenon from the standpoint of rate of coagulation.

It has been demonstrated that the addition of the electrolyte does not influence the Brownian motion of the colloidal particle *per se*, but rather the electrolyte removes the barrier to the union of the particles upon collision. When observed under the ultramicroscope, before the addition of the electrolyte, the particles never appear to unite upon collision; as soon, however, as the electrolyte is present, a clumping is observed which increases until the particles become so large that they settle rapidly to the bottom of the vessel.

The following experimental threshold values have been obtained by Freundlich and his co-workers. It is to be remembered that these values will vary according to the method and concentration of the sol, and are therefore not to be given any weight as absolute constants.

TABLE 17.10

COAGULATION CONCENTRATIONS OF As_2S_3 SOL. (1.85 G./LITER)

Electrolyte	Conc. millimole/ liter	Electrolyte	Conc. millimole/ liter
K_3 Citrate/3	>240	Crystal Violet	0.165
K Acetate	110	Fuchsine	0.11
K Formate	86	$MgCl_2$	0.72
LiCl	58	$MgSO_4$	0.81
NaCl	51	$CaCl_2$	0.65
KCl	49.5	$SrCl_2$	0.635
KNO_3	50	$BaCl_2$	0.69
$K_2SO_4/2$	65.5	$ZnCl_2$	0.685
HCl	31	$AlCl_3$	0.093
$H_2SO_4/2$	30	$Al(NO_3)_3$	0.095
Aniline Chloride	2.5	$Al_2(SO_4)_3/2$	0.096
Morphine Chloride	0.42	$Ce(NO_3)_3$	0.080

The data given may be taken as typical of the experimental facts from which one may deduce the general theory of the coagulation of lyophobe sols. The data are restricted in their significance, as outlined above, and must therefore be looked upon as of secondary importance when compared with the measurements of the rate of coagulation. However, it is possible to draw a number of important generalizations from the above facts. In the first place, it is to be noted that, with a negatively charged colloid, the valence of the cation is of primary importance in fixing the threshold concentration of the electrolyte. This rule is not always reliable for it is also to be noted that certain electrolytes containing univalent cations are more effective in bringing about coagulation than other bivalent cations. In addition, the influence of the anion is not entirely negligible, for considerable variation is associated with changes in the nature of the same.

TABLE 17.11

COAGULATION CONCENTRATIONS OF Fe_2O_3 SOL. (.823 G./LITER)

Electrolyte	Conc. millimole/ liter	Electrolyte	Conc. millimole/ liter
NaCl	9.25	$Ba(OH)_2/2$	0.42
KCl	9.0	K_2SO_4	0.205
$BaCl_2/2$	9.65	Tl_2SO_4	0.22
KBr	12.5	$MgSO_4$	0.22
$Ba(NO_3)_2/2$	14.0	$K_2Cr_2O_7$	0.195
HCl	>400	H_2SO_4	0.5

All the above observations may be correlated as follows: The micelle owes its charge and therefore its stability to the presence of a certain amount of adsorbed electrolyte. This material may be considered as constituting an ionic double layer that gives rise to the charge and the potential. The addition of other electrolytes to the inter-micellar liquid brings about a rearrangement of this adsorbed layer of the micelle, and, with it, a change in the potential difference. This change may be either an increase or decrease in the existing charge of the micelle. If the charge is diminished, then the opposition to impacts between particles resulting in a union is decreased and therefore the stability is diminished. It is obvious that the cations will be most effective in decreasing the negative charge of the micelle, and also that a strongly adsorbed univalent cation may be more effective than a weakly held polyvalent cation. Just as in the effect on the potential difference, here in the case of coagulation there is ever present the valence effect and the extent of adsorption of the various ionic species.

Freundlich and his co-workers have experimentally proven most of the statements made in the above paragraph. They show, in the first place, that the most effective ion in bringing about coagulation is more strongly adsorbed by the colloid than an ion of lesser effect of the same valence. The following table illustrates the idea in a quantitative manner.

With the exception of the picrate the equivalent amounts adsorbed are the same, while the molar quantities differ widely but always parallel the threshold concentration. Similar experiments have been conducted with a great number of sols and with various coagulants, and the result is always a substantiation of the above. That the equivalent quantity adsorbed should be the same is a significant fact and leads directly to the supposition that the coagulation results from the replacement of the ion in the micellar layer by another ion. This assumption would easily explain the inconstancy of the threshold values with various colloidal solutions, in other words the "purity" of the micelle determines the amount of added electrolyte necessary for coagulation.

TABLE 17.12

AMOUNTS OF ANIONS ADSORBED IN THE COAGULATION OF Al_2O_3 SOLS

	Threshold Value $\frac{\text{millimole}}{\text{liter}}$	Millimole Adsorbed per g. Al_2O_3	Milli-equivalent per g. Al_2O_3
Salicylate	8	0.46	0.46
Picrate	4	.275	.275
Oxalate	.36	.275	.55
Ferricyanide	.10	.14	.42
Ferrocyanide	.08	.11	.44

18. Lyophile Colloidal Solutions: It is possible to obtain fairly correct conceptions of the various factors that determine the properties of the lyophobe class of colloidal solutions, or, more definitely, with the aid of the principles of thermal agitation, adsorption, and electrical charge a more or less rational explanation of the properties of such sols may be formulated. In dealing with the other class, the lyophile, there is immediately felt the crying need for guiding generalizations. It is generally accepted that such sols, as distinguished from the lyophobe, are more closely related to the dispersion medium, i.e., the disperse phase is hydrated or in combination with the solvent. While this explanation is undoubtedly the reason for the peculiar behavior of such systems, a quantitative insight into the properties of the lyophile sols cannot be had until we understand much more of the nature of solvation or hydration.

This section of colloidal chemistry may therefore be said to be in almost a purely empirical state. There is no guiding generalization except the vague idea of solvation, which is imperfectly understood. Nevertheless, a vast amount of data has been collected regarding such sols. Lyophile sols are characterized by (1) Stability in fairly concentrated solutions of electrolytes, (2) High viscosity, often exhibiting elastic properties, (3) Difficulty of being resolved under the ultramicroscope, (4) Setting to gels.

These characteristics, together with other minor ones, serve to distinguish such solutions from the lyophobe class. The latter solutions show the opposite behavior in all the above four points and therefore may be regarded as being fundamentally different in nature. It must be constantly borne in mind that these two great classes of colloidal solutions are connected by a class of intermediate solutions that show some of the properties of both classes. In other words, the distinction between the two groups is not always sharp, but may be made difficult in certain cases. For example aluminum hydroxide sols show many of the properties of the lyophiles but are nevertheless classed as lyophobe due to their sensitiveness to coagulation by electrolytes. Furthermore, it is often possible to convert a distinctly lyophile sol into a characteristically lyophobe sol, by changing the dispersion medium. In this case it is obvious that it is possible to arrest the change in the nature of the medium at such a point that the system will exhibit the properties of both classes to a certain degree.

With both types of solutions, there is, however, a disperse phase of greater than molecular dimensions. In the case of the lyophile systems this conclusion is drawn from their small diffusion coefficients and their low osmotic pressures. The ultramicroscopic channel of investigation is practically closed with this type of sol due to the small difference between the refractive indices of the two phases. Further, the stability in the presence of electrolytes shows that they do not possess a well-defined electric charge, which fact is well illustrated by the inability of the ordinary electrokinetic phenomena to furnish much helpful information. In addition, most of these colloids are composed of substances that are much more chemically active than those comprising the lyophobe class, there being always therefore the possibility of such changes beclouding the ordinary colloidal reactions.

The ordinary aqueous lyophile colloids are represented by such substances as gelatin, sulfur, silicic acid, stannic acid, various albumins, starch, soaps, and many dyes.

19. **Mutual Effects of Colloids:** If a lyophilic colloid is added to a lyophobic sol there may be mutual interaction of the stabilizing agents of the two sets of particles. If the two contain ions of opposite sign in excess, there will be mutual neutralization with partial reduction of charge on the suspensoid. This will have the effect of an equivalent addition of coagulant and a lower concentration of electrolyte will be sufficient to produce a given degree of coagulation. This effect is termed a *sensitization* of the suspensoid by the lyophilic colloid Positive Fe_2O_3 sols are sensitized by the addition of a negative serum albumin sol.

With excess of a lyophilic colloid opposite in sign of charge to that of the suspensoid, the latter may be protected against coagulation. This action is termed *protective action* or *stabilization.* Even small amounts of a lyophilic colloid of the same charge as the suspension have the same stabilizing effect. Larger amounts of coagulants will now be required to effect a given degree of coagulation. Gelatine, sodium caseinate, albumin, gum arabic, dextrin and potato starch are all protective colloids to the red gold sol delaying the coagulation which produces the change from red to blue sol when sodium chloride solutions are added. These protective colloids are operative in the production of a number of metal sols prepared by several different methods. Also, the new synthetic polymers function also as protective agents. Polyvinyl alcohol proves to be an excellent protective agent for platinum and palladium colloidal catalysts. The 'gold numbers' of a group of colloids are shown in Table 17.13.

TABLE 17.13

GOLD NUMBERS OF PROTECTIVE COLLOIDS

Colloid	Gold Number	Colloid	Gold Number
Gelatin	0.005–0.0125	Gum Arabic	0.10–0.125
Egg Albumin	0.08 –0.10	Dextrin	125–150
Protalbinic Acid	0.15 –0.20	Soluble Starch	10–15
Lysalbinic Acid	0.10 –0.125	Sodium Oleate	2–4

20. **Peptization:** The reversal of coagulation is termed peptization. This can be effected with a colloidal precipitate in two ways. The addition of a peptizing agent will in many cases serve to produce a colloidal solution from a colloidal precipitate. Precipitated sulfides can be peptized by washing with water containing hydrogen sulfide, or with dilute solutions of alkali sulfides. Silver halides can be peptized by using dilute solutions of silver salts or univalent halide solutions. The phenomenon of peptization is easily recognized in the latter example during volumetric precipitation of chloride ion by silver nitrate. The milky liquid, containing the partially peptized silver chloride, formed during titration, changes to the characteristic curdy precipitate when halogen and silver ion are approximately equivalent. Reversal of coagulation can also in certain cases be secured by washing the precipitate more completely free from the electrolytes which, as already discussed, play an integral part in the coagulation process. Thus a coagulated precipitate of hydrous chromic oxide on repeated washing with distilled water gradually peptizes, the onset of the process being readily recognized by the increasing length of time required for the precipitate to settle after each washing process. Since the valence of the electrolyte is an important factor in coagulation, it follows that peptization by washing will be more difficult when salts of high valences have been employed as coagulating agents.

21. **Gels:** The term gel is now generally restricted to the product of coagulation of a colloid which is a coherent, more or less elastic solid enclosing a part or all of the dispersion medium. An apparently homogeneous, transparent, amorphous semi-rigid structure with a high liquid content is often termed a *jelly*. Some reasonably firm jellies may contain as much as 99 per cent of the liquid component. Gels with a low liquid content, desiccated gels or bodies behaving like them are termed *xerogels*. Both naturally occurring and synthetic materials belong to this class. We may cite opal, limonite, natural and synthetic zeolites, silica gel, soap, leather, natural and artificial textiles, wood, paper, plastics, paint films, rubber, starch, certain food-stuffs, muscle tissue and cell membranes.

The formation of gels is the result of partial or incomplete precipitation of a sol, as is obvious in the case of silica gel and the hydrous oxide gels where uncontrolled precipitation will give slimy or gelatinous precipitates. The optimum conditions for gel formation are intermediate between those for stability and those for precipitation. Conditions must be chosen, generally by trial and error, so that the reinforcing structure of the gel may form without the coagulation which leads to precipitation; in all probability the solvent is involved in the gel structure in many cases, but in others, as, for example dibenzoyl cysteine, which forms jellies in very low concentrations, the structure may be practically anhydrous. The evidence, now accumulating, from studies of polymerization processes indicates the formation of long molecular chains with cross-linking between the chains; this may be typical of the processes operative in gel formation and the solvent may take part in the architecture of the gel structure. Minimum concentrations of the disperse phase are necessary for the formation of gel structure. When the system is too dilute coagulation fails to immobilize the dispersion medium and a gelatinous precipitate forms. The more highly dispersed the colloidal substance is, the more dilute the concentration which will yield a jelly. In several cases stable jellies contain only a few tenths per cent of disperse phase.

The structure of the dilute gels is in all probability a more or less coherent framework of disperse phase formed by long chains of molecules, with cross-linking, so spaced that the regions of free liquid between the units of structure are not much greater than molecular dimensions. Evidence from the X-ray and optical examination of the natural zeolites as typical xerogels indicates that the arrangement of the molecules is extraordinarily regular and the pores resulting from their desiccation are in several cases extremely uniform.

Dilute gels are extremely porous to small molecules or ions. This is readily shown by measurements of diffusion velocity with small molecules (Graham), or of electrical conductivity in the case of electrolyte solutions (Arrhenius). The diffusivity and electrical conductivity differ little from that in the dispersion medium alone. This fact has led to one method of determining ion migration using agar jellies. Friedman and Kraemer have also used diffusion experiments in gelatine jellies to determine effective pore sizes in different concentrations. Some of the results are shown in Table 17.14.

TABLE 17.14

EFFECTIVE PORE-SIZE IN GELATINE GELS BY DIFFUSION METHODS

Diffusing Substance	Effective Pore Diameter		
	5 Per Cent Gelatine	10 Per Cent Gelatine	15 Per Cent Gelatine
Urea	9.4 $m\mu$	3.0 $m\mu$	1.6 $m\mu$
Glycerol	11.4	3.4	2.0
Sucrose	11.0	2.8	1.0

Gel structure minimizes disturbances due to vibration and convection currents, common difficulties in diffusion processes. The counter diffusion in gels of reactants which yield precipitates leads to novel crystal forms and under suitable conditions to banded precipitates, generally known as Liesegang's rings. These discontinuous, periodic depositions of precipitate are dependent on concentration gradients due to diffusion, causing the concentrations of the reactants to rise at given positions to the degree of supersaturation necessary for precipitation. The concentration is reduced thereby to the saturation value not only where the precipitate is deposited but also in the adjacent regions of lower supersaturation. The diffusing reactant must then advance beyond this region before a sufficient supersaturation for precipitation is again reached.

In the desiccation of gels distinction may be drawn between lyophiles and lyophobes. These latter are sometimes termed *irreversible* gels. In the case of a typical lyophilic gel the fall in vapor pressure and liquid content traces an S-shaped curve, the volume of the gel continuously decreasing to a horny residue. With lyophobic gels, for example, silicic acid gel, the conditions initially are similar to the case of lyophilic gels. A point is reached, however, beyond which no further shrinkage of the gel occurs. Solvent is then removed for a period without much change in vapor pressure and ultramicroscopic pores are formed. The gel is opaque at this stage. Further solvent removal brings transparency but becomes progressively more difficult; gels such as silica, alumina and chromic oxide gel will retain up to as much as 5 per cent of water after evacuation at 300° C.

Lyophobic xerogels will adsorb and imbibe any liquid which will wet the gel. A maximum volume of liquid can be so imbibed depending essentially on the pore volume of the gel since little or no swelling occurs.

Such gels are also able to adsorb gases and vapors in large amounts partly by surface adsorption on the relatively large surface, partly as liquid by capillarity. Lyophilic gels show both imbibition and swelling. The dispersion medium penetrates into the interior of the gel and actually separates the structural units of the gel from each other. This swelling is evidently dependent on the relations between the adhesional energy between solvent and gel structure and the cohesional energy of the structure. Within certain limits the processes of imbibition and swelling on the one hand and desiccation on the other are reversible in the case of lyophilic gels. The imbibition-swelling process involves both gel structure and solvent. Thus, with gelatine gels, the process occurs with water but not with benzene. Combination must occur between the water and particular units of the gelatine chains. With rubber, swelling occurs with benzene, much less so with paraffinic hydrocarbons, and not at all with water. Obviously, there may exist intermediate cases where limited imbibition and swelling occur involving certain types of linkages in the gel structure but not all. Diffusible constituents retained within the gel structure may also account for some cases of imbibition by osmosis.

Gels are unstable systems in common with all colloidal states of matter. Their breakdown occurs generally in two stages; first a *syneresis*, shrinkage of the gel with exudation of liquid medium, which may be followed by a process of crystallization. Increase of temperature accelerates such changes. Chromic oxide gel illustrates these changes spectacularly. The gel is quite stable if the removal of water is conducted slowly even up to temperatures of 550–600° C. Rapid removal of the water causes collapse of structure and this is followed by recrystallization, in this case sufficiently exothermic to cause an incandescence known as the 'glow phenomenon.'

Kistler developed a technique for removal of water from fairly dilute gels by progressive displacement with solvents of increasing volatility. Thus, by displacing water with alcohol, alcohol with ether, etc., he was finally able to replace the water of various gels by air without collapse of the gel structure. The products are known as *aerogels*. In such structures solvation of the gel-forming material cannot be an essential of the structure.

Certain clays, especially the bentonites, hydrated silicates of alumina, swell under water, in some cases with large volume increase, by imbibition, and set to jellies or gels, with characteristic setting times. The clay sol is often sensitive to the content of electrolyte present. Gels so formed may be termed *suspensoid* gels. The ready dispersion of the clays is associated with a relatively large content of combined alkalis or alkaline earths. Purification of the dispersion, for example by electrodialysis, profoundly affects the reversibility of the dispersion. On removal of the metal ions the acidic clay residue, after drying, does not readily redisperse.

Dilute bentonite gels show the phenomenon of *thixotropy*. The gel liquefies on agitation to a fluid suspension of low viscosity. On standing without agitation the gel re-forms. The phenomenon is of industrial importance, for example in the utilization of paints.

22. **Emulsions:** Systems in which both disperse phase and dispersion medium are fluids are known as emulsions. The term is generally restricted to the case in which both fluids are liquids. The dispersion of a gas in a liquid medium is sometimes termed a gas emulsion but more usually a foam. Liquid emulsions have a considerable technical importance and foams are of importance in the use of soaps and other detergents as well as in the phenomena of ore concentration by flotation.

Liquid emulsions are formed between immiscible or between partially miscible liquids, and, as an example, we may cite emulsions of oil and water. Violent agitation, spraying and the use of homogenizers or colloid mills will serve to break up both liquids and eventually to produce an emulsion of one liquid in the other. Such emulsions are stabilized by an electric charge on the surface of the droplets. With oil-water emulsions the oil drop carries a negative charge as shown by electrophoretic measurements (Section 15, Fig. 17.5). These emulsions are known as *hydrosols*. They are, at best, not very stable when the two liquids are pure but they can be rendered very stable by the presence of *emulsifiers*. By suitable choice of emulsifiers the two possible emulsions may be produced, for example oil-in-water or water-in-oil. A small amount of sodium oleate yields an emulsion of oil-in-water with water and a hydrocarbon. Calcium oleate on the other hand yields a water-in-oil emulsion. Finely divided solids also function as emulsifying agents. Hydrous oxides, basic sulfates and clays yield oil-in-water emulsions, while carbon black and mercuric iodide yield water-in-oil emulsions.

In general it can be said that emulsifiers will cause the liquid for which they have the greater affinity to become the dispersion medium. This is borne out by the examples of solids already cited. Hydrophilic agents such as alkali soaps, gelatine, gum, favor oil-in-water and hydrophobic agents water-in-oil. The emulsifying agent accumulates in the interface between the droplets and medium. It forms a film which is more effective in preventing coalescence of drops of A in B than B in A when the final emulsion is an A in B emulsion. Undoubtedly the relative adsorptions of A and B by the agent are of importance as first pointed out by Bancroft and orientation in the adsorption process (Chap. 6, 17) must also play a role. Viscous agents are more effective in general than non-viscous, hence the efficiency of solid emulsifiers.

The particle size in ordinary suspensions and emulsions is in general larger than that in ordinary colloidal solutions. The range of size is from 10^{-2} cm. to 1 μ, the ordinary cream globule falling within this range. Emulsification effects notable changes in the physical characteristics of the constituent liquids. Mayonnaise which is an oil-in-water emulsion with egg-yolk as the emulsifying agent is a good example of such changes in, for example, viscosity.

EXERCISES (17)

1. Calculate the increase in surface area when 1 cm.^{3} of material is dispersed into colloidal particles 10^{-6} cm.^{3} in volume.

2. Calculate the number of atoms in a colloidal gold particle whose radius is 5 mμ; the density of gold is 19.3.

3. Perrin obtained a mean horizontal displacement of gamboge particles of 7.09 μ in 30 sec. at 290° K. The particle radius was 0.212 μ and the viscosity of the medium 0.011. Calculate the Avogadro number.

4. Calculate the Avogadro number from the sedimentation data in Table 17.2 for gold sols in water.

5. Show by plotting $\log x_{\text{obs.}}$ against $\log c$ for the data in Table 17.5 that n in the Freundlich adsorption isotherm for acetic acid on charcoal is 0.425.

6. Combine the relation for the volume of liquid flowing through a capillary under an applied potential with Poiseuille's equation and show that the maximum pressure difference $P = 2\zeta ED/\pi r^2$. Hence calculate the zeta-potential for glass-water, for a tube of radius 0.0449 cm. under an applied potential of 76 volts when a difference of 0.0011 cm. in the level of the water at the ends of the tube was observed.

7. Using 0.5 per cent $ZnSO_4$ solution and a clay diaphragm Saxèn found 1.585 cc. water transported in 1829 sec. using 0.024 amp. With the same system a streaming potential of 0.00147 volt was found for a pressure difference of 31.4 cm. mercury. Show that $V/I = E'/P$ expressing the ratios in cm.$^{5/2}$ g.$^{-1/2}$ units.

8. Horse hemoglobin is found to contain 0.335 per cent iron. Calculate the minimum molecular weight of the protein.

APPENDIX 1

Maxwell's Distribution Law of Velocities: Experience shows that the molecules of a gas in a container under a fixed set of conditions will have a random motion. This randomness is in reality twofold. In the first place the molecules are travelling in all directions. No one particular direction is favored over another. There is, we say, an isotropic distribution. In the second place the velocities of the molecules are not identical, some will be moving very slowly, others very rapidly and still others at an intermediate pace. It is the purpose of Maxwell's law to show precisely what is this distribution of velocities. It must be realized at the outset that it is almost impossible to answer the question: "how many molecules have a velocity c at a particular instant?", since it may so happen that at that particular instant not a single molecule would have that specified velocity. Rather must the question be worded so that a certain latitude is permissible in the velocities: "how many molecules have velocities lying in the range of velocity dc between c and $c + dc$?", where dc may have any physical value not necessarily mathematically infinitesimally small. Furthermore the latitude must be extended for the instant for which the statement is made, so as to yield an average result over a period of time rather than at a specified instant.

Consider a system of N molecules. The velocity c of one of them may be resolved into its rectangular component velocities u, v and w such that:

$$c^2 = u^2 + v^2 + w^2. \tag{1}$$

The fraction of all the molecules which have a component of velocity in a specified direction between u and $u + du$ will depend on the particular magnitude of u, in some way to be determined, as also on the magnitude of the velocity range du. Let this be represented as $f(u)\,du$. Similarly for the other component velocities, $f(v)dv$ and $f(w)dw$ will be the fraction of the molecules with respective component velocities in the ranges dv and dw. Hence the fraction of the total number of molecules having simultaneously component velocities in the specified ranges will be:

$$f(u)f(v)f(w)du\,dv\,dw. \tag{2}$$

Owing to the isotropic distribution of direction of motion of the molecules the function $f(u)\ f(v)\ f(w)$ must represent the same fraction of all the molecules whatever the individual values of u, v and w may be, so long as equation (1) is satisfied. That is, it must be a constant and the first derivative of equations (1) and (2) must therefore be zero. Letting f'

represent the first derivative of the function f gives:

$$u\,du + v\,dv + w\,dw = 0 \tag{3}$$

and

$$f'(u)f(v)f(w)du + f(u)f'(v)f(w)dv + f(u)f(v)f'(w)dw = 0. \tag{4}$$

Dividing the latter by the constant factor $f(u)f(v)f(w)$ gives:

$$\frac{f'(u)}{f(u)}\,du + \frac{f'(v)}{f(v)}\,dv + \frac{f'(w)}{f(w)}\,dw = 0 \tag{5}$$

and equations (3) and (5) hold simultaneously. To express them as a single equation, (3) is multiplied by a constant λ and added to (5), giving

$$\left(\frac{f'(u)}{f(u)} + \lambda u\right)du + \left(\frac{f'(v)}{f(v)} + \lambda v\right)dv + \left(\frac{f'(w)}{f(w)} + \lambda w\right)dw = 0.$$

Now du, dv and dw are the specified velocity ranges and are therefore not necessarily zero. Hence their coefficients must be zero to satisfy the above zero identity. That is:

$$\frac{f'(u)}{f(u)} + \lambda u = 0; \qquad \frac{f'(v)}{f(v)} + \lambda v = 0; \qquad \frac{f'(w)}{f(w)} + \lambda w = 0.$$

Solving the first of these as an example, the equation may be written:

$$d \ln f(u) = -\lambda u\,du.$$

On integration

$$\ln f(u) = -\tfrac{1}{2}\lambda u^2 + \text{constant},$$

or

$$f(u) = Ae^{-\lambda u^2/2}.$$

Similarly $f(v) = Ae^{-\lambda v^2/2}$; $f(w) = Ae^{-\lambda w^2/2}$. Hence the fraction of the number of molecules dN/N, which have simultaneously components of velocity in the specified ranges du, dv and dw, becomes

$$dN/N = A^3 e^{-\lambda(u^2+v^2+w^2)/2}\,du\,dv\,dw.$$

The constant A may first be determined since the sum of all the fractions dN/N for all possible values of u, v and w must be equal to unity, that is:

$$\int \frac{dN}{N} = 1 = A^3 \iiint_{-\infty}^{+\infty} e^{-\lambda(u^2+v^2+w^2)/2}\,du\,dv\,dw.$$

The triple integral is easily found as the product of the three separate integrals in u, v and w. Now

$$\int_{-\infty}^{\infty} e^{-\lambda u^2/2}\,du = \sqrt{\frac{2\pi}{\lambda}}\,.$$

Hence the triple integral will have the value $(2\pi/\lambda)^{3/2}$ and $A^3 = (\lambda/2\pi)^{3/2}$ whence

$$\frac{dN}{N} = \left(\frac{\lambda}{2\pi}\right)^{3/2} e^{-\lambda(u^2+v^2+w^2)/2}\, du\, dv\, dw. \tag{6}$$

This equation specifies the fraction of all the molecules which have velocities lying in a particular range between c and $c + dc$ not only so far as their magnitude is concerned but also for their direction, since the component velocities are also restricted. To determine the fractional number of molecules having velocities in the range c to $c + dc$ regardless of their direction, the former equation must be integrated over all possible directions of motion. To do this most conveniently the polar co-ordinates of the velocity rather than the rectangular co-ordinates may be considered. Thus in place of u, v and w, the velocity is designated in terms of its magnitude c and its direction in space by the two angles θ and ϕ, the co-latitude and longitude respectively. The volume element corresponding to $du\, dv\, dw$ may then be expressed in terms of dc, $d\theta$ and $d\phi$. Thus in the figure a surface, distance c from the origin, is designated together with a surface element equivalent to $du\, dv$. The angles subtended by the sides of this element are $d\theta$ and $d\phi$. From the geometry of the figure it follows that:

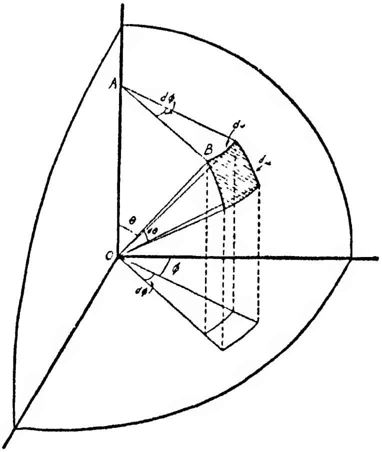


FIG. A.1

$$\begin{aligned} du\, dv &= c \sin d\theta \cdot AB \sin d\phi \\ &= c\, d\theta \cdot c \sin\theta \cdot d\phi = c^2 \sin\theta\, d\theta\, d\phi, \end{aligned}$$

since the sine of a small angle is equivalent to the angle. Hence the volume element equivalent to $du\, dv\, dw$ becomes the product of this surface element and the velocity range dc, or $c^2 \sin\theta\, d\theta\, d\phi\, dc$. Substituting this in equation (6) gives

$$\frac{dN}{N} = \left(\frac{\lambda}{2\pi}\right)^{3/2} e^{-\lambda c^2/2}\, c^2 \sin\theta\, d\theta\, d\phi\, dc. \tag{7}$$

Integrating over all possible values of θ and ϕ, namely, θ from 0 to π and

ϕ from 0 to 2π, gives

$$\begin{aligned} dN/N &= \left(\frac{\lambda}{2\pi}\right)^{3/2} e^{-\lambda c^2/2}\, c^2dc \int_0^{2\pi}\int_0^{\pi} \sin\theta\, d\theta\, d\phi \\ &= \left(\frac{\lambda}{2\pi}\right)^{3/2} e^{-\lambda c^2/2}\, c^2dc\cdot 2\pi \int_0^{\pi} \sin\theta\, d\theta \\ &= \left(\frac{\lambda}{2\pi}\right)^{3/2} e^{-\lambda c^2/2}\, c^2dc\cdot 2\pi\cdot 2 \\ &= 4\pi\left(\frac{\lambda}{2\pi}\right)^{3/2} e^{-\lambda c^2/2}\, c^2dc. \qquad (8) \end{aligned}$$

The quantity λ can now be easily determined by relating it to the root mean square velocity $\bar{u}$ which is given by the expression:

$$\bar{u}^2 = \frac{1}{N}\int_0^{\infty} c^2dN,$$

or, substituting for dN:

$$\bar{u}^2 = 4\pi\left(\frac{\lambda}{2\pi}\right)^{3/2}\int_0^{\infty} e^{-\lambda c^2/2}c^4dc.$$

The definite integral is related to the gamma function 5/2 and has a value

$$\int_0^{\infty} e^{-\lambda c^2/2}c^4dc = \frac{3}{2}\sqrt{\frac{2\pi}{\lambda^5}}\,.$$

Hence

$$\bar{u}^2 = 4\pi\left(\frac{\lambda}{2\pi}\right)^{3/2}\cdot\frac{3}{2}\sqrt{\frac{2\pi}{\lambda^5}} = 3/\lambda.$$

But by kinetic theory $\bar{u}^2 = 3RT/Nm = 3kT/m$, where k is the gas constant per molecule. Hence

$$\lambda = m/kT.$$

The Maxwell distribution law therefore becomes:

$$dN/N = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT}c^2dc. \qquad (9)$$

APPENDIX 2

Planck's Expression for the Average Energy of a Linear Vibrator: The problem to be solved is what is the average energy, $\bar{\epsilon}$, of an oscillator or vibrator if the system can only receive energy in definite increments or quanta, ϵ, 2ϵ, ... $r\epsilon$, but not in intermediate amounts. The quantity ϵ is equal to $h\nu$. We employ the relation established by Maxwell's law that the number of vibrators N_r having r quanta of vibrational energy is

$$N_r = Ae^{-r\epsilon/kT}. \tag{1}$$

The constant A is a proportionality factor whose magnitude is determined by the fact that the summation of all the N_r's is equal to the total number of vibrators, N; that is,

$$\Sigma N_r = N = A\Sigma e^{-r\epsilon/kT}, \tag{2}$$

where the sign of summation Σ indicates the inclusion of all integral values of r from zero to infinity.

The average value of the vibrational energy, $\bar{\epsilon}$, is, by definition, the summation of all values of $N_r \cdot r\epsilon$ divided by the total number, N; hence,

$$\begin{aligned}\bar{\epsilon} = 1/N[(N_0 \times 0) + (N_1 \times \epsilon) + (N_2 \times 2\epsilon) + \dots\dots \\ + (N_r \times r\epsilon) + \dots\dots] \end{aligned} \tag{3}$$

which may be abbreviated thus, using expressions (1) and (2),

$$\bar{\epsilon} = \frac{\Sigma r\epsilon A e^{-r\epsilon/kT}}{A\Sigma e^{-r\epsilon/kT}} = \frac{\Sigma r\epsilon e^{-r\epsilon/kT}}{\Sigma e^{-r\epsilon/kT}}. \tag{4}$$

If, for the summation $\Sigma e^{-r\epsilon/kT}$, we write

$$J = 1 + e^{-\epsilon/kT} + \epsilon^{-2\epsilon/kT} + \dots\dots,$$

then

$$J = \frac{1}{1 - e^{-\epsilon/kT}} \tag{5}$$

and the expression for the average energy $\bar{\epsilon}$ becomes

$$\bar{\epsilon} = (kT)^2 \frac{d \ln J}{d(kT)}. \tag{6}$$

Substituting in this expression the value of J in (5) we obtain

$$\bar{\epsilon} = \frac{\epsilon}{e^{\epsilon/kT} - 1}. \tag{7}$$

Equation (7) is the Planck expression desired. The classical result for continuous increments of energy is approached when we allow the quantity ϵ/kT to approach zero. Expanding expression (7) according to the exponential theorem yields

$$\bar{\epsilon} = \frac{\epsilon}{1 + \epsilon/kT + \ldots\ldots - 1} = kT. \tag{8}$$

That is, upon classical grounds of continuous energy values, the average energy of the vibrator is kT. This obtains at sufficiently high temperatures T. At very low temperatures, as T approaches 0° K., the average quantized vibrational energy $\bar{\epsilon}_0$ is zero since

$$\bar{\epsilon}_0 = \frac{\epsilon}{\infty} = 0. \tag{9}$$

We may obtain from equation (7) the contribution from quantized vibrational energy to the heat capacity by differentiating the total vibrational energy $N\bar{\epsilon}$ with respect to temperature, thus obtaining

$$C_{vib} = \frac{d(N\bar{\epsilon})}{dT} = Nk\frac{x^2e^x}{(e^x - 1)^2} = R\frac{x^2e^x}{(e^x - 1)^2}, \tag{10}$$

where x is equal to ϵ/kT, and $Nk = R$, the gas constant per mole.

APPENDIX 3

The Limiting Law of Debye and Hückel: The fundamental problem involved in the treatment, is the calculation of the electrical free energy of the solution originating from the uneven distribution of the ions. The free energy is obtained from the mutual electrical potential of the ions and this latter is calculated on the basis of the applicability (1) of Coulomb's law to the electrical forces between ions and (2) of Boltzmann's principle to the distribution of the ions.

To simplify the derivation, a dilute solution of KCl will be considered first. The result obtained may be easily generalized. Imagine that it would be possible to see a particular ion, say a K^+, and to follow that ion as it moves through the solution. If there were no charges on the ions and the solution was ideal, a completely random distribution of particles would prevail and the chance that the potassium would approach another potassium at a given instant would be equal to the chance of its approaching a chlorine. Owing to the inter-ionic electrical forces, however, the K^+, in order to approach another K^+, must overcome the electrostatic repulsion exercised between them while its approach to a chloride ion would be aided by their mutual attractions. If ψ represents the average electrical potential of an ion of charge ϵ, the work performed in the approach of two K^+ ions will be $\epsilon\psi$. The particular K^+ ion being watched therefore acquires an additional potential energy of $\epsilon\psi$. In like manner its approach to a chloride ion, of charge $-\epsilon$, causes a changed potential energy of $-\epsilon\psi$.

On the basis of these potential energies, by means of Boltzmann's principle, the probable number of each kind of ion in the neighborhood of a particular ion may be stated. Thus the number of positive ions n_+ out of a total number of ions n in the solution will be:

$$n_+ = ne^{-\epsilon\psi/kT}$$

and of negative ions likewise

$$n_- = ne^{-(-\epsilon\psi/kT)} = ne^{\epsilon\psi/kT}.$$

If these numbers of ions are expressed as the number per unit volume, that is, as a density, the corresponding electrical density is easily found. Thus the electrical density ρ is the algebraic sum of charges present in unit volume:

$$\rho = n_+\epsilon + n_-(-\epsilon) = n\epsilon(e^{-\epsilon\psi/kT} - e^{\epsilon\psi/kT})$$

which to a first approximation becomes

$$\rho = -2n\epsilon(\epsilon\psi/kT). \tag{1}$$

According to Coulomb's law the force acting between two charges ϵ_1 and ϵ_2 a distance r apart in a medium of dielectric constant D is given by:

$$F = \epsilon_1\epsilon_2/Dr^2.$$

The application of this to the simple case of three or four particles may be directly made by considering the charges in pairs. Where, however, there are a large number of charges such as are present in a solution containing ions such a simple treatment is impossible. Poisson has shown that in such a case, assuming a spherical charged particle, the electrical potential at a distance r from the charge is related to the average density of electricity ρ by the differential equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(\frac{r^2 d\psi}{dr}\right) = -\frac{4\pi\rho}{D}. \tag{2}$$

Accepting this and combining with equation (1)

$$\frac{1}{r^2}\frac{d}{dr}\left(\frac{r^2 d\psi}{dr}\right) = -\frac{4\pi}{D}(-2n\epsilon^2\psi/kT)$$

$$= \frac{8\pi n\epsilon^2\psi}{DkT} = \kappa^2\psi \tag{3}$$

where $\kappa = (8\pi n\epsilon^2/DkT)^{1/2}$. Equation (3) may be integrated to give the general solution:

$$\psi = \frac{Ae^{-\kappa r}}{r} + \frac{Be^{\kappa r}}{r},$$

where A and B are integration constants to be determined. Since ψ must approach zero as r is made larger and larger, the constant B must be zero, otherwise ψ would be infinite when r was infinite. Hence:

$$\psi = Ae^{-\kappa r}/r. \tag{4}$$

Now by Coulomb's law the potential of a single point charge ϵ is:

$$\psi = \epsilon/Dr. \tag{5}$$

This therefore should be applicable to a single ion in the solution, that is, to an infinitely dilute solution or when κ is equal to zero. From equation (4) when $\kappa = 0$, $\psi = A/r$ and equating to (5) $A = \epsilon/D$ or $\psi = \epsilon e^{-\kappa r}/Dr$ which may be written

$$\psi = \frac{\epsilon}{Dr}[1 - (1 - e^{-\kappa r})] = \frac{\epsilon}{Dr} - \frac{\epsilon(1 - e^{-\kappa r})}{Dr},$$

whereby the total potential at a distance r from a given ion in the solution has been split into two terms, the first being the contribution of the ion itself unaffected by other ions, the other due to the presence of the surrounding ions. This is the quantity desired and is seen to be a function of κ and therefore of the concentration of the solution. For dilute solutions when κ is small $(1 - e^{-\kappa r})$ reduces to κr. Thus the potential due to the surrounding ions becomes

$$\psi = -\epsilon\kappa/D. \tag{6}$$

In other words, $1/\kappa$ behaves in equation (6) as does r in equation (5), that is, κ has the dimensions of a reciprocal length. Substituting for the values in equation (3) at 0° C. $\kappa = 0.327 \times 10^8 \sqrt{c}$ cm.$^{-1}$ where c is the molar concentration. In a molar solution therefore $1/\kappa$ has molecular dimensions. It was termed by Debye and Hückel the radius of the ionic atmosphere.

From the value of the potential due to the surrounding ions in equation (6) the free energy may be calculated. Since it is assumed that the uncharged particles would constitute an ideal solution, the extent of deviation from ideality will be measured by the work done in discharging the ions. This process is similar to the discharge of a condenser and is to be carried out without changing the concentration, that is, at constant κ. With κ constant the potential will be proportional to the charge and the work done will be given by:

$$F_e = \int_0^{\psi} \epsilon d\psi = \int_0^{\psi}\left(-\frac{D}{\kappa}\right)\psi d\psi = -\frac{1}{2}\frac{D}{\kappa}\psi^2 = -\frac{\epsilon^2\kappa}{2D}.$$

But this electrical free energy is related to the activity coefficient:

$$\bar{F}_e = kT \ln f.$$

Therefore:

$$\ln f = -\frac{\epsilon^2 \kappa}{2DkT} = -\frac{\epsilon^2}{2DkT}\sqrt{\frac{8\pi n\epsilon^2}{DkT}}, \tag{7}$$

where f is the activity coefficient of the particular K^+ ion considered. It must be particularly noted that the dependence of f on the other ions in the solution is involved in κ, that is, on the quantities under the root sign in equation (7).

Passing now to the general case of a solution containing a number of different kinds of ions $1,2,3 \ldots\ldots i \ldots\ldots s$, of valence z and number per unit volume n with corresponding subscript, the value of κ can readily be seen to be

$$\kappa = \sqrt{\frac{4\pi\epsilon^2}{DkT}\sum n_i z_i^2},$$

for now the charge on an ion instead of being ϵ will be $z_i\epsilon$ and the factor $8\pi n$ in equation (3) was obtained from the 4π in Poisson's equation and the $2n$ in equation (1) involving the sum of the valences of a K^+ and Cl^- ion.

Hence equation (7) becomes in the general case

$$\ln f_i = -\frac{(z_i\epsilon)^2}{2DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT}\sum n_i z_i^2}$$

for the activity coefficient of an ion of the ith kind. The term under the root sign will again involve all the other ions in the solution.

To determine the activity coefficient of an electrolyte dissociating into ν_+ cations and ν_- anions, use is made of its relation to the activity coefficients of its ions:

$$f = (f_+^{\nu_+} \cdot f_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$$

or

$$\ln f = \frac{1}{\nu_+ + \nu_-}(\nu_+ \ln f_+ + \nu_- \ln f_-).$$

Considering this electrolyte in the general solution considered above as a solvent, substitution for f_+ and f_- gives:

$$\ln f = \frac{1}{\nu_+ + \nu_-}\left[-\frac{\nu_+ z_+^2\epsilon^2}{2DkT} - \frac{\nu_- z_-^2\epsilon^2}{2DkT}\right]\sqrt{\frac{4\pi\epsilon^2}{DkT}\sum n_i z_i^2}$$

$$= -\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-}\cdot\frac{\epsilon^2}{2DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT}\sum n_i z_i^2}.$$

Now

$$\nu_+ z_+ = \nu_- z_-.$$

Therefore

$$\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-} = z_+ z_-.$$

Also

$$\Sigma n_i = 6.02 \cdot 10^{20} c \Sigma \nu_i = 6.02 \cdot 10^{20} m \Sigma \nu_i = 6.02 \cdot 10^{20} \Sigma m_i,$$

where n_i is the number of ions of each kind per unit volume, c is the molar and m the molal concentration. Hence:

$$\ln f = - z_+ z_- \frac{\epsilon^2}{2DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \cdot 6.02 \cdot 10^{20} \Sigma m_i z_i^2}.$$

But $\Sigma m_i z_i^2 = 2\mu$, where μ is the ionic strength. When $\epsilon = 4.8025 \cdot 10^{-10}$ e.s.u., $k = 1.381 \cdot 10^{-16}$ ergs and D for water at 25° C. is 78.8, this becomes the limiting law

$$\log f = - 0.507 z_+ z_- \sqrt{\mu}.$$

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