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CHEMICAL ENGINEERING FUNDAMENTALS

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Chemical Engineering Fundamentals

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CHEMICAL ENGINEERING FUNDAMENTALS

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TO

BILLIE S. KIRKBRIDE, MY WIFE

WITHOUT WHOSE CONTINUAL ENCOURAGEMENT AND ASSISTANCE
THIS BOOK WOULD NOT HAVE BEEN PREPARED

PREFACE

For many years teachers of chemical engineering have expressed their desire to give more intensive instruction to second-year students in applied chemistry, applied physics, and applied mathematics. This book was written originally to facilitate such instruction at the Agricultural and Mechanical College of Texas. Its chief purpose is to introduce the primary fundamentals of chemical engineering so that the student can proceed later at a faster pace with his more advanced studies in the applications of these fundamentals to the unit operations and chemical processes.

The text is introduced at the A and M College of Texas in the second semester of the second year. It is covered in two semester courses of three credit hours each. The first five chapters, through "The Material Balance," are studied during the first course. The remaining five chapters are studied during the second course, which comes in the first semester of the third year.

The only prerequisites for the first six chapters are courses in general college chemistry, differential calculus, and the physics of mechanics, sound, and heat. Physical chemistry is not a prerequisite. Chapter IV, "Important Concepts of Physics and Chemistry," covers the essential physicochemical principles so that the student can *begin* the elementary study of chemical-engineering fundamentals in the second year without a detailed knowledge of physical chemistry. Integral calculus does not become of importance until Chap. VII is reached. Therefore, the student is not at a disadvantage if integral calculus is taken during the second semester of the second year.

Experience at the A and M College of Texas has shown that students who take the course in elementary fundamentals are able to handle far more advanced and intensive instruction than those who have not had this preparation. Furthermore, it has been interesting to note that the second- and third-year students generally have been able to grasp the underlying philosophy of the fundamentals with little more apparent difficulty than fourth-year or even graduate students who have taken these courses as "refreshers."

Because of the emphasis that has been placed on the unit-operation concept of chemical engineering in the past, many students have been graduated with the erroneous belief that the unit operations are themselves the fundamentals of chemical engineering, rather than mere applications of the fundamental principles to which this text is devoted. A lack of appreciation of this distinction is a common cause of difficulty for the beginner in professional practice. Until the practicing engineer recognizes the errors in this viewpoint and grasps the alternative philosophy of thinking in terms of the real fundamentals, his progress is likely to be retarded. Too often he becomes unhappy in his job because he feels that he is not practicing his professional training unless he is working with the unit operations. However, once he gets a thorough and philosophical insight into the fundamentals of chemical engineering he will develop a more wholesome attitude. He will approach all problems in terms of the true fundamentals that underly chemical-engineering applications.

In view of the foregoing reasons, the number of unit operations and chemical processes discussed in the text has been held to a minimum. Furthermore, the extent of treatment of each of these applications has been limited to that required to stimulate thinking in terms of the basic fundamentals rather than in terms of the specific unit operation or chemical process involved. A number of the example problems were taken from the petroleum industry, which provides an excellent basis on which to teach and learn the fundamentals of chemical engineering. These are broad and never change, although there are many and frequent variations in their applications through the unit operations and chemical processes. Once the student develops the philosophy of attacking problems with the fundamentals, the industry in which he practices chemical engineering will make little difference and he will be able to handle almost any problem that comes to him.

Considerable attention is also devoted to human relations and the reporting of technical results. These are integral parts of chemical-engineering practice and can hardly be overemphasized in the mind of the embryonic engineer. Too often the student develops the misconception that technical ability is the only important basis for advancement in the profession. The author believes that this misunderstanding is largely a result of the lack of emphasis by most teachers on these nontechnical phases of chemical-engineering education. Although not always apparent, the student is prone to adopt unconsciously the patterns and professional values manifested by his chemical-engineering teachers. Thus, if only the technical side of chemical-engineering practice is taught, the student is likely to be graduated with the subconscious feeling that technical ability is the only thing of real importance. To avoid this, the chemical-engineering teachers should emphasize continually the importance of human relations throughout the entire academic training of their students. Such emphasis by the chemical-engineering staff will usually carry more weight than similar instruction in courses given by other college departments.

Numerous surveys of practicing engineers and chemists have shown that the weakness in their academic training most frequently emphasized is lack of practice in the preparation of technical reports. Until the chemical engineer develops some proficiency in presenting the results of his work to others, his progress is sorely handicapped. The experience of the author indicates that the most common cause of trouble lies in the engineering rather than the rhetorical phases of the report. Too often report writing is taught only in the English department. Too often the instruction is given by some teacher whose livelihood has never depended upon presenting results of technical work in unequivocally clear and understandable reports.

Here again chemical-engineering teachers can be most helpful. In the first place, they should make certain that the desired type of instruction is given. They should advise on the assignments because the average English instructor can seldom suggest subjects that provide proper breadth and depth for a technical report. The course in report writing should come early in the curriculum and the initial instruction should be augmented thereafter by assigning the preparation of reports, both oral and written, in every chemical-engineering course that presents such an opportunity. By such a procedure, the student will gain valuable experience and be more fully impressed with the importance of his technical reports.

Thus the fundamentals that make for success in the practice of chemical engineering are both technical and nontechnical. If this book can contribute to their recognition and use by the young engineer in the early and formative stages of his career, it will serve its most important purpose and fully justify the effort and time expended in its preparation. In this connection, the author wishes to express his deep appreciation to the many persons who assisted in making the text possible.

In particular, the author is grateful to J. D. Lindsay of the A and M College of Texas for his encouragement and wholehearted cooperation in the preparation of the book, as well as for the opportunity to try out the plan of instruction in the chemical-engineering curriculum. Also, thanks are due J. W. Kilmer, E. H. Ivey, and F. F. Bishop of the same institution for their many helpful suggestions on improving the original manuscript.

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CHALMER G. KIRKBRIDE

WALLINGFORD, PENNA.
September, 1947

CONTENTS

CHAPTER I

INTRODUCTION

This book presents a broad perspective of the fundamentals of the chemical-engineering profession. This includes a treatment of the humanistic side of the profession as well as of the technical principles. The primary purpose is to present the beginner with the philosophy of chemical engineering before he initiates an intensive study of any of the specific principles. Hence the purpose is to introduce the fundamentals of chemical engineering to the beginner. If the student has a general perspective of chemical engineering as a whole, his intensive study of each principle should be more fruitful.

Chemical engineering is one of the youngest branches of the engineering profession. Even so, it has enjoyed extensive development and expansion during the past three decades. Furthermore, it is in a very healthy state for development and growth at an even greater rate in the future, for it has not been confined within any arbitrarily defined boundary by those who are practicing the profession.

Since chemical engineering is a profession, the value of each chemical engineer to society is measured in terms of his accomplishments rather than on the basis of the "time" he devotes to his work. The industrial arts or trades are on the latter basis, but no engineer can expect to enjoy a truly professional status if his work is reduced to a clock-hour basis.

Contrary to the usual concept, the work of the chemical engineer is rarely done with test tubes, beakers, etc. Unfortunately there is a tendency on the part of students to assume that the beginning college courses in chemistry are indicative of what chemical engineering is. This is far from true. In view of this misconception, it is desirable to devote some attention at the outset to orientation so that the student will have a clearer view of the work he will do if he pursues the study of chemical engineering.

The Chemical Engineering Education Accrediting Committee of the American Institute of Chemical Engineers accepted the following definition of chemical engineering:

> Chemical engineering is that branch of engineering concerned with the development and application of manufacturing processes in which chemical or certain physical changes of materials are involved. These processes may usually be resolved into a coordinated series of unit physical operations and chemical processes.

The work of the chemical engineer is concerned primarily with the design, construction, and operation of equipment and plants in which these unit operations and processes are applied. Chemistry, physics, and mathematics are the underlying sciences of chemical engineering, and economics is its guide in practice.

The unit operations mentioned in the definition are physical in nature and can be classified into specific types. They deal for the most part with determination of the size and type of equipment needed to carry out the various kinds of physical changes. Some of the unit operations are described briefly as follows:

1. Fluid flow. This deals with the laws that govern the flow of any fluid from one point to another.
2. Heat transfer. This consists primarily in a study of the laws which govern the rate at which heat can be transferred from one point to another.
3. Evaporation. This is a means of separating a solvent from a nonvolatile solute. The study covers chiefly the laws that govern the rate of evaporation and the energy required.
4. Distillation. This is a means of separating mutually soluble volatile components in a mixture.
5. Absorption. This is a method of separating components in a gaseous mixture.
6. Extraction. This is an operation by which mutually soluble components of a mixture can be separated by means of a solvent which selectively dissolves one or more of the components.
7. Drying. This consists in the removal of small concentrations of volatile liquids (such as water) from nonvolatile materials, usually solid.
8. Filtration. This deals with the separation of a solid phase from a liquid phase.

There are several other unit operations, but it should be apparent from the above examples what is meant by the classification of physical operations into specific types.

The chemical processes mentioned in the definition given above consist in chemical changes (reactions). Much controversy has centered in the classification of chemical reactions into specific types. One of the classifications is as follows:

1. Oxidation
2. Reduction
3. Combustion
4. Hydrogenation
5. Halogenation
6. Hydrolysis
7. Fermentation
8. Calcination

The significance of this scheme of classification of chemical reactions on an industrial scale will be apparent to the student on the basis of his knowledge of general chemistry. It must be emphasized, however, that the principles involved in different processes of a given classification are frequently as diverse as those involved in different classifications. Thus, no satisfactory scheme of classifying chemical processes has been determined as yet.

The unit operations deal chiefly with the transfer and transformation of energy and the transfer, separation, and conditioning of materials by physical means, whereas the chemical processes involve primarily the conversion of materials of given chemical classification to materials of another chemical classification by means of chemical reaction. The chemical engineer is concerned primarily with the development, design, and operation of processes and process equipment. He is concerned with construction and structural details particularly insofar as they affect his functions in the process development, process design, and operation of the process. Actually, it might have been more significant had chemical engineering been named "process engineering," for the work deals so much with processes.

Although chemical engineering is defined in terms of unit operations and chemical processes, these are not fundamentals. They are, instead, merely specific applications of the fundamentals of chemical engineering. There are only five technical fundamentals, *viz.*, (1) material balance, (2) energy balance, (3) static equilibria, (4) rates of transfer and transformation of mass and energy, and (5) the economic balance.

Chemical engineering (process engineering) might have been defined as the application of material balances, energy balances, static equilibria, rates of transfer and transformation of energy and mass, and economic balances to the development, design, and operation of processes and process equipment in which materials undergo chemical and/or physical change. The chemical engineer must be able to accept direction as well as to direct the efforts of subordinates and must be able to work with associates in a harmonious manner toward a rapid and effective attainment of a common objective.

Chemical engineering is distinguished from the pure sciences merely by a philosophy, attitude, or viewpoint in obtaining and applying technical information to the development, design, and operation of processes and process equipment. It is this philosophy that is so very important to the successful chemical engineer. He attacks almost all technical problems by means of five fundamentals. He analyzes his objectives and any information given him on the basis of these fundamentals. This becomes habitual with the successful chemical engineer. The problems he encounters are so varied in nature and so complicated that unless he develops the habit of analyzing them in terms of fundamentals his value and corresponding success are limited. Often the work of the chemical engineer will involve neither unit operations nor chemical processes, but the fundamental philosophy will be used to the fullest extent. It is not entirely satisfactory, therefore, to define chemical engineering in terms of unit operations and chemical processes. The chemical engineer who thinks merely in terms of these applications instead of in terms of the fundamentals upon which they are based is likely to be narrow and inflexible. It will be difficult for him to follow the rapidly changing profession. The applications of the fundamentals change with time, but the fundamentals never change. Mathematics is the primary tool. No one should embark upon a career in chemical engineering unless he is fond of mathematics and proficient in its use.

Work of the Chemical Engineer.—The fundamentals of chemical engineering and the philosophy of their application having been briefly discussed, attention will now be devoted to a general description of the work of the chemical engineer at the present time. In order to describe how the chemical engineer fits into the picture it will be helpful to consider the history of a process from its inception to and including its commercial application.

The inception of a process may consist merely in an idea for converting certain materials into products of higher value. There must be a sizable economic advantage to such conversion, or the process will have no commercial application. The idea may originate with a chemical engineer, with a chemist, with a physicist, or with other persons. Possibly the idea can be shown to be sound by use of existing data, but frequently chemical research must be carried out to provide a more quantitative basis for evaluating the economic feasibility of the process. Information on product yields and rate of conversion is needed. Ordinarily the chemical research in this case is done by highly trained chemists and physicists, although chemical engineers may do much of the experimental work. In any event, the chemical engineer usually appraises the process on the basis of the results obtained on small-scale laboratory equipment. Thus, the chemical engineer follows the chemical-research work very closely even though he may not be directly involved in the experimental work. It is very desirable that he be fully informed on the experimental technique, including methods of analysis. Also, he should have a clear understanding of the limits of accuracy of the research results and should make certain that all the data are being obtained which he needs to make his process appraisal.

The process appraisal usually consists in a preliminary process design of a commercial plant of suitable size and an estimate of investment cost, processing cost, and profit. This is of a preliminary nature, for it involves extrapolation of the results obtained on small laboratory equipment to full-scale commercial equipment. Much judgment must therefore be exercised by the chemical engineer in regard to what commercial performance can be expected, based on the research results. A background of experience that provides a basis for comparison of commercial performance with chemical-research results for other processes is almost essential for this work. Rarely does commercial performance equal that obtained on small laboratory equipment. In the extrapolation of research data to full-scale commercial plants it is frequently necessary to set up the process design for a continuous unit on the basis of chemical-research data that were obtained with batch equipment. The translation of data from batch equipment to a basis for a continuous unit is indeed dangerous, and unless the chemical engineer stays on the solid foundation of fundamentals he is likely to arrive at a process design for the continuous unit that is far different from what actually is feasible.

Chemical-research work usually is done on an extensive basis so that the effect of process variables such as temperature, pressure, product yields, catalyst concentration (if a catalytic process), reaction rate, etc., can be established within desired limits in a relatively short time. The chemical engineer may therefore have to make several preliminary process appraisals in order to define the probable economic optimum range of process variables for commercial operation.

Assuming that the preliminary appraisals show that the process is economically feasible on a commercial scale, the next step may be to investigate the process in semicommercial-scale equipment called a pilot plant. This step is desirable if the investment cost of the commercial unit is relatively high compared with the cost of pilot-plant investigation. A decision in such a case is predicated upon an economic study that compares the probable cost of pilot-plant investigation with the cost of a full-scale commercial unit. Occasionally, however, a pilot plant is desirable because a market must be developed for the product. The pilot plant can be used effectively in this case to supply the market in its infancy.

In order to determine the probable cost of the pilot-plant investigation the chemical engineer must prepare a preliminary plan of investigation that will provide all the data he needs for detailed process design of a full-scale commercial unit. Also, a process design and estimate of investment cost for the proposed pilot plant must be prepared. Based on the preliminary plan of pilot-plant investigation, an estimate is made of the time that will be required to carry out the projected pilot-plant program. The total operating cost for the pilot-plant program can then be estimated. This cost, together with the estimated investment cost of the proposed pilot plant, represents the total probable cost of pilot-plant investigation. If this figure is relatively high compared with the cost of a commercial unit, the decision may be to avoid completely a pilot-plant investigation. Instead, a commercial unit may be installed directly on the basis of chemical-research data. In this case the chemical-research work should be more intensive than in the case in which a pilot-plant investigation is carried out.

Assuming, however, that it is decided to conduct a pilot-plant investigation, a structural (mechanical) design should be made on the basis of the process design. The mechanical design involves engineering that is primarily mechanical, electrical, etc.

The chemical engineer may or may not have the responsibility of the mechanical design. In any event, he should approve the arrangement of equipment and make certain that the pilot plant as installed provides him with the equipment needed to obtain the desired process data. Also, he should make certain that the plant as installed is consistent with safe working conditions from an operating standpoint.

After the pilot plant is installed, it may be operated by chemical engineers or skilled nontechnical operators. The latter are usually preferable, for operation of a unit is an art at which the young chemical engineer does not usually excel. Steady operation is essential if reliable data are to be obtained. It requires years to develop the desired skill at operation of process equipment.

Operation of the pilot plant is ordinarily supervised by one or more chemical engineers. The chemical engineer instructs the operators on what conditions to maintain, and the operators hold these conditions while the desired data are obtained. The data are then analyzed by chemical engineers, which entails calculations to translate the operating data to the desired basis. Information on product yield, product quality, and rate of conversion may be obtained. These results are then correlated with the process variables.

As the pilot-plant investigation proceeds, process appraisals should be made. These are valuable as a guide to the pilot-plant work. They show where important improvements would be desirable from an economic standpoint. Effort can then be directed toward making such improvements. Improvements that have little economic significance hardly justify the cost of investigation.

After the pilot-plant program has progressed far enough so that a precise appraisal can be made, it may be decided to install a commercial unit. This will require a detailed process design, detailed mechanical design, and firm estimate of investment cost and processing cost. The chemical engineer usually does not have an active part in the detailed mechanical design and firm estimate of investment cost. Nor does he ordinarily have more than an advisory status in the construction of the unit.

When the unit is installed, it is usually the responsibility of the chemical engineer to make it operate under conditions that yield the greatest economic returns. In general, the operation will be carried out by skilled nontechnical operators, who may work under the supervision of the chemical engineer.

Chemical engineers also will continuously study the performance of the commercial unit after it is put into operation with the objective of maintaining its performance at the optimum economic point. This work is commonly known as technical service. It is one of the best places for the newly graduated chemical engineer to begin his chemical-engineering practice, for there he will be able to develop that indefinable judgment factor. He will be able to correlate the application of chemical-engineering theory with what is actually obtained in full-scale commercial units. He will learn the limits to which he can trust his calculations based on theory and the size of safety factors he should use to compensate for the inaccuracies. Also, in technical service he will learn to question the process arrangement as it exists in his continuous effort to improve upon it. He will find at times that even rather major revisions in the existing process will show attractive economic returns. Such conclusions must, of course, be based on calculations, which in turn are predicated upon fundamentals. This will involve process designs and economic appraisals in much the same way as for the original installation.

Frequently those working in technical service will wish to investigate novel features in the process—features not previously investigated. This might be done on the commercial unit, though it is often quite expensive to carry out experimental work in this way. For this reason pilot plants are frequently used in technical-service work to evaluate changes considered for the commercial units.

Thus, the chemical engineer may be involved from the inception to and including the operation of the commercial unit. This may include chemical-engineering research; preliminary process design and process appraisal; pilot-plant design, evaluation, and investigation; detailed process design, process appraisal, and operation of commercial units; and technical service. It is apparent that this is a particularly good training ground for future executives of a company.

It should be emphasized that the method of handling chemical-engineering work described above is not used by every organization. It is one method, however, that is sound and that is used by a number of progressive companies. It should be realized, further, that the work of the chemical engineer also involves research and development of unit operations as well as chemical processes. Opportunities for work of a supervisory nature are numerous.

Another field for application of chemical engineering is technical sales. In the past, the requirements for technical ability were not important. In recent years, however, the more progressive equipment and engineering organizations are demanding high-caliber technical ability of their sales engineers. Possibly the cause of this is that technical sales are based on logic rather than on an appeal to the customer's emotions. The customer frequently does not have a staff of engineers and is dependent upon the sales engineer for his technical advice. Consequently, the sales engineer must be able to make a complete economic appraisal to show the customer how much profit can be made by investing in what he has to sell. Such appraisals must be honest in every respect if repeat business is expected. Furthermore, the sales engineer must become thoroughly acquainted with the customer's business in order to give him the best advice. Such advice must be supported by calculations. It must be on the basis of logic. Hence, the sales engineer must have high technical ability as well as pleasing personal qualities.

Still another field in which chemical engineers find desirable employment is patent law. This requires additional training, but it is an attractive field. The application of the fundamentals of chemical engineering is very broad.

Nontechnical Aspects.—In academic training the technical aspects of chemical engineering are of necessity stressed. Nevertheless, the human relations of the profession, are of at least as great importance. The student should understand this, for when he begins the practice of chemical engineering he will find that though his technical training is a prerequisite his success will depend chiefly upon his ability to deal with the nontechnical aspects. This is so very important that an entire chapter (Chap. II) is devoted to this subject. The student will profit if he begins the practice of these principles of human relations early in his academic training.

Plan of Presentation.—The purpose of this chapter up to this point is to orient the student with regard to what chemical engineering is and the type of work chemical engineers do. The subject matter to be covered in the succeeding chapters will now be described.

Chapter II discusses in some detail the principles of human relations in chemical engineering. The chemical engineer is very much a human being and is associated closely with other human beings. It is essential that he learn to deal harmoniously and effectively with his associates, supervisors, and subordinates. This phase of chemical-engineering practice unfortunately is frequently neglected and thus causes the young chemical engineer endless trouble until he has adjusted himself. He must have a good understanding of human relations if outstanding success is to be realized.

Chapter III presents certain mathematical tools that will be used throughout a career in chemical-engineering practice.

Chapter IV covers various principles of physics and chemistry that are useful in the application of the technical fundamentals of chemical engineering. The chief reason for presentation of these principles is that the student may not have completed a study of physical chemistry at this point in his academic work. Chapter IV, therefore, is intended to make it possible for the student to begin his study of chemical engineering without first having a knowledge of physical chemistry.

Chapter V is the first to take up the technical fundamentals of chemical engineering. It discusses the material balance and its application to chemical processes and unit operations. The purpose is to teach the philosophy of the use of the law of conservation of mass. Information presented on the unit operations and chemical processes is merely incidental.

Chapter VI teaches the philosophy of the application of the energy balance in combination with the material balance. This is merely the application of the laws of conservation of mass and conservation of energy. Examples of certain unit operations and chemical processes are used to facilitate the presentation.

Chapter VII discusses static equilibria, which involve also the mass balance and energy balance. Static equilibria involve the calculation of final conditions after all driving forces within a system are zero.

Chapter VIII covers the application of rates of transfer and transformation of mass and energy. The study of unit operations and chemical processes involves the prediction of these rates, but there is much that the student can learn about their importance before he begins the more advanced study of unit operations and chemical processes.

Chapter IX treats the application of the economic balance. This is the final chapter on the technical fundamentals of chemical engineering. It involves the fundamentals as presented in the preceding four chapters but brings out the important aspects of profit and loss. The chemical engineer will find in his practice that maximum profit per unit time is the guide which he must always follow.

Chapter X discusses the presentation of technical results. The chemical engineer in practice is eternally faced with the necessity of selling the products of his professional services. Unless he is able to do so, he will accomplish very little. It is most essential, therefore, that the student learn as early as possible in his academic training the proper presentation of technical results.

QUESTIONS

1. Name five unit operations, and state what each deals with.

2. What is the fundamental distinction between the unit operations and chemical processes?

3. What are the technical fundamentals of chemical engineering?

4. Define chemical engineering in terms of the fundamentals.

5. What is the distinction between chemical engineering and the pure sciences?

6. What is the primary requirement of a process before it can be considered for development?

7. What may be the first step by the chemical engineer when the mere idea of a process is disclosed?

8. What does the preliminary process appraisal consist of?

9. Is chemical research usually done on an extensive or an intensive basis?

10. What are three common process variables?

11. If the preliminary process appraisals on the early research are favorable, what may be the next step of the chemical engineer?

12. When is pilot-plant development desirable?

13. How is the cost of pilot-plant investigation determined?

14. If it is decided to carry out a pilot-plant development, what is the first step?

15. Is the pilot plant operated by chemical engineers?

16. After the pilot-plant program is under way, what is the function of the chemical engineer?

17. When the commercial unit is installed, what is the function of the chemical engineer?

CHAPTER II

HUMAN RELATIONS IN CHEMICAL ENGINEERING

Unfortunately the chemical-engineering curriculum is usually so crowded with technical courses that too little time is devoted to the nontechnical features so continuously encountered by the practicing chemical engineer. Consequently, the recent graduate is seldom properly impressed with the great importance of human relations. This is unfortunate, for his progress is slow until he appreciates fully that his accomplishments depend chiefly upon his ability to handle the nontechnical aspects of chemical engineering.

As individuals we can accomplish very little. It is only through organized efforts of a number of individuals that substantial accomplishments are made. It is easily visualized how disastrous it would be for an army to operate as so many individuals instead of on the basis of organized cooperative endeavor. The same is true of any group of people with a common objective. It is desirable, therefore, that the chemical engineer begin to develop early in his academic training the spirit of cooperative endeavor. Some persons are born with this spirit, but in the great majority of cases it seems that it must be developed and cultivated. There is no better time than during the period of academic training to practice cooperative endeavor. The chemical engineer who is strong in technical knowledge but weak in understanding of human relations ordinarily will not enjoy so much success as one whose technical training is only fair but whose training in human relations is sound. Of course, the engineer whose practice is sound both technically and nontechnically will be outstanding.

Soon after the chemical engineer begins his professional practice, he should decide between two possibilities. Does he prefer to be an expert (specialist) in a particular phase of chemical engineering, or does he prefer to develop executive capacity and direct the efforts of others? The failure to make such a decision is often responsible for later dissatisfaction. Sometimes the young engineer will express a desire to do a certain type of work, such as process design, and later become dissatisfied because he really does not want to be an expert in this line. He does not know what he wants because he has not clarified his own mind. After he once becomes clear in his own mind what course he wishes to pursue, he can go about his work in a much happier frame of mind and with somewhat greater success.

In deciding between these two possibilities, the young chemical engineer should be guided by his potential abilities. Some persons do not have the ability to direct the efforts of a large organization and yet are forever dissatisfied because they have the false conception that success lies only in executive work. As one progresses along the route of an executive, he becomes less able to practice his technical chemical engineering. The nontechnical side becomes of greater and greater importance. It does not follow that a good chemical engineer makes a good executive. As a matter of fact, those who elect to become executives may be disappointed to find how little time can then be devoted to technical chemical engineering.

As a guide in deciding what course one should take, King [1] has suggested the characteristic qualities given in Table 1.

TABLE 1.—CHARACTERISTIC QUALITIES FOR THE EXECUTIVE AND THE INDIVIDUAL WORKERS

Executive	Individual Worker
Extrovert	Introvert
Cordial, affable	Reserved
Gregarious, sociable	Prefers own company
Likes and interested in people	Likes technical work
Interested in	Interested in
Business	Sciences
Costs	Mathematics
Profit and loss	Literature
Practices	Principles
Ability to get many things done	Ability to get intricate things done
Practical	Idealistic
Broad perspective	Detailed perspective
Synthesist	Analyst
Fast, intuitive	Slow, methodical
Talent for leadership	Independent, self-sufficient
Uses inductive logic	Uses deductive logic
Has competitive spirit	Prefers to "live and let live"
Bold	Modest
Courageous	Retiring
Noisy	Quiet
Aggressive	Restrained
Tough, rugged	Vulnerable, sensitive
Confident	Deferential
Impulsive	Intellectual
Vigorous, energetic	Meditative, philosophical
Opinionated, intolerant	Broad-minded, tolerant
Determined	Adaptable
Impatient	Patient
Enterprising	Conservative

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[1] KING, W. J., *Mech. Eng.*, **66**, 323–326, 398–402, 459–462 (1944).

The qualities of any given individual will usually lie between these two extremes, but they should be an aid in deciding upon the course of progress best suited to one's natural traits.

Requirements for Leadership.—It is possible to be a leader in either capacity, as an executive or as an individual worker. Of course, the requirements for leadership for the executive are far more severe. Even so, the leadership qualities for success in any phase of chemical engineering have certain things in common. It is therefore desirable to discuss the requirements in some detail.

There are numerous publications dealing with leadership, but six[1] form the basis for much of the following discussion. There are possibly nine essential qualities of leadership, *viz.*, (1) determination, (2) self-confidence, (3) courage, (4) integrity, (5) responsibility, (6) energy, (7) skill in human relations, (8) ability to express one's thoughts, and (9) technical ability. Actually, leadership may be regarded as ability to influence people. In the dictatorship (country or organization) it is not at all necessary that the leader have a pleasing personality and be able to get along with people. He may be the opposite type and still retain his leadership. In a democratic organization, however, the leader will find his road very rough unless he has that invaluable quality of being able to get along with people.

Determination.—This quality is probably the most important of all the essential qualities of leadership. It is a trait that involves neither intellect nor emotion. It is a quality of character. It is that deep-rooted force in the leader that drives him on to the goal no matter how many difficulties he encounters. It is a quality that the leader manifests at all times—a dogged persistence in holding steadfast to the course that leads him to his final objective. This persistence must, of course, be tempered with several of the other essential qualities discussed below. Even so, it is a strong force that is evident at all times. The leader does not seek to convince anyone that the force exists. It is obvious to all.

The leader analyzes himself to make certain what he wants. Then he carefully plans his course of action and follows it. The smart leader will not be given to bullheadedness and dogmatism but will revise his course if new evidence shows it foolish to continue his original plan. On the other hand, he will not be influenced by everyone who voices objections to his selected course of action. No person qualifies as a leader whose opinion depends on the person to whom he has talked last.

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[1] *Ibid.*; KIRKBRIDE, C. G., *Arch. Eng. Ind.* (*Univ. Texas*), **4** (No. 4), 19 (1942); WILLIAMS, E. C., *Chem. Ind.*, **56**, 397 (1945); SHEPARD, N. A., *Ind. Eng. Chem. News*, **23**, 104 (1945); KIRKBRIDE, C. G., *Mich. Technic.* (*Univ. Mich.*), **57** (No. 1), 6 (1938); WRIGHT, MILTON, "Getting Along with People," McGraw-Hill Book Company, Inc. New York, 1935.

The leader gets results. He rarely starts anything he does not complete. He gets things done. The fact that a person has put in his regular working hours on the job has little significance if he does not get results. He might just as well have loafed, for apparently the period was one of wasted effort. The chemical engineer should understand that chemical engineering is a profession, not a trade. His remuneration is based, not on the number of hours he puts in at the office, but upon what he accomplishes—the results he gets. His employer has appointed him, not because he thinks he is a nice fellow or because he thinks chemical engineering is interesting, but because he expects to make a profit on his services. Unless he does, there is little justification for continued employment.

The young engineer is prone to feel that after he has placed an order for material or work to be done he must sit down and wait for the results. This is far from the case. "The squeaking wheel gets the grease"; therefore, it is highly desirable to follow up orders to learn of their status and advise those concerned of one's active interest. Of course, discretion must be exercised so that people will not be offended. Furthermore, every effort should be made to pursue the project with partial effectiveness without the material or work requested. One of the marks of a good engineer is that he can get results with a minimum of materials and service from others. It is better to make some progress under adverse circumstances than to delay the work until the adverse circumstances can be avoided and thus make no progress.

Self-confidence.—This quality is also one that the leader does not seek to prove. It is taken for granted. It will show unmistakably in his actions. If the leader does not have confidence in himself, he can be sure that others will not have confidence in him. He must feel certain that he will reach his goal. Furthermore, his feeling must be so evident to his followers that there is not the slightest doubt in their minds that he knows exactly what he is doing. This quality should be most evident under fire. Actually, among his followers is frequently his boss, who will value him most highly if he can hold his course with confidence and attain the objective. All executives want men of this type as subordinates, for they are strongest during the storm when strength of character is most needed.

The leader must be able to make decisions without procrastinating. He will weigh the factors available to him and make a decision with all the confidence in the world. He will not "ride the fence," for this is an evidence of weakness.

The leader does not stampede when trouble is encountered. As a matter of fact, he will be found to minimize rather than magnify trouble. The trouble will not affect his confidence in reaching his objective. His persistence will be very evident.

All leaders must take chances, but the chances they take will be reduced to the minimum so that the odds are in their favor. The chemical engineer will find that he frequently must estimate the time it will take to complete a job or the amount of production which can be realized in a given period of time. His estimate will be based on as many facts as he can obtain; with experience, he will become quite proficient. He will have confidence in his estimates, although he will occasionally miss them by a substantial margin. The same thing applies to his designs. If his designs are based on fundamental facts, they should perform accordingly. Frankly, a new process seldom performs initially as intended; but eventually the difficulties are removed, and usually satisfactory performance is attained. The chemical engineer who is a leader will be persistent throughout the troubles. He will find the difficulties and eliminate them.

Courage.—This quality is akin to determination and self-confidence yet is quite different. Both physical and moral courage are required. No coward can lead. The leader often finds himself under persistent attack. Yet he never shows weakness; he is not afraid of the outcome. Moral courage is vital in a crisis. The leader does not ask someone to do something he would not do.

The leader has the courage to express his thoughts and promote his ideas. A large percentage of young chemical engineers are too inclined to do only what they are asked to do. Often the young engineer has suggestions that would influence his superior in the course of action he requests. He should therefore express himself, or it will be assumed that he has nothing to contribute. This is particularly true in the case of technical conferences that are held for the purpose of framing a program or plan. Such conferences are attended by a number of persons who, it is felt, can contribute to the final plan or program. The reason why such conferences are held is that it is uncertain just what should be done. Consequently, each person should express his feelings on the subject. The first one to propose a reasonable plan will have the best chance of taking the lead. The leaders will be quite prominent in the discussion. It will ordinarily be observed that there is no clear-cut solution. This is all the more reason why all thoughts should be presented to the group for consideration. Each thought tends to stimulate further thought and discussion.

Above all, the leader will not let proposals and recommendations be influenced by what he thinks his superior would like. He can be sure that his boss wants to do what is best for the enterprise; therefore, his thoughts should be confined to a fundamental and objective analysis predicated upon what is best for the enterprise. The program or plan of procedure will always be regarded by the person in charge as tentative and will be in force only until a better program is proposed. Thus, the leader will have the courage to propose a change in the program that he feels is an improvement.

The leader has the courage to make decisions. There are many people who avoid making decisions because of the fear of making a mistake. Those who let this fear influence them are not leaders. The chemical engineer should realize in the beginning that he will make mistakes and plenty of them. His value will depend upon how much above the value of 1.0 he can keep the ratio of his correct decisions to his erroneous decisions. The only people who do not make erroneous decisions are those who never do anything to promote progress. The leader does not procrastinate in making a decision, nor does he ride the fence.

The leader has the courage to tell those who are responsible to him how they stand. He will make it clear to them what is expected of them and will point out ways in which they can improve. It is always advisable to talk with a man if he is not doing work consistent with his ability. He will appreciate your advice. If he cannot be guided so that he can do satisfactory work, the boss has failed as well as he.

Integrity.—This quality is probably the most valuable of personal qualities. The factor that most commonly distinguishes the outstanding executives is their personal integrity and loyalty. The leader must be loyal to the cause at all times. He may be able to betray a follower and retain the lead, but he can never betray the cause and retain the lead. Even so, he will find that the heights of leadership which he can attain are limited if he even on rare occasions betrays his followers.

It is surprising how accurately one's character is appraised after a short period of time in an organization. Each individual in the organization will be appraised for exactly what he is. This appraisal will be far more accurate than that the individual can make of himself. It is therefore important that the leader not try to impress on his associates that he is anything other than himself. Furthermore, the chemical engineer will find it to his advantage to maintain his conduct on a basis that can stand inspection by any of his associates. He will be respected for this. He will find it well to assume that the moral and ethical standards of his associates are as high as his.

The young chemical engineer should understand at the very beginning that he is working for his superior or boss. His boss must know what is being done in his organization or he cannot intelligently manage the work. Therefore, in loyalty to him the young engineer must keep him informed of the activities. Of course, the young engineer is also working for the enterprise, but everything he does his boss is responsible for. If he is the right kind (which is usually the case), he will take the responsibility of all the acts of his subordinate. The mistakes and errors of the subordinate will be accepted by the boss as his as far as those outside the immediate organization are concerned. Therefore, the subordinate owes his boss his complete loyalty. The young engineer must not ignore the boss in his rush to get results. It might appear on the surface at times that things can be accomplished with a saving in time by not working with and through the boss, but in the final analysis it will be found that actually time can be saved by taking cognizance of him. This is particularly true in a large organization.

If an engineer cannot give his boss his complete loyalty, for his own sake he should make a change. He should get a boss whom he can respect and to whom he can give his complete loyalty. Otherwise, he will establish himself as not being of the highest integrity. The chemical engineer cannot afford this if his objective is the heights of leadership.

Of course, the young engineer must exercise judgment in his contacts with his boss. His boss will expect him to use his own judgment and come forth with definite proposals in his work. He should therefore not plague his boss with incessant questions or with too frequent reports on his activities. At least he should get a reasonable amount accomplished before notifying the boss.

Whatever the boss requests should be given first-order priority. If it seems that his request is not feasible or is not for the best interests of the enterprise, arguments should be presented to him with a definite alternative plan that is believed to be better. If after the arguments and proposed plan are presented he still wishes to proceed according to his original request, the engineer should do his very best to accomplish what the boss wishes. He may have reasons he is not free to disclose for wanting his original plan carried out. If the additional information could be disclosed, in all probability it would be agreed that his request is the most reasonable. Loyalty to the boss includes furthering his interests, and this means keeping him from making a move that is not to his best advantage. Therefore, the engineer should never act on a request by his boss until it has been analyzed in the light of probable results and the effect they will have on the enterprise. The engineer must not be a "yes man"—that is not an expression of loyalty. The progress of boss and enterprise is the progress of the engineer.

Responsibility.—This essential quality of leadership is in some respects similar to integrity and in some respects different. The leader must be eager to accept responsibility. Furthermore, he is not given to "passing the buck." He accepts not only the responsibility for his own acts but also that for the acts of his subordinates, even though the latter may have acted contrary to his requests. Of course, he may severely reprove the subordinate or even discharge him, but to all other parties the leader accepts all the responsibility and takes all the blame. In general, people fear responsibility because of the possibility of blame. On the average, they are timid and lazy. They want a leader to shoulder their burdens and plan their course of action. They hope for gain without the possibility of penalty. The leader must therefore take all responsibility.

The leader does not become a leader because he is a hard worker, although he usually is. He becomes a leader because he assumes the responsibility for making plans and getting results. Furthermore, no leader is a "bottleneck" to his organization. If the leader finds that he is unable to digest the results that his organization is getting, he takes immediate steps to correct the situation.

The young chemical engineer must learn to handle all assignments effectively, no matter how insignificant they seem. He will develop his capacity for responsibility in this way. More and more responsibility will be given him if he handles effectively jobs entailing little responsibility.

The engineer should be very careful of the accuracy of his results and statements. It is very important to be able to give an immediate answer to a question; but if the limits of accuracy are not known, they should be determined at once. A reputation for dependability and reliability is an index of the capacity for responsibility. Before submitting a report to a superior, the engineer should check the results carefully himself. There is nothing that shakes the confidence of a superior more than to have reports submitted to him for approval that are full of errors. Unfortunately, this is a blunder often made by young chemical engineers. As long as they do this, they need not ask why they are not given more responsibility. The answer is that they are not handling satisfactorily the responsibility they now have. If the engineer handles his present job well, the future will almost always take care of itself. He must learn to analyze his data and results from the standpoint of fundamental concepts to determine whether or not they are sound. Stupid conclusions are frequently drawn from poor data because these are improperly analyzed. The engineer must learn to question the reliability of his results and conclusions in order to determine whether or not they are consistent with other well-established facts. He should feel deeply his responsibility for the results and conclusions he presents.

Energy.—In general, people are lazy and indolent. Many persons of greater ability are willing to submit to the leader owing to sheer laziness. The leader devotes more time to the job than his followers. In addition, he works faster; and, above all, he gets results. He thinks more about the job while away from it.

Initiative is an expression of energy. The leader does not wait to be told about a job that should be done. He precedes the mass of people.

He is endlessly on the watch for things that need doing and seeing that they are done. He is a trail blazer. The majority of persons are in a rut and are willing to follow a leader who will get them out of it. The path of leadership is an untried one. It does not follow tradition. Tradition is a challenge to the leader. He is always starting and doing something new and different that is an improvement over what has been accepted previously.

The real leader never becomes a bottleneck. He never gives the answer that he has not had the time to direct work to a final conclusion. In a very short time he either accepts the results or states his objections, with a request for further development. One of the most common blunders of persons in a supervisory position is to hold up results that subordinates have submitted. This will kill initiative and disrupt morale. If the work of a group of persons is piling up on your desk, it is either because you are trying to do too much of the detail work yourself or because you do not have the ability to handle the job. If you wish to develop leadership capacity, get the habit of driving yourself with the minimum of waste effort. Take frequent inventory of what you have undertaken and what was accomplished. Profit from the mistakes you made that can be classified as waste motion. Keep driving at top speed toward your objective. You can acquire the habit of working continuously at high speed as easily as at low speed. Strive continuously to increase your speed, consistent with accuracy. It is significant that one is never paid for more than he does until he does more than he is paid for.

Skill in Human Relations.—This is a quality that is very important to those who are striving for executive positions. It is of far greater importance than technical ability, for the executive who understands people and directs their efforts can surround himself with persons who have the required technical chemical-engineering knowledge. The executive deals with people, whereas the individual worker deals primarily with subject matter. Of course, other things being equal, the executive who has both knowledge of people and knowledge of subject will be the best qualified.

The leader should have a thorough understanding of organization. He must be capable of organizing, deputizing, and directing. He must never be caught napping. There is nothing so detrimental to the prestige of a leader as to be caught "asleep at the switch."

Charles Steinmetz once stated, "Cooperation is not a sentiment. It is an economic necessity." Develop the habit of getting along with all kinds of people. Several books have been written on this subject. Cultivate the habit of reading such literature. In general, a strict observance of the golden rule and sincere interest in the welfare of your fellow man will lead to the desired end. King[1] presents several "do's" and "don'ts" that are worthy of thought.

1. Cultivate the tendency to appreciate the good qualities rather than the shortcomings of each individual.

2. Do not give vent to impatience and annoyance on slight provocation. Some offensive individuals seem to develop a striking capacity for becoming annoyed in which they indulge with little or no restraint.

3. Do not harbor grudges after disagreements involving honest differences of opinion. Keep your arguments on an objective basis and leave personalities out as much as possible. The purpose of argument is to persuade your opponent to accept your viewpoint, not merely to prove that you are right. You should be open to accept his viewpoint as well as to "sell" yours to him. Occasionally you will oppose a course of action which is being proposed. If you see that your opposition is futile, it is frequently more desirable to go with the tide and help control it than to be swept off your feet as it passes over you.

4. Form the habit of considering the feelings and interests of others.

5. Do not become unduly preoccupied with your own selfish interests. It may be natural to "look after Number One first," but when you do your associates will leave the matter entirely in your hands, whereas they will be much readier to defend your interests for you if you characteristically neglect them for unselfish reasons.

This applies particularly to the matter of credit for accomplishments. It is wiser to give your principal attention to the matter of getting the job done or to building up your men than to spend too much time pushing your personal interests ahead of everything else. You need have no fear of being overlooked; about the only way to lose credit for a creditable job is to grab for it too avidly.

6. Make it a rule to help the other fellow whenever the opportunity arises. Even if you are mean-spirited enough to derive no personal satisfaction from accommodating others, it is a good investment. The business world demands and expects cooperation and teamwork among the members of an organization. It is smarter and more pleasant to give it freely and ungrudgingly up to the point of unduly neglecting your own responsibilities.

7. Be particularly careful to be fair on all occasions. This means a good deal more than just being fair upon demand. All of us are frequently unfair, unintentionally, simply because we do not habitually view the matter from the other fellow's point of view to be sure that his interests are fairly protected. For example, when a man fails to carry out an assignment, he is sometimes unjustly criticized when the real fault lies with the executive who failed to give him the tools to do the job. Whenever you enjoy some natural advantage or whenever you are in a position to injure someone seriously, it is especially incumbent upon you to "lean over backward" to be fair and square.

8. Do not take yourself or your work too seriously. A normal healthy sense of humor, under reasonable control, is much more becoming, even to an executive, than a chronically soured dead pan, a perpetually unrelieved air of deadly serious-

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[1] KING, *op. cit.*

ness, or the pompous solemn dignity of a stuffed owl. The Chief Executive of the United States [the late President Roosevelt] smiled easily or laughed heartily on appropriate occasions, and even his worst enemies did not attempt to criticize him for it. It is much better for your blood pressure and for the morale of the office to laugh off an awkward situation now and then than to maintain a tense, tragic atmosphere of stark disaster whenever matters take an embarrassing turn. To be sure, a serious matter should be taken seriously and a man should maintain a quiet dignity as a rule, but it does more harm than good to preserve an oppressively heavy and funereal atmosphere around you.

9. Put yourself out just a little to be genuinely cordial in greeting people. True cordiality is, of course, spontaneous and should never be affected, but neither should it be inhibited. We all know people who invariably pass us in the hall or encounter us elsewhere without a shadow of recognition. Whether this be due to inhibition or to preoccupation, we cannot help feeling that such unsociable chumps would not be missed much if we never saw them again. On the other hand, it is difficult to think of anyone who is too cordial, although it can doubtless be overdone like anything else. It appears that most people tend naturally to be sufficiently reserved or overreserved in this respect.

10. Give the other fellow the benefit of the doubt if you are inclined to suspect his motives, especially when you can afford to do so. Mutual distrust and suspicion breed a great deal of absolutely unnecessary friction and trouble, frequently of a very serious nature. This is a very common phenomenon which can be observed among all classes and types of people in international as well as in local affairs. It is derived chiefly from misunderstandings, pure ignorance, or an ungenerous tendency to assume that a man is guilty until he is proved innocent. No doubt the latter assumption is the "safer" bet; but it is also true that if you treat the other fellow as a depraved scoundrel, he will usually treat you likewise, and he will probably try to live down to what is expected of him. On the other hand, you will get much better cooperation from your associates and others if you assume that they are just as intelligent, reasonable, and decent as you are, even when you know they are not (although the odds are 50:50 that they are). It is not a question of being naïve or a perpetual sucker; you will gain more than you lose by this practice, with anything more than half-witted attention to the actual odds in each case.

Although it is very noble to get along with all kinds of people, the leader will not tolerate being run over. The leader will command the respect of his associates. He will not be given to appeasement just to avoid a fight. He will not look for fights; but if they come his way, he will put up such a fight that his opponent will not forget it and will respect him. He will keep his arguments on an objective basis and "slug it out" with a smile on his face. The smile will permit him to fight more effectively, particularly if his opponent gets angry.

The great majority of chemical engineers will be employed in enterprises having many workers. The leader will always be a good representative of the enterprise. He will be one that his executives will be proud of. His personal appearance will be good at all times. His clothes will be well kept, his hands and nails clean, his manners of the best. Good manners are a result of habit and are merely an outward expression of the personality beneath the surface. If a man is inwardly inconsiderate of his associates, this will be obvious from his manners. The leader will not indulge in profanity. There is a difference between rough talk and profanity. The latter is repulsive to most persons. The chemical engineer cannot afford to be anything other than a gentleman.

In all transactions, whether a discussion of a project, a letter or memorandum, or entertainment of visitors, be sure to take cognizance of all those who are concerned. It is almost impossible to carry out a transaction involving persons who have not had a hand in it without producing bad feeling. A leader will always tell his subordinates in advance about changes that will affect them. He will tell them "why" and, if possible, will convince them that the change is desirable.

The smart leader will never let his friendliness affect discipline. His subordinates will know that even though he is friendly he is serious and must get results. He will always use disciplinary measures when needed, but they will be impartial and fair. He will likewise be just as ready or even readier to give recognition to the accomplishments of his followers. If the supervisor does not handle each issue effectively, he is not a leader and is not competent to hold his position. The leader cannot be too lax in dealing with his men. He will criticize them individually and privately with "straight from the shoulder" remarks. This will prevent the necessity of serious disciplinary measures later.

The leader will not try to do too much himself. Whenever the remark is made that a certain transaction cannot be handled for some time because a given person will not be available until then, the business is not properly organized. No leader should be so indispensable that the business must wait until he can "carry the ball." He should appoint a responsible assistant to act in his behalf.

If the leader has a complaint to make, he will go directly to the person responsible and make it. If he does not get satisfaction, he may then go to the executive in charge. Above all, he will not indulge in "bellyaching."

Ability to Express One's Thoughts.—The need for this essential quality of leadership is obvious to everyone; yet the average technical man is given too little training in it. If a person cannot express his thoughts so that others can benefit by them, he might just as well not have any thoughts, as far as society is concerned. The chemical engineer who has leadership ambitions must be able to express himself verbally and in writing clearly, concisely, and rapidly. This is a busy world, and people do not have the time to listen to a chemical engineer who rambles in circles while expressing his thoughts. Furthermore, people are lazy, and unless the chemical engineer can express himself so that his audience or readers can understand his ideas with little effort they will not listen to him or read what he has to say.

The busy executive will not assign responsibility to the chemical engineer who has the bad habit of surrounding his answer to a simple question with so many qualifications that the answer can hardly be detected. It is always best to give a direct and concise answer. The qualifications can then be presented, but they should be "boiled down" so that the executive will be able to understand them easily. Usually the reason why the average young chemical engineer cannot express himself clearly, concisely, and rapidly is that his own mind is confused. Do not let the trees obscure the forest. Form the habit of reducing everything to its fundamental elements. Leadership is the supreme example of influencing people, and thus the leader must be able to convey his thoughts effectively.

Ordinarily the pertinent questions of an executive will center in the following six words:

What Who
Why When
How Where

If the chemical engineer is prepared to answer such questions on his subject rapidly and concisely, he will be developing his leadership capacity.

Perhaps the weakest point in the work of a young chemical engineer is his written reports. It is so essential that he be able to prepare reports of high quality that the last chapter of this book is devoted to this subject.

Technical Ability.—This essential quality of leadership is perhaps the least important of the nine. It is, however, essential; do not assume that the heights of leadership in chemical engineering can be attained without it. There is one thing the chemical engineer must understand: when he completes his academic training, he has not received his education—he has merely been equipped with a few tools with which to obtain it. He has reached the threshold of his professional education and is headed in the right direction. The remainder of his professional life will be spent in getting his education. From about thirty-five to fifty-five years of age is the period of greatest productivity. Certainly up to thirty-five the young engineer should concentrate on gaining knowledge that broadens his capacities.

It also should be understood thoroughly that chemical engineering is a *profession*, not a trade. The chemical engineer cannot hope to succeed as a leader if he evaluates his work in terms of the number of hours he devotes to his job. Certainly he cannot expect to accomplish much if he devotes merely 40 to 48 hr per week to his professional interests. Actually he will find it to his advantage to devote not less than 12 hr per week to study directed toward developing and expanding his factual knowledge of chemical engineering and related subjects. Thus, it may be stated that the leader will devote not less than 56 hr per week to his professional interests, including his job. Even so, he will evaluate his efforts in terms of accomplishments and results rather than in terms of time devoted to the subject. He will not be mercenary. His objective will be to do a good or excellent job and to achieve professional distinction. The monetary return will come sooner or later—mostly later—but it will be on a sound foundation and accompanied with much more satisfaction.

Professional pride is very desirable. The leader is not satisfied with merely doing a job; instead, he is satisfied only by doing the best job. It is not necessary that the leader know the most about any given phase of the enterprise—as a matter of fact, this is sometimes undesirable. Nevertheless, the leader must have the broadest knowledge, the best perspective, and the greatest foresight. He must not be caught napping. He must be prepared for eventualities. He must understand the functions of the entire organization and should have the best concept of the economic factors involved. The wider his knowledge of the economic background, the greater his ability to guide and direct the efforts of his organization to the best advantage of the enterprise.

The leader can see the individual phases and at the same time the whole. He knows how each phase fits into the whole. He handles problems in the proper order with respect to importance. He reduces things to their fundamental parts. In the preparation and execution of a plan he will probably follow this procedure:

1. Set up an objective.
2. Plan and devise steps to reach the objective.
3. Follow the plan.
4. Take frequent inventory to determine results and desirable changes.
5. Complete the job.

The leader will investigate a project to establish its economic feasibility before he proposes it. He will support his proposal with the arguments that favor it but will also present any unfavorable factors. Above all, he will do no camouflaging to support the proposal. He will deal in terms of facts and logic. A complete plan is desirable to show how the proposal can be carried out. The smart leader will know when accuracy can be slighted in favor of saving time. Very frequently in process design and process calculations the chemical engineer will have the option of furnishing an approximation or long tedious calculations to determine the magnitude of an intermediate figure in the calculations. He should form the habit of determining quickly what the effect would be on the final answer of an error in the intermediate figure, which corresponds to the limits of accuracy of the approximate method. In many cases it will have no important effect, and therefore time should be saved by using an approximation.

The chemical engineer must be very careful in respect to accuracy. He must be reliable in what he says as well as in what he writes. It is better to qualify a statement in regard to accuracy and confirm it at once than to have one's unqualified statements found later to be in error by others. Rapid answers are very desirable only if they are sufficiently accurate.

Fundamental knowledge should be kept well in hand. If one is adept in the application of fundamentals, he can arrive at answers quickly without carrying so much bulk factual information in his head. Imagination is one of the greatest assets of the chemical engineer. With a keen imagination and a thorough knowledge of fundamentals, the chemical engineer can become outstanding technically.

Conclusion.—Chemical engineering is a profession. The chemical engineer can enjoy the same position in his community as that of any other professional man such as the doctor or lawyer. However, his position will be about proportional to his efforts in the affairs of the community. The chemical engineer cannot bury himself in his professional work and expect to maintain leadership in the community. It has become of increasing importance that the technically trained man take an active part in the affairs of the community, state, nation, and world. Certainly the Second World War showed the relative value of the chemical engineer in the affairs of the nation. Chemical engineers were given a top position on the deferment list. The same knowledge required to carry on a war is needed to maintain the peace. What the chemical engineer does is of such great importance to society that society needs him to help in the affairs of the community, state, nation, and the world.

The chemical-engineering profession has hitherto been uncontaminated by shady politics, and it must remain so. The chemical engineer can influence people because of this fine record. He must do so in order that the affairs of our nation be properly handled.

QUESTIONS

1. What important decision should the young chemical engineer make early in his professional practice?

2. Which phase of chemical engineering becomes of greatest importance as the chemical engineer enters executive work?

3. Give the opposite quality to the following, and state whether they indicate the executive or individual-worker type:

Extrovert
Idealistic
Ability to get many things done
Cordial, affable
Slow, methodical
Retiring
Noisy
Impulsive
Bold
Adaptable

4. What are the nine essential qualities of leadership?

5. By which of the two routes (that of the executive or the individual worker) may the chemical engineer become a leader?

6. Discuss the essential quality determination. Does it involve intellect? What is it? How does the follower know the leader has determination?

7. After an order for material or work is placed by the chemical engineer, what should be his procedure?

8. Why does a company employ a chemical engineer?

9. What is self-confidence, and how do the leader's followers recognize it?

10. Why is self-confidence so important in the leader?

11. Should the leader be willing at all times to change his plan or program? Why?

12. Why do most people avoid decisions?

13. How should the chemical engineer conduct himself? Why?

14. How should the chemical engineer look upon his associates?

15. Should the chemical engineer determine what he thinks the boss wants before he proceeds?

16. Why do people want a leader to take responsibility?

17. If the chemical engineer is assigned to an unimportant task, what should be his reaction?

18. What should the chemical engineer do before he submits a report to his boss?

19. Why are persons often willing to follow a leader with less ability than they have?

20. How do initiative and tradition fit into the life of the leader?

21. What is the chief distinction between the work of an executive and the work of an individual worker?

22. What is a good general policy to follow in dealing with one's fellow men?

23. What are 5 of the 10 "do's" and "don'ts" in dealing with one's fellow men?

24. What is the purpose of argument?

25. How should one conduct an argument?

26. To what extent does the leader practice getting along with all kinds of people?

27. In the discussion of a proposed action that you are opposing should you stand your ground to the bitter end? Why?

28. How must the chemical engineer be able to express himself?

29. What plan should be followed by the chemical engineer in any project?

30. Why should the chemical engineer devote efforts to the affairs of society?

CHAPTER III

USEFUL MATHEMATICAL TOOLS

Now that some of the nontechnical aspects of chemical engineering have been covered briefly, the technical features will be considered. Before these are discussed, however, it is desirable to devote some attention to certain mathematical "tools" that will be found invaluable throughout the professional career of the chemical engineer. It is the purpose of this chapter to describe them. To some extent their discussion here will represent mere repetition for the reader. Even so, this will emphasize their importance and serve as a review.

TRIAL-AND-ERROR CALCULATIONS

In the average course in abstract mathematics each problem will usually have a definite analytical solution. In such cases the correct answer will be definite and fixed. If the correct answer is 2.0, a result of 1.99 or 2.01 will not be acceptable. In the practice of chemical engineering, however, such accuracy is in general quite acceptable, for it is usually well within the required accuracy for engineering purposes. The chemical engineer does not seek an abstract answer. Instead, he wishes to determine the size of some piece of equipment in a design or perhaps the most economical conditions under which to operate existing equipment. Mathematics will be applied only as a means to the desired end. Furthermore, the basis he selects for his design or process calculations will be of far greater importance than any inaccuracy that may be incurred owing to reading his slide rule. Thus, for the purpose of the chemical engineer 2.01 will be as acceptable as 2.0 in most cases.

Many of the process calculations will involve the use of mathematical functions that are represented graphically. The functions may be correlations of data that have been obtained experimentally and at times may not be reliable within ±10 per cent. Even so, if the chemical engineer knows the limits of accuracy, he can make due allowance in his final results.

It is not infrequent that the chemical engineer must solve his mathematical problems by a trial-and-error procedure. This is true particularly when tabular or graphical functions are used in the solution. The method of attack involves first the assumption of the answer or sometimes an intermediate figure. Then the calculations are carried out, based on the assumed figure. When the final answer is obtained, it is checked by independent relations to determine whether it is consistent when tested by these relations. The trial-and-error type of solution is illustrated in Example 1.

Example 1. It is found that the amount of water at 70°F that will flow through a length of pipe can be calculated from the following equation:

$$\Delta P = \frac{0.0269 f L V^2}{D}$$

where ΔP = pressure drop through the pipe, lb/sq in.
L = length of pipe, ft
V = average linear velocity of water flowing through the pipe, ft/sec
D = inside diameter (i.d.) of pipe, ft
f = friction factor, which is dependent upon the product DV, as shown in the tabulation below

f	DV
0.0100	0.0454
0.0080	0.1077
0.0060	0.378
0.0050	1.077
0.0042	3.78
0.0037	10.77
0.0032	37.8

It is desired to calculate the amount of water that will flow through 1000 ft of pipe having an inside diameter of 6.065 in. if the available pressure is sufficient to provide only 1.21 lb/sq in. pressure drop through the 1000 ft of pipe.

Solution: Since the value of f is dependent upon the value of V, which in turn is directly related to the final answer desired, it will be necessary to assume values of V or f and then calculate ΔP from the equation to determine whether or not it is consistent with the value given.

Assume $f = 0.0042$.

Then

$$V = \frac{3.78}{6.065/12} = 7.48 \text{ ft/sec}$$

$$\Delta P = \frac{(0.0269)(0.0042)(1000)(7.48)^2}{0.505} = 12.5 \text{ lb/sq in.}$$

which is too high compared with the available ΔP of 1.21 lb/sq in.

Assume $f = 0.0050$.

Then

$$V = \frac{1.077}{0.505} = 2.13 \text{ ft/sec}$$

$$\Delta P = \frac{(0.0269)(0.0050)(1000)(2.13)^2}{0.505} = 1.21 \text{ lb/sq in.}$$

which checks with the available ΔP.

Thus, the amount of water that will flow through the pipe is

$$\frac{(3.14)(0.505)^2(2.13)}{4} = 0.426 \text{ cu ft/sec}$$

or

$$(0.426)(7.48)(60) = 191.5 \text{ gal/min}$$

The solution of Example 1 above is quite simple inasmuch as a sharp negative convergence occurs. That is, as f is *increased* in small increments, the values of V and ΔP *decrease* sharply. Hence, the calculated value of ΔP converges rapidly in an opposite direction to the change in the assumed values of f. Sometimes negative convergence will occur at a low rate. For large changes in the assumed values of the key variable, rather small changes will occur in an opposite direction in the final answer. Nevertheless, as long as the convergence is negative, the solution is usually not so time-consuming. Trial-and-error solutions will be encountered, however, in which the convergence is positive. These are usually more time-consuming.

If an equation were available in Example 1 that gave f as a function of DV, it might be possible to solve directly for V. Even so, it is likely that the function would be so complicated that, in the end, time would be saved by resorting to the trial-and-error type of solution. This is true particularly when the graphical or tabular functions are quite complicated. The trial-and-error type of solution is very common in chemical-engineering calculations, and therefore the student must develop his skill in such solutions.

DIMENSIONAL CONSISTENCY

One of the most common sources of error in chemical-engineering calculations is the confusion of dimensions. It is very desirable that the student develop the habit of examining mathematical expressions he uses or develops to determine whether or not they are dimensionally sound. For example, any relation that expresses linear velocity should have the dimensions of length/time. Otherwise it is not fundamentally sound for general application. All fundamental equations are dimensionally consistent.

In this connection it will be noted that the equation

$$\Delta P = \frac{0.0269fLV^2}{D}$$

as given in Example 1 is dimensionally inconsistent. The dimensions of the left member correspond to force[1] per unit area where the force

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[1] It is common practice to state the dimensions of pressure and pressure drop in terms of pounds per unit area. This is pounds of force—not pounds of mass. The chemical engineer must be cautious not to confuse the use of pounds in this instance with pounds of mass.

is expressed in pounds of force. The unit of force of one pound is that which the earth exerts on one pound of mass at sea level or a force which gives a mass of one pound an acceleration equal to that of gravity g. It is therefore 32.2 times as great as the force of one poundal. The dimensions of the poundal are (lb)(ft $\sec^{-2}$) since force is equal to the product of mass and acceleration. The dimensions of the force of one pound are (lb)(G $\sec^{-2}$), where G is a unit length that is equivalent to g ft or 32.2 ft. Thus, the dimensions of the left member of the above equation are (lb of force)(in.$^{-2}$) or (lb)(G $\sec^{-2}$)(in.$^{-2}$).

The right member includes the friction factor, f, which is dimensionless, as will be found in Chap. VI. If this fact is accepted, it will be apparent that the dimensions of the right member, exclusive of the proportionality constant, are (ft)(ft $\sec^{-1}$)^2(ft^{-1}), or ft^2 $\sec^{-2}$. Thus it is apparent that three different units of length appear, *viz.*, in., ft, and G.

In order to utilize only one unit of length, two of the units must be converted to the third. If the foot is selected, it will be necessary to multiply the dimensions of the left member by (ft G^{-1}) to convert G to feet and by (in.^{2} ft^{-2}) to convert in.$^{-2}$ to ft^{-2}. The dimensions of the left member would then be (lb ft^{-1} $\sec^{-2}$), which is poundals per square foot.

The numerical value of the left member would therefore be (32.2)(144), or 4637 times as large as with the previous dimensions of pounds of force per square inch. Furthermore, to maintain the equality, the proportionality constant of the right member must be multiplied by 4637.

Although not apparent to the beginner the pressure drop is proportional to the density of the flowing fluid, ρ, which for water at 70°F is 62.3 lb/cu ft. Thus, if ρ is inserted in the right member, the proportionality constant must be divided by 62.3. The new value of the proportionality constant is therefore (0.0269)(4637)/62.3, or 2.0. With ρ included, the dimensions of the right member become (ft^2 $\sec^{-2}$)(lb ft^{-3}) or lb ft^{-1} $\sec^{-2}$, which is identical with the dimensions of the left member when converted to poundals per square foot.

Although the equation with the conversions as indicated is entirely consistent, pressure drop is usually quoted in pounds force per unit area. Consequently, if this is done, the numerical value of the left member will be g^{-1}, or 1/32.2 times as large as when expressed in poundals per unit area. Also, in order to maintain the equality, the right member must be divided by g or 32.2, which gives the final equation (3.1). This is dimensionally consistent and generally applicable.

$$\Delta P = \frac{2fLV^2\rho}{gD} \tag{3.1}$$

This is known as the Fanning equation.

An equation that is referred to as dimensionally homogeneous or dimensionally consistent will be equally applicable with any consistent set of units such as feet, pounds, and seconds. It will make no difference whether the English or metric system is used as long as consistent units are used for each dimension. It is not advisable to substitute values of the variables that involve different units of the same dimension, such as feet and inches. It is suggested in particular that the beginner in chemical engineering follow this rule. Also, in complicated equations it is a good plan to set up equations involving only the dimensions, to be sure that the dimensions cancel out consistently.

Dimensional Analysis.—Many of the scientific and technical phenomena that are encountered are so complicated that a direct fundamental mathematical analysis is hopeless. Of course, such an analysis is always the most informative in regard to the relationship between the various independent variables if it can be made. Nevertheless, in the more complicated systems a direct analytical solution is almost always beyond the available knowledge. In such cases, a considerable amount of valuable information can be obtained by the mathematical tool, dimensional analysis. This approach will not provide a complete knowledge of the relationships between the independent variables. Nevertheless, much can be learned that will reduce the amount of experimental work necessary to establish the relationships. The full benefits of dimensional analysis can be realized only when combined with experimentation.

Dimensional analysis can be applied when an incomplete knowledge of the system is available. Even so, this method of attack can be used effectively only when all the factors or variables that affect the system are known. Dimensional analysis will indicate the logical combination of the variables into dimensionless groups. This is particularly valuable in the interpretation of data that were obtained while two or more variables were not held constant.

Bridgman [1] has shown that dimensional analysis is applicable because of two important properties of all fundamental equations as customarily presented, *viz.*: (1) The numerical value of the ratio of the measurements of any two concrete things (for example, the velocities of two objects) is independent of the system of units used in the measurements, provided that the same units are used in each case. (2) The type of equations in scientific and technical use is given in a form such that they are independent of the system of units of measurement employed. Based on these two properties of all fundamental equations, a relation known as the π theorem was developed.[1] The form of any fundamental equation is

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[1] BRIDGMAN, P. W., "Dimensional Analysis," Yale University Press, New Haven, 1922.

unaffected by the system of units, and the dimensional constants and variables can be arranged so that they are combined into dimensionless groups. Also, the variables and dimensional constants of any fundamental equation may be expressed as products and powers of the units of measure used to evaluate them. That is, the dimensions of the variables may be substituted directly for the variables in a dimensional analysis.

Application of dimensional analysis to any situation is carried out on the basis of the π theorem. There are three steps in the method, *viz.*, (1) identification of all variables that affect the phenomenon, (2) substitution of the respective dimensions for each variable, and (3) calculation of the proper arrangement of variables into dimensionless groups. The final equation that involves the dimensionless groups will have the following form:

$$X_0 = CX_2^aX_3^bX_4^c \cdots X_n^z \tag{3.2}$$

where X = variable
C = proportionality factor

The subscripts refer to different variables, and the exponents are to be determined. In regard to the third step in this procedure, according to the π theorem the number of dimensionless groups will usually be equal to the difference between the number of variables (including dimensional constants) and the number of dimensions involved. Occasionally, however, the number of dimensionless groups may be greater or less than this difference. This will be easily detected, however, by inspection of the condition equations developed in the third step of the procedure mentioned above as, for example, when two or more of them are identical. The procedure of application of dimensional analysis will become somewhat clearer from the following example given by Bridgman.[1]

Example 2. Assuming the time of swing of a simple pendulum is dependent upon its length, mass, and acceleration due to gravity, develop a relation between these variables by dimensional analysis.

Solution:

Step 1:

Variable	Symbol	Dimensions
Length of pendulum	l	L
Mass of pendulum	m	M
Gravity	g	LT^{-2}
Time of swing	t	T

---

[1] *Ibid.*

Step 2:

$$t = Cl^a m^b g^c$$

Substituting the dimensions for each variable,

$$T = L^a M^b (LT^{-2})^c$$

Since the dimensions of each member of the equation must be identical, the condition equations are obtained by equating the exponents of each unit in the left member of the equation to the exponents of the same unit in the right member of the equation.

For T, $1 = -2c$, since the exponent of T is unity in the left member and is $-2c$ in the right member.

For L, $0 = a + c$, since the exponent of L is zero in the left member and is $a + c$ in the right member.

For M, $0 = b$, since the exponent of M is zero in the left member and b in the right member.

Thus,

$$c = -\tfrac{1}{2}$$

$$a = \tfrac{1}{2}$$

$$b = 0$$

$$t = Cl^{1/2} m^0 g^{-1/2}$$

$$t = C\sqrt{\frac{l}{g}} \quad \text{or} \quad C = t\sqrt{\frac{g}{l}}$$

Thus, it is seen that mass of the pendulum has no effect on the time of swing. Of course, this was known from the early study of physics. Also, by the direct analytical solution it was found that the proportionality constant C in the above equation is equal to 2π. It will be noted, however, that, even though the solution by dimensional analysis did not provide the value of C, it gave the relation of the variables with respect to each other. This is of great assistance in determining the complete relationship by experimentation.

In order to give further demonstration of the application of dimensional analysis, this method of attack will be applied to a problem in fluid flow.

Example 3. It is believed that the pressure drop through a straight pipe is a function of the length of the pipe, the diameter, density of the fluid flowing, linear velocity of the fluid through the pipe, and viscosity[1] of the fluid. Determine a relationship between these variables by dimensional analysis.

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[1] Viscosity is a property of a fluid that represents the resistance to the flow of the molecules of the fluid over each other. It has been found that the resistance force to the flow of molecules in one plane, in a direction parallel to the molecules in a second (parallel) plane, is directly proportional to the area in the first plane covered by the molecules, directly proportional to the linear velocity of flow in the first plane relative

Solution:

Variables	Symbols	Dimensions
Length of pipe	l	L
Diameter of pipe	D	L
Density of fluid	ρ	ML^{-3}
Linear velocity	V	LT^{-1}
Viscosity	μ	$ML^{-1}T^{-1}$
Pressure drop	ΔP	$ML^{-1}T^{-2}$

It seems apparent that the pressure drop would be proportional to the length of the pipe. Thus,

$$\frac{\Delta P}{l} = CD^a\rho^bV^c\mu^d$$

There are five variables and three dimensions, and thus two dimensionless groups would be expected. Substituting the dimensions of each variable,

$$ML^{-2}T^{-2} = (L)^a(ML^{-3})^b(LT^{-1})^c(ML^{-1}T^{-1})^d$$

Condition equations:

$$\text{For } M, \quad 1 = b + d$$

$$\text{For } L, \quad -2 = a - 3b + c - d$$

$$\text{For } T, \quad -2 = -c - d$$

Thus, there are three equations and four unknowns; thus one of the unknowns will be retained.

Retaining d,

$$b = 1 - d$$

$$c = 2 - d$$

$$a = -2 + 3(1 - d) - (2 - d) + d = -1 - d$$

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to the second, and inversely proportional to the distance between the two planes. Thus,

$$\text{Force} = \mu\left(\frac{\text{area} \times \text{velocity}}{\text{distance}}\right)$$

where μ is the proportionality constant.

Thus,

$$MLT^{-2} = \mu L^2LT^{-1}L^{-1} = \mu L^2T^{-1}$$

$$\mu = ML^{-1}T^{-1}$$

The dimensions of μ are pounds per foot per second in English units or grams per centimeter per second in the metric system. The dimensional constant μ is the absolute viscosity of the fluid.

Then,

$$\frac{\Delta P}{l} = CD^{-1-d}\rho^{1-d}V^{2-d}\mu^{d}$$

$$= C\left(\frac{\rho V^2}{D}\right)\left(\frac{\mu}{DV\rho}\right)^{d}$$

$$\frac{\Delta PD}{l\rho V^2} = C\left(\frac{\mu}{DV\rho}\right)^{d}$$

or

$$\Delta P = \frac{l\rho V^2}{D} C\left(\frac{DV\rho}{\mu}\right)^{-d} = \frac{l\rho V^2}{D} f'\left(\frac{DV\rho}{\mu}\right)$$

f' and C are functions to be determined. It will be noted by comparison with the Fanning equation, presented earlier in this chapter, that the above equation is quite similar. If f' is replaced with $2f$ and the right member is divided by the constant g (poundals/pound force), the equations are identical.

It is apparent from the above examples that dimensional analysis can be of great assistance in the investigation of complex scientific and technical phenomena. Perhaps its greatest value as far as the student is concerned at this time will be in providing a knowledge of the properties of fundamental mathematical expressions with respect to dimensions. This knowledge should be helpful to the student in chemical engineering in avoiding the common errors in calculations due to confusion of units of dimensions.

GRAPHICAL REPRESENTATION

The chemical engineer uses graphical representation of technical data and mathematical functions quite freely because this method provides a much clearer understanding of the relation between variables than tabular presentations of data and algebraic equations. Usually, fundamental physical and chemical data are presented graphically to greatest advantage. In general, the purposes for graphical presentation may be summarized as follows: (1) to provide a clearer concept and more complete knowledge of the phenomenon under consideration; (2) to simplify the correlation of data with respect to pertinent variables; (3) to utilize a simplified and convenient method of calculation.

For the purpose of this text, it is neither necessary nor desirable to present a complete treatment of graphical representation. It is the objective merely to give some of the essential items that will facilitate the application of chemical-engineering fundamentals by the student in the later chapters. For a more complete treatment of the subject the reader is referred to Sherwood and Reed,[1] Perry,[2] and Lipka.[3]

Flow Sheets.—In all calculations that involve processes and process equipment even the experienced chemical engineer should begin by drawing a diagrammatic representation of the process or process equipment. This is especially important in the case of material balances and energy balances. A very common error in such calculations is to forget one of the streams of material and the energy which it contains and which enters or leaves the process. In the case of performance investigations of commercial units it is very desirable that the plans of the investigation be based on an accurate flow sheet of the process. Too frequently much costly investigation is carried out and when calculations are being made it is discovered with much embarrassment and loss of prestige that one or more pertinent streams were not included in the performance test. Thus, in all probability the work must be repeated. Flow sheets help to avoid such stupid errors. Also, they will be found very convenient for reporting process data in connection with performance studies. The reader can see at once the significance of a temperature, pressure, or flow rate.

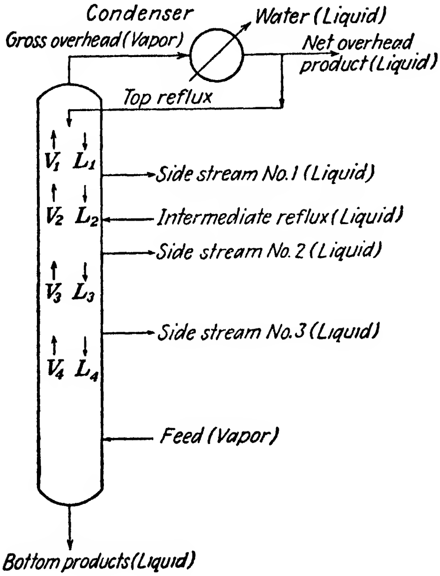

FIG. 3.1.—Distillation column.

As an example of the use of a flow sheet or flow diagram, consider a heat and material balance on a distillation column. The flow diagram is given in Fig. 3.1.

Although the reader may not be familiar with the theory of distillation, perhaps from his study of general chemistry and physics he has become familiar with such fundamental laws as the conservation of mass and the

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[1] SHERWOOD, T. K., and C. E. REED, "Applied Mathematics in Chemical Engineering," McGraw-Hill Book Company, Inc., New York, 1939.

[2] PERRY, J. H., "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

[3] LIPKA, J., "Graphical and Mechanical Computation," John Wiley & Sons, Inc., New York, 1921.

conservation of energy. Only these features will be considered at this time.

It will be noted from Fig. 3.1 that there are a number of streams which enter and leave the process. If *all* these streams are not considered, neither the material nor energy balance will be valid. It is apparent that without a diagram it would be relatively easy to overlook one of the streams. In view of this, it will be agreed that a flow diagram is quite essential in such calculations. The chemical engineer will occasionally be tempted to avoid making a flow sheet in order to save time in obtaining results. This is a bad practice, for errors are made most often in working rapidly in an effort to complete a job in the minimum amount of time. It is far better to consume a few more minutes and have everything in the calculations that is necessary than to get a result that is in error. Usually time will be saved by first drawing a flow diagram.

Graph Paper.—There are several types of graph paper with which the beginner in chemical engineering should become acquainted. Each type has its advantages for certain applications. Several different types are marketed by the Codex Book Company, New York; Schleicher and Schull, New York; the Educational Exhibition Company, Providence, R. I.; and Keuffel and Esser Company, New York.

The most common graph paper is the arithmetic type shown in Fig. 3.2. It is supplied in various forms, such as 10 lines per centimeter (sometimes called millimeter paper), 10 lines per inch, and 20 lines per inch. Also, it is available in thin paper suitable for blueprinting or ozaliding and in heavier paper. The lines of the graph are obtainable in different colors such as orange, green, and blue. The first two colors will photograph and ozalide, but with the standard processes the blue lines will not. The chief advantage of the blue lines is that lines, letters, and symbols to be reproduced can be drawn on the graph in ink or pencil and only these will be reproduced by photostating, planographing, or ozaliding. This effects a great saving in time in the preparation of reports, manuscripts, etc. The arithmetic type of graph paper is best for presenting straight-line functions such as

$$y = mx + b$$

where y = ordinate
x = abscissa
m = slope
b = intercept of the y axis

It is almost always desirable to use the type of graph paper that permits the representation of theoretical and experimental relations as straight lines, for a straight line is the simplest type of curve and lends itself readily to extrapolation and interpolation.

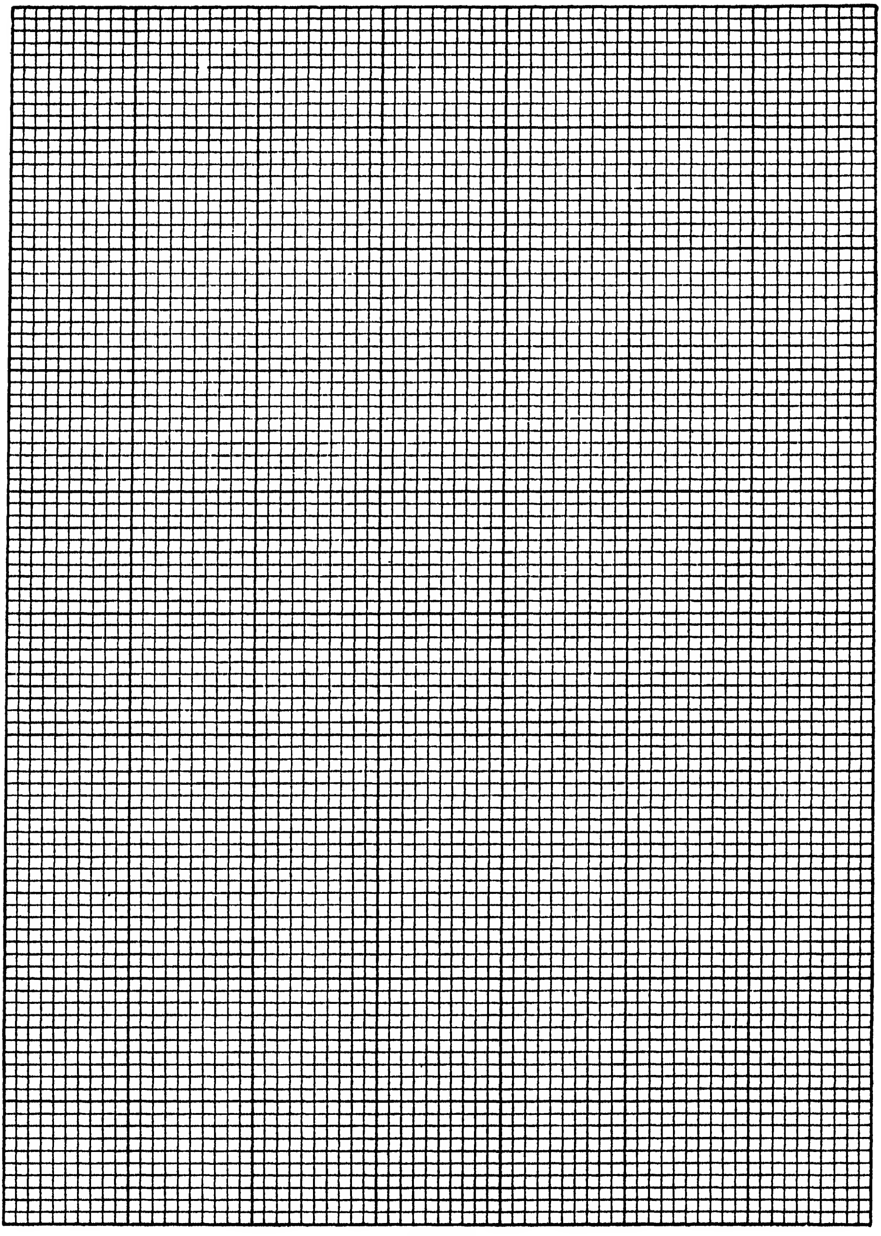

Fig. 3.2.

Another quite common graph paper is the logarithmic type shown in Fig. 3.3. The coordinates represent the logarithm of the variables on an arithmetic type of graph, but instead of identifying the coordinate lines with the values of the logarithms the corresponding values of the variables

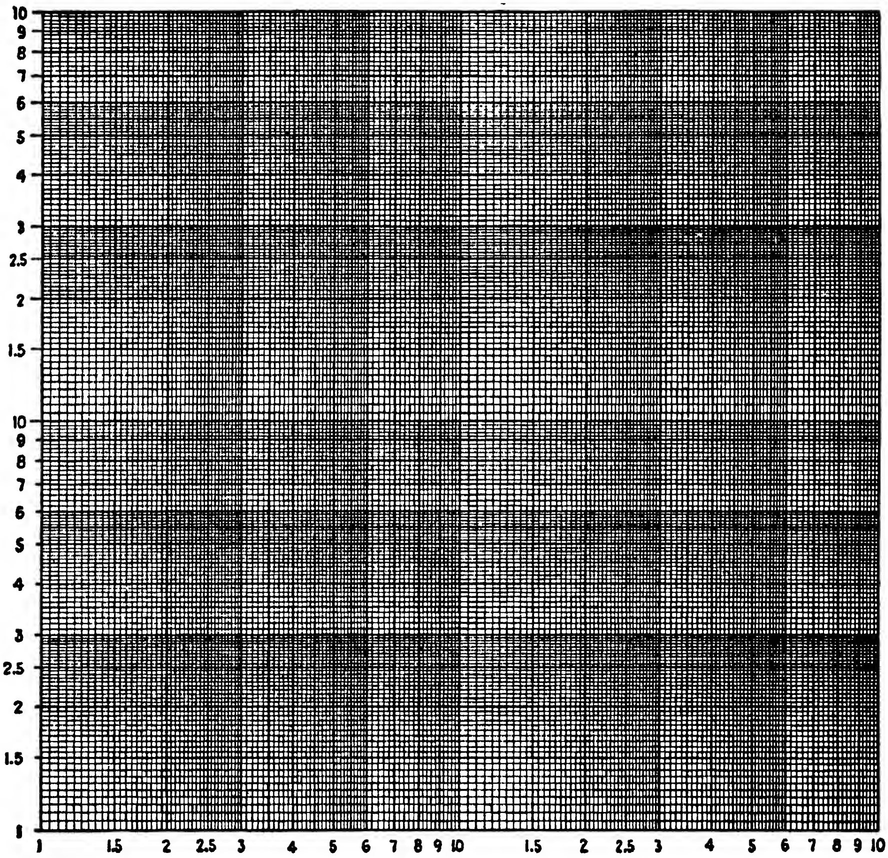

Fig. 3.3.

(antilogarithms) are substituted. Thus, considering one complete cycle such as 1 to 10, the distance from 1 to another coordinate line corresponds to the logarithm of the number that identifies this line. The logarithmic type of graph paper is therefore particularly suited for the representation of functions of the following type,

$$y = mx^n$$

where m and n are constants. Many functions of this type or approaching this type are encountered in chemical engineering. They can be repre-

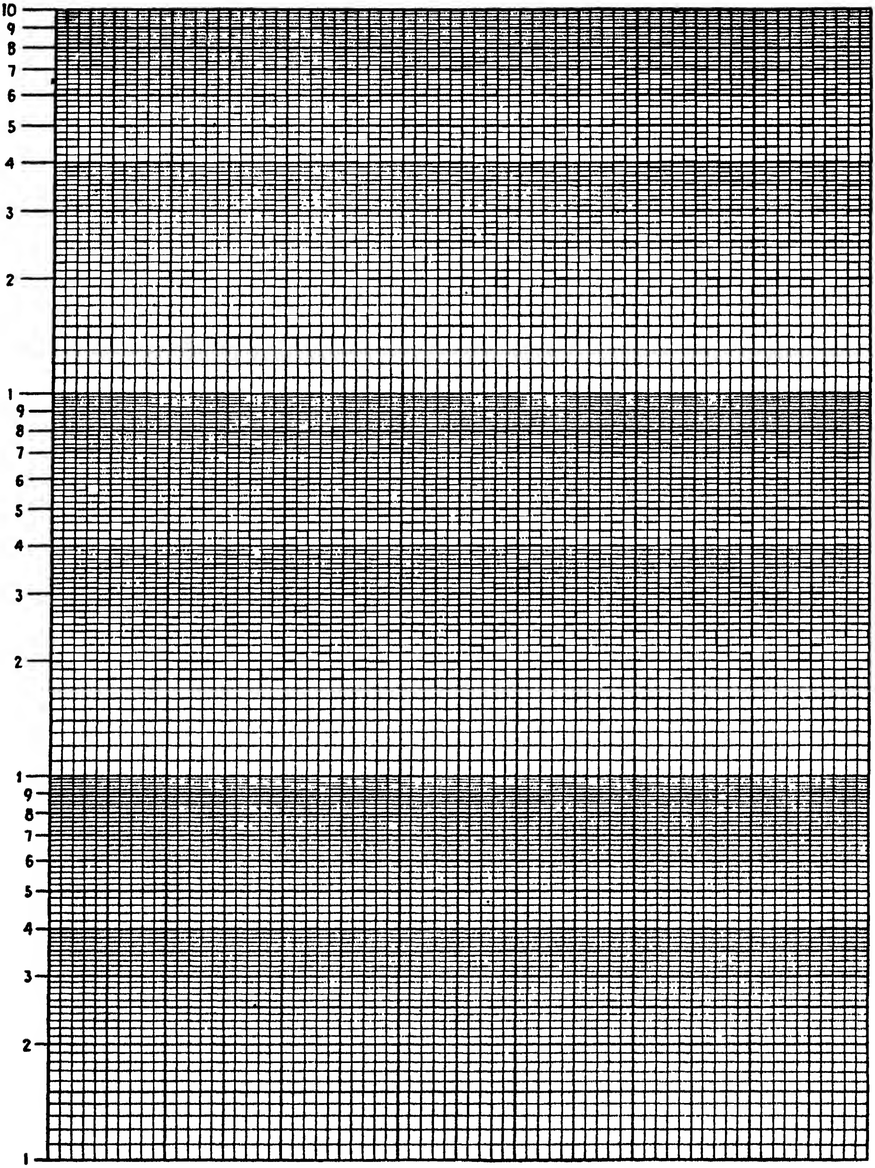

FIG. 3.4.

sented as straight lines or nearly straight lines on logarithmic paper. An important property of the logarithmic graph is that a fixed vertical distance or a fixed horizontal distance represents the same percentage change in the respective coordinate at any place on the graph.

The semilogarithmic graph paper (Fig. 3.4) has one coordinate laid off as a logarithmic scale and the other coordinate as an arithmetic scale.

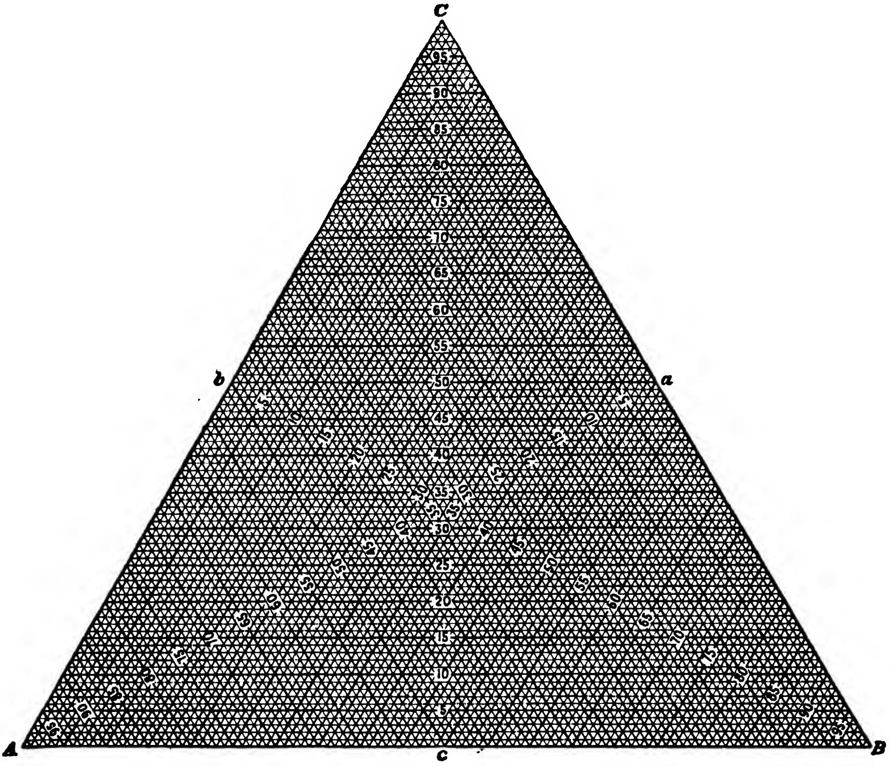

Fig. 3.5.

It is well suited for the representation of functions of the following type,

$$\log y = mx + b$$

where m and b are constants. This function can be represented as a straight line on semilogarithmic paper. Here again this type of function is frequently encountered in chemical engineering. Also, any given distance along the logarithmic coordinate, any place on the graph, represents the same percentage change in the logarithmic coordinate.

In addition to the more common types of graph paper mentioned above, there are three less common types that are sometimes quite useful. These are probability, reciprocal, and triangular graphs. Probability graphs have one arithmetic coordinate and one coordinate that is laid off as a probability scale. A probability curve will therefore be represented by a straight line. The reciprocal type of paper has one coordinate laid off as a logarithmic scale and one coordinate as a reciprocal scale. The advantage of this type of graph paper is that the vapor pressure vs. temperature curves for liquids and the absolute viscosity vs. temperature curves for liquids and gases are represented as approximately straight lines. This is due to the fact that the logarithm of viscosity is almost inversely proportional to the corresponding absolute temperature. The triangular (trilinear) graph paper (Fig. 3.5) is especially adapted for representing the concentrations of a three-component system. It has the unique property that the sum of the perpendicular distances from any point within the triangle to the three sides is equal to the perpendicular distance from any apex to the opposite base. Because of this fact, trilinear graph paper is convenient for the study of three-component systems.

There are other types of graph paper that are used in chemical engineering, but their application will be apparent as they are encountered. If a more detailed treatment of the subject is desired, the reader is referred to Lipka,[1] Perry,[2] and Sherwood and Reed.[3]

GRAPHICAL SOLUTIONS

As the student in chemical engineering progresses through his academic training, he will find that there are many different calculations which can be carried out most conveniently by graphical or semigraphical methods. All the various types of graphical solutions cannot be taken up at this time, nor is it desirable to do so, for most such solutions are peculiar to a specific process or operation. But there are a few that are generally applicable throughout the study and practice of chemical engineering. At this point, therefore, graphical integration, graphical differentiation, and alignment charts will be discussed.

Graphical Integration.—Perhaps in the majority of cases in which the chemical engineer is faced with the integration of a function, the integration will be feasible only by graphical means. Even when an algebraic expression of a function has been developed, it will frequently be necessary to carry out the integration graphically because some of the variables in the algebraic expression can be evaluated only from graphical representations. Consequently, it is essential that the student in chemical engineering

[1] *Ibid.*

[2] *Op. cit.*

[3] *Op. cit.*

learn the operation of graphical integration at an early date. The method proposed is identical with that described by Running.[1]

If

$$y = F(x) \tag{3.3}$$

and

$$dy = f(x)\,dx \tag{3.4}$$

then

$$\int_a^b dy = \int_m^n f(x)\,dx = F(n) - F(m) \tag{3.5}$$

Thus, the area under the differential curve between two limits n and m is equal to the difference between the ordinates on the integral curve at values of the abscissas of n and m.

Consider the graphical function as presented in Fig. 3.6. Construct a series of small rectangles between the two limits so that the area between the top of each rectangle and the curve is divided into two segments of equal area. The width of the rectangles (dx) can be so chosen that the areas of the segments are sufficiently small for very accurate division of the segments to be attained by eye. The integration can then be carried out by determining the area of each rectangle and obtaining the summation of these areas between the limits. The integral curve can be constructed in accordance with Eq. (3.5) so that the difference between the ordinates which correspond to the two sides of each rectangle is equal to the area of the rectangle. The difference between the ordinates of the integral curve that correspond to the two limits m and n should be equal to the summation of the areas of the rectangles between these two limits. Perhaps the operations involved in graphical integration will be clearer by following through Example 4.

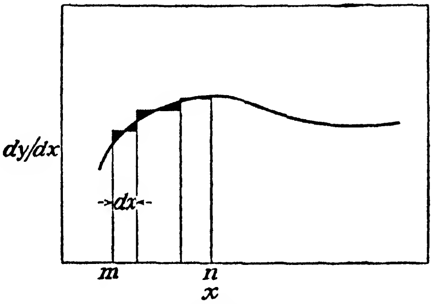

FIG. 3.6.

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[1] RUNNING, T. R., "Graphical Calculus," George Wahr, Ann Arbor, Mich., 1937.

Example 4. A gas is expanded at constant temperature from a volume of 100 cu ft at 300 lb/sq in. pressure to a volume of 300 cu ft at 125 lb/sq in. pressure. How much work is done by the gas if the volume and pressure observed during expansion are as follows:

Lb/Sq In.	Cu Ft
300	100
210	150
165	200
140	250
125	300

Solution. The work done by the gas is represented by $\int_{100}^{300} P\,dV$. Therefore, construct the function P vs. V on arithmetic graph paper with P as the ordinate and V as the abscissa (Fig. 3.7). The integral for the amount of work can then be evaluated by obtaining the area under the curve from $V = 100$ to $V = 300$. Construct the small rectangles, and determine their area.

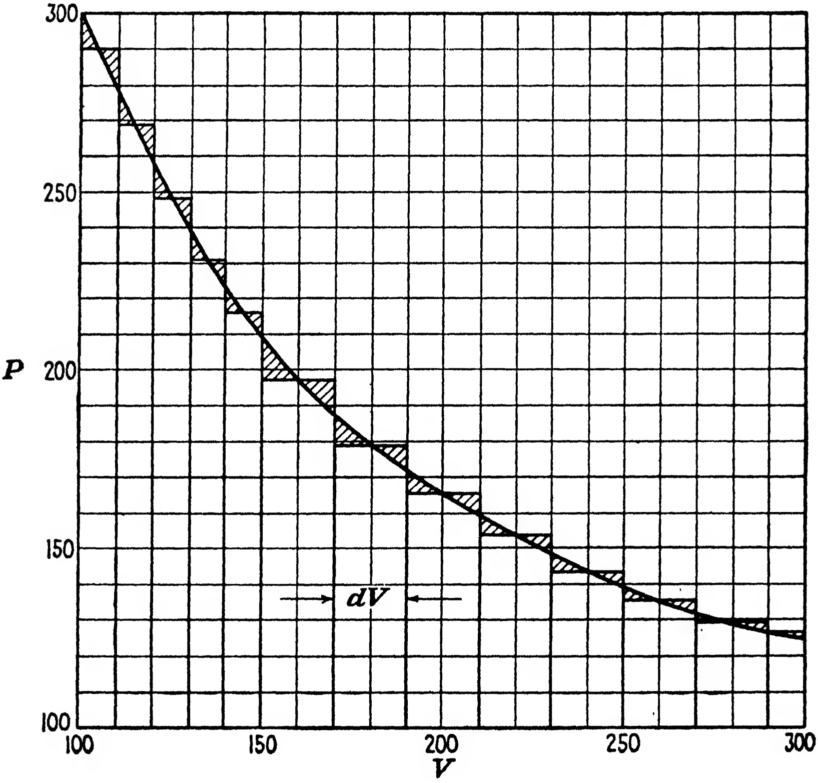

FIG. 3.7.

V	Av. P *	dV	$P\,dV$	$\int P\,dV$
100–110	290	10	2,900	2,900
110–120	268.5	10	2,685	5,585
120–130	248	10	2,480	8,065
130–140	231	10	2,310	10,375
140–150	216	10	2,160	12,535
150–170	197.5	20	3,950	16,485
170–190	179	20	3,580	20,065
190–210	165	20	3,300	23,365
210–230	153.5	20	3,070	26,435
230–250	143.5	20	2,870	29,305
250–270	135.5	20	2,710	32,015
270–290	129.5	20	2,590	34,605
290–300	126	10	1,260	35,865
			35,865	

* Height of the top of the rectangle, which is equal to the area under the curve between the same two values of the abscissa.

Thus, the total amount of work done was (35,865)(144) = 5.16×10^6 ft-lb.[1] The integral curve $\int P\,dV$ could be constructed from the column of figures headed by $\int P\,dV$. This would show the amount of work done in expanding the gas from 300 lb/sq in. to any intermediate pressure.

Graphical Differentiation.—The method for this operation is the reverse of the method for integration as described above. It was proposed by Running.[2]

From Eq. (3.5) it is seen that the area under the differential curve between two limits is equal to the difference between the two ordinates of the integral curve corresponding to the same limits. Thus, in order to differentiate a function, the integral curve should be divided into small segments, and the difference between the ordinates limiting each segment should be determined. That difference represents the area under the differential curve between the limits of the same two ordinates. Therefore, since the height of a rectangle is equal to its area divided by its

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[1] Do not be confused by the use of pounds here. It has reference to pounds of force—not pounds of mass.

[2] *Op. cit.*

width, each difference between two ordinates on the integral curve must be divided by the difference between the abscissas corresponding to the two ordinates. This will give the height of each rectangle. The differential curve should then be drawn through the top of each rectangle so that the area between the top and the differential curve is divided into segments of equal area. The differential curve should be smooth, and therefore care must be taken to see that its shape is not influenced by inherent inaccuracies in locating the tops of the rectangles.

The method of graphical differentiation will be clearer after following through Example 5.

Example 5. Water is delivered from an elevated tank for irrigation. The elevated tank is 12 ft in diameter by 20 ft in height. The drop in level in the tank was observed at various times as follows:

Outage, Ft	Min
0	0
3	30
5.5	60
7.5	90
9.0	120
10.0	180

Determine the instantaneous flow rate in gallons per minute as a function of time.

Solution: Convert the outage figures to gallons.

Outage		Time, min
Ft	Gal	
0	0	0
3	2535	30
5.5	4650	60
7.5	6340	90
9.0	7610	120
10.0	8450	180

The outage figures in gallons vs. time represents the integral curve that can be constructed on an arithmetic graph. Its actual construction, however, is not necessary inasmuch as the operations involved in differentiation can be carried out as a tabulation. The ordinate would be gallons; the abscissa, time. In this way dy/dx represents gallons per minute.

Integral curve				Differential curve, Δ gal/Δ min
Gal	Min	Δ gal	Δ min	
0	0			
		2535	30	84.5
2535	30			
		2115	30	70.5
4650	60			
		1690	30	56.3
6340	90			
		1270	30	42.3
7610	120			
		840	30	28.0
8450	~~180~~ 150			

In the above tabulation under Integral curve the difference between each two adjacent ordinates (gallons) was obtained and recorded under the heading of Δ gal. This represents the area of each of the rectangles or the area under the differential curve between the two corresponding abscissas (minutes). Then the difference between the corresponding abscissas was obtained and recorded under the heading of Δ min. The height of each rectangle is obviously the area (Δ gal) divided by the width of the rectangle (Δ min). This is recorded under Differential curve, Δ gal/Δ min. The top of each rectangle was drawn in Fig. 3.8. Then a smooth curve was drawn through the tops

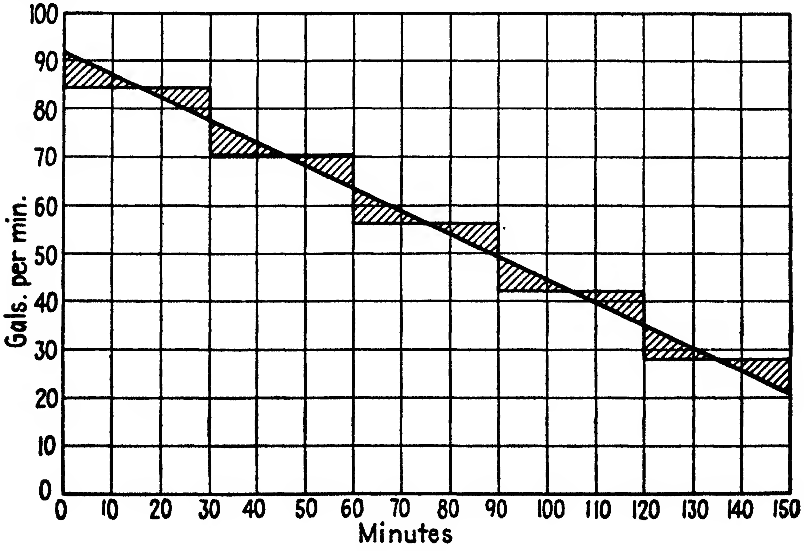

Fig. 3.8.

of the rectangles so that the area between each top and the smooth curve was divided into segments of equal size. The smooth curve happens to be a straight line. The straight line is the differential curve, and it gives the instantaneous rate of flow at any time during the period covered.

Alignment Charts.—Although graphs are of great assistance in many chemical-engineering calculations, in general it is not feasible to present the relationship between more than three variables on any one graph. If more than three variables are shown, the graph is complicated with so many curves that its utility is reduced owing to the difficulty of reading it.

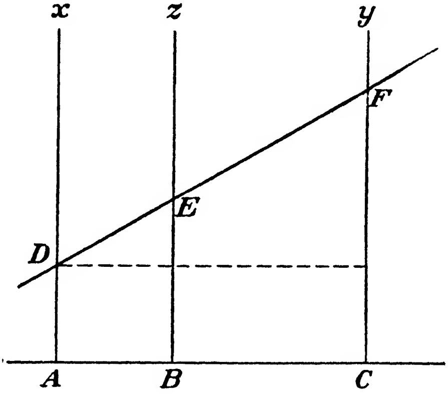

Fig. 3.9.

When it is desired to present the relationship between more than three variables, this can usually be done more effectively with an alignment, or nomographic, chart. The advantages of alignment charts are that (1) the relationship between several variables can be presented conveniently, clearly, and concisely; and (2) calculations can be made very rapidly. Alignment charts are especially helpful in calculations that involve repeated use of the same mathematical functions.

There are several types of alignment charts, but it is the purpose here merely to acquaint the reader with the subject, and thus only two types will be discussed. For a comprehensive treatment of the subject including detailed instruction on the construction of such charts, the reader is referred to Lipka.[1]

The most common and perhaps the most useful alignment chart is made up of three or more vertical parallel lines. Multiplication, division, addition, and subtraction can be done with this type of chart. Its simplest form, *viz.*, that made up of three parallel lines, will now be described.

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[1] *Op. cit.*

Construct three parallel vertical lines, spaced in any desired way, as in Fig. 3.9. These lines will represent x, y, and z. Then construct a line that is oblique to the three parallel lines and intersects the x line at D, the z line at E, and the y line at F. Then, by similar triangles, it is apparent that

$$\frac{CF - AD}{AB + BC} = \frac{BE - AD}{AB} \tag{3.6}$$

or

$$BE = \left(\frac{AB}{AB + BC}\right) CF + \left(\frac{BC}{AB + BC}\right) AD \tag{3.7}$$

Thus, it is seen that the length of the segment BE is directly related to the spacing of the lines and the length of the segments (above the base) on the x and y lines. If the x, y, and z lines are marked off in terms of the same unit length, it is apparent that

$$z = \left(\frac{AB}{AC}\right) y + \left(\frac{BC}{AC}\right) x \tag{3.8}$$

Also, if the x, y, and z lines are marked off with different scales so that

n = units of z/unit length

m = units of x/unit length

p = units of y/unit length

then

$$BE = \frac{z}{n} \qquad AD = \frac{x}{m} \qquad CF = \frac{y}{p}$$

and, by substitution in Eq. (3.7),

$$z = \left(\frac{AB}{AC}\right)\left(\frac{n}{p}\right) y + \left(\frac{BC}{AC}\right)\left(\frac{n}{m}\right) x \tag{3.9}$$

If it is desirable to construct the chart so that

$$z = x + y \tag{3.10}$$

then

$$\left(\frac{BC}{AC}\right)\left(\frac{n}{m}\right) = 1$$

$$\left(\frac{AB}{AC}\right)\left(\frac{n}{p}\right) = 1$$

and

$$\frac{BC}{AB} = \frac{m}{p} \tag{3.11}$$

Also,

$$BC = \left(\frac{m}{p}\right)(AB) = AC - AB$$

$$\frac{AB}{AC} = \frac{p}{p+m} \tag{3.12}$$

and

$$\frac{BC}{AC} = \frac{m}{p+m} \tag{3.13}$$

Then

$$BE = \frac{p}{p+m}(AD) + \frac{m}{p+m}(CF) \tag{3.14}$$

$$BE = \frac{1}{p+m}[p(AD) + m(CF)] \tag{3.15}$$

From Eqs. (3.9) and (3.10),

$$\frac{1}{p+m} = \frac{1}{n} \tag{3.16}$$

or

$$n = p + m \tag{3.17}$$

Thus, the spacing of the three lines is directly related to the scales that will be marked off on the parallel lines. As long as the spacing is maintained in accordance with the required relationship between m, n, and p as set forth in Eq. (3.17), a straightedge laid between a value of x and a value of y on the x and y lines, respectively, will intersect the z line at a value of z that is equal to the sum of x and y. Addition of two functions can be done graphically with such a chart. Furthermore, subtraction can be accomplished by laying the straightedge between a value on either the x or the y line and a value on the z line. The difference ($z - x$ or y) can then be read on the third line.

Multiplication can be carried out merely by substituting for x, y, and z the logarithms of the variables. Thus

$$z = \log u \qquad x = \log v \qquad y = \log w$$

and

$$\log u = \log x + \log w$$

In much the same way as in the case of logarithmic paper, described above, a logarithmic scale is marked off on the x, y, and z lines, but instead of the values of the logarithms the values of the antilogarithms are inserted.

Division, of course, involves the same operation as in the case of subtraction, except with logarithmic scales. Also, by the use of more parallel lines, addition, subtraction, multiplication, and division can be carried out on the same alignment chart.

Another type of alignment chart that is relatively common is the Z chart. This consists of two parallel lines connected by an oblique line, which extends from the base of one to the top of the other, as shown in Fig. 3.10. The relationship between the scales on the x, y, and z lines will not be developed here but can be obtained by reference to Lipka.[1]

The chart is used primarily for multiplication and division because the relationship is such that in these operations the scales on the x and y lines are linear. The scale on the z line is, of course, directly related to the scales on the x and y lines but is neither linear nor logarithmic. Each value on the z line must be calculated to fit the required relationship between the scales on the x and y lines.

In the case of multiplication a straightedge is laid from the value C on the x line to the value E on the y line. The product $(C)(E)$ is found at D on the z line. The operation in the case of division is apparent, since it is the reverse of multiplication.

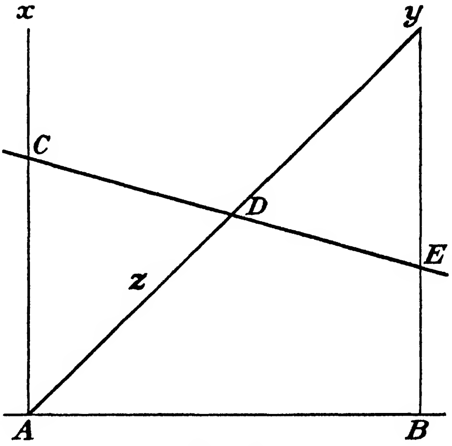

FIG. 3.10.

PROBLEMS

1. Convert the following values, as indicated, by use of conversion factors that consist of the ratio of units for the same dimension; *i.e.*, velocity in mph would be converted to feet per second by multiplying by feet per mile and hours per second.

Given	Convert To
10 mph	Meters/sec
5000 cal/(g)(deg C)	Btu/(lb)(deg F)
50 lb/sq in.	G/sq cm
45 lb/cu ft	G/cu cm
5 g/(cm)(sec)	Lb/(ft)(sec)
50 lb/1000 bbl	G/cu ft

Table A.13 provides the necessary conversion factors.

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[1] *Op. cit.*

2. It is believed that the resistance force R to the fall of a sphere in a liquid is a function of the diameter of the sphere, the viscosity of the liquid, and the linear velocity at which the sphere falls relative to the liquid. Derive an equation by dimensional analysis that gives the resistance force as a function of these variables.

3. A vapor is condensing on the surface of a vertical tube. It is believed that the thickness of the condensate film is a function of the diameter of the tube, the acceleration of gravity, the mass rate of condensation, the viscosity of the condensate, and the density of the condensate. Derive an equation that expresses the film thickness as a function of these variables.

4. Temperature of the atmosphere was recorded during a 24-hr cycle as follows:

Deg F	Time
55.0	6 A.M.
60.0	8 A.M.
68.0	10 A.M.
74.0	12 M.
78.0	2 P.M.
76.0	4 P.M.
72.0	6 P.M.
66.0	8 P.M.
62.0	10 P.M.
59.0	12 P.M.
57.0	2 A.M.
55.0	4 A.M.
54.0	6 A.M.

Determine the average temperature by graphical integration.

5. The speed of an automobile during a 6-hr period was varied uniformly as follows:

Time, hr.	0	1	2	3	4	5	6
Mph.	35	42	43	48	52	58	60

How far did the automobile travel in the 6-hr period?

6. Oil is being transferred by pipe line to a storage tank. The gauge on the tank at various times read as follows:

Bbl.	15,000	21,000	26,700	30,600	32,000
Hr.	0	2	5	8	10

Determine the instantaneous rate of flow over the 10-hr period in gallons per minute.

7. Convert the following values, as indicated, by use of conversion factors that consist of the ratio of units for the same dimensions, *i.e.*, inches to feet, seconds to hours, grams to pounds.

Given	Convert To
5 mph	Meters/sec
10,000 cal/g	Btu/lb
150 lb/sq in.	Kg/sq cm
60 lb/cu ft	G/cu cm
1.0 lb/(ft)(sec)	G/(cm)(sec)

8. A mass is dropped from an airplane, and the distance it had fallen at various times was determined to be as follows:

Sec.......	0	1	2	3	4	5	6	7	8	9	10
Ft........	0	16	56	115	189	276	375	483	598	717	837

Determine the acceleration at each of the times at which distance was determined. Show all supporting calculations.

CHAPTER IV

IMPORTANT CONCEPTS OF PHYSICS AND CHEMISTRY

This chapter deals with a number of fundamental laws and principles that will be found of great utility in the application of the fundamentals of chemical engineering. In many cases their presentation and discussion will be repetition to the student, from courses in elementary chemistry and physics. Nevertheless, a review at this time will be advantageous. It will provide those who are unfamiliar with these important concepts with essential tools for frequent application in the following chapters.

At this point the bare essentials will be presented so that the beginner can initiate his study of the fundamentals of chemical engineering without the prerequisites of physical chemistry and thermodynamics. The average beginning courses in general chemistry, chemical qualitative analysis, and physics of mechanics, sound, and heat should suffice if the student becomes quite familiar with the principles presented in this chapter. The development of the various concepts will be obtained in the study of physical chemistry and thermodynamics as usually afforded in any modern chemical-engineering curriculum. Thorough courses on these subjects are prerequisites to the study of chemical engineering beyond the scope of this text.

MISCELLANEOUS DEFINITIONS

Law of Conservation of Mass.—This law states that mass cannot be destroyed.[1] In any chemical reaction the total mass of the reactants is equal to the total mass of products. Also, the mass of any element which enters a chemical reaction is equal to the mass of that element in the products. For example, in the chemical reaction

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

every 98 units of mass of sulfuric acid will react with 80 units of mass of sodium hydroxide to produce 142 units of mass of sodium sulfate and 36 units of mass of water. Furthermore, the masses of hydrogen, sulfur, sodium, and oxygen on each side of the equation are 4, 32, 46, and 96 units, respectively.

Molal Expressions.—The molecular weight of a material is a dimensionless number. In many calculations, however, it is frequently convenient

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[1] Mass can be converted into energy by atomic fission or disintegration, but for the purposes of this text the law of conservation of mass is entirely rigorous.

to use quantities of mass that correspond to the molecular weight of each material involved. This quantity of mass is called the mole. A mole of a material is therefore a quantity whose mass expressed in any convenient unit of weight is equal numerically to the molecular weight. Thus, a pound-mole of water vapor (H_2O) is 18 lb of water, and a gram-mole of methane (CH_4) is 16 g of methane. In this text the word mole will refer always to the pound-mole unless otherwise indicated.

The significance of the mole is apparent in the case of a pure compound. The expression, however, is also commonly used for homogeneous mixtures of materials. The molecular weight of a mixture is equal to the mass of a given quantity of the mixture divided by the number of moles in the mixture. Thus, in a mixture that contains 40 lb of oxygen, 40 lb of nitrogen, and 120 lb of carbon dioxide the number of moles and average molecular weight are calculated as follows:

	Lb	Mol. wt.	Moles
O_2	40	32	1.25
N_2	40	28	1.43
CO_2	120	44	2.73
	200	37	5.41

The weight of each component is divided by its molecular weight to obtain the corresponding number of moles. Then the total number of moles (5.41) is obtained by addition of the moles of each component of the mixture. The average molecular weight (37) is obtained by dividing the total mass of 200 lb by the total number of moles. Thus, 1 mole of the mixture is 37 lb.

Another common expression in connection with homogeneous mixtures is the mole fraction or mole percentage. The mole fraction of a component is the number of moles of that component in a given quantity of a mixture divided by the total number of moles in the mixture. The mole percentage is 100 times the mole fraction. Thus, in the above example,

	Moles	Mole fraction	Mole %
O_2	1.25	0.231	23.1
N_2	1.43	0.264	26.4
CO_2	2.73	0.505	50.5
	5.41	1.000	100.0

The number of moles of each component is divided by the total number of moles (5.41) to obtain the corresponding mole fraction. The composition of a homogeneous mixture is frequently expressed in terms of mole fraction or mole percentage.

In like manner the molecular weight of air can be calculated. The following analysis of moisture-free air has been reported by Paneth:[1]

	Vol. %
Oxygen	20.95
Nitrogen	78.08
Carbon dioxide	0.03
Argon, etc.	0.94
Total air	100.00

Since the volume of one mole of gas at low pressure is the same for all compounds, the volumetric percentage of a gaseous mixture is identical with the mole percentage. Thus, the calculations can be made as follows:

	Mole fraction	Mol. wt.	Wt.
O_2	0.2095	32.00	6.70
N_2	0.7808	28.02	21.88
CO_2	0.0003	44.00	0.01
A, etc.	0.0094	39.94	0.38
	1.0000	28.97	28.97

Thus, for all practical purposes the molecular weight of air is 29. Also, the molecular weight of that portion of air excluding oxygen is (28.97 − 6.70)/(1.0000 − 0.2095), or 28.2. This material (inerts) is commonly referred to as "nitrogen in air." In computations in which it is involved, the molecular weight of 28.2 should be used.

Temperature Scale.—The two most common temperature scales are the centigrade and Fahrenheit. Both scales are based on the freezing point and boiling point of water at atmospheric pressure. The freezing point of water corresponds to 0° on the centigrade scale and 32° on the Fahrenheit scale. The boiling point of water on the centigrade scale corresponds to 100°, whereas on the Fahrenheit scale it corresponds to 212°. Thus, the temperature range between the freezing point and boiling point of water is divided into 100 equal increments on the centigrade scale and

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[1] Paneth, F. A., *Sci. J. Roy. Coll. Sci.*, **6**, 120 (1936).

into 180 equal increments on the Fahrenheit scale. The relationship between the two scales is therefore

$$\text{Deg F} = 32 + (1.8)(\text{deg C}) \tag{4.1}$$

or

$$\text{Deg C} = \frac{\text{deg F} - 32}{1.8} \tag{4.2}$$

In an effort to obtain a suitable standard for the measuring of temperature Lord Kelvin introduced the fundamental absolute thermodynamic scale. This is based on a reversible (frictionless) heat engine that absorbs heat from a heat reservoir at T_1 and rejects heat to a reservoir at T_2. The scale is so defined that the ratio of the heat absorbed Q_1 to the heat rejected Q_2 is in direct proportion to the ratio of the two temperatures. Thus,

$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2} \tag{4.3}$$

Also, it follows that

$$\frac{T_1 - T_2}{T_1} = \frac{Q_1 - Q_2}{Q_1} \tag{4.4}$$

From Eq. (4.4) the concept of absolute zero is suggested since, when

$$Q_2 = 0$$

then

$$T_2 = 0$$

If all the heat is converted into work and no heat is rejected, Q_2 is zero. It is evident that this can occur only when T_2 is zero.

If, as in the case of the centigrade scale, the temperature range between the freezing point and boiling point of water is divided into 100 equal increments, the absolute zero will be −273°C. The absolute centigrade scale is expressed in degrees Kelvin, and thus 0°C = 273°K. Similarly, the Fahrenheit scale may be used, in which case absolute zero is −460°F. When this basis is used, the absolute scale is expressed in degrees Rankine, and thus 0°R = −460°F or 60°F = 520°R. In this text the Fahrenheit and Rankine scales will be used unless otherwise noted. Degrees Fahrenheit and centigrade will be denoted by t, whereas absolute temperature (degrees Rankine and degrees Kelvin) will be represented by T.

System and Process.—Two terms that will be used frequently throughout the text should be defined at this point. A *system* consists of the mass and energy that are confined by known boundaries. It may be either static (no movement) or dynamic (in motion). A *process* is the method by which a change takes place within the system. Energy and mass that enter and leave a system through its boundaries are indicative of the changes within the system, and the method by which these changes take place represents the process in which the system is involved.

Processes are frequently classified as isothermal, adiabatic, isobaric, isopiestic, or isometric. Those terms are so common that the student should understand instantly their significance. *Isothermal* processes are those which take place at constant temperature. *Adiabatic* processes take place with no exchange of heat energy between the system and the surroundings. *Isobaric* and *isopiestic* processes occur at constant pressure. *Isometric* processes in a system are at constant volume.

There are two distinct types of process, *viz.*, batch and continuous. In the *batch process*, the mass is charged to the system at one time, and the process is then carried to completion. In the *continuous process*, the mass is charged to the system continuously, and the products are removed continuously. In industrial application the continuous process is perhaps the more common, but in experimental work the batch process is probably the more frequently employed.

Density and Specific Volume.—The density of a material is its mass per unit volume. In English units the density of a material is usually quoted as pounds per cubic foot. Another common method of expressing density is in terms of specific gravity. Specific gravity (sp. gr.) of a liquid or solid is the ratio of its density at the given conditions to the density of water at 60°F. The specific gravity of a gas is its density divided by the density of air at atmospheric pressure and the same temperature. Essentially then the specific gravity of a gas is its molecular weight divided by the molecular weight of air, or 29.

There are several arbitrary scales in use in industry and commerce for expressing the density of liquids in arbitrary units. Degrees Baumé is used mostly in the chemical industry and is related to specific gravity as follows:

For liquids heavier than water,

$$\text{Deg Bé} = 145 - \frac{145}{\text{sp. gr.}} \tag{4.5}$$

Table A.1 gives the degrees Baumé of several liquids heavier than water.

For liquids lighter than water,

$$\text{Deg Bé} = \frac{140}{\text{sp. gr.}} - 130 \tag{4.6}$$

In the petroleum industry, degrees API (American Petroleum Institute) is the scale. It is related to specific gravity as follows:

$$\text{Deg API} = \frac{141.5}{\text{sp. gr.}} - 131.5 \tag{4.7}$$

Table A.2 is a tabular representation of Eq. (4.7).

Density is also commonly expressed in terms of specific volume. *Specific volume* is the volume per unit mass. In English units it is the cubic feet per pound. Thus, it is merely the reciprocal of density.

Pressure.—From the study of elementary physics it was learned that pressure is force per unit area. In engineering practice, pressure is given as gauge pressure or absolute pressure. *Gauge pressure* is the pressure above atmospheric pressure, whereas *absolute pressure* includes atmospheric pressure. Thus, absolute pressure is above zero pressure. In most of the technical calculations that the chemical engineer makes he will deal with absolute pressure instead of gauge pressure. If gauge pressure is given, atmospheric pressure must be added to obtain absolute pressure. Since pressure is quoted in atmospheres, pounds per square inch, pounds per square foot, etc., the proper value of atmospheric pressure must be used. Atmospheric pressure is 14.7 lb/sq in. Of course, the value varies, but this is the accepted average value at sea level. If a highly accurate value of absolute pressure is desired, the barometric pressure should be obtained at the time and this value should then be added to the gauge pressure.

Another common method of expressing pressure is in terms of *head.* The pressure exerted by a column of fluid is equal to the weight of the column that has a cross-sectional area of unity. Hence, a column of fluid having a cross-sectional area of 1 sq ft would have a weight that corresponds to its density in pounds per cubic foot multiplied by its height in feet. If density is constant, the pressure can then be expressed in terms of the height of the column, which is called the head. Thus, when pressure is expressed in terms of heads, the expression must also include conditions that fix density. For example, atmospheric pressure is commonly quoted in terms of head of mercury. The standard density of mercury corresponds to 32°F. The average value of atmospheric pressure corresponds to 760 mm or 29.9 in. of mercury head.

When the pressure on a system is below atmospheric pressure, it is frequently expressed in terms of vacuum instead of absolute pressure. *Vacuum* is merely an expression of negative gauge pressure, *i.e.*, the difference between atmospheric pressure and the absolute pressure. Vacuum is perhaps most commonly expressed in head of mercury relative to a barometric pressure of 30.0 in. of mercury. A 26-in. vacuum would therefore correspond to $30.0 - 26.0$, or 4.0, in. of mercury absolute pressure.

Units of Energy and Power.—Inasmuch as energy is expressed in different terms, the student must be very familiar with the conversion of the terms of one expression to another. Since mechanical energy (work) is force multiplied by the distance through which it operates, it has the dimensions of foot-pounds if the force is in terms of pounds force. In chemical-engineering practice, force is usually expressed in terms of pounds so that the foot-pound is a common expression of energy. Even so, the chemical engineer frequently deals with other expressions of mechanical energy such as the erg and the joule. The erg has the dimensions of centimeter-grams. Owing to the fact that the erg is such a small unit of energy, the joule is more commonly used. It is equivalent to 10^7 ergs.

There are four very common expressions of heat energy, *viz.*, the calorie, the kilogram-calorie, the pound-centigrade unit (pcu), and the British thermal unit (Btu). One calorie is one one-hundredth ($1/100$) the amount of heat energy required to raise the temperature of one gram of water from 0 to 100°C. One kilogram-calorie is one one-hundredth ($1/100$) the amount of heat energy required to raise the temperature of one kilogram of water from 0 to 100°C. One pcu is one one-hundredth ($1/100$) the amount of heat energy required to raise the temperature of one pound of water from 0 to 100°C. One Btu is one one-hundred and eightieth ($1/180$) the amount of heat required to raise the temperature of one pound of water from 32 to 212°F. The Btu is equivalent to 778 ft-lb. Since 1°C is equivalent to 1.8°F and there are 453.6 g in a pound (Table A.13), it is apparent that 1 Btu is equivalent to 252 cal or 0.252 kg-cal.

There are other common expressions of energy, but these are related to units of power. *Power* is the rate of doing work. In the English system of units the *horsepower* is a common unit that is equivalent to 33,000 ft-lb/min. The watt or kilowatt, however, is the common expression for electric power. One horsepower is equivalent to 746 watts or 0.746 kw.

Since power is the rate of doing work, it follows that energy may be expressed in terms of the product of power and time. Hence, the kilowatt-hour and horsepower-hour are units of energy. Table A.13 presents conversion factors for several of the more common units of energy and power. The student will have occasion for frequent reference to this table throughout the remainder of the text.

GASES

The Ideal Gas.—There is no ideal gas, but the concept is very convenient since deviations from the ideal gas can be dealt with quite effectively. The ideal-gas law applies to most real gases over a wide range of conditions well within the required degree of accuracy for chemical-engineering calculations. It may be stated as follows:

$$PV = nRT \tag{4.8}$$

	Dimensions
where P = pressure	$ML^{-1}T^{-2}$
V = volume	L^3
n = number of moles	M
R = the gas constant (energy per degree per unit mass)	$L^2T^{-2}\theta^{-1}$
T = absolute temperature	θ

It will be noted that the gas constant R has the dimensions of energy per degree temperature per unit mass and therefore is dependent upon the units used for P, V, n, and T. If P is expressed in pounds per square inch absolute,[1] V in cubic feet, n in pound-moles, and T in degrees Rankine, the value of R is 10.7. Since the constant R has the dimensions of energy per degree temperature per unit mass, it may be expressed in mechanical or heat energy per degree of temperature per unit of mass. Its value expressed in Btu per degree Fahrenheit per mole or calories per degree centigrade per gram-mole is 1.99.

One pound-mole is equivalent to 359 cu ft at 32°F and 14.7 lb/sq in. abs. Another basis commonly used in chemical-engineering calculations is 60°F and atmospheric pressure, in which case one pound-mole occupies 379 cu ft. In this text this basis will be implied unless other conditions are specified when a volume of gas is given or requested.

The ideal-gas law was arrived at on the basis of laws developed by Boyle and Charles. *Boyle's law* states that for any gas or mixtures of gases the following relation holds:

$$PV = \text{a constant} \tag{4.9}$$

Charles's law states that the volume of a given mass of gas is directly proportional to the absolute temperature.

$$\frac{V}{T} = \text{a constant} \tag{4.10}$$

By combining Eqs. (4.9) and (4.10), Eq. (4.11) is obtained.

$$\frac{PV}{T} = \text{a constant} \tag{4.11}$$

For one mole of an ideal gas the constant in Eq. (4.11) is R, the gas constant.

The ideal-gas law is usually sufficiently reliable for most chemical-engineering calculations below 50 lb/sq in. gauge pressure. It becomes more accurate the lower the pressure on the system.

There are two other laws that might be classified under the heading of the ideal-gas law, although they were not involved in its development. These are Dalton's law and Amagat's law. Both apply to gas mixtures. *Dalton's law* states that the pressure exerted by each component of a

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[1] Atmospheric pressure is on the average 14.7 lb/sq in. at sea level, but at high pressure a value of 15 lb/sq in. is frequently used because the 0.3 lb/sq in. has no significant effect on the accuracy. For example, a gauge pressure of 500 lb/sq in. would represent for all practical purposes an absolute pressure of 515 lb/sq in.

gaseous mixture is the same as if the component existed alone at the same temperature in the volume occupied by the mixture. This pressure (exerted by a component of a mixture) is called its partial pressure. Obviously, the summation of the partial pressures of the components of a mixture is equal to the total pressure on the mixture. Thus, it follows that

$$p = \pi y \tag{4.12}$$

where π = total pressure of the mixture
p = partial pressure of a component
y = mole fraction of the component in the mixture

Since the summation of the mole fractions is unity, the summation of the partial pressures is equal to π.

As pointed out previously, based on the concept of the ideal-gas law, an analysis of a gas mixture reported in volume percentage is numerically equivalent to mole percentage of the components. Since analyses of gases are usually conducted at low pressure, this is applicable to real gases.

Whereas Dalton's law is based on constant temperature and volume, *Amagat's law* is based on constant temperature and pressure. It states that the volume of a gaseous mixture is equal to the sum of the volumes of the individual components at the same temperature and pressure as the mixture.

$$V = v_1 + v_2 + v_3 + \cdots + v_n \tag{4.13}$$

where v = volume of a component
V = total volume of the mixture

Amagat's law is somewhat more representative of real gases than Dalton's. As a matter of fact, it is quite reliable even at fairly high pressures.

A corollary that can be drawn from Amagat's law is set forth as Eq. (4.14),

$$v = yV \tag{4.14}$$

where y = mole fraction of a component

Equation (4.14) is not as reliable for real gases, however, as Eq. (4.13), particularly at high pressures. At high pressures the volume occupied by one mole of a real gas is not the same for all gases. Therefore, Eq. (4.14) will not apply in all cases.

Critical Properties.—Before discussing various principles concerning real gases, it will be desirable to digress somewhat in order to take up a few principles that are related to both liquids and real gases. It was learned in elementary physics that liquids exert a vapor pressure which is a result of the molecules in the liquid tending to evaporate. It will be found later in the chapter that when both the liquid and the vapor phase of a given pure compound coexist in equilibrium with each other *the vapor pressure is a function only of temperature.* For example, water at 212°F in equilibrium with water vapor at that temperature will always exert a vapor pressure of 14.7 lb/sq in. abs. At 300°F it will always exert a vapor pressure of 67.0 lb/sq in. abs. The curve of vapor pressure vs. temperature for two such phases in equilibrium is called the vapor-pressure curve for the material under consideration. It is also called the equation of state at conditions of saturated vapor. *Saturated vapor* means merely that the vapor is under conditions which are identical with those when the vapor is in equilibrium with the liquid phase.

As liquid water in equilibrium with its vapor phase is heated, the temperature and pressure rise until finally a temperature is reached at which the liquid phase and vapor phase merge. This is called the *critical point.* Furthermore, *for a pure compound,*[1] above that temperature two phases cannot be produced no matter how high the pressure is extended. This temperature is called the *critical temperature,* and for a pure compound[1] it is the maximum temperature on the vapor-pressure curve.

The vapor pressure at the critical-point temperature is the *critical pressure.* The volume per unit mass *at the critical temperature and pressure is the critical volume.* For a pure compound the critical pressure is the maximum pressure on the vapor-pressure curve.[1]

It has been found that the critical properties of pure compounds are related to the pressure, volume, and temperature behavior of the compounds in the vapor phase. On the other hand, when mixture of gases are encountered, their behavior is not directly related to the actual critical properties as in the case of pure compounds. It has been found by Kay,[2] however, that their behavior is related to what he calls *pseudocritical properties.* These properties are merely values that, if used in the equations of state,[3] permit the same procedures to be followed in calculations as are used for pure compounds. The *pseudocritical temperature* is calculated by taking the sum of the products of mole fraction and critical temperature of each component. Likewise, the *pseudocritical pressure* is calculated by taking the sum of the products of mole fraction and critical pressure of each component. Thus, the pseudocritical temperature and pseudocritical pressure of a mixture of 10 moles of ethane, 15 moles of

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[1] It will be found later that mixtures behave differently from pure compounds.

[2] KAY, W. B., *Ind. Eng. Chem.*, **28**, 1014 (1936).

[3] Equation of state for a gas is a relationship of P, V, and T.

propane, and 25 moles of normal butane would be calculated as follows:

	Moles	Mole fraction	Critical temp.,* deg F	(Critical temp.) × (mole fraction)	Critical pressure,* lb/sq in. abs	(Critical pressure) × (mole fraction)
Ethane	10	0.200	90	18.0	712	142.4
Propane	15	0.300	206	61.8	617	185.1
n-Butane	25	0.500	306	153.0	550	275.0
	50	1.000		232.8		602.5

* See Table A.8.

The pseudocritical temperature is therefore 232.8°F, and the pseudocritical pressure is 602.5 lb/sq in. abs.

Real Gases.—Now that critical and pseudocritical properties have been defined, it will be possible to proceed with the discussion of certain principles related to the behavior of real gases.

It was pointed out in the discussion of the ideal-gas law that real gases do not behave in accordance with the law at pressures above about 50 lb/sq in. gauge but that it is convenient to deal with deviations from the ideal-gas law. The deviations vary considerably from one gas to another.

There have been many attempts to establish a universal correlation that would satisfy all real gases. Although such a universal equation has not been attained, several very useful relations have been developed in the attempt. One of these is the van der Waals equation as given by Eq. (4.15).

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{4.15}$$

where V = molal volume (volume of one mole)
a and b = constants, characteristic of each gas

This equation will not be applied as such in the later chapters of this book. It is presented now primarily because of its classical significance. It is reliable for the ordinary chemical-engineering calculations at temperatures at least 100°F above the critical temperature down to a molal volume of about 5 cu ft and at temperatures near or below the critical temperature down to a molal volume of about 50 cu ft.

For pure compounds, it has been found by experimentation that an approximate relation exists between the constants a and b of the van der Waals equation and the critical properties. This is as follows:

$$T_c = \frac{8a}{27bR} \qquad P_c = \frac{a}{27b^2} \qquad V_c = 3b$$

If the ratio of the values of P, V, and T to the respective critical properties is represented by P_r, V_r, and T_r, the values of P, V, and T are given by P_rP_c, V_rV_c, and T_rT_c, respectively. By substituting these products for P, V, and T, respectively, in Eq. (4.15) and then substituting the values for P_c, V_c, and T_c in terms of a, b, and R as given above, the equation reduces to

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r \tag{4.16}$$

where $P_r = P/P_c$, or reduced pressure
P_c = critical pressure
$V_r = V/V_c$, or reduced volume
V_c = critical volume
$T_r = T/T_c$, or reduced temperature
T_c = critical temperature

Equation (4.16) is the *reduced van der Waals equation of state* and is based on an important concept known as the *law of corresponding states.* According to the law of corresponding states the ratio of the volume of a given mass of gas to its volume at the critical point is related to the reduced temperature T/T_c and reduced pressure P/P_c by the same function for all similar substances. Equation (4.16) is the equation of state for any gas in terms of its critical properties, and according to the law of corresponding states it should hold for any gas. Even so, the law of corresponding states is not rigorous. It is a close approximation, however, and provides much better correlation than the ideal-gas law for P, V, and T at high pressures and at low temperatures that approach saturation conditions.

Another reduced equation of state that has been developed on the basis of the law of corresponding states is presented in Fig. A.29. This figure provides the compressibility factor z to be used in Eq. (4.17).

$$PV = znRT \tag{4.17}$$

Thus, Fig. A.29 provides an approximate relation for the deviation of real gases from the ideal-gas law. The factor z is dimensionless.

Example 6. *a.* What is the volume occupied by 100 moles of ethane vapor at 500 lb/sq in. abs and 200°F?

b. What is the volume occupied by a gaseous mixture of 10 moles of ethane, 20 moles of propane, and 50 moles of *n*-butane at 500 lb/sq in. abs and 400°F?

Solution: a. The deviation from the ideal-gas law can be estimated by means of Fig. A.29 and Table A.8.

From Table A.8,

$$T_c \text{ of ethane} = 549°\text{R}$$

$$P_c \text{ of ethane} = (48.8)(14.7) = 716 \text{ lb/sq in. abs}$$

$$T_r = \frac{200 + 460}{549} = 1.20$$

$$P_r = {}^{500}\!/_{716} = 0.698$$

From Fig. A.29,

$$z = 0.855$$

$$PV = znRT$$

$$V = \frac{(0.855)(100)(10.7)(660)}{500} = 1207 \text{ cu ft}$$

b. The deviation from the ideal-gas law can be determined from Fig. A.29 and Table A.8, but pseudocritical conditions must be used to determine reduced conditions.

	Moles	Mole fraction	T_c	(Mole fraction) (T_c)	P_c	(Mole fraction) (P_c)
Ethane............	10	0.125	549	68.6	716	89.5
Propane............	20	0.250	665	166.2	617	154.2
n-Butane...........	50	0.625	766	479.0	550	344.0
	80	1.000		713.8		587.7

Thus, the pseudo-critical temperature and pressure are 713.8°R and 587.7 lb/sq in. abs, respectively.

$$T_r = \frac{400 + 460}{713.8} = 1.207$$

$$P_r = \frac{500}{587.7} = 0.85$$

From Fig. A.29,

$$z = 0.817$$

$$PV = znRT$$

$$V = \frac{(0.817)(80)(10.7)(860)}{500} = 1203 \text{ cu ft}$$

GIBBS PHASE RULE

Before taking up the subject of behavior of liquids, the Gibbs phase rule will be briefly discussed since it will facilitate the presentation of liquids. The phase rule was formulated by Willard Gibbs. It is a criterion of phase equilibrium. It states how many phases may exist at equilibrium or how many degrees of freedom exist for a given system. It provides no further information. The rule is given as follows:

$$F = 2 + C - P \tag{4.18}$$

where F = degrees of freedom
C = number of components
P = number of phases

Equation (4.18) is applicable to any system. The *degrees of freedom* is the number of independent variables such as temperature, pressure, and concentrations of the components that must be fixed in order to define the system completely. Thus, the number of degrees of freedom is the number of independent variables that can be varied (within limits) without changing the number of phases in the system. A *phase* is any part of a system that is completely homogeneous, bounded by a surface, and capable of being separated mechanically from the system. Thus, a system that consists of a liquid and vapor in equilibrium has two phases, *viz.*, gaseous and liquid. A system that includes a homogeneous solid mass in equilibrium with a liquid and a vapor phase consists of three phases. More than one solid phase and more than one liquid phase can exist in equilibrium together, but only one gas phase can exist.

The *number of components* is the *smallest* number of independently variable constituents with which the composition of each phase in the system can be defined. If the system can be defined as a chemical equation, sometimes only one constituent in the equation will define the composition of each phase even though there are several constituents shown in the equation. The components must be chosen from the constituents with which the composition of each phase in the system can be defined.

The phase rule gives no indication of the rate at which equilibrium is attained, nor does it throw any light on the composition, relative amount, and nature of any of the phases.

LIQUIDS

Equation of State for Pure Compounds.—It was pointed out earlier that the vapor pressure of a pure compound is a function only of temperature when the liquid and vapor phases coexist at equilibrium. A check on this statement is afforded by application of the phase rule. The number of components is unity. The number of phases is two. Thus,

$$F = 2 + 1 - 2 = 1$$

and thus there is one degree of freedom and it is necessary to fix only one of the independent variables (temperature or pressure) to define the system completely.

It is apparent that if three phases (vapor, liquid, and solid) existed in equilibrium there would be no degrees of freedom and therefore both temperature and pressure would be fixed. This phenomenon is consistent with the fact that the "triple point" in the system of ice, water, and water vapor occurs at a fixed temperature and pressure.

The presentation of the equation of state for a liquid-vapor system in equilibrium can be conveniently represented graphically on semilogarithmic paper, as pointed out in Chap. III. By plotting vapor pressure on the logarithmic scale against the recriprocal of the absolute temperature, a vapor-pressure curve is obtained that is almost a straight line over the entire range of temperature. Such a plot is very convenient for extrapolation of the vapor-pressure curve.

A second method commonly used for presenting vapor-pressure curves graphically is by means of a Cox chart. The Cox chart is constructed by first setting up a logarithmic scale as an ordinate to represent pressure. Second, a straight line is drawn at a convenient angle (usually about 45 deg) with the horizontal or abscissa lines. Third, an abscissa scale is constructed to represent temperature. The temperature at, say, 10°F intervals is inserted on the base line so that the 45-deg straight line represents the vapor-pressure curve of a chosen reference compound. After the graph is completed by filling in the ordinate and abscissa lines, the vapor-pressure curves for other compounds, which are chemically similar to the reference compound chosen, will be represented by essentially straight lines on this graph. Chemical similarity means merely that if hydrocarbons are being represented a hydrocarbon should be chosen as a reference. If alcohols are being represented, water would be a good reference, etc. A Cox chart is shown in Fig. A.1.

More recently, Othmer[1] has developed a very useful method of presenting vapor-pressure curves. He has shown that the logarithm of the vapor pressure of a liquid (or solid and solutions) is a straight-line function of the logarithm of the vapor pressure of a reference substance at the same temperature below the critical region. Hence on log-log paper such functions would be straight lines. Furthermore, the slope of the functions is the

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[1] Othmer, D. F., *Ind. Eng. Chem.*, **32**, 45 (1940).

ratio of the amount of heat required for vaporization to that of the reference substance.

Dühring's rule is another useful tool in the presentation, correlation, extrapolation, and interpolation of vapor-pressure data. This rule is applied on arithmetic coordinate paper. The temperature of a given liquid is represented on the abscissa; but instead of plotting the vapor pressure of this liquid as the ordinate the temperature at the same vapor pressure is plotted as the ordinate, for a reference compound. Thus, if water is the reference compound and if at a temperature of 100°F the compound under consideration exhibits a vapor pressure of 14.7 lb/sq in. abs, the ordinate would be 212°F and the abscissa would be 100°F. By using a reference compound that is similar chemically to the compounds under consideration, straight lines are obtained by this method of presenting vapor-pressure curves. Figure 4.1 shows a Dühring curve for ethyl alcohol, with water as the reference.

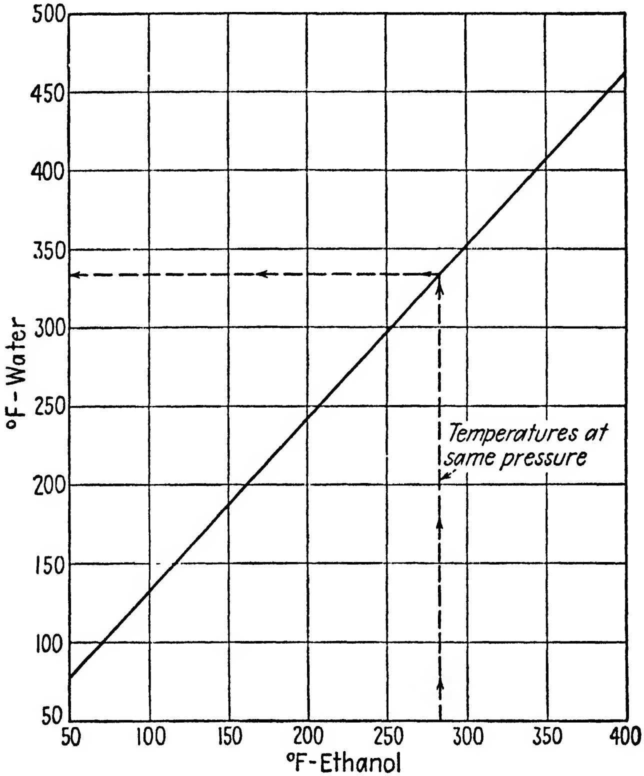

FIG. 4.1.—Dühring curve for ethanol vs. water.

Solutions.—Before proceeding with the discussion of solutions certain terms that will be used frequently will be defined. The principles of solutions depend to a considerable extent upon whether the components are [illegible] or nonpolar. Polar components are those which have free electrons. That is, they ionize readily and will conduct electricity. Nonpolar materials do not ionize to any appreciable extent and consequently are poor conductors of electricity.

Materials that are *miscible* will form a solution of one with the other. If the materials are mutually soluble, each can be dissolved in the other. Sometimes, however, one material can be dissolved in a solvent, but the solvent will not dissolve in the solute. This is commonly true when the solute is a solid and the solvent is a liquid.

Substances that are *immiscible* are insoluble in each other. There are instances, however, when substances are partly miscible, which presents additional complications to be considered in chemical-engineering calculations. For example, if two liquids A and B are partly miscible in each other, there may be two liquid phases. The phase in which A predominates will be saturated with B, and the phase in which B predominates will be saturated with A.

Equations of State for Solutions.—In the case of liquid solutions [1] the equation of state is somewhat more complicated than for pure compounds. Even so, the vapor-pressure curve is very similar to that of a pure compound, if *none* of the liquid is allowed to vaporize. The peculiarities of equations of state for mixtures of mutually soluble liquids can best be explained by reference to Fig. 4.2, which is a generalized phase diagram for a nonelectrolyte solution of fixed composition.

The curve DBA represents the vapor-pressure curve for 100 per cent liquid, and the curve KCA represents the temperature and pressure relationship for 100 per cent vapor at conditions of saturation. These curves are called the *boiling-point* or *bubble-point curve* and the *dew-point curve*, respectively. The critical point is at A. At this point both the liquid and the vapor phase are of identical composition. It will be noted, too, that the curves which represent intermediate amounts of vaporization converge at the critical point. The critical temperature is the highest temperature on the 100 per cent liquid–vapor-pressure curve but unlike the case of a pure compound the critical pressure is not necessarily the highest vapor pressure on the 100 per cent liquid curve.

If the temperature is reduced at constant pressure from a point on the 100 per cent liquid curve just below the critical temperature T_c, it will be noted that vaporization will occur at first and then condensation will occur

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[1] **Only nonpolar solutions will be considered in this text.**

until the 100 per cent liquid curve is again reached. The phenomenon of vaporization at constant pressure as temperature is reduced is called *retrograde vaporization* because it is a reverse effect to that observed with pure compounds. Likewise, if the pressure is reduced at constant temperature from a temperature on the 100 per cent vapor curve just above the critical temperature T_c, condensation will occur at first and then vaporization will occur until the 100 per cent vapor line is reached. The phenomenon of condensation by reduction in pressure at constant temperature is called *retrograde condensation* because it is an opposite effect to that observed with pure compounds. Retrograde vaporization can occur in the pressure range between P_c and P_M, and retrograde condensation can occur in the temperature range between T_c and T_M. For example, if a point is selected below the 100 per cent vapor curve in the temperature range between T_c and T_M and the pressure is increased, the two-phase region will be reached at the 100 per cent vapor or dew-point line. At this point the liquid phase begins to appear, and further condensation occurs as pressure is increased until a maximum is reached. As pressure is increased beyond the point of maximum condensation, vaporization occurs until the dew-point curve is again reached. The range above the point of maximum condensation and below the dew-point line is the range of retrograde condensation. Point C is the maximum temperature at which both liquid and vapor phases can

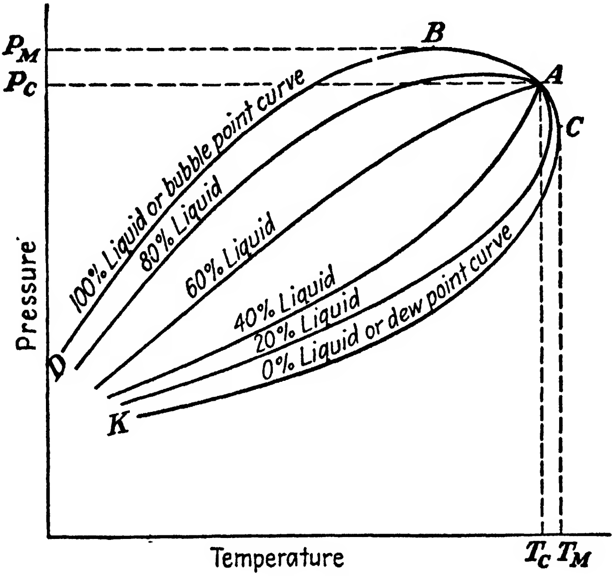

FIG. 4.2.

coexist in equilibrium. It should be understood, however, that at this point the compositions of the vapor and liquid phases are different. *In the case of mixtures the compositions of the liquid and vapor phases are identical only at the critical point.* It will be noted, too, that point B is the maximum pressure at which both liquid and vapor phases can coexist in equilibrium. In the case of a single component, points A, B, and C are the same.

With reference to the phase rule for a system of more than one component it is apparent that the number of degrees of freedom for a two-phase two-component system is two.

$$F = 2 + 2 - 2 = 2$$

Thus, either temperature and pressure or the concentration of one component plus either temperature or pressure must be fixed in order to define the system in a two-phase region. For a three-component system the system will be completely defined in a two-phase region by fixing the concentration of two components and either temperature or pressure. Of course, as the number of components in a system increases, the number of possible phases increases. For example, in a two-component system there is a possibility of four phases,

$$F = 0 = 2 + C - P$$

or

$$P = 2 + 2 = 4$$

For each increase in the number of components there is a corresponding increase in the number of possible phases. There might be different solids and/or liquid phases, but only one gaseous phase can exist.

Calculation of Phase Equilibria of Solutions.—In general, the chemical engineer encounters systems that consist of more than one component more frequently than he does single-component systems. It is often necessary to calculate the equation of state for solutions of nonpolar components. Several useful methods have been developed that facilitate such calculations.

The relationship between composition of the liquid phase and vapor pressure is given by two well-known laws, *viz.*, *Raoult's law* and *Henry's law*. Raoult's law states that partial pressure of the solvent is directly proportional to its mole fraction in the solution, or

$$p_i = P_i x_i \tag{4.19}$$

where p_i = partial pressure of solvent
P_i = vapor pressure of pure solvent at same temperature
x_i = mole fraction of solvent in liquid phase

Henry's law states that the amount of gas which dissolves in a liquid is directly proportional to the partial pressure of the gas in equilibrium with the liquid phase, or

$$p_v = kx_v \tag{4.20}$$

where p_v = partial pressure of vapor
k = a constant
x_v = mole fraction of gas in liquid phase

Henry's law is applicable to each component of a gaseous mixture as well as to a single-component gas. The constant k varies with the temperature and is also dependent upon the gas solvent. Equations (4.19) and (4.20) are quite similar. They differ only in the proportionality constants. At high concentration of the solvent [low value of x_v in Eq. (4.20)] Raoult's law is at its most reliable and Henry's law at its most accurate range of application. The deviations from both laws increase with increasing pressure.

At pressures below 50 lb/sq in. gauge Raoult's law is reasonably reliable even for components at low concentration. Thus, Eq. (4.19) may be combined with Eq. (4.12) (Dalton's law) to give a very important equation [Eq. (4.21)] that provides a relationship between the compositions of the liquid and vapor phases,

$$\pi y_i = P_i x_i \tag{4.21}$$

or

$$\frac{y_i}{x_i} = \frac{P_i}{\pi} \tag{4.22}$$

where y_i = mole fraction of component i in vapor
x_i = mole fraction of same component in liquid
P_i = vapor pressure of same component in pure state at same temperature
π = total pressure on the system

Since

$$\Sigma x = 1.0 \tag{4.23}$$

$$\Sigma y = 1.0 \tag{4.24}$$

the compositions of the liquid and vapor phases can be calculated on the basis of the equations of state for the pure components in the system. This is a very useful relationship and is applied in Example 7.

Example 7. Calculate the composition of the vapor phase in equilibrium with the liquid phase for *all* proportions of normal pentane and normal hexane. The total pressure on the system is 40 lb/sq in. abs.

Solution: By inspection of Eq. (4.22) it is apparent that the ratio of the mole fraction of hexane (or pentane) in the vapor phase to that of the liquid phase is a function only of temperature because π has been fixed at 40 lb/sq in. abs and P, the vapor pressure of pure hexane (or pentane), is a function only of temperature.

Let x_h = mole fraction of hexane in liquid
P_h = vapor pressure of pure hexane
P_p = vapor pressure of pure pentane

Then, from Eq. (4.23),

$$1 - x_h = \text{mole fraction of pentane in liquid}$$

$$\pi = 40 \text{ lb/sq in. abs}$$

	Mole fraction, x	Vapor pressure pure component, P	P/π	$Px/\pi = y$
$n\text{-}C_6H_{14}$	x_h	P_h	$0.025P_h$	$0.025P_hx_h$
$n\text{-}C_5H_{12}$	$1 - x_h$	P_p	$0.025P_p$	$0.025P_p - 0.025P_px_h$
Solution	1.000		1.000	$0.025P_hx_h + 0.025P_p - 0.025P_px_h$

Since the summation of the mole fractions in the vapor phase Σy is unity [Eq. (4.24)], it follows that

$$0.025P_hx_h + 0.025P_p - 0.025P_px_h = 1.000$$

and

$$x_h = \frac{1.00 - 0.025P_p}{0.025(P_h - P_p)} = \frac{P_p - 40}{P_p - P_h}$$

Now that an equation for the mole fraction of hexane in the liquid phase in terms of the vapor pressures of hexane and pentane has been derived, the procedure is to assume temperatures between the points that correspond to 100 per cent pentane and 100 per cent hexane (at 40 lb/sq in. vapor pressure) and calculate the mole fraction of hexane in the liquid phase from the equation. Then the mole fractions in the vapor phase are calculated from Eqs. (4.21), (4.23), and (4.24).

Deg F	P_p *	P_h *	$P_p - 40$	$P_p - P_h$	x_h	y_h	x_p	y_p
155	40	14.3	0	25.7	0.000	0.000	1.000	1.000
175	54	20	14	34	0.410	0.205	0.59	0.795
200	75	30	35	45	0.778	0.583	0.222	0.417
220	96	40	56	56	1.000	1.000	0.000	0.000

* Figure A.1.

With the four values of x_h, y_h, x_p, and y_p vs. temperature, curves can be constructed as in Fig. 4.3 that show the relationship between composition of the liquid phase and composition of the vapor phase and temperature.

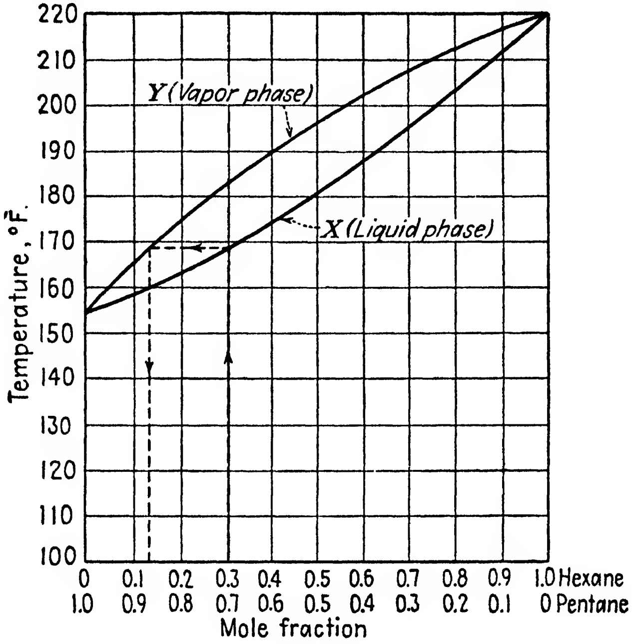

FIG. 4.3.

It would be possible to calculate the relationship between liquid and vapor phases over any temperature and pressure ranges by the method of Example 7 except for the fact that both Raoult's and Dalton's laws become unreliable as pressure is increased much above 65 lb/sq in. abs. A method will be described in Chap. VII, however, that is reliable at substantially higher pressure.

Raoult's law is a special case of a more general concept known as the *perfect solution.*[1] As in the case of the ideal-gas concept, there is perhaps no solution that has the properties of a perfect solution. Even so, it is a useful concept with which real solutions can be compared. It will not be possible at this point to define the perfect solution completely, but some of its properties can be stated. The volume of the perfect solution is equal to the sum of the volumes of its components in the pure state at the same conditions. Also, when the components in the pure state are dissolved to form the solution, there is no heat given off or absorbed and the temperature remains constant. It should be understood, however, that the perfect-solution concept

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[1] LEWIS, G. N., *J. Am. Chem. Soc.*, **30**, 668 (1908).

applies to gaseous solutions as well as to liquid solutions. Later chapters will bring out more clearly the usefulness of the perfect-solution concept.

Expressions of Liquid Composition.—The compositions of solutions are expressed in three different ways, *viz.*, as liquid-volume percentage, weight percentage, and mole concentration. The expression in terms of liquid-volume percentage has significance only if the solution approaches the perfect-solution concept, *i.e.*, if the volumes of the components are additive. This is found to be essentially true in the case of hydrocarbons and many other organic compounds. Weight percentage, on the other hand, is based on the law of conservation of mass and is perhaps the most fundamental method of expressing composition. The student must be familiar with the conversion of each type of concentration to the other. Example 8 illustrates the conversion of liquid-volume percentage to weight percentage and finally to mole percentage.

Example 8. Convert the following liquid solution (60°F) to weight percentage and mole percentage.

	Liquid Volume 70
Propane	25
n-Butane	35
n-Pentane	40
	100

It may be assumed that this is a perfect solution.

Solution: Since this is a perfect solution, the volume of the solution is equal to the volumes of the components in the pure state. The method of calculation is to convert the volume of each component to pounds and weight percentage. Then the pounds are converted to moles and mole percentage. Basis of 100 gal of solution:

	Gal	Lb/gal *	Lb	Wt. %	Mol. wt.	Moles	Mole %
Propane	25	4.329	108.2	22.1	44	2.455	29.5
n-Butane	35	4.863	170.5	34.9	58	2.940	35.4
n-Pentane	40	5.251	210.0	43.0	72	2.915	35.1
	100		488.7	100.0		8.310	100.0

* Table A.9.

Viscosity.—There is a resistance force that tends to prevent the molecules of any fluid or plastic from moving over each other. This internal friction is called viscosity. The property of viscosity is perhaps more important in the case of nonrigid materials such as liquids and gases. Nevertheless, it is sometimes quite important in the case of solids, which behave under certain conditions as nonrigid materials.

Viscosity is analogous to the friction incurred in a deck of playing cards by sliding them about. If the top card is moved in any direction in its plane, it tends to move the card next to it in the same direction. Likewise, the second card tends to move the card next to it, etc. In the case of a fluid an area of molecules of unimolecular thickness behaves in much the same way, as is indicated in Fig. 4.4. It has been found that the force required to overcome the resistance to the movement of an area of molecules of unimolecular thickness is proportional to the area, proportional to the velocity at which the area of molecules moves with respect to another area in a parallel plane, and inversely proportional to the distance between the parallel planes which include the two areas of molecules. Equation (4.25) represents this observation.

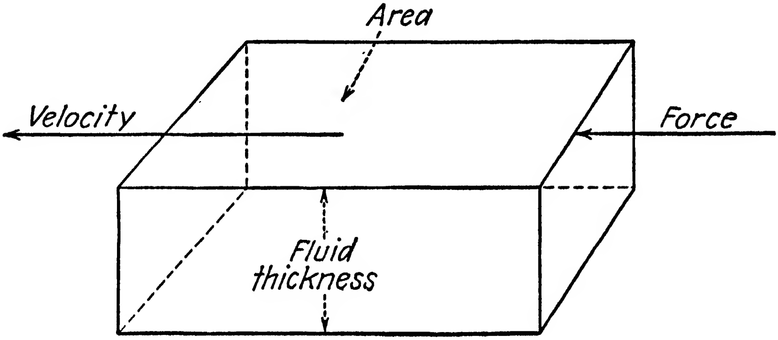

FIG. 4.4.

$$\text{Force} = \mu \frac{(\text{area})(\text{velocity})}{\text{thickness}} \tag{4.25}$$

where μ = proportionality constant

The value of μ is dependent on the fluid, temperature, and pressure, though, in noncompressible fluids, pressure has no effect on it. The proportionality constant μ is called absolute viscosity and has the dimensions of mass/(length)(time). In English units absolute viscosity has the dimensions of lb/(ft)(sec). The absolute viscosity in metric units is called the *poise* and has the dimensions of g/(cm)(sec). Thus, the poise is equivalent to 0.0672 English unit (lb/(ft)(sec)) of viscosity. It will be found in chemical-engineering practice that absolute viscosity is perhaps most frequently quoted in *centipoises.* A centipoise is equivalent to 0.01 poise. Therefore, to convert centipoises to English units multiply by 0.000672. *Relative viscosity* is the absolute viscosity of a material divided by the absolute viscosity of water in the same units at a temperature of 68°F. At this temperature the relative viscosity of water is essentially

1 centipoise, and thus relative viscosity is for all practical purposes numerically equal to the viscosity in centipoises.

Viscosity varies with temperature in much the same way as vapor pressure. Therefore, it can be represented as an essentially straight line if the logarithm of absolute viscosity is plotted vs. the reciprocal of absolute temperature.

Surface Tension.—Another important property of liquids is surface tension, or interfacial tension as it is sometimes called. Owing to molecular attraction it requires work to increase the surface of a liquid. The energy expended in increasing the area is directly proportional to the increase in area. The proportionality constant is the surface tension, which has the dimensions of energy divided by area or force divided by length. Surface tension is usually expressed in dynes per centimeter, which is equivalent to ergs per square centimeter. In order to convert to English units of pounds of force per foot the value in dynes per centimeter must therefore be multiplied by 6.85×10^{-5}.

ENERGY TRANSFORMATION

Types of Energy.—Energy may be divided into two types, *viz.*, potential and kinetic. Each type may also be subdivided into internal and external potential and kinetic energies. Internal has reference to the energies stored within the molecules themselves, whereas external pertains to the energies of the mass as a whole. The potential energy of a system is a result of its position. For example, an elevated weight possesses potential (external) energy since it can do work if allowed to descend to the surface of the earth. Also, the shell in a gun contains potential (internal) energy because it can expel the bullet if fired, owing to the energy released by chemical reaction. Kinetic energy, on the other hand, is a result of the motion of the system. In a continuous process, mass enters the system continuously and leaves continuously. It possesses kinetic (external) energy that corresponds to the velocity at which it enters and leaves. This kinetic energy is equivalent to $mV^2/2g$, where m is the mass, V the velocity, and g the acceleration of gravity. The internal kinetic energy of a system is due to the movement of the molecules within the system, whereas the internal potential energy is a result of the molecular structure or form. Potential and kinetic energy will be discussed more fully in Chap. VII.

Law of Conservation of Energy.—Energy cannot be created or destroyed.[1] It may be converted from one form into another, but without

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[1] To be absolutely rigorous, the laws of conservation of mass and energy should be combined; but as long as atomic fission or disintegration is not involved, the laws may be regarded as entirely rigorous for chemical-engineering purposes when applied separately.

destruction. The natural tendency is for all forms of energy to pass into heat energy. The law of conservation of energy (the first law of thermodynamics) is one of the most useful of the fundamentals of chemical engineering. It may be defined for a static system by the equation

$$Q = \Delta U + W \tag{4.26}$$

where Q = heat *transferred* to the system *from* the surroundings
ΔU = *increase* in internal energy of the system
W = work done by the system *on the surroundings*

Obviously Eq. (4.26) can be applied only when each term in the equation is expressed in the same units of energy. This can be done with any energy equivalent such as Btu, foot-pounds, calories, etc. (see Table A.13) as long as the same unit of energy is used throughout. Thus, when any static system is involved in a change, the amount of heat transferred to the system from the surroundings is equal to the amount of work done by the system on the surroundings plus the change in internal energy of the system. Equation (4.26) may be applied to a dynamic system, but in this case additional terms must be added to take cognizance of all forms of external energies.

The work done by the system on the surroundings may consist of mechanical, electrical, magnetic, etc., energies. If the work consists only of expansion or compression, the work term is as follows:

$$W = \int_{V_1}^{V_2} P\,dV \tag{4.27}$$

If the pressure is constant during compression or expansion,

$$W = P(V_2 - V_1) = P\,\Delta V$$

If pressure is not constant, the relationship between pressure and volume must be known in order to evaluate the integral of Eq. (4.27).

The change in internal energy of a system may be expressed as $U_2 - U_1 = \Delta U$. This quantity is always evaluated as a *difference*. Internal energy U is not given an absolute value. Unlike the work term of Eq. (4.27) the value of ΔU is independent of the path the change in the system passes over. The value ΔU is a result of a change in temperature, pressure,[1] volume,[1] mass, phase condition, or chemical composition of the system.

The internal energy of a system is a result of movement of the molecules and the atoms of which the molecules are composed. For example, the internal energy of a gas is the summation of the different internal kinetic energies, and the intrinsic energy, which is not a function of temperature. The internal kinetic energies are due to linear vibrations of the molecules

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[1] In the case of an ideal gas the value of ΔU is independent of pressure and volume.

and the atoms composing them, as well as to rotational movement. The intrinsic energy may be, for example, the energy of a chemical reaction.

Although ΔU is a property of the system, Q and w are *not* properties of the system. A system at both the beginning and the conclusion of a change has internal energy, but the system has no Q or w, for these are observed only *during* a change in the system from one state to another as they affect the surroundings. Heat is energy *transferred* from the surroundings to the system. A system *never* contains heat; instead, it contains internal energy. Heat is energy being transferred. Likewise, w is work done by the system on the surroundings. Consequently, a system *never* contains work energy. *Neither heat nor work is a property of the system.*

Even so, chemical engineers in practice commonly refer to the "heat contained by a system." This is not strictly correct, for this so-called "heat" is internal energy. If this distinction is kept in mind, there is less possibility of confusion.

Enthalpy.—Consider a system that consists of two pistons in respective cylinders that are connected by a tube. A valve is located in the tube between the two cylinders, as shown in Fig. 4.5. The initial condition of the system is such that gas at high pressure is contained at rest in the small cylinder and there is no gas in the large cylinder ($V_2 = 0$). Then, a change is started that consists in heat being transferred from the surroundings to the small cylinder, and simultaneously the valve between the two cylinders is opened. The piston in the small cylinder is moved by an outside force so that the pressure P_1 is maintained constant while the gas expands into the large cylinder. Likewise, the piston in the large cylinder is allowed to move against an outside force so that P_2 is maintained constant. During the entire change the amount of heat transferred to the system is represented by Q.

If Eq. (4.27) is applied to the process, it is apparent that the amount of work done by the system on the surroundings, W, is equal to the amount of work done by the system on the piston in the large cylinder minus the work done by the surroundings on the piston in the small cylinder; or since pressure was maintained constant at P_1 in the small cylinder and at P_2 in the large cylinder,

$$W = P_2V_2 - P_1V_1 \tag{4.28}$$

where V_1 and V_2 represent the change in volumes in the respective cylinders. Thus, *for a static system when the pressure at any given point remains constant,*

$$Q = U_2 - U_1 + P_2V_2 - P_1V_1 = \Delta U + \Delta PV \tag{4.29}$$

The student must keep well in mind the fact that Eq. (4.29) is theoretically valid only for static systems when the pressure at any given point in the system remains constant. It will be found in Chap. VI that Eq. (4.29) is not *strictly* applicable to *dynamic* systems because of kinetic energies that are involved. The sum $\Delta U + \Delta PV$ is a property of the system that is dependent *only* upon the initial and final conditions of the system. Since this sum is frequently encountered in chemical-engineering processes and since it is a property of the system, it has been identified as enthalpy, or heat content, in accordance with Eq. (4.30).

$$\Delta H = \Delta U + \Delta PV \tag{4.30}$$

It is noted that ΔH is equivalent to Q only when there is no variation in pressure at any given point in the system during the change in the system.

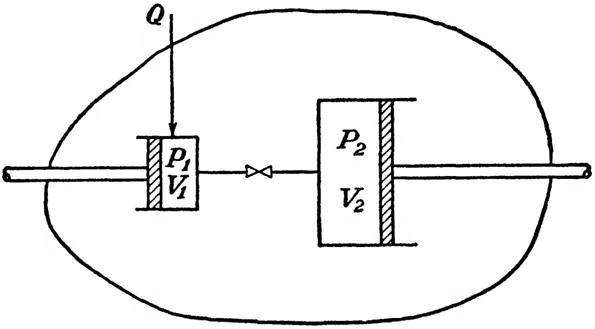

FIG. 4.5.

Obviously the work term of Eq. (4.26) as expressed in Eq. (4.27) would not be equivalent to ΔPV if there were any variation in pressure in either cylinder during expansion. It is apparent also from the above analysis of the change in the system as represented in Fig. 4.5 that if adiabatic expansion ($Q = 0$) had occurred ΔH would be zero. It will be learned later that in a dynamic system ΔH is not necessarily zero for an adiabatic process.

Datum Plane.—Those terms which depend only upon initial and final conditions are called *integral quantities*, whereas those which depend upon the path of change as well as the initial and final conditions are called *differential quantities*. In view of the fact that the integral quantities depend upon a difference rather than an absolute value it is convenient in calculations to use the same reference state and conditions in establishing the differences involved. Such a reference is commonly called the *datum plane.*

Heat of Reaction.—In a chemical reaction, heat may be absorbed or liberated. Heat of reaction is the change in enthalpy of a system that accompanies a chemical reaction relative to a specific temperature. The heat of reaction is the net change in enthalpy that occurs when the process (reaction) begins at the datum-plane temperature and the products of the reaction are brought to the same temperature at the end of the process. The heat of reaction must therefore be defined by specifying the initial and final states (chemical equation) as well as whether the reaction took place at constant pressure or constant volume.

At constant pressure, ΔH is identical with Q, or the heat transferred to the system (static), whereas at constant volume no work is done on the surroundings and Q is equivalent to ΔU or $\Delta H = Q + \Delta PV$. Unless otherwise specified, heats of reaction are quoted on the basis of constant pressure of 1 atm. The heat of reaction that accompanies a chemical change is expressed in two different ways as shown by the following equations:

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 383{,}000 \text{ Btu } (60°\text{F}) \tag{4.31}$$

or

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (\Delta H_{60°} = -383{,}000 \text{ Btu}) \tag{4.32}$$

The heat of reaction is frequently expressed in terms of heat energy per mole of one of the products or reactants, which therefore defines the chemical equation to which the heat of reaction corresponds. If the gram-mole is used as the basis, the heat of reaction will be expressed in calories or kilogram-calories; but if the pound-mole is used, the heat of reaction will usually be in Btu. In the above equations the heat of reaction is expressed in Btu per pound-mole of CH_4. In the first equation the heat of reaction is expressed as part of the results of the reaction. In the second equation the heat of reaction is expressed as the change in enthalpy that occurred in the static system. This corresponds to a reaction that takes place at atmospheric pressure with the initial and final temperature of the system at 60°F.[1] Since Q is equal to ΔH at constant pressure, it is apparent that 383,000 Btu was transferred to the surroundings (relative to 60°F) for every mole[2] of methane converted to CO_2 and H_2O.

In the case of Eq. (4.32) the heat of reaction $H_{60°}$ is also referred to as the *heat of combustion*. The heat of combustion is merely the change in enthalpy, relative to a specific temperature, at constant pressure of 1 atm (unless stated otherwise), when a combustible material is burned completely with oxygen. Tables A.5 to A.7 give the heats of combustion of specific compounds, petroleum oils (liquids), and hydrocarbon gaseous mixtures, respectively, relative to 60°F at constant pressure. It will be noted that heats of combustion are given as *gross* and *net*. The gross heat of combustion includes the change in enthalpy due to the condensation at the reference temperature of the water vapor formed. The net heat of combustion does not include the change in enthalpy due to condensation of the water

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[1] In this text 60°F will be used as the basis. The temperature basis should always be known for any heat-of-reaction data used.

[2] The pound-mole will be used throughout this text unless otherwise mentioned.

vapor in the products of combustion. Of course, the gross and net heats of combustion are identical if no water vapor is formed.

In addition to heats of reaction as a result of chemical reaction, there are others such as *heat of solution.* When concentrated sulfuric acid is diluted with water, it will be noted that the temperature increases rapidly. This is owing to the fact that the heat of solution is rather large. In some cases, however, the heat of solution is positive (heat absorbed), and a reduction in temperature occurs if the system is maintained under adiabatic conditions. Table A.4 presents the *integral heat of solution* for several rather common materials. The integral heat of solution is the change in enthalpy when a unit mass of solute is dissolved in a given mass of solvent at constant temperature and atmospheric pressure.

Heat of Formation.—Since ΔH is an integral quantity, it is feasible to calculate the ΔH that corresponds to the formation of methane from its elements C and H. This can be done if the heats of combustion of carbon and hydrogen to CO_2 and H_2O are available. Thus

$$C + O_2 \rightarrow CO_2 \quad (\Delta H = -169{,}000 \text{ Btu})$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad (\Delta H = -122{,}900 \text{ Btu})$$

Thus, by addition,

$$\begin{array}{c} C + \cancel{O}_2 \rightarrow \cancel{CO_2} + 169{,}000 \\ 2H_2 + \cancel{O}_2 \rightarrow \cancel{2H_2O} + 245{,}800 \\ \cancel{CO_2} + \cancel{2H_2O} \rightarrow CH_4 + \cancel{2O_2} - 383{,}000 \\ \hline C + 2H_2 \rightarrow CH_4 + 31{,}800 \end{array}$$

or

$$\Delta H = -31{,}800 \text{ Btu}$$

In this case ΔH is called the "heat of formation" of CH_4 (methane). If methane were decomposed into hydrogen and carbon, 31,800 Btu would be absorbed by the system from the surroundings per mole of methane decomposed. The heat of reaction for any reaction can be calculated by this procedure if the heats of formation of each of the products of the reaction and reactants are known.

Heat Capacity and Specific Heat.—The rate of change in Q with respect to temperature of a system is called its heat capacity and may be defined mathematically as follows on the basis of one mole:

$$C = \frac{dQ}{dT} \tag{4.33}$$

where C is the heat transferred per degree Fahrenheit per unit mole.

From Eq. (4.27) it is apparent that if the only work done is by expansion or compression

$$C = \frac{dU}{dT} + P\frac{dV}{dT} \tag{4.34}$$

At constant volume the second term of the right member of Eq. (4.34) becomes zero, and

$$C_v = \frac{dU}{dT} \tag{4.35}$$

This is called the *heat capacity at constant volume.* It represents the amount of heat required to increase the temperature of one mole by 1°F at constant volume.

At *constant pressure* it is apparent from Eq. (4.34) that

$$C_p = \frac{d(U + PV)}{dT} = \frac{dH}{dT} \tag{4.36}$$

This is the *heat capacity at constant pressure.* The relation in Eq. (4.36) is also apparent from the development of Eqs. (4.29) and (4.30) since $Q = \Delta H$ at constant pressure. It follows from Eq. (4.36) that at constant pressure

$$Q = \Delta \mathrm{H} = \int_{T_1}^{T_2} C_p\, dT \tag{4.37}$$

This is a very useful and important relationship.

In the case of solids and liquids C_v is essentially equivalent to C_p, but in the case of gases C_p is somewhat larger than C_v. For an ideal gas it can be shown that

$$C_p - C_v = R \tag{4.38}$$

Note that the gas constant R has the same dimensions as heat capacity.

The expression "specific heat" is perhaps more common in the practice of chemical engineering than is the expression "heat capacity." These expressions are very closely related, and the distinction should be understood. Actually, specific heat is dimensionless; it is the amount of heat required to increase the temperature of one unit mass of a system 1°F relative to the amount of heat required to increase the temperature of one unit mass of water from 60 to 61°F. Inasmuch as the amount of heat required to increase the temperature of 1 lb of water from 60 to 61°F is 1 Btu, specific heat is equivalent numerically to the amount of heat required to increase the temperature of a unit mass of a system 1°F. The heat capacities *per unit mass* at constant volume and constant pressure will be denoted by c_v and c_p, respectively, throughout this text. They are related to molal heat capacities as follows:

$$c_vM = C_v \tag{4.39}$$

$$c_pM = C_p \tag{4.40}$$

where M = molecular weight

The enthalpy of a material owing to its temperature (commonly called heat energy in practice) is called its *sensible heat.* Thus, the sensible heat is the enthalpy of a substance with reference to some datum-plane temperature and is equal to the average heat capacity multiplied by the temperature difference. Average molal heat capacities relative to 60°F are given in Table A.3 for several common gases.

Latent Heat.—It was stated earlier that internal energy is dependent, among other things, upon the phase condition. The reason for this is that, when a change of phase occurs, heat is usually liberated or absorbed. This is shown graphically in Fig. 4.6 for the case of heating ice from 0°F to steam at 250°F at atmospheric pressure. If ice at 0°F and atmospheric pressure is heated, its temperature will rise continuously as heat is absorbed, owing to its heat capacity, until the ice changes from the solid phase to the liquid phase. The amount of heat absorbed in order to effect the change of phase in this case (2580 Btu/mole) is called the *heat of fusion.* Then, after the change from solid to liquid phase, the temperature of the water will rise continuously as heat is absorbed until the temperature reaches 212°F. At this temperature, vaporization of the water occurs as heat is absorbed. The heat required (change in internal energy) to change the water from the liquid to the vapor phase in this case (17,500 Btu/mole) is called the *latent heat of vaporization* or merely latent heat. After all the liquid is converted to steam, the temperature of the steam will rise continuously

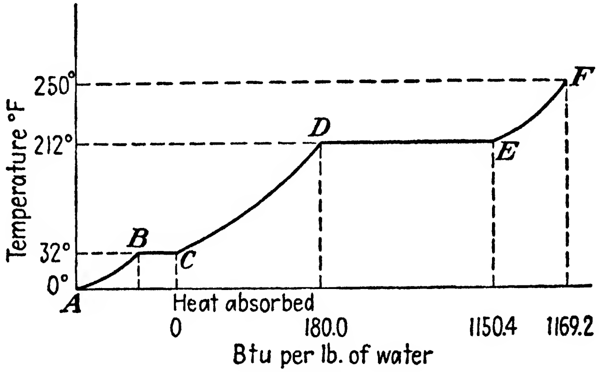


FIG. 4.6.

as heat is absorbed. As the temperature of equilibrium between the vapor and liquid phases increases, the latent heat of vaporization decreases until at the critical temperature it is zero. Table A.11 presents latent heats of several compounds at atmospheric pressure.

Enthalpy Tables and Charts.—Tables A.14 and A.15 present as a function of temperature and pressure the enthalpy of liquid water and steam in Btu per pound relative to liquid water at 32°F as the datum plane. These tables are commonly called steam tables.

In Table A.14 the specific volume (cubic feet per pound) of water and of steam at equilibrium conditions is given as a function of the temperature. Obviously, since the table is for a two-phase system in equilibrium, the pressure is fixed for any specific value of temperature. Also, the enthalpy (Btu per pound) of water and of steam at equilibrium conditions (saturated) is given relative to the datum plane of liquid water at 32°F. The change in enthalpy between any two conditions can be obtained merely by obtaining the difference between the enthalpies for the two conditions under consideration as given in the table.

Table A.15, on the other hand, is for superheated steam, and therefore in this case only one phase exists. Hence it is necessary to fix both temperature and pressure in order to define the system completely. This table gives the specific volume and enthalpy per pound of steam as a function of temperature and pressure. The change in enthalpy between any two conditions can be obtained by taking the difference between the enthalpies as given in the table.

Inasmuch as both specific volume and pressure are given in Tables A.14 and A.15, it is apparent that internal energies can be computed easily, based on Eq. (4.30).

Figures A.9 to A.14 are graphical representations of enthalpies (Btu per pound) of some of the hydrocarbons as a function of temperature and pressure relative to liquid at 32°F. Latent heats of vaporization can be obtained for any specific condition of temperature or pressure merely by taking the difference between the enthalpy of saturated vapor and saturated liquid. Also, sensible heats can be obtained for liquid or for vapor at constant pressure. The constant-pressure curves are for vapor.

Each chart is for a specific hydrocarbon in the pure state but may be applied to the hydrocarbon in a mixture with sufficient accuracy for chemical-engineering calculations. The reason for this is that the enthalpy of a mixture of hydrocarbons is equal to the summation of the enthalpies of its components. This is owing to the fact that hydrocarbon solutions approximate perfect solutions. In the case of mixtures it was learned earlier in the chapter that a specific component may exist in the vapor phase under conditions which would correspond to liquid phase only if the component existed in the pure state. Also, it was learned that a component of a mixture can exist in the liquid phase under conditions which would correspond to vapor only if the component existed in the pure state. In order to apply Figs. A.9 to A.14 to mixtures under such circumstances the following procedure should be followed:

1. When the temperature of a liquid mixture is above the critical temperature of some of the components, the enthalpy of each of these components is represented by the curve marked For liquid phase, which lies above the critical temperature. This was calculated on the basis of the extrapolated vapor-pressure line. For the other components of the mixture their enthalpies are given by the saturated-liquid curve.
2. When the pressure on a mixture is above the vapor pressure of some of the heavier components in the pure state, their enthalpies should be obtained from the saturated-vapor curves at the temperature of the mixture. For the other components their enthalpies are represented by the curves that correspond to the pressure on the mixture.
3. The enthalpies of the components of a mixture are additive on a weight basis because heat of solution is nil.

The application of Figs. A.9 to A.14 to mixtures is illustrated by Example 9.

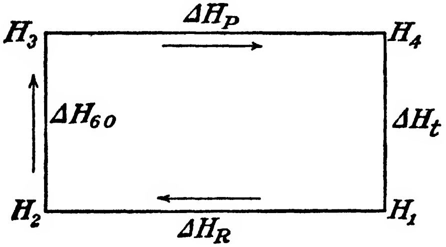
Example 9. Calculate the enthalpy of the following mixtures at the conditions indicated:

	Lb	
	Liquid at 110°F	Vapor at 275 lb/sq in. abs and 113°F
Methane	26	37
Ethane	785	213
Propane	10,840	1,097
Total	11,651	1,347

Solution:

	For liquid			For vapor		
	Lb	Btu/lb	Btu	Lb	Btu/lb	Btu
Methane	26	48	1,280	37	136	4,870
Ethane	785	102	80,070	213	192	40,100
Propane	10,840	39	423,000	1,097	173	189,700
	11,651		504,300	1,347		234,670

Enthalpy for Different Datum Plane.—Since enthalpy is given relative to a specific datum plane, it is frequently necessary in chemical-engineering calculations to compute enthalpy relative to another datum plane. For example, assume that it is desirable to calculate the heat of reaction for combustion of methane at temperature t, based on the heat of reaction given by Eq. (4.32). Inasmuch as the enthalpy change is independent of the path, the calculation can be made on the basis of the following diagram:



The enthalpy change $H_3 - H_2 = \Delta H_{60} = -383{,}000$ Btu is known, and it is desirable to calculate $\Delta H_t = H_4 - H_1$. It is apparent therefore that

$$\Delta H_t = \Delta H_R + \Delta H_{60} + \Delta H_p$$

because the value of ΔH_t is independent of the path. The enthalpy change ΔH_R is the change in sensible heat energy owing to heating (or cooling) the reactants of Eq. (4.32) from 60 to t°F. Thus, $\Delta H_R = H_2 - H_1$. The change in enthalpy ΔH_P is the change in sensible heat energy owing to cooling (or heating) the products of reaction in Eq. (4.32) from 60 to t°F. Thus,

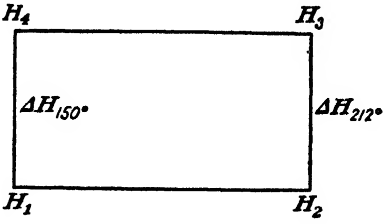
$$\Delta H_p = H_3 - H_2$$

This identical procedure is applicable to the calculation of enthalpies of any type with reference to other datum planes. Heats of fusion, latent heats of vaporization, heats of formation, etc., can all be referred to a different datum plane by this procedure.

Example 10. The latent heat of water at 212°F and atmospheric pressure is 970.3 Btu/lb. Using a specific heat for liquid water as 1.0 and for steam as 0.40, calculate the latent heat of water at 150°F and saturation pressure.

Solution: It is always most convenient to set up such calculations by following through a diagram, with the starting point at the state of the system for which the change in enthalpy is desired and with the finishing point at the final state of the system for which the enthalpy change is desired.

Thus, since latent heat at 150°F is desired, the starting point will be liquid water at 150°F and the finishing point will be steam at 150°F.



Thus, $$\Delta H_{150°} = H_4 - H_1 = (H_2 - H_1) + (H_3 - H_2) + (H_4 - H_3)$$

But $H_2 - H_1$ is the sensible heat of water (change in internal energy) from 150 to 212°F, or

$$H_2 - H_1 = 1.0(212 - 150) = 62.0 \text{ Btu/lb}$$

$$\Delta H_{212} = H_3 - H_2 = 970.3 \text{ Btu/lb}$$

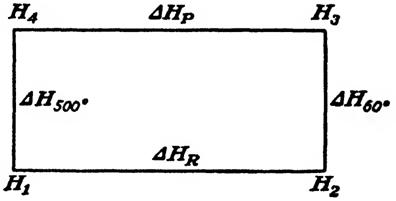
Also, $H_4 - H_3$ is the sensible heat of steam above 212°F, or

$$H_4 - H_3 = 0.40(150 - 212) = -24.8 \text{ Btu/lb}$$

Then, $$\Delta H_{150°} = 62.0 + 970.3 - 24.8 = 1007.5 \text{ Btu/lb}$$

It will be noted by referring to Table A.14 that the correct latent heat at 150°F is 1007.8 Btu/lb. The difference is a result of using specific heats that are not quite correct.

Example 11. Calculate the heat of reaction of Eq. (4.32) relative to a datum plane of 500°F.



Solution: First construct a diagram.

Then, starting with the reactants at 500°F,

$$\Delta H_{500°} = \Delta H_R + \Delta H_{60°} + \Delta H_P$$

The heat of reaction at 60°F is given by

$$\Delta H_{60°} = -383{,}000$$

The mean molal heat capacities of CH_4, O_2, CO_2, and H_2O are given in Table A.3. At 500°F the values relative to 60°F are as follows:

	CH_4	O_2	CO_2	H_2O
Btu/(mole)(deg F)...........	9.91	7.23	9.98	8.19

$$\Delta H_R(\text{sensible heat}) = [9.91 + (2)(7.23)](60 - 500) = -10{,}700$$
$$\Delta H_P(\text{sensible heat}) = [9.98 + (2)(8.19)](500 - 60) = 11{,}600$$

Then $$\Delta H_{500^\circ} = \Delta H_R + \Delta H_{60^\circ} + \Delta H_P = -10{,}700 - 383{,}000 + 11{,}600$$
$$= -382{,}100 \text{ Btu}$$

It is noted that in this particular case the heat of reaction is not much affected by temperature.

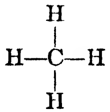
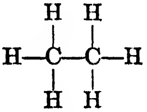
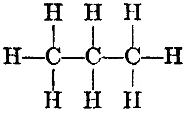
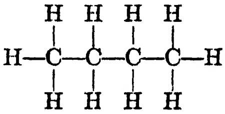
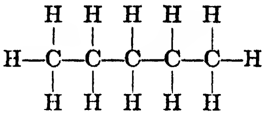
CLASSIFICATION OF ORGANIC CHEMICALS AND REACTIONS

Inasmuch as it will be necessary to deal in the following chapters with the application of the technical fundamentals of chemical engineering to certain of the chemical processes, the student should have some conception of the chemical reactions upon which these processes are based. Many of the examples in the subsequent chapters involve organic chemical compounds and organic chemical reactions. Hence, a slight knowledge of these will help the student to a fuller understanding of the conditions surrounding the application of the fundamentals.

Organic chemistry deals primarily with carbon and its compounds. The compounds with which the student will be concerned in this text may be divided into three classifications, *viz.*, aliphatic, naphthenic, and aromatic. The molecules of the aliphatic series are of the form of a chain, whereas the molecules of both the naphthenic series and the aromatic series are of the form of a ring. This, however, will become clear as the discussion proceeds.

With rare exceptions the valence of the carbon atom is 4. This fact will be found of great help in completely identifying and understanding the different compounds.

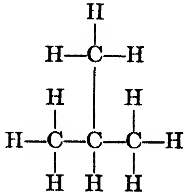
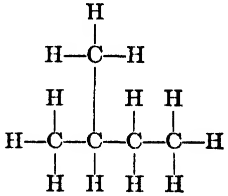
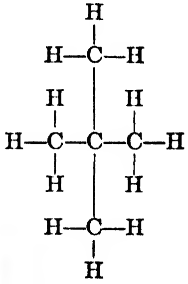
Important Aliphatic Compounds. *Paraffin Hydrocarbons.*—The general chemical formula for the paraffin hydrocarbons is C_nH_{2n+2}. These are commonly referred to as the saturated hydrocarbons because the carbon chain is completely saturated with hydrogen. Some of the more common paraffin hydrocarbons are listed below, with their chemical and structural formulas:

Compound	Chemical formula	Structural formula
Methane..........	CH_4	 $\begin{array}{ccc} & H & \\ & \vert & \\ H- & C & -H \\ & \vert & \\ & H & \end{array}$
Ethane..........	C_2H_6	 $\begin{array}{cccc} & H & H & \\ & \vert & \vert & \\ H- & C- & C & -H \\ & \vert & \vert & \\ & H & H & \end{array}$
Propane..........	C_3H_8	 $\begin{array}{ccccc} & H & H & H & \\ & \vert & \vert & \vert & \\ H- & C- & C- & C & -H \\ & \vert & \vert & \vert & \\ & H & H & H & \end{array}$
n-Butane....	C_4H_{10}	 $\begin{array}{cccccc} & H & H & H & H & \\ & \vert & \vert & \vert & \vert & \\ H- & C- & C- & C- & C & -H \\ & \vert & \vert & \vert & \vert & \\ & H & H & H & H & \end{array}$
n-Pentane.........	C_5H_{12}	 $\begin{array}{ccccccc} & H & H & H & H & H & \\ & \vert & \vert & \vert & \vert & \vert & \\ H- & C- & C- & C- & C- & C & -H \\ & \vert & \vert & \vert & \vert & \vert & \\ & H & H & H & H & H & \end{array}$

The series extends to higher molecular weight merely by extension of the carbon chain, as shown by the structural formulas. Normal hexane has 6 carbon atoms in the chain, normal heptane has 7, normal octane has 8, normal nonane has 9, normal decane has 10, and so on. It will be noted from the structural formulas that each carbon atom has four valence bonds each of which is taken up with either another carbon atom or a hydrogen atom.

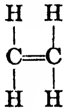
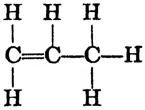
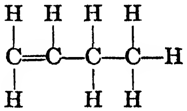
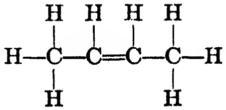
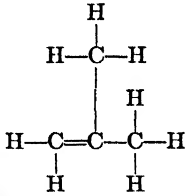
In addition to the straight-chain or normal paraffins, as they are called, branched-chain paraffins, or isoparaffins, fall in the same classification. The isoparaffins have the same general chemical formula but somewhat different structural formulas. Some of these are given in the following table.

As the molecular weight increases, the number of isomers increases at a rapid rate. The term "isomer" is applied to the different configurations that can be made out of an individual molecule. Thus, in a strict sense, the normal paraffins are isomers although their name does not have the prefix "iso." Thus, butane has 2 isomers, that is, normal butane and isobutane. Pentane has 3 isomers, namely, normal pentane, isopentane, and neopentane. Hexane has 5 isomers, heptane has 9, octane has 18 and so on.

Compound	Chemical formula	Structural formula
Isobutane.....	C_4H_{10}	
Isopentane....	C_5H_{12}	
Neopentane..	C_5H_{12}	

In the study of organic chemistry the student will learn a system of names for the different isomers, but this is not essential knowledge for the purpose of this text.

Olefins.—Another series of chain-type hydrocarbons has the general formula C_nH_{2n}. These are called olefins. They are unsaturated, for each molecule has one double bond between two carbon atoms. Some of the more common olefins are the following:

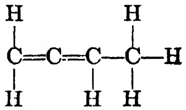
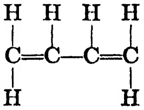
Compound	Chemical formula	Structural formula
Ethylene	C_2H_4	
Propylene	C_3H_6	
Butene-1 (or α)	C_4H_8	
Butene-2 (or β)	C_4H_8	
Isobutylene	C_4H_8	

In the case of four carbon atoms there are three isomers. One has the double bond between the first two carbon atoms in the chain. Another has the double bond between the second two carbon atoms in the chain. The third corresponds to the removal of two hydrogen atoms from isobutane. It is seen, therefore, that isomers occur as a result of the position of the double bond as well as of rearrangement of the carbon atoms.

As might be expected, the olefins are more reactive than the saturated hydrocarbons owing to the double bond.

Polyolefins.—In addition to the olefins, there are compounds that have more than one double bond. For example, butadiene possesses two double bonds. (See p. 94.)

The prefix numbers denote the position of the double bonds. By inspection of the structural formula it can be seen that there can be no butadiene which corresponds to isobutane because the valence of each carbon atom is 4.

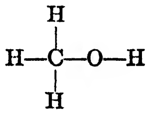
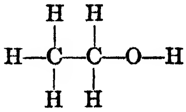
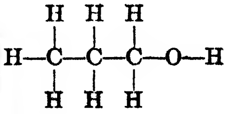
Compound	Chemical formula	Structural formula
1-2 Butadiene....	C_4H_6	 $H_2C{=}C{=}CH{-}CH_3$
1-3 Butadiene....	C_4H_6	 $H_2C{=}CH{-}CH{=}CH_2$

As the molecular weight increases, the number of possibilities for diolefins increases. Likewise, it becomes possible to have more than two double bonds in a given molecule. The diolefins are very reactive and were very important during the Second World War in the production of synthetic rubber.

Acetylenes.—Another series of unsaturated chain-type hydrocarbons is the acetylenes. These have triple bonds and are very reactive. They have the general formula of C_nH_{2n-2}. Acetylene itself has the following chemical and structural formulas:

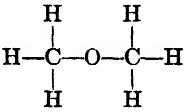
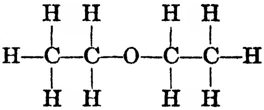
$$C_2H_2 \qquad H{-}C{\equiv}C{-}H$$

Alcohols.—By the addition of an atom of oxygen to the molecule of a paraffin hydrocarbon, the corresponding alcohol is formed. Some of the more common primary alcohols are as follows:

Compound	Chemical formula	Structural formula
Methanol...	CH_3OH	 $H{-}CH_2{-}O{-}H$
Ethanol.....	C_2H_5OH	 $H{-}CH_2{-}CH_2{-}O{-}H$
Propanol....	C_3H_7OH	 $H{-}CH_2{-}CH_2{-}CH_2{-}O{-}H$

As in the case of the hydrocarbons, alcohols have corresponding isomers. These need not be discussed, however.

Ethers.—Another type of compound that is formed by addition of an oxygen atom to a paraffin hydrocarbon is the ethers. The oxygen atom is located between two carbon atoms in this case.

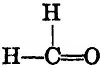
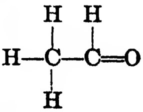
Compound	Chemical formula	Structural formula
Dimethyl ether...	C_2H_6O	 $H-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-H$
Diethyl ether.....	$C_4H_{10}O$	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$

The ethers may be produced from alcohols. For example,

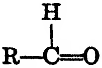
$$2C_2H_5OH = C_4H_{10}O + H_2O$$

Diethyl ether is commonly referred to as "ether," but there are many different types.

Aldehydes.—By the further oxidation of primary alcohols a series of compounds called aldehydes is formed.

Compound	Chemical formula	Structural formula
Formaldehyde....	CH_2O	 $H-\overset{H}{C}=O$
Acetaldehyde.....	C_2H_4O	 $H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=O$

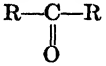
Higher molecular weight aldehydes are formed, which correspond to the basic paraffin hydrocarbon or primary alcohol. The aldehydes always have the characteristic group as follows:



$$R-\overset{H}{C}=O$$

where R is a methyl, ethyl, propyl, or similar group.

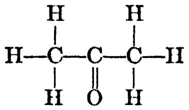
Ketones.—A series of compounds somewhat similar in structural formula to the aldehydes is produced if the oxygen atom is attached farther in the hydrocarbon molecule. These have the characteristic group of



$$R-\underset{\underset{O}{\|}}{C}-R$$

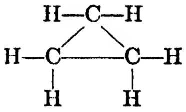
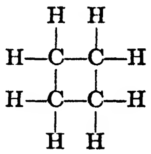
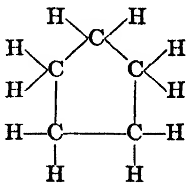
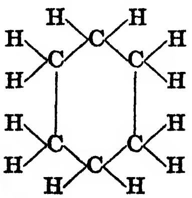
Acetone, the most common of the ketones, has the following formulas:

C_3H_6O



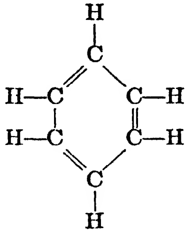
$$H-\overset{H}{\underset{H}{C}}-\underset{\underset{O}{\|}}{C}-\overset{H}{\underset{H}{C}}-H$$

Naphthene Hydrocarbons.—Up to this point only straight-chain and branched-chain compounds have been considered. Another important type is the cycloparaffins, or naphthenes. The molecules of this type are in the form of a ring. They have the general chemical formula of C_nH_{2n}, which is identical with that of olefins. The structural formulas are quite different, however, for these are saturated compounds. Some are as follows:

Compound	Chemical formula	Structural formula
Cyclopropane......	C_3H_6	
Cyclobutane.......	C_4H_8	
Cyclopentane......	C_5H_{10}	
Cyclohexane.......	C_6H_{12}	

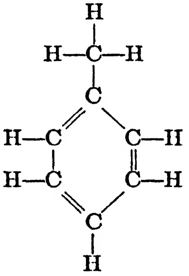
Important Aromatic Compounds.—Although there are many more types of aliphatic hydrocarbons of great importance, they need not be discussed now. Instead, some aromatic types of hydrocarbons will be considered.

Benzene Ring.—The aromatic hydrocarbons are those compounds which include the benzene ring. Benzene, or benzol as it is sometimes called, has the chemical formula C_6H_6. Its structural formula is as follows:



The benzene ring has three double bonds and as would be expected is quite reactive. This ring is also known as the phenyl ring.

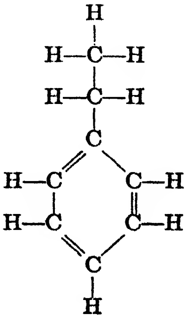
Toluene.—Toluene is a phenyl ring with a methyl group (CH_3). Its chemical formula is C_7H_8, and its structural formula is



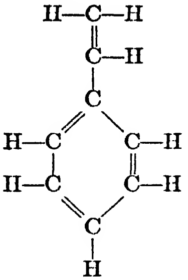
Toluene was the base used for production of trinitrotoluene (TNT) during the Second World War.

Ethyl Benzene and Styrene.—By the addition of an ethyl group (C_2H_5) to the benzene ring, ethyl benzene is formed. Its chemical and structural formulas are as follows:

C_8H_{10}



By removing two of the hydrogen atoms from the ethyl group, the compound styrene is obtained. Its chemical formula is C_8H_8, and its structural formula is as follows:



Styrene is reacted with butadiene to produce one of the best grades of synthetic rubber.

There are many other types of aromatic hydrocarbon, but a discussion of them at this time would not help the student particularly in understanding the subjects covered in the later chapters.

Important Reactions.—A discussion of a few organic chemical reactions is in order at this time. The purpose of this discussion is merely to acquaint the student with the primary chemical reactions involved in certain of the chemical processes.

Isomerization.—The chemical reaction involved in isomerization is the conversion of a compound to one or more of its isomers. For example, *n*-butane is isomerized to isobutane in the unit process, isomerization. Butene-1 is isomerized to butene-2. Also, *n*-pentane is isomerized to isopentane, and normal hexane is isomerized to its isomers. As the number of possible isomers increases, the number obtained in the reaction products increases.

Alkylation.—This consists in the reaction of an olefin with an aromatic, naphthenic, or saturated aliphatic type of compound so that the olefin is merely joined to the aromatic, naphthenic, or aliphatic molecule. For example, ethylene is alkylated with benzene to produce ethylbenzene. Butene-1, butene-2, and isobutylene are alkylated with isobutane to produce iso-octane isomers.

Polymerization.—This involves the reaction of an unsaturated type of compound so that large molecules are produced by the complete addition of the reacting molecules. For example, butadiene will polymerize first by the reaction between two butadiene molecules; then the product will react with another butadiene molecule; this product will react with still another butadiene molecule, etc., until huge molecules are formed. Likewise, styrene molecules will react among themselves so that polymers of high molecular weight are formed.

Another type of polymer is formed by the reaction between styrene and butadiene. This polymer is the source of some of the best synthetic rubber. Polymers thus formed by the reaction between unlike molecules are called copolymers. Another example is the copolymerization of isobutylene with butene-2 to form the olefin, iso-octene. In this case the polymerization reaction is controlled so that for each mole of product formed, one mole of isobutylene and one mole of butene-2 are consumed.

Hydrogenation.—The conversion of unsaturated compounds to saturated compounds by the addition of hydrogen is called hydrogenation. For example, isobutylene can be converted to isobutane by hydrogenation. Iso-octene can be converted to iso-octane by hydrogenation. Also, benzene can be converted to cyclohexane by hydrogenation.

Dehydrogenation.—This chemical process is the reverse of hydrogenation. Cyclohexane can be converted to benzene and *n*-butane can be converted to butene-1 and butene-2 by dehydrogenation.

Dehydration.—This consists in removal of two hydrogen and one oxygen atoms (H_2O) from one or two molecules to produce a new compound. For example, ethylene can be produced by dehydration of ethanol. One molecule of diethyl ether can be produced by dehydration of two molecules of ethanol.

PROBLEMS

1. Calculate the volume of a mole of methane at 100°C and 60 cm of mercury.

2. Calculate the pressure there would have to be on methane for it to have the same density as air at the same temperature but at atmospheric pressure.

3. What is the volume of a balloon that has a lifting power (over its own weight) of 1 ton (short) at 100°F if filled with helium? The dead weight of the balloon (without the helium) is 100 lb.

4. A drum of 100 cu ft is under a vacuum of 1.0 in. of mercury relative to a 30-in. barometer. If the contents of the drum is entirely air, how many pounds of nitrogen is in the drum at 60°F?

5. The following mixture of gases is at a pressure of 50 lb/sq in. gauge:

	N_2	O_2	NH_3	H_2	Total
Lb.	40	55	10	35	140

What is the partial pressure of each component?

6. A large drum is vented to the atmosphere by means of a 1-in. pipe. There is a small amount of water in the bottom of the drum. The drum and its contents are at 150°F. What is the partial pressure of water vapor in the vapor space in the drum?

7. Calculate the volume occupied by the following mixture at 500°F and 300 lb/sq in. gauge:

	Lb
Methane (CH_4)	100
Ethane (C_2H_6)	240
Propane (C_3H_8)	150
Nitrogen (N_2)	50
Hydrogen (H_2)	60
Total	600

8. The following gaseous mixture is saturated with water vapor. The pressure and temperature are atmospheric and 130°F, respectively. How many moles of water vapor are present?

	CO_2	N_2	O_2	Total
Moles	10	100	12	122

9. A system contains two components. What is the maximum number of phases possible with this system if pressure and temperature are the only variables to be considered. Give basis for answer.

10. A two-phase system is completely defined by fixing temperature, pressure, and the amount of one component. How many components are there in the system?

11. Prepare a Düring plot of isopentane with isobutane as a reference between 15 lb/sq in. abs and 150 lb/sq in. abs. Show in tabular form the pertinent data used to prepare the plot.

12. A liquid solution of the following composition is at a temperature of 100°F:

	Wt. %
Propane	20.0
Isobutane	20.0
n-Butane	30.0
Isopentane	30.0
Total	100.0

What is the vapor pressure of the solution?

13. Calculate the composition vs. temperature curve of the vapor phase in equilibrium with a liquid phase composed of propane and *n*-butane. The vapor-phase composition curve should cover the range of 0 per cent propane to 0 per cent *n*-butane in the liquid phase. The pressure on the system is 50 lb/sq in. abs.

14. Calculate the average molecular weight of the following gas mixture:

	Vol. %
CO_2	12.0
O_2	8.0
N_2	75.0
H_2O	5.0
Total	100.0

15. Calculate the density of the following gas mixture at 500 lb/sq in. gauge and 250°F:

	Lb
Methane (CH_4)	100
Ethane (C_2H_6)	240
Propane (C_3H_8)	150
Nitrogen (N_2)	50
Total	550

16. Calculate the pressure there would have to be on methane for it to have the same density as air at the same temperature but at 20 lb/sq in. gauge.

17. Air is saturated with water vapor at 100°F and atmospheric pressure. What is the partial pressure of the water vapor? How many moles of water vapor is there per 100 moles of dry air?

18. The following mixture of gases is at 40 lb/sq in. gauge:

	CO_2	CO	N_2	H_2	Total
Lb	100	50	50	10	210

What is the partial pressure of each component expressed in grams per square centimeter?

19. The sensible heat of a gas at constant pressure above 60°F is given as follows:

Deg F	Btu/Mole
60	0
250	1,120
500	2,970
750	5,395
1000	8,520
1250	12,470
1500	17,320

Determine the instantaneous molal heat capacity at constant pressure of the gas over the range of 60 to 1500°F.

20. The latent heat of evaporation of normal pentane at 100°F and its vapor pressure is 153 Btu/lb. The specific heat of liquid *n*-pentane is 0.595 between 100 and 300°F. The specific heat of *n*-pentane vapor over the same range is 0.300. Calculate the latent heat of evaporation in Btu per pound at 300°F.

21. Calculate the composition of liquid (mole per cent or mole fraction) in equilibrium with the following vapor at 100°F:

	Wt. %
Propane (C_3H_8)	10.0
Isobutane (C_4H_{10})	30.0
n-Butane (C_4H_{10})	20.0
Isopentane (C_5H_{12})	20.0
n-Pentane (C_5H_{12})	20.0
Total	100.0

22. The following gas at 40 lb/sq in. gauge and 150°F is saturated with water vapor. How many moles of water vapor does it contain per mole of dry gas?

	Mole %
Methane	45.0
Ethylene	30.0
Ethane	20.0
Propane	5.0
Total	100.0

23. Calculate the heat of formation of normal pentane at 60°F and constant pressure.

24. Calculate the volume of the following gas mixture at 500 lb/sq in. gauge and 300°F.

	Moles
Ethane	30.0
Propane	25.0
Isobutane	25.0
n-Butane	20.0
Total	100.0

25. Calculate the composition (as mole per cent or mole fraction) of the vapor phase in equilibrium with the liquid phase of the following composition at 120°F.

	Liq Vol % (60°)
Isobutane (C_4H_{10})	15.0
n-Butane (C_4H_{10})	25.0
Isopentane (C_5H_{12})	30.0
n-Pentane (C_5H_{12})	30.0
	100.0

26. Calculate the composition of the liquid phase (as mole fraction or mole per cent) in equilibrium with vapor which has the following composition at 30°F:

	Vol. %
Propane	50.0
Isobutane	20.0
Isopentane	20.0
n-Pentane	10.0
	100.0

27. Calculate the amount of heat transferred, the work done on the surroundings, the change in internal energy, and the change in enthalpy when 1 lb of water is evaporated at 1 atm from and at 212°F.

28. If in Prob. 27 the evaporation took place into a total vacuum that has a volume of 26.83 cu ft, what would be the value of Q, W, ΔU, and ΔH?

29. The heat of formation of Al_2O_3 is $\Delta H = -380{,}000$ cal/g. mole at 18°C and atmospheric pressure. Calculate the change in internal energy, the heat transferred to the system, and the work done on the surroundings for the reaction

$$2Al + 1\tfrac{1}{2}O_2 = Al_2O_3$$

Assume that the volume of 2Al is equal to that of Al_2O_3 and that the oxygen is a perfect gas.

30. Calculate the theoretical minimum amount of energy required to move 100 cu ft of water at 60°F to the roof of a building 100 ft in height if 25 cu ft of the water is available on a floor 50 ft above the ground and a large reservoir filled with water at 60°F is located 10 ft below the ground surface.

31. Calculate the heat transferred to the system, the work done on the surroundings, the change in internal energy, and the change in enthalpy when 1 cu ft of methane and excess oxygen (both at 60°F) is reacted in a constant-volume bomb to form CO_2 and H_2O. The contents of the bomb after reaction is cooled to 60°F.

32. Calculate the heat of formation of benzene based on the data given in Table A.5.

33. Calculate the net heat of combustion of ethylene at 500°F, based on the data in Tables A.3 and A.5.

34. The heat of formation at 20°C of $KClO_3$ is $\Delta H = 89{,}870$ cal/g. mole, and the heat of formation at 20°C of KCl is $\Delta H = -104{,}300$ cal/g. mole. If the heat of combustion at 20°C of $C_6H_5NO_2$ is as follows:

$$C_6H_5NO_2(l) + {}^{25}\!/_4O_2 = \tfrac{1}{2}N_2 + 6CO_2 + \tfrac{5}{2}H_2O(l) \qquad \Delta H_c = -1{,}478{,}000 \text{ cal/g. mole}$$

calculate the heat of reaction at 20°C for the following reaction:

$$2C_6H_5NO_2(l) + {}^{25}\!/_3KClO_3 = 12CO_2 + 5H_2O(l) + N_2 + {}^{25}\!/_3KCl \qquad \Delta H = ?$$

Also calculate the change in internal energy, the work done on the surroundings, and the heat transferred to the system. Assume that the ideal-gas law applies.

35. Assume $H_2O(l)$ incompressible and steam a perfect gas. Also assume that the specific heat is 1.0 for water and 0.5 for steam. Given the latent heat of water from and at 212°F and 1 atm pressure is 970.3 Btu/lb, calculate the change in enthalpy, the change in internal energy, the work done on the surroundings, and the heat transferred to the system when water at 300°F is flashed isothermally into steam at 1 atm pressure.

36. If the water in Prob. 35 at 300°F is flashed into steam at 1 atm under adiabatic conditions, what would be the value of Q, W, ΔU, and ΔH?

CHAPTER V

THE MATERIAL BALANCE

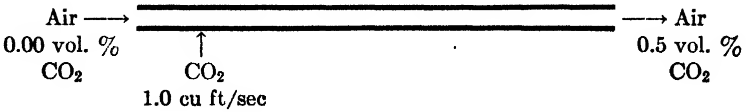
The material balance is one of the five technical fundamentals of chemical engineering. It is a detailed, quantitative account (preferably written) of all materials that enter, leave, and accumulate in a system. It may be expressed as input = output + accumulation. The last term will, of course, be negative if there is a depletion of mass in the system. The material balance is based on the law of conservation of mass. Consequently, it is rigorous for the purposes of chemical engineering even though mass is convertible into energy under certain conditions, as explained in Chap. IV. The energy equivalent of mass is so huge that changes in mass owing to its conversion into energy are not detected in the application of chemical-engineering fundamentals.

The material balance is frequently referred to as a *mass balance* or *weight balance* in chemical-engineering practice. These terms will therefore be used interchangeably throughout the text. The material balance is one of the most powerful tools in chemical engineering when applied proficiently. The concept is so simple, however, that the student is prone to assume erroneously that he can apply the material balance skillfully without much training in its application. Thus, it is the purpose of this chapter to provide preliminary training in its use. Somewhat more intensive training in this field should be received, however, before the student is prepared to practice chemical engineering.

In general, there are two types of chemical process with which the chemical engineer deals, *viz.*, static and dynamic, or in more common terminology the "batch process" and the "continuous process." In the batch process the charge is entered in one operation. Then the process is carried out. In some cases the products are removed during this period, but in others they are removed after the processing is completed. In the continuous process the charge (input items) and products (output items) are entered and removed continuously. In contrast with the batch process the flow rates, temperatures, pressures, and compositions at any point in a continuous process should be constant at all times. The material balance is useful in its application to either a batch or a continuous process. Of course, when it is applied to a batch process, input is equivalent to the output. There is no accumulation of mass in the system except in the form of loss, which rightfully belongs with the output items. The time variable usually does not enter into the material balance in a batch process. The balance is made over a complete cycle, which involves merely the processing of a single charge. In the case of a continuous process, however, the time variable must enter the material balance. The balance must be made over a specified period of time. Also, there may be an accumulation of mass in the system. This can be made insignificant, however, by selecting a sufficiently long period of time over which the balance is made so that the material in the system will be negligible compared with the input and output items. Thus, any change in the mass of the system would have no measurable effect on the balance. This eliminates the necessity of measuring the accumulation of material in the system so that input may be equated to output. Material balances on continuous processes should always be set up so that input is equal to output unless special circumstances require that the accumulation of mass in the system be measured. In essentially all process designs of continuous processes the material balance will be predicated on no accumulation of mass in the system.

One of the many useful applications of the material balance is in technical service when the performance of a given process unit is being investigated. If each item of the input and output is measured, the material balance will serve to check the accuracy of the measurements. If a balance is not obtained within desired accuracy, it is apparent that one or more of the measurements is in error. Usually, streams can be metered within an accuracy of ±1.5 per cent. Thus, if all streams are measured, the balance should check within this degree of accuracy. In many of the processes with which the chemical engineer will deal it will not be possible to measure directly all the items of input and output. The material balance will be particularly useful in such cases for measuring streams that cannot be metered. One of the simplest examples of such a case is a performance test on a furnace. It would be difficult in the great majority of cases to meter the air supplied for combustion. It would be quite costly to meter the products of combustion. But the fuel can be metered and analyzed, and the products of combustion can be analyzed. By the application of a material balance the quantity of air for combustion and the quantity of products of combustion can be calculated with a high degree of accuracy, as will be seen later.

Sometimes a stream can be metered by intentionally admitting to it at a constant rate a component that can be easily detected in low concentration. Based on the rate at which the component is admitted and its concentration in the effluent stream (by analysis), a material balance will permit the calculation of the rate of flow of the stream in question. For example, a stream of air that contained no CO_2 was metered by admitting CO_2 at the rate of 1.0 cu ft/sec. A sample of the air was taken on the downstream side of the point of CO_2 admission during the period when the CO_2 was being admitted at constant rate. The sample was analyzed and found to contain 0.5 per cent by volume CO_2 (equal to 0.5 mole per cent).



Let A = cu ft of air/min

$$CO_2 \text{ admitted} = (1.0)(60) = 60 \text{ cu ft/min}$$

$$\frac{60}{A + 60} = 0.005$$

$$A = 11{,}940 \text{ cu ft/min}$$

This balance was made on the basis of volumes, which in the special case of gases is the same as a mole balance when under conditions that the gases follow the ideal gas law. Since the mole is merely the weight (mass) of a material equal numerically to its molecular weight, the volumetric balance in the special case of gases (at low pressure) is the same as a material balance.

Another example of the use of a material balance for metering is the admission of a highly concentrated dye solution at a fixed rate to a stream of water. Rhodamine B, which is deep red and highly soluble in water, is suitable. The concentrated dye solution is prepared at any suitable concentration. A sample of the water is taken on the downstream side during the period when the dye is being admitted at a fixed rate. A sample of water also is taken on the upstream side. The latter is used to prepare a dilute solution of the dye that is about of the same color intensity as the sample of water taken when dye was being admitted to the water stream. The same concentrated dye solution is used to prepare the dilute solution so that the amount of the concentrated dye solution in the dilute solution is known. By use of a true-color colorimeter the concentration of dye in the unknown sample can be determined by reference to the dilute solution of known dye concentration. Once the concentration of dye in the unknown sample has been determined, the rate of flow of the stream of water can be calculated by material balance based on the known rate at which dye was admitted to the water stream.

Both the above examples illustrate the use of the material balance for measuring streams when one item enters in a single metered stream and leaves in a single unmetered stream. Had the air in the first example contained any CO_2, it would have been necessary to know the concentration; otherwise, the material balance could not have been used to measure the air. If an item enters a system by one stream and leaves by two or more streams, it is necessary that all the exit streams except one be metered by other means and analyzed. Otherwise, the amount of the given item in the unmetered stream will not be known and the material balance cannot be used to measure it.

Types of Balance.—The material-balance principle may be applied either on the basis of units of weight such as pounds or on the basis of moles. Since the mole is merely a unit of mass that is numerically equal to the molecular weight, it is a very convenient unit to use in material balances. If no chemical change takes place in the system on which a material balance is being made, the weight unit such as the pound can ordinarily be used quite conveniently. There are many applications, however, in which the mole unit is most convenient even though no chemical change takes place. Of course, if chemical change occurs, the mole unit is almost always the most convenient.

The material balance may be applied to a process as an over-all balance of the incoming items with the outgoing items. Also, it may be applied to intermediate parts of a *continuous* process. Each independent balance provides one equation. There must be as many balances as there are unknowns. Frequently intermediate balances will provide additional equations. If a chemical reaction takes place, balances can be set up for each element. If the ratio of two elements or components in each stream entering a process is the same as the ratio in each stream through which they leave the process, only one independent equation can be obtained by a material balance. Nothing is accomplished under such conditions by setting up a material balance on each element or component. It is apparent, therefore, that if no chemical change takes place, it is useless to set up material balances on each element involved.

Occasionally a sufficient number of data will be available so that a larger number of independent material-balance equations will be possible than there are unknowns. In such cases the selection of the balances for calculating the unknowns will depend largely upon the possibilities for error. If all analyses were precise, it should make no difference which of the material-balance equations are selected. This, of course, is never the case because of the limits of error in the analytical methods. In particular, the value of an unknown should never be calculated by the difference of two numbers of the same general magnitude. For example, $A + B = C$. The values of B and C have been determined to be 10,000 ± 100 and 10,500 ± 100, respectively. Note that both values are known within a probable error of

±1.0 per cent. If the value of A were calculated by taking the difference between C and B, a value of 500 ± 200 would be obtained. Thus, the maximum probable error of the value of A by this method would be ±40 per cent, or 40 times as great as the maximum probable error of the figures used in the calculations. It is apparent, therefore, that the selection of material balances for determining unknowns should always exclude those which would involve the evaluation of an unknown by the difference between two numbers of about the same size. Accuracy is usually the highest when an unknown can be evaluated by the sum of two or more figures. If, in the above example, A were known to be 400 ± 4 and B were known to be $10{,}000 \pm 100$, the value of C would be $10{,}400 \pm 104$. Thus, the maximum probable error in C would be ±1.0 per cent, which is the same as for the two factors used in its determination.

Under limited conditions a volumetric balance can be applied to liquids in conjunction with a mass balance. *Nonpolar* mutually soluble liquids in general blend so that the volume of the blend is essentially equal to the sum of the liquid volumes of the components at the same temperature. Hydrocarbons are good examples of this. To illustrate, a petroleum gas oil which has a specific gravity of 0.85 is being separated into a light oil fraction of 0.80 sp. gr. and a heavy oil fraction of 0.93 sp. gr. It is desired to know the yields of the light and heavy oil fractions.

Let L = gal of light oil/100 gal of gas oil
H = gal of heavy oil/100 gal of gas oil

Then, by material balance,

$$\text{Gas oil} = \text{light oil} + \text{heavy oil}$$

or $$(100)(8.33)(0.85) = (L)(8.33)(0.80) + (H)(8.33)(0.93)$$

and $$0.80L + 0.93H = 85.0$$

By liquid volumetric balance,

$$L + H = 100$$

Thus, $$0.80L + 0.93(100 - L) = 85.0$$

$$L = 61.5 \text{ gal or \% (by vol.) on gas oil}$$

$$H = 38.5 \text{ gal or \% (by vol.) on gas oil}$$

The volumetric balance may be applied to polar liquids if information is available on the relationship between volume of the blend and the volumes of its components in the pure state. This involves a trial-and-error type of solution.

Procedure for Material Balance.—In making a material balance there are a number of preliminary steps that are very helpful and desirable. Each of these steps is essential if careless errors are to be avoided.

1. Prepare a simplified flow sheet of the system or process on which the material balance is to be made.
2. Put on the flow sheet all pertinent data to be used in the material balance.
3. Set down all chemical equations for the chemical reactions that occur in the process.
4. Select a convenient basis upon which all the calculations will be predicated.

It is recommended that the beginning student take each of these steps, even in the case of relatively simple systems. Almost invariably the habit of avoiding any of the steps will eventually lead to serious careless errors. After the student has gained considerable experience with material balances, the first step may be avoided in the case of a simple system. Even so, it is difficult to avoid the oversight of some phase of a process that must be considered. A simplified flow sheet of the system that includes all the features pertinent to the material balance will help to keep careless errors to a minimum. It is well to develop the habit of always sketching a simplified flow sheet even for the simple systems.

All the data that will be used in the material balance can be located on the flow sheet so that they are identified with the proper phases of the system. The connection between the data and the various items to be taken into account in the balance can be seen at a glance. Furthermore, in the case of preparations for a material balance on some process in operation this procedure will be helpful in determining what data must be obtained. It is very embarrassing and damaging to prestige to find after a costly test on an operating unit that certain essential data were not obtained.

Also, it is highly desirable to locate on the flow sheet the equations of the chemical reactions that occur in the process if these equations will be used in the material balance. Sometimes the chemical reactions are so complicated that they cannot be written to show the exact changes that occur. In such cases the material balance would not involve the chemical equations. An example of this is the cracking of petroleum oil.

The fourth step is by no means the least important. One of the most common and most inexcusable of errors is the confusion of bases in material-balance calculations. It is very important that all calculations be made on a convenient common basis. This may be a period of time or a unit of weight of one of the items in the process. For example, an aqueous solution contains 10 per cent by weight of calcium chloride. It is concentrated by evaporating some of the water so that after evaporation there is 25 per cent by weight of calcium chloride. How much water was evaporated per 1000 lb of the original solution? The correct answer cannot be arrived at by a direct subtraction of the two percentages, for each percentage is referred to a different basis. By selecting a common basis of 100 lb of calcium chloride the correct answer can be calculated. There was 100/0.10, or 1000, lb of the original calcium chloride solution. When this was concentrated to 25 per cent by weight, there remained 100/0.25, or 400, lb of concentrated solution. The amount of water evaporated was therefore 1000 − 400, or 600, lb. As the study of the material balance progresses, it will become quite apparent why the selection of a common basis of calculation is essential.

MATERIAL BALANCES IN UNIT OPERATIONS

Distillation.—Distillation is the separation of two or more miscible components of a liquid solution by means of vaporization and condensation. Almost always the components are volatile, although distilled water is separated from nonvolatile minerals. In all cases, however, part of the condensed vapor that is separated from the liquid is returned to the distillation process. Distillation is feasible for the separation of miscible liquid (solution) components only if the composition of the liquid phases to be separated into components is different from the composition of the vapor phase in equilibrium with it. Obviously, if the vapor phase were identical, no change in composition could be obtained by separating it from the liquid phase with subsequent condensation. If there is a difference in compositions as shown in Fig. 5.1, it is apparent that by separating the vapor phase from the liquid with subsequent condensation the liquid would be enriched in the higher boiling component A and the condensate would contain a higher concentration of the more volatile component B than the original liquid mixture. For example, a liquid that contains 0.70 mole fraction A and 0.30 mole fraction B is in equilibrium with vapor of 0.23 mole fraction A and 0.77 mole fraction B. This can be seen by tracing the line from N to O to P in Fig. 5.1. If the vapor of composition corresponding to P is separated and condensed, the condensate will be in equilibrium with vapor of composition at R, or 0.03 mole fraction A and 0.97 mole fraction B. If this vapor is separated and condensed, it will be in equilibrium with vapor that is richer in component B and leaner in component A. Theoretically, an entirely pure product can be obtained only by carrying out an infinite number of successive vaporization and subsequent condensation steps. For all practical purposes, however, a pure product can be obtained with a finite number of such steps. The impurities can be reduced to such a low concentration that they cannot readily be detected. It is apparent that pure A can be produced by vaporizing all but a minute amount of the original liquid. The vapor will be in equilibrium with liquid of 0.95 mole fraction *A* and 0.05 mole fraction *B*. By following a number of steps such as from *O* to *K* to *L*, and so on, a pure product can be obtained.

Obviously, the procedure as outlined would not be a practical process, for only an infinitesimal amount of product could be obtained. In practice, however, the mechanism is carried out in distillation columns, or fractionating columns as they are frequently called. These usually consist of cylinders which contain several plates or trays for contacting the liquid and vapor so that equilibrium between the two can be reached almost instantly. Figure 5.2 presents a diagrammatic sketch of a continuous fractionating column. In this specific case there are five trays. Those above tray 3 (feed tray) are called rectifying trays, and those below the feed tray are called stripping trays. The trays are arranged so that vapor can go through them but no liquid can pass through the holes through which the vapor passes. The liquid flows over the tray and passes over a weir into a downspout. The weir assures that there will be liquid on the tray at all times. The liquid passes down the downspout onto the tray below, where it flows across in contact with rising vapor and passes over a weir into another downspout, and so on. This is the method of contacting the liquid and vapor phases.

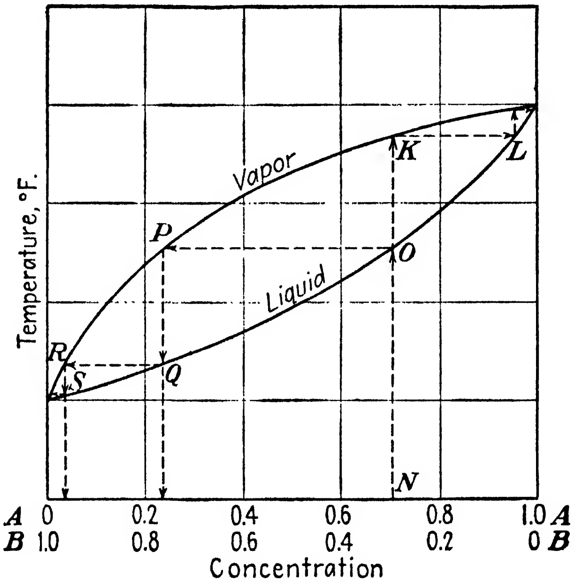


FIG. 5.1.

The feed is admitted to the column on the feed tray. Here it comes in contact with vapor from the tray below. The vapor condenses when it contacts the colder liquid, but in doing so it gives up its latent heat of vaporization so that a corresponding amount of vapor, richer in the lower boiling component than the feed, is produced. This then results in a depletion of the lower boiling component in the feed, and thus the remaining liquid contains less of the lower boiling component than the feed. The remaining liquid on the feed tray passes over the weir into the downspout and onto tray 4 below. Here the liquid comes in contact with hotter vapor from tray 5. The vapor condenses, and a corresponding amount of vapor is produced, which contains more of the lower boiling component than the liquid from the feed tray. Thus, the remaining liquid on tray 4 contains

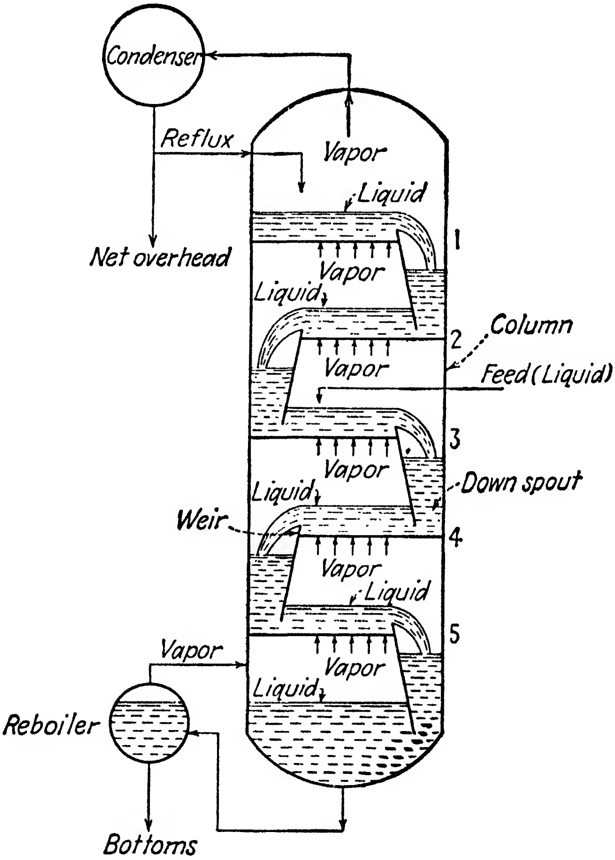


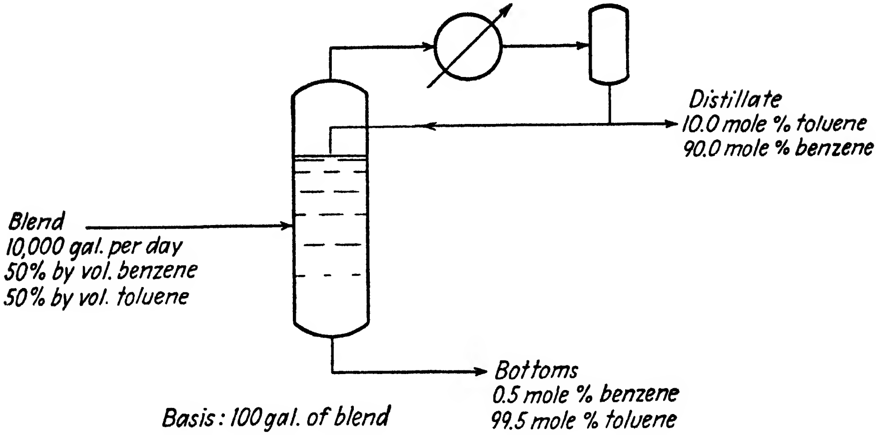
FIG. 5.2.

less of the lower boiling component and more of the higher boiling component than the liquid from tray 3. The liquid from tray 4 passes down to tray 5, where it comes in contact with vapor from the reboiler, or kettle as it is sometimes called. The vapor condenses and thus vaporizes a lower boiling vapor, which further depletes the liquid of the lower boiling component and enriches it in the higher boiling component. The liquid from tray 5 goes to the reboiler, where part of it is vaporized. The remaining liquid is removed as bottoms product, whereas the vapor from the reboiler passes to tray 5. It is apparent that the bottoms are leaner in the low-boiling component and richer in the higher boiling component than the liquid from tray 5. It should be noted that the vapor leaving the reboiler is condensed on tray 5, whence it returns to the reboiler and is again vaporized. Thus, it is seen that *the vapor from each tray is merely recycled from the tray below to the tray above, where it condenses and is returned to the tray below.* This is merely a means of transferring heat from one tray to the tray above, as will be learned in Chap. VI.

In considering the rectification section, the student will be able to see on the basis of the above discussion of the stripping section what takes place. The vapor rising from the feed tray enters tray 2, where it contacts the liquid from tray 1. Here it condenses and thus vaporizes material that is richer in the lower boiling component. The vapor from tray 2 enters tray 1, where it comes into intimate contact with some of the overhead product (reflux) that is returned from the condenser. The vapor from tray 1 is richer in the lower boiling component than the vapor from tray 2. The vapor from tray 1 leaves the column and is condensed. Part is returned as reflux, and the remainder is eliminated from the system as overhead product, or net overhead as it is usually called.

This is the function of a fractionating, or distilling, column. The more nearly pure the products must be, the larger the number of trays required. This is apparent from Fig. 5.1. The material balance is a very useful tool in the calculation of the number of trays needed, as will be learned when the student studies unit operations. There are many other applications of the material balance in the design and operation of fractionating columns. Example 12 illustrates one type of balance encountered.

Example 12. A blend of 50 per cent toluene liquid volume and 50 per cent benzene liquid volume is being separated by fractionation into an overhead product that has 10.0 mole per cent toluene and a bottoms product that has 0.5 mole per cent benzene. The blend is fractionated at the rate of 10,000 gal/day. How many gallons of each product is produced?



Solution: From Table A.9 it is found that the densities of benzene and toluene are 7.346 and 7.259 lb/gal, respectively. Since these are hydrocarbons, a liquid volumetric balance can be employed.

	Gal	Lb/gal	Lb	Mol. wt.	Moles
Benzene	50	7.346	367.3	78	4.71
Toluene	50	7.259	362.9	92	3.95
	100		730.2		8.66

Let D = moles of distillate
B = moles of bottoms

By component material balance:

$$\text{Benzene} = 4.71 = 0.900D + 0.005B$$

$$\text{Toluene} = 3.95 = 0.995B + 0.10D$$

Solving the simultaneous equations for B and D,

$$B = 3.447$$

$$D = 8.66 - 3.447 = 5.213$$

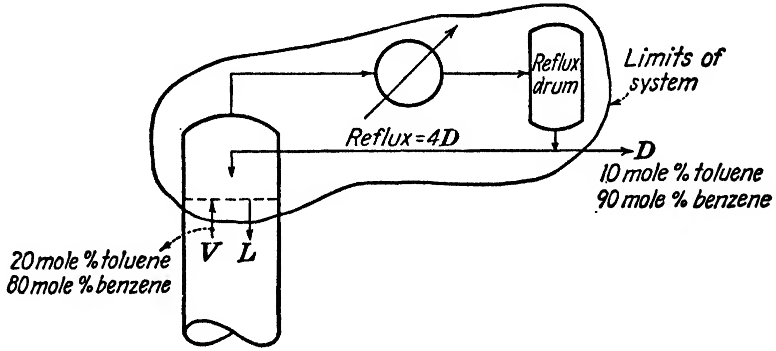
Distillate:

	Moles	Gal
Benzene	4.692	49.8
Toluene	0.521	6.6
Total	5.213	56.4

$$\text{Bottoms} = 100 - 56.4 = 43.6 \text{ gal}$$

Another application of the material balance in distillation is the calculation of liquid and vapor flow rates and compositions at intermediate points in a fractionating column.

Example 13. A test was made on the fractionating column of Example 12. The ratio of reflux to distillate on a mole basis was 4.0/1.0. A sample of vapor from one of the trays above the feed tray was taken and found to contain 20 per cent toluene. What was the composition of the liquid from the tray above the point at which the sample of vapor was taken? It may be assumed that the flow rate of liquid in the column on a mole basis is equal to the reflux rate.



Solution:

Basis: 100 moles of distillate.

$$V = L + D = L + 100$$

$$L = 4D = 400$$

$$V = 500$$

By benzene balance,

Let x_b = mole fraction of benzene in L
x_t = mole fraction of toluene in L

Then
$$0.80V = x_lL + (0.90)(100)$$

$$x_b = \frac{0.80V - 90}{L} = \frac{(0.80)(500) - 90}{400}$$

$$= 0.775$$

Since
$$x_b + x_t = 1.000$$

$$x_t = 0.225$$

Fractionation in commercial units is generally of the continuous type. Even so, *batch* fractionation is frequently used, particularly in laboratory-size installations. This type of fractionator (Fig. 5.3) consists of a kettle, or reboiler, to which the batch is charged. The fractionating column is located above the kettle. Contact between rising vapor and descending liquid in the column is usually effected by different types of packing. In some cases, however, small trays are used. Batch distillation is carried out by transferring heat to the kettle, where the charge is gradually vaporized. Reflux is admitted to the top of the column. This provides the desired enrichment of the rising vapors in much the same way as in continuous columns. As the distillation proceeds, the temperature of the material in the kettle increases owing to the gradual removal of the less volatile component or components. Separations are obtained by collecting the distillate in different vessels. Each vessel will represent product collected between definite limits of temperature at the top of the column. This corresponds to product of specific purity.

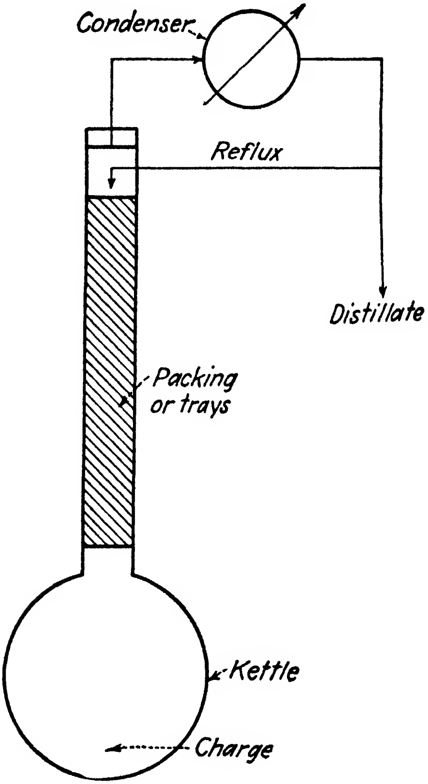


FIG. 5.3.

Example 14. A binary mixture of miscible liquids is being vaporized in the kettle of a batch distillation column. No liquid is allowed to run back from the column into the kettle. Determine a general mathematical expression that relates the change in composition of the liquid in the kettle to the amount vaporized.

Solution: Using Fig. 5.3 as a guide,

Let L = moles of liquid charged
x = mole fraction of one component in the charge

Then xL = moles of the component charged

Vaporize an infinitesimal amount of the charge, $-dL$.

Let y = mole fraction of the given component in $-dL$

Thus $-y\,dL$ = moles of the component vaporized

The depletion of the component in the kettle is $-d(Lx)$ or $-L\,dx - x\,dL$. By material balance,

$$-L\,dx - x\,dL = -y\,dL$$

or

$$\frac{dL}{L} = \frac{dx}{y - x}$$

This equation was first presented by Lord Rayleigh.[1] It may be integrated between the limits of L_1 and L_2 and x_1 and x_2 to give the following equation:

$$\ln \frac{L_2}{L_1} = \int_{x_1}^{x_2} \frac{dx}{y - x}$$

This equation may be used to calculate the change in composition of the liquid in the kettle with the amount vaporized if the equilibrium relationship between x and y is known. Such relationships are usually given graphically, and thus the solution is one of graphical integration in most cases.

Drying.—One of the unit operations that is frequently encountered in chemical engineering is drying. This usually involves the removal of water from solid material by vaporization when the water content is small. Sometimes, however, it involves the removal of low concentrations of water from gases or liquids.

In the application of the material balance to problems in drying the chief difficulties lie in maintaining a common basis of calculations.

Example 15. Slabs of building boards contain 17.0 per cent moisture by weight. They are dried to a water content of 1.0 per cent by weight by circulating hot air over them. The fresh air contains 0.017 lb of moisture per pound. The exhaust air contains

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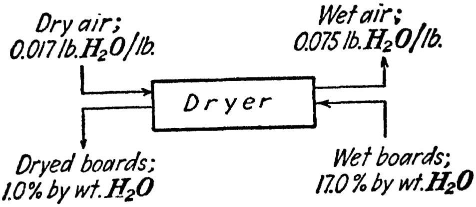
[1] RAYLEIGH, LORD, *Phil. Mag.*, **8**, 534 (1904).

0.075 lb of moisture per pound. How many cubic feet of fresh air at standard conditions must be used per ton of the wet building boards?



Solution:

Basis: 100 lb of water-free boards

$$H_2O \text{ in wet boards} = x$$

$$\frac{x}{100 + x} = 0.17$$

$$x = \frac{17}{0.83} = 20.5 \text{ lb}$$

$$H_2O \text{ in dried boards} = y$$

$$\frac{y}{100 + y} = 0.01$$

$$y = \frac{1}{0.99} = 1.0 \text{ lb}$$

$$H_2O \text{ evaporated} = 20.5 - 1.0 = 19.5 \text{ lb}$$

$$\text{Moisture in wet air} = \frac{0.075}{0.925} = 0.0810 \text{ lb/lb of } H_2O\text{-free air}$$

$$\text{Moisture in dry air} = \frac{0.017}{0.983} = 0.0173 \text{ lb/lb of } H_2O\text{-free air}$$

$$H_2O\text{-free air/100 lb of } H_2O\text{-free boards} = \frac{19.5}{0.0810 - 0.0173} = 306 \text{ lb}$$

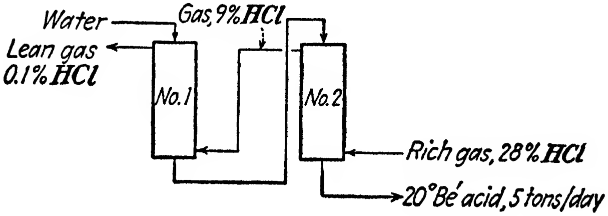
$$\text{Fresh air required} = \frac{(306/0.983)(2000)}{(100/0.83)} = 5170 \text{ lb/ton of wet boards}$$

	Lb	Mol. wt.	Moles
Water-free air	5082	29	175
Water in fresh air	88	18	4.9
Fresh air	5170		179.9

$$V = \frac{nRT}{P} = \frac{(179.9)(10.7)(520)}{14.7} = 68{,}000 \text{ cu ft}$$

Absorption.—The separation of components of a gaseous mixture by contacting the mixture with a liquid solvent that selectively dissolves one or more of the components is called absorption. This is one of the more important unit operations. It is perhaps the most frequently used means of recovering specific components from a gaseous mixture.

Example 16. Hydrochloric acid is produced by absorbing HCl in water. Absorption is carried out by countercurrent (flow in opposite directions) contact of the gas and liquid in two packed columns. Fresh water enters at the top of column 1. The dilute solution from the bottom of column 1 is pumped to the top of column 2. A 20°Bé solution of HCl is eliminated from the bottom of this column. The rich gas contains 28 per cent by volume HCl (H_2O-free basis), and the remainder is inert. The rich gas enters at the bottom of column 2, passes out the top, and enters column 1 at the bottom. The lean gas leaves column 1 at the top. The HCl content (H_2O-free basis) of the lean gas is 0.1 per cent by volume. The HCl content of the gas from column 2 is 9.0 per cent by volume (H_2O-free basis). How much water must be used to produce 5 tons of 20°Bé acid per day? What percentage of the absorbed HCl is absorbed in each column? What is the volume rate of flow of rich gas at standard conditions?



Solution:

Basis: 100 moles of inert gas; 1 day.

$$\text{HCl in rich gas} = (100)(28/72) = 38.9 \text{ moles}$$

$$\text{HCl in gas from column 2} = (100)(9/91) = 9.9 \text{ moles}$$

$$\text{HCl in lean gas} = (100)\left(\frac{0.1}{99.9}\right) = 0.1 \text{ mole}$$

$$\text{Total HCl absorbed} = 38.9 - 0.1 = 38.8 \text{ moles}$$

$$\text{HCl absorbed in column 2} = 38.9 - 9.9 = 29.0 \text{ moles}$$

$$\%\ \text{HCl absorbed in column 2} = \frac{(29.0)(100)}{38.8} = 74.8\%$$

$$\%\ \text{HCl absorbed in column 1} = 25.2\%$$

Conc. of HCl in 20°Bé acid = 31.45% by wt. (Table A.1)

$$\text{HCl absorbed} = (5.0)(2000)(0.3145) = 3145 \text{ lb/day}$$

$$= \frac{3145}{36.5} = 86.2 \text{ moles/day}$$

$$\text{Water required} = \frac{(5)(2000)(0.6855)}{(8.33)(24)} = 34.3 \text{ gal/hr}$$

$$\text{Rich gas} = \left(\frac{86.2}{38.8}\right)(100 + 38.9) = 308.5 \text{ moles/day}$$

$$V = \frac{nRT}{P} = \frac{(308.5)(10.7)(520)}{14.7} = 117{,}000 \text{ cu ft/day}$$

MASS BALANCES IN CHEMICAL PROCESSES

Combustion.—The combustion of fuel is the chief source of heat energy in the process industries. Combustion is defined as the chemical reaction of oxygen with materials, accompanied by the emission of light and rapid generation of heat. If the reaction of oxygen with materials takes place without the emission of light, the process is termed oxidation. Usually oxidation is a slower process, and heat is not generated rapidly.

Materials may be divided into combustible and noncombustible types. If they burn freely in air, they are called combustibles. Fuel is a combustible that is employed for the generation of heat energy by combustion because it is sufficiently inexpensive to be used merely for this purpose. Solid, liquid, and gaseous fuels are used. The solid fuels consist chiefly of coal, although lignite, peat, and wood are used to some extent. Liquid fuels are essentially always obtained from petroleum, whereas gaseous fuels may be a by-product of petroleum refining, natural gas, or gas manufactured from coal.

In the study of any combustion process much information can be obtained by means of the material balance, though its application to combustion problems usually requires a knowledge of the analyses of the fuel and of the products of combustion. Such analyses will now be discussed.

There are two types of analysis used for coals, *viz.*, *ultimate* and *proximate*. Coals are classified on the basis of these analyses. The ultimate analysis may be reported on a moisture-free or "as fired" basis. It is the most detailed and costly analysis to make. The percentages of carbon, hydrogen, nitrogen, sulfur, and ash are determined. Oxygen is obtained by difference after these five components are determined. It may be assumed in all calculations that the oxygen is present as combined water even though it is actually present in very complex organic chemical compounds. The details of the method of ultimate analysis will not be considered in this text. The reader is referred to Parr [1] in case such information is desired.

The proximate analysis of coal provides the percentage moisture, volatile

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[1] PARR, S. W., "The Analysis of Fuel, Gas, Water and Lubricants," 3d ed., McGraw-Hill Book Company, Inc., New York, 1922.

TABLE 2.—TYPICAL ANALYSES OF SOLID FUELS AS RECEIVED

	Proximate analyses, wt. %			Ultimate analyses, wt. %						Heating value, Btu/lb.
	Moisture	Volatile combustible	Fixed carbon	Ash	Sulfur	Hydrogen	Total carbon	Nitrogen	Oxygen	
Wood	.....	.....	.....	.....	....	6.25	49.50	1.10	43.15	5,800
Peat	56.70	26.14	11.17	5.99	0.64	8.33	21.03	1.10	62.91	3,586
Lignite	34.55	35.34	22.91	7.20	1.10	6.60	42.40	0.57	42.13	7,090
Subbituminous	24.28	27.63	44.84	3.25	0.36	6.14	55.28	1.07	33.90	9,376
Bituminous	3.24	27.13	62.52	7.11	0.95	5.24	78.00	1.28	7.47	13,919
Semibituminous	2.03	14.47	75.31	8.19	2.26	4.14	79.97	1.26	4.18	14,081
Semianthracite	3.38	8.47	76.65	11.50	0.63	3.58	78.43	1.00	4.86	13,156
Anthracite	2.80	1.16	88.21	7.83	0.89	1.89	84.36	0.63	4.40	13,298

combustible matter, fixed carbon, and ash; fixed carbon obtains by difference. The volatile combustible matter consists of hydrocarbons, and thus the fixed carbon does not represent the total carbon in the coal. This is perhaps the most frequently used analysis in combustion calculations, although a knowledge of the "total carbon" is usually required also. The method of analysis is described in detail by Parr.[1] Typical analyses of different types of solid fuel are given in Table 2.[2] The various coals are classified on the basis of proximate analyses according to the *U.S. Geological Survey Professional Paper* 100-A.

The products of combustion are analyzed by an Orsat, which is also fully described by Parr.[1] The analysis is carried out over concentrated salt water; thus at all times the gas contains water vapor in accordance with the partial pressure of the salt-water solution. Essentially the analytical procedure is to take a sample of 100 cu cm of gas over salt water at atmospheric pressure. Then, the CO_2 is removed by scrubbing the gas with NaOH solution. The remaining gas is then measured over salt water at atmospheric pressure. The loss in volume is the volume of CO_2 plus the water vapor it contained. After this, the gas is scrubbed with a liquid to remove oxygen. Pyrogallate is sometimes used for this, although better materials are available. The gas volume is again measured at atmospheric pressure over salt water after removal of oxygen. The second loss in volume is owing to the removal of the oxygen plus the water vapor it contained. Finally, the gas is scrubbed with cuprous chloride to remove CO, and the gas is again measured over salt water at atmospheric pressure. The loss in volume is the CO content plus the water vapor it contained. The balance of the gas is the nitrogen content plus the water vapor it contains. Since all measurements are made over the same salt water at constant temperature, the percentage of water vapor in the gas during each measurement is identical. *Thus, the Orsat analysis is automatically on a "water-free" basis.*

It is apparent from the above description that any SO_2 in flue gas will be absorbed with the CO_2. About 150 to 250 cu ft of dry flue gas (N_2, O_2, CO_2, CO, and SO_2) will be produced from 1 lb of fuel (solid, liquid, and gas). For each per cent by weight sulfur in the fuel only $(378)(0.01)/32 = 0.118$ cu ft of SO_2 will be produced. This corresponds to only about 0.08 per cent of the minimum amount of dry flue gas required for combustion of 1 lb of fuel. Inasmuch as the accuracy of the Orsat analysis is ±0.2 per cent, it is apparent that it is not necessary to consider the sulfur

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[1] Parr, S. W., "The Analysis of Fuel, Gas, Water and Lubricants," 3d ed., McGraw-Hill Book Company, Inc., New York, 1922.

[2] Haslam, R. T., and R. P. Russell, "Fuels and Their Combustion," p. 53, McGraw-Hill Book Company, Inc., New York, 1925.

in combustion calculations until its concentration in the fuel exceeds 2.5 per cent by weight.

Since liquid fuels are almost always derived from petroleum, they consist entirely of hydrogen, carbon, and sulfur. The latter item can be ignored if it is less than 2.5 per cent by weight, which is usually the case. The weight ratio of hydrogen to carbon and heating value can be estimated quite accurately from Table A.6.

In the case of gaseous fuels both natural gas and by-product gas from petroleum refining consist primarily of hydrocarbons. Natural gas is usually not less than 90 per cent methane, whereas the by-product gas from petroleum refining may be less than 50 per cent methane. The hydrogen to carbon weight ratio and heating values of hydrocarbon gases may be estimated quite accurately from Table A.7. Occasionally hydrocarbon gas will contain a high concentration of sulfur as H_2S, but in general the sulfur content may be ignored in combustion calculations. Of course, in the handling of hydrocarbon gas some air contamination may occur. An Orsat analysis will show this, as well as the extent of contamination.

Table 3 presents average analyses for the four most common gases manufactured from coal. In the case of carbureted water gas, petroleum gas oil is decomposed (cracked) in the manufacturing process to increase the heating value of the water gas otherwise produced.

TABLE 3.—ANALYSES OF MANUFACTURED GASES *

	% by volume			
	Coke-oven gas	Producer gas	Water gas	Carbureted gas
Carbon monoxide	6.3	27.0	42.8	33.4
Carbon dioxide	1.8	4.5	3.0	3.9
Hydrogen	53.0	14.0	49.9	34.6
Nitrogen	3.4	50.9	3.3	7.9
Oxygen	0.2	0.6	0.5	0.9
Methane	31.6	3.0	0.5	10.4
Ethylene	2.7	.....	.....	6.7
Benzene	1.0	.....	.....	2.2
Total	100.0	100.0	100.0	100.0
Net heating value, Btu/cu ft	521	140	281	496

* PERRY, J. H., "Chemical Engineers' Handbook," p. 363, 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

Combustion of fuel is seldom carried out with merely the theoretical amount of air. *Excess air* is used to ensure complete and economical combustion. Excess air is always quoted as a percentage on the theoretical amount of air required for complete combustion. For example, 25 per cent excess air signifies that, of the air used, only 80 per cent of the oxygen was required to combine with the fuel to produce CO_2, H_2O, or SO_2.

Example 17. Flue gas from a combustion chamber of a furnace was analyzed and found to contain 15.0 per cent CO_2, 2.0 per cent CO, and 1.5 per cent O_2. What was the amount of excess air used?

Solution: The amount of excess air in combustion problems is calculated by making material balances on the carbon, oxygen, nitrogen, and hydrogen. These are made most conveniently by tabular or column calculations.

Basis: 100 moles of H_2O-free flue gas.

	%	Moles	
		C	O_2
CO_2	15.0	15.0	15.0
CO	2.0	2.0	1.0
O_2	1.5	—	1.5
N_2	81.5	—	—
Total	100.0	17.0	17.5

Thus, it is seen that for every 100 moles of dry flue gas 17.0 moles (or atoms) of carbon and 17.5 moles of O_2 are accounted for by the analysis. Since air contains 21 per cent oxygen and 79 per cent "nitrogen," the total air used was 81.5/0.79 = 103.2 moles. The amount of oxygen in the air was (103.2)(0.21), or 21.7 moles. This leaves 21.7 − 17.5, or 4.2, moles of O_2 not accounted for in the analysis. Since the analysis is on a water-free basis, it is apparent that the oxygen which combined with the hydrogen in the fuel did not show up in the analysis. The 4.2 moles of O_2, therefore, combined with hydrogen to form H_2O.

Water formed by combustion was therefore (4.2)(2), or 8.4, moles. In order to convert the CO to CO_2, 1.0 mole of O_2 would be required. Thus, the theoretical O_2 for complete combustion is 17.0 + 4.2, or 21.2, moles to convert the carbon to CO_2 and hydrogen to H_2O.

$$\text{Excess oxygen} = 21.7 - 21.2 = 0.5 \text{ mole}$$

$$\%\text{ excess air} = \frac{(0.5)(100)}{21.2} = 2.36\%$$

Example 18. Coal that has the following proximate analysis is being burned in a grate-fired furnace:

	Wt. %
Moisture	3.0
Volatile combustibles	27.0
Ash	7.0

The total carbon content of the coal is known to be 78.0 per cent by weight. The refuse is removed from the ashpit and wetted down to facilitate handling. A sample of the refuse was analyzed as follows:

	Wt. %
Moisture	30.0
Ash	55.0

The flue-gas analysis was as follows:

	Vol. %
CO_2	14.0
O_2	5.0

What percentage excess air was used? Also, what percentage of the carbon was burned? How much coal is consumed per 100 moles of dry flue gas?

Solution: It may be assumed that all the ash in the coal was collected in the ashpit. This is the component that is common to both the coal and the refuse. All of it enters in a single stream and leaves in a single stream.

By material balance on the ash the loss of carbon in the refuse can be calculated.

Basis: 100 lb of coal as fired.

Ash in coal = 7.0 lb

Ash in refuse = 55.0 wt. %

$$\text{Wt. ratio of fixed carbon}^1 \text{ to ash in refuse} = \frac{15.0}{55.0} = 0.273$$

$$\text{Fixed carbon in refuse} = (0.273)(7.0) = 1.9 \text{ lb}$$

It may be assumed that the carbon content of the refuse is identical with the fixed carbon. Thus,

$$\frac{(1.9)(100)}{78.0} = 2.44\% \text{ of total carbon was unburned}$$

or 97.56% was burned.

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[1] As indicated on p. 122 fixed carbon is obtained by difference between 100.0 and the total of moisture, volatile combustible matter, and ash.

By component balances on flue gas:
Basis: 100 moles of dry flue gas.

	%	Moles	
		C	O_2
CO_2	14.0	14.0	14.0
O_2	5.0	0.0	5.0
N_2	81.0	—	—
Total	100.0	14.0	19.0

$$\text{Total } O_2 \text{ to furnace} = \frac{(81)(21)}{79} = 21.5 \text{ moles}$$

$$O_2 \text{ that combined with hydrogen} = 21.5 - 19.0 = 2.5 \text{ moles}$$

$$\text{Carbon in flue gas} = 14.0 \text{ moles}$$

$$\text{Carbon in refuse} = (14.0)\left(\frac{2.44}{97.56}\right) = 0.35 \text{ mol}$$

$$\text{Coal consumed} = \frac{(14.0 + 0.35)(12)}{0.78} = 221 \text{ lb}$$

$$O_2 \text{ for carbon in refuse} = 0.35 \text{ mole}$$

$$\text{Excess air} = \frac{5.0 - 0.35}{14.0 + 2.5 + 0.35} = 27.6\%$$

Example 19. If the nitrogen content of the coal in Example 18 was 1.5 per cent by weight, what was the extent of the error involved by neglecting it?
Solution:

Basis: 100 moles of dry flue gas.

The amount of coal consumed was calculated to be 221 lb/100 moles of dry flue gas. This calculation was independent of nitrogen content of the coal.

$$N_2 \text{ in coal} = (221)(0.015) = 3.3 \text{ lb}$$

$$= \frac{3.3}{28} = 0.118 \text{ mole}$$

Since the accuracy of the nitrogen determination in the flue-gas analysis was ±0.2 per cent, it is apparent from Example 19 that no measurable error was incurred by neglecting the nitrogen content of the coal.

Example 20. Producer gas of the composition given below is burned in a combustion chamber. The analysis of the flue gas is also given.

	Vol. %	
	Producer	Flue
CO	27.5	—
CO_2	5.0	16.5
H_2	14.0	—
N_2	50.0	80.4
O_2	0.5	3.1
CH_4	3.0	—
Total	100.0	100.0

How many cubic feet of air is required per cubic foot of fuel gas? How many cubic feet of total flue gas is produced per cubic foot of fuel gas?

Solution:

Basis: 100 moles of dry flue gas.

	%	Moles	
		C	O_2
CO_2	16.5	16.5	16.5
O_2	3.1	—	3.1
N_2	80.4	—	—
Total	100.0	16.5	19.6

A nitrogen balance cannot be used directly in this case, for the fuel gas contains an appreciable quantity of N_2. A carbon balance can be made, however, since all the carbon in the flue gas enters with the fuel gas. The ratio of moles of nitrogen to moles of carbon in the fuel gas is

$$\frac{N_2}{C} = \frac{50.0}{27.5 + 5.0 + 3.0} = 1.41$$

Thus, the moles of N_2 in flue gas that entered with the fuel gas = (1.41)(16.5) = 23.3 moles.

$$\text{Air supplied} = \frac{80.4 - 23.3}{0.79} = 72.3 \text{ moles}$$

$$O_2 \text{ in air} = (72.3)(0.21) = 15.2 \text{ moles}$$

Fuel gas consumed based on carbon balance:

$$\text{Moles of fuel gas/mole of carbon} = \frac{100.0}{27.5 + 5.0 + 3.0} = 2.82$$

$$\text{Moles of fuel gas consumed} = (2.82)(16.5) = 46.5$$

$$\text{Air required} = \frac{72.3}{46.5} = 1.56 \text{ cu ft/cu ft of fuel gas}$$

The ratio of moles of oxygen to moles of carbon in the fuel gas is

$$\frac{O_2}{C} = \frac{(27.5/2) + 5.0 + 0.5}{27.5 + 5.0 + 3.0} = 0.542$$

$$\text{Oxygen in flue gas from fuel gas} = (0.542)(16.5) = 8.9 \text{ moles}$$

$$\text{Total oxygen} = 8.9 + 15.2 = 24.1 \text{ moles}$$

$$\text{Oxygen that combined with hydrogen to form } H_2O = 24.1 - 19.6 = 4.5 \text{ moles of } O_2$$

$$H_2O \text{ produced} = (4.5)(2) = 9.0 \text{ moles}$$

$$\text{Total flue gas} = \frac{100.0 + 9.0}{46.5} = 2.35 \text{ cu ft/cu ft of fuel gas}$$

If the analytical work is reliable, it should be possible to arrive at the amount of H_2O produced by a hydrogen balance.

$$\text{Moles of } H_2\text{/mole of fuel gas} = \frac{14.0 + (2)(3.0)}{100} = 0.20$$

$$\text{Moles of } H_2O \text{ produced} = (0.20)(46.5) = 9.3$$

Thus, by hydrogen balance, 9.3 moles of "water formed" was calculated, compared with 9.0 moles by an oxygen balance. This is a reasonable check, for it is within the limits of accuracy of the analytical methods.

Boiler-feed-water Conditioning.—Steam is the primary source of power in the process industries. It is also an important heating medium. Hence, some of the chemical-engineering aspects of steam generation will now be discussed.

Steam is generated by the evaporation of water in boilers. It is produced in many different types of boiler at pressures ranging up to about 1400 lb/sq in. As far as the immediate purpose is concerned, however, a consideration of the different types of boiler is not necessary. The chemical-engineering student will obtain such information in his elective courses in mechanical engineering. The discussion here will be confined to boiler-feed-water conditioning for scale prevention. Even so, it will not be possible to describe in any detail all the various methods of conditioning boiler feed water. It is the purpose here merely to acquaint the student with the use of the material balance in water softening. Only the lime-soda process with internal phosphate treatment will be considered at any length.

Boiler feed waters are usually obtained from wells, rivers, or fresh-water lakes. They therefore contain dissolved solids and oxygen in various concentrations. Also, they sometimes contain suspended solids. The purpose of boiler-feed-water conditioning is to remove those materials from the water which are undesirable from the standpoint of boiler performance. Some of the ingredients cause boiler scale, which is a solid deposit on the heating surface of the boiler. Others cause embrittlement or corrosion of the boiler metal. It is important that the undesirable materials be removed from the boiler feed water or counteracted so that their bad effects are prevented. For the purposes of this text, however, no consideration will be given to boiler-water treatment for prevention of embrittlement or corrosion.

Suspended solids are removed by sedimentation and filtration. Dissolved solids, on the other hand, must be removed by other means. The most common boiler scales are $CaCO_3$, $CaSO_4$, and calcium silicate ($CaSiO_3$). They are called carbonate, sulfate, and silicate scales, respectively. Scale-forming ingredients are those which decrease in solubility with increasing temperature. Since the highest temperature is on the tube surface through which heat is being transferred, scale will form on this surface. When scale is forming, it will act as a binder for other materials that may be suspended in the boiler water. Thus, scale deposition will take place at a more rapid rate if suspended solids are present.

In water conditioning for prevention of boiler scale the chief objective is to remove the calcium and magnesium ions (Ca^{++} and Mg^{++}). Also, it is desirable to remove the bicarbonate ions (HCO_3^-). The bicarbonate ion is usually removed by treatment with lime, whereas Ca^{++} is removed by treatment with soda ash. The excess lime used is ordinarily about 0.05 mole per 1,000,000 lb of water (with dissolved solids). The chemical reactions are as follows:

$$2(HCO_3)^- + Ca(OH)_2 = CaCO_3 \downarrow + CO_3^{--}$$

$$Ca^{++} + Na_2CO_3 = 2Na^+ + CaCO_3 \downarrow$$

An overtreatment of Na_2CO_3 is ordinarily used so that the excess CO_3^{--} is about 0.3 mole per 1,000,000 lb. Actually, complete removal of Ca^{++} cannot be attained, for the $CaCO_3$ is slightly soluble. After the treatment with Na_2CO_3 the amount of Ca^{++} remaining is about 0.15 mole per 1,000,000 lb, but the Ca^{++} may be reduced to essentially zero by proper treatment with sodium phosphate. This is frequently done by admitting the phosphate [usually metaphosphate ($NaPO_3$)] directly to the boiler for internal treatment. The reaction may be represented for purpose of material balance as follows:

$$2NaPO_3 + 3CaCO_3 = Ca_3(PO_4)_2 \downarrow + Na_2CO_3 + 2CO_2$$

It must be emphasized, however, that even $Ca_3(PO_4)_2$ has a very slight solubility. In order to ensure good treatment it is necessary to overtreat slightly so that there is an excess of PO_4^{---} of about 0.5 mole per 1,000,000 lb. Note that according to the following equation metaphosphate ($NaPO_3$) will reduce alkalinity by the equivalent of 2 moles of NaOH per mole of metaphosphate ($NaPO_3$):

$$NaPO_3 + H_2O = NaH_2PO_4$$

Usually magnesium salts are present in the water along with the calcium salts. They are removed in the lime-soda treatment in accordance with the following reaction:

$$Mg^{++} + Ca(OH)_2 = Mg(OH)_2 \downarrow + Ca^{++}$$

Unlike $CaCO_3$, $MgCO_3$ is quite soluble, but it is almost completely removed by $Ca(OH)_2$ at the time when HCO_3^- is removed. It is undesirable from the standpoint of sludge formation in the boiler and will represent suspended solids if not removed. Of course, as a suspended solid it will aggravate scale formation if scale-forming ingredients are present. The solubility of $Mg(OH)_2$ is about 0.02 mole per 1,000,000 lb.

Although the soluble salts in treated boiler feed water do not form scale, it is apparent that they must be removed from the boiler. The best method for doing this is to draw off continuously a stream of water from the point of highest dissolved solids concentration in the boiler. This is called the continuous blowdown. In addition to this, it is desirable to remove a stream of water from the bottom of the boiler intermittently (once every 8 to 24 hr). The intermittent blowdown will dispose of suspended solids (sludge) that settle to the bottom of the boiler (called the mud drum). The extent of continuous blowdown will depend on how high the solids concentration can be maintained without foaming, or priming, of the boiler. When foaming or priming occurs, solids are rejected from the boiler with the steam. This is detrimental to turbines as well as to other equipment. Thus, the solids concentration within the boiler, which is the same as the solids concentration of the continuous blowdown, should be maintained sufficiently below the foaming or priming point so that difficulties from this cause will not be encountered. This point must be determined by performance tests for each type of boiler for different boiler feed waters. It is common practice to control the solids concentration by controlling the chloride content of the continuous blowdown. If the ratio of total solids to chloride is known by previous analyses, the solids concentration of the blowdown is known by material balance.

Example 21. Water of the following composition will be treated by the lime-soda process:

Constituents	Parts per Million (ppm)
OH^-	—
CO_3^{--}	—
HCO_3^-	172.0
Cl^-	17.7
SO_4^{--}	28.8
SiO_2	15.5
Ca^{++}	45.0
Mg^{++}	12.1
Na^+	15.4
Total dissolved solids	309.5

The total dissolved solids in the continuous blowdown can be maintained at 2500 ppm without priming. Sodium metaphosphate will be used in an internal treatment. Assume that 80 per cent of the excess Na_2CO_3 will hydrolyze into CO_2 and NaOH.

Calculate (*a*) the amount of each chemical required to treat 1,000,000 lb of water, (*b*) the composition of treated water, and (*c*) the percentage blowdown.

Solution:

Basis: 1,000,000 lb of raw water.

Constituents	Ppm	Moles per 1,000,000 lb
OH^-	—	—
CO_3^{--}	—	—
HCO_3^-	172.0	2.82
Cl^-	17.7	0.50
SO_4^{--}	28.8	0.30
SiO_2*	15.5	0.26
Ca^{++}	45.0	1.125
Mg^{++}	12.1	0.50
Na^+	15.4	0.67

* $SiO_2 + H_2O = H_2SiO_3$.

In order to simplify the calculations, they will be based on the following ionic reactions:

(1) $2HCO_3^- + Ca(OH)_2 = CaCO_3\downarrow + H_2O + CO_3^{--}$

(2) $Mg^{++} + Ca(OH)_2 = Mg(OH)_2\downarrow + Ca^{++}$

(3) $Ca^{++} + Na_2CO_3 = 2Na^+ + CaCO_3\downarrow$

(4) $2NaPO_3 + 2H_2O + 3Ca^{++} = Ca_3(PO_4)_2 + 2Na^+ + 4H^+$

a. Chemicals required.

	Moles per 1,000,000 Lb
Lime for	
Bicarbonate = 2.82/2 =	1.41
Magnesium	0.50
Excess lime (see text)	0.05
Total	1.96

Since the molecular weight of lime is 74, the lime required = (1.96)(74) = 145 lb.

	Moles per 1,000,000 Lb
Soda ash for	
Calcium	1.125
Calcium, from Eq. (2)	0.50
Excess lime	0.05
Excess soda ash	0.30
Total	1.975
Equiv. Na_2CO_3, from Eq. (1)	1.41
Net soda ash to be added	0.565

Soda ash required = (0.565)(106) = 59.9 lb
Phosphate. Calculate under part *c*.

b. Composition of treated water. After treating, there would be no HCO_3^-, Ca^{++}, and Mg^{++} if $CaCO_3$ and $Mg(OH)_2$ were absolutely insoluble. However, owing to the slight solubility there will be 0.15 mole of Ca^{++} and 0.02 mole of Mg^{++} per 1,000,000 lb (see text). Also, by addition of Na_2CO_3 there is a gain of (0.565)(2), or 1.13, moles of Na^+ per 1,000,000 lb, and by addition of excess lime there will be (0.05)(2), or 0.1, mole of OH^-. Owing to dissolving the 0.15 mole of $CaCO_3$ the total increase in CO_3^{--} will be 0.3 + 0.15, or 0.45, mole per 1,000,000 lb.

Constituents	Moles	Ppm	Net change, ppm
OH^-	0.10	1.7	+1.7
CO_3^{--}	0.45	27.0	+27.0
HCO_3^-	—	—	−172.0
Cl^-	0.50	17.7	—
SO_4^{--}	0.30	28.8	—
SiO	0.26	15.5	—
Ca^{++}	0.15	6.0	−39.0
Mg^{++}	0.02	0.5	−11.6
Na^+	1.80	41.6	+26.2
Total dissolved solids		141.8	−167.7

c. Blowdown.

Phosphate for Ca^{++} = $(\frac{2}{3})(0.15)$ = 0.10 mole per 1,000,000 lb

Increase in Na^{+} = 0.10 mole = 2.3 ppm

Decrease in Ca^{++} = 0.15 mole = 6.0 ppm

Decomposition of CO_3^{--} = (0.8)(0.45) = 0.36 mole

Decrease due to CO_2 evolved = (0.36)(44) = 15.8 ppm

Net change in dissolved solids = −19.5 ppm

Net dissolved solids = 141.8 − 19.5 = 122.3 ppm

Blowdown contains 2500 ppm dissolved solids, which includes 0.5 mole per 1,000,000 lb or 47.5 ppm as PO_4^{---}. This is equivalent to $\left(\frac{102}{95}\right)(47.5) = 51.0$ ppm of $NaPO_3$.

Total dissolved solids in blowdown excluding $NaPO_3$ = 2500 − 51.0 = 2449 ppm

Let B = lb of blowdown/1,000,000 lb of treated water

$$(B)(2449) = \text{dissolved solids excl. } NaPO_3 = 122.3$$

$$.B = \frac{122.3}{2449} = 0.05$$

Blowdown = 5.00%
Metaphosphate required = (0.10)(102) + (51.0)(0.05) = 12.8 lb

Caustic Soda Manufacture.—A large amount of caustic soda (NaOH) is produced by the action of hydrated lime [$Ca(OH)_2$] on soda ash [Na_2CO_3] in accordance with the following reaction:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$$

The essential steps in the process are given by the flow sheet in Fig. 5.4.

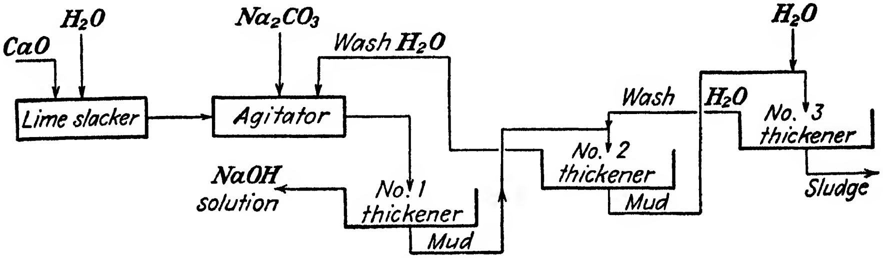

FIG. 5.4.

Only enough water is mixed with the lime in the slacker to produce $Ca(OH)_2$. The soda ash and hydrated lime are agitated with wash water from thickeners. In order to reduce the caustic soda loss in the $CaCO_3$, the mud is washed countercurrently, *i.e.*, the mud and wash water flow through the process in opposite directions. This permits the fresh water to come in contact with the mud of lowest caustic concentration and the caustic solution to contact mud of highest caustic concentration. Such processes are quite common and afford many problems of a chemical-engineering nature.

Example 22. A process for producing caustic soda similar to that shown in Fig. 5.4 eliminates 2500 gal/day of a 15°Bé solution of NaOH. The $CaCO_3$ is pumped as a slurry (mud) that consists of 50 per cent by weight $CaCO_3$. Assume that all the lime and soda ash are consumed in the reaction. What is the loss of NaOH in the slurry from the last thickener?

Solution: From Table A.1, 15°Bé caustic is 10.3 per cent by weight NaOH and is 9.289 lb/gal.

$$\text{NaOH solution} = (2500)(9.289) = 23{,}200 \text{ lb/day}$$

$$\text{NaOH in solution} = (0.103)(23{,}200) = 2390 \text{ lb/day}$$

$$H_2O \text{ in solution} = 20{,}810 \text{ lb/day}$$

$$CaO + H_2O = Ca(OH)_2$$

$$Ca(OH)_2 + Na_2CO_3 = 2NaOH + CaCO_3$$

Thus, 56 lb of CaO plus 18 lb of water plus 106 lb of Na_2CO_3 will produce 80 lb of NaOH plus 100 lb of $CaCO_3$.

Basis: 80 lb of NaOH produced in agitator.

Let x = lb of NaOH/lb of solution from No. 2 thickener
y = lb of NaOH/lb of solution from No. 3 thickener

Over-all balance: The sludge from No. 3 thickener consists of 100 lb of $CaCO_3$ and 100 lb of solution.

$$\text{Caustic in sludge from No. 3} = 100y$$

$$\text{Caustic in solution from No. 1} = 80 - 100y$$

$$\text{Water in solution from No. 1} = \left(\frac{0.897}{0.103}\right)(80 - 100y) = 695 - 870y$$

$$\text{Water in sludge from No. 3} = 100 - 100y$$

$$\text{Fresh water to No. 3} = H_2O \text{ in solution from No. 1} + \text{water in sludge from No. 3}$$
$$= 695 - 870y + 100 - 100y = 795 - 970y$$

Balance on No. 3:

$$\text{Caustic in sludge leaving} = 100y$$

$$\text{Caustic in slurry entering} = 100x$$

$$\text{Caustic in wash water leaving} = 100x - 100y$$

$$\text{Water in sludge leaving} = 100(1 - y)$$

$$\text{Water in slurry entering} = 100(1 - x)$$

$$\text{Water in wash water leaving} = 795 - 970y + 100(1 - x - 1 + y)$$
$$= 795 - 870y - 100x$$

$$\text{Total wash water including caustic} = (795 - 870y - 100x) + (100x - 100y)$$
$$= 795 - 970y$$

Thus, the weight of wash water including caustic is identical with the weight of fresh water. This is apparent by inspection since the weights of the slurry to and from the thickener are the same by definition.

The concentration of caustic in the wash water leaving is therefore

$$\frac{100x - 100y}{795 - 970y} = y$$

or

$$x = \frac{y(895 - 970y)}{100}$$

Caustic balance on No. 2:

$$\begin{aligned}
\text{Caustic in slurry leaving} &= 100x \\
\text{Caustic in slurry entering No. 2} &= 10.3 \\
\text{Caustic in wash water from No. 3} &= 100x - 100y \\
\text{Caustic in wash water leaving} &= 10.3 + 100x - 100y - 100x \\
&= 10.3 - 100y
\end{aligned}$$

The weight of wash water leaving is the same as that entering, or $795 - 970y$. Thus,

$$\frac{10.3 - 100y}{795 - 970y} = x$$

Solving the two simultaneous equations,

$$x = \frac{y(895 - 970y)}{100} = \frac{10.3 - 100y}{795 - 970y}$$

$$\begin{aligned}
9400y^3 - 16{,}390y^2 + 7120y &= 10.3 \\
y &= 0.00143 \\
x &= 0.0128
\end{aligned}$$

The loss of caustic in the slurry from the last thickener = $(0.00143)(100) = 0.143$ lb, or $[2390/(80 - 0.143)](0.143) = 4.3$ lb/day.

Most of the caustic soda (NaOH) is produced by the electrolysis of NaCl. The brine charged to the electrolytic cells is usually very nearly saturated with NaCl. About 30 to 50 per cent of the NaCl is converted into NaOH. Chlorine is liberated at the anode, and an almost equivalent amount of hydrogen is liberated at the cathode. There are a few secondary reactions at the anode all of which result in the liberation of oxygen. These result in the hydrogen elimination at the cathode not being exactly equivalent to the chlorine liberation at the anode. The NaOH solution is withdrawn from the cathode compartment of the cell. The cathode and anode compartments are separated by a porous diaphragm. The details of the process are described by Badger and Baker.[1]

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[1] BADGER, W. L., and E. M. BAKER, "Inorganic Chemical Technology," 1st ed., p. 165, McGraw-Hill Book Company, Inc., New York, 1928.

Example 23. An electrolytic cell is charged continuously with a 22 per cent by weight solution of NaCl. The products leave the cell at 125°F. Assuming no secondary reactions, calculate the concentration of the NaOH in the solution removed from the cathode compartment if 40 per cent of the NaCl is decomposed. The water vapor in the gaseous products corresponds to 90 per cent of saturation.

Solution:

Basis: 1 mole of NaCl charged.

The reaction that occurs is

$$0.4H_2O + 0.4NaCl = 0.4NaOH + 0.2H_2 + 0.2Cl_2$$

NaCl in solution = 58.5 lb

H_2O in solution = $(58.5)(^{78}\!/_{22}) = 207.5$

Solution = 266.0 lb

Vapor pressure of H_2O at 125°F = 1.94 lb/sq in. abs (Table A.14)

Vapor pressure of H_2O in gas = (0.90)(1.94) = 1.74 lb/sq in.

$$\text{Concentration of } H_2O \text{ in gas} = \frac{(1.74)(100)}{14.7} = 11.8 \text{ mole } \%$$

$Cl_2 + H_2$ liberated = 0.4 mole

$$H_2O \text{ in gas} = \left(\frac{11.8}{88.2}\right)(0.4) = 0.054 \text{ mole}$$

$$= (0.054)(18) = 0.97 \text{ lb}$$

H_2O consumed in chemical reaction = 0.4 mole or 7.2 lb

Total water disappearance = 7.2 + 0.97 = 8.17 lb

	Charge		Product solution		Gas product, lb
	Lb	Wt. %	Lb	Wt. %	
NaCl	58.5	22.0	35.10	14.0	—
H_2O	207.5	78.0	199.33	79.6	0.97
NaOH	—	—	16.00	6.4	—
Cl_2	—	—	—	—	14.20
H_2	—	—	—	—	0.40
Total	266.0	100.0	250.43	100.0	15.57

The sum of the weights of the total products is identical with the charge, which is a check on the accuracy of the calculations. The concentration of NaOH in the product solution is 6.4 per cent by weight.

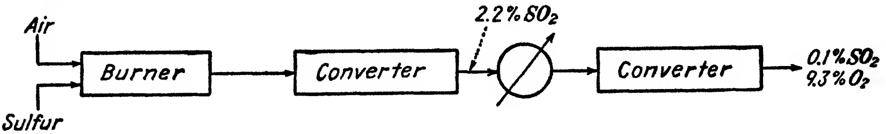
Sulfuric Acid Manufacturing.—Two processes are used generally for the manufacture of sulfuric acid from sulfur dioxide, the chamber process and the contact process. These are described in considerable detail by Badger and Baker [1] and by Shreve.[2] In the chamber process SO_2 is converted to SO_3 in a lead-lined chamber. This is accomplished in the presence of oxygen and oxides of nitrogen. The oxygen is consumed, but the oxides of nitrogen act as a catalyst and are not consumed in the chemical reaction. The recovery of the oxides of nitrogen, however, is not complete, and thus there is a net consumption. In the contact process SO_2 is reacted directly with O_2 to form SO_3 by means of a catalyst.

Most of the SO_2 supplied to the chamber and contact processes is produced by burning sulfur with air. Nevertheless, some is produced in the chamber process by burning iron pyrites (FeS_2). When sulfur is the raw material, no appreciable amount of SO_2 is oxidized to SO_3 in the sulfur burner. In the case of iron pyrites, however, the Fe_2O_3 formed in the burner acts as a weak catalyst, and as much as 2 to 10 per cent of the SO_2 is oxidized in the burner to SO_3.

In the analysis of the products of combustion from a sulfur burner the results are automatically obtained on a moisture-free basis as in the case of combustion products from fuels. Also, any SO_3 in the gas reacts at once with H_2O when it is collected in the measuring burette of the analytical apparatus and condenses as H_2SO_4. Thus, the SO_3 does not appear in the analysis.

Example 24. A contact sulfuric acid plant burns essentially pure sulfur with air. The products of combustion pass to a converter, where some of the SO_2 is converted to SO_3 at a high rate owing to the high temperature of the gas. The gas is then cooled and sent to a final converter, where the oxidation can be carried further at the lower temperature that is more favorable from the standpoint of greater conversion of SO_2 to SO_3. The gas from the first converter was found to contain 2.2 per cent SO_2. The gas from the final converter contained 0.1 per cent SO_2 and 9.3 per cent O_2. What percentage of the total SO_2 was converted to SO_3 in the first and second converters? What was the excess air used to burn the sulfur?

Solution:



Basis: 100 moles of SO_3-free gas from second converter.

$$(1)\quad S + 1.5O_2 = SO_3$$

$$(2)\quad S + O_2 = SO_2$$

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[1] *Ibid.*

[2] Shreve, R. N., "The Chemical Process Industries," McGraw-Hill Book Company, Inc., New York, 1945.

Gas from second converter:

	%	Moles	
		S	O_2
SO_2	0.1	0.1	0.1
O_2	9.3	—	9.3
N_2	90.6	—	—
Total	100.0	0.1	9.4

O_2 in air to sulfur burner $= (90.6)(^{21}/_{79}) = 24.1$ moles

O_2 converted to $SO_3 = 24.1 - 9.4 = 14.7$ moles

SO_2 converted to SO_3 in both converters $= (14.7)(\frac{2}{3}) = 9.8$ moles

Total SO_2 produced $= 9.8 + 0.1 = 9.9$ moles

Overall conversion of $SO_2 = 98.99\%$

Since the moles of nitrogen remained unchanged at 90.6 and ½ mole of O_2 was consumed per mole of SO_2 converted to SO_3 in the second converter, the oxygen and nitrogen contents of the gas from the first converter may be calculated.

Let D = moles of SO_2 consumed in 2nd converter

Then $0.5D$ = moles of O_2 consumed

Total moles of gas to 2nd converter $= 100 + 1.5D$

Also,

$$\frac{D + 0.1}{100 + 1.5D} = 0.022$$

$$D = 2.17 \text{ moles}$$

$$\text{Conversion of } SO_2 \text{ in 2nd converter} = \frac{(2.17)(100)}{9.9} = 21.9\%$$

Conversion of SO_2 in 1st converter $= 98.99 - 21.9 = 77.09\%$

Moles of O_2 to convert SO_2 from 2nd converter to $SO_3 = (0.5)(0.1) = 0.05$

$$\% \text{ excess air} = \frac{(9.3 - 0.05)(100)}{24.1 - (9.3 - 0.05)} = 62.3$$

Thermal Cracking of Petroleum.—Applications of the material balance have been given for a few of the inorganic chemical processes. Other inorganic chemical processes will be covered in later chapters, in which the mass balance will be applied in connection with other chemical-engineering fundamentals. The applications of the material balance in organic chemical processes are as numerous as in the inorganic chemical processes, but the reactions are not usually so clean-cut. For this reason it is more advantageous to consider the applications of the material balance to organic chemical processes in connection with the energy balance and equilibrium balance. This is done in the following chapters. However, one organic chemical process will be discussed before concluding this chapter.

Petroleum refining, since about 1930, has progressed continuously in the direction of isolated chemical reactions. Nevertheless, many of the more important refining processes deal with a multitude of simultaneous chemical reactions, few of which, if any, can be expressed in the form of a chemical equation. Furthermore, the chemical composition of the products with the exception of gas is not known with any precision. Under such conditions it might be concluded that the application of fundamentals such as the material balance would offer little advantage. This is not the case, however. For example, in one of the oldest processes, thermal cracking, the application of the material balance provides much information.

Thermal cracking is one means of producing gasoline from petroleum fractions that boil above the gasoline boiling range. Distillate oil, called gas oil, which has a boiling range from 450 to about 700°F, may be separated by distillation from the crude petroleum and cracked to its ultimate yields of gas, gasoline, and black fuel oil (tar). The thermal cracking operation is usually carried out by pumping the gas oil through a coil of tubes in a furnace. The extent of thermal cracking of the charge to the cracking coil is limited by the formation of coke in the tubes. It is not practicable to crack the gas oil from the crude petroleum to its ultimate yields by pumping it through the coil only once (once-through operation). It is necessary to crack the oil only partly and recycle the uncracked portion through the cracking coil after removal of the gas, gasoline, and tar produced during each pass through the coil. Figure 5.5 gives a very much simplified flow sheet of the process. Virgin gas oil (gas oil not yet exposed to cracking conditions) is charged to a coil in the furnace in admixture with recycle gas oil that has been separated from products of previous cracking. On a once-through basis the gasoline produced (called crack per pass) will range from 5 to 20 per cent by liquid volume at 60°F. The maximum ultimate gasoline yield from the virgin gas oil will usually vary from 50 to 70 per cent by volume. The effluent from the cracking coil passes to fractionator 1, where the tar is separated. The overhead from this fractionator passes to fractionator 2, where the recycle gas oil is separated and returned to the cracking coil. The overhead from this fractionator passes to fractionator 3, where the gas and gasoline are separated.

The maximum ultimate yield of gasoline from the virgin oil is based on a sharp separation of gasoline from the recycle gas oil in fractionator 2. In practice, however, a sharp separation is usually not obtained. Thus, the recycle gas oil contains some gasoline of which about 15 per cent by volume is cracked to gas and tar. The net gasoline produced per pass (called crack per pass) is therefore equal to the gross gasoline produced minus the amount destroyed owing to the lack of sharp fractionation. Consequently, the net ultimate yield in industrial practice will be lower than could be realized if sharp fractionation were attained in fractionator 2. Under such conditions, the charge rate to the cracking coil is, of course, greater than with sharp fractionation. This process offers a good opportunity for application of the material-balance principle.

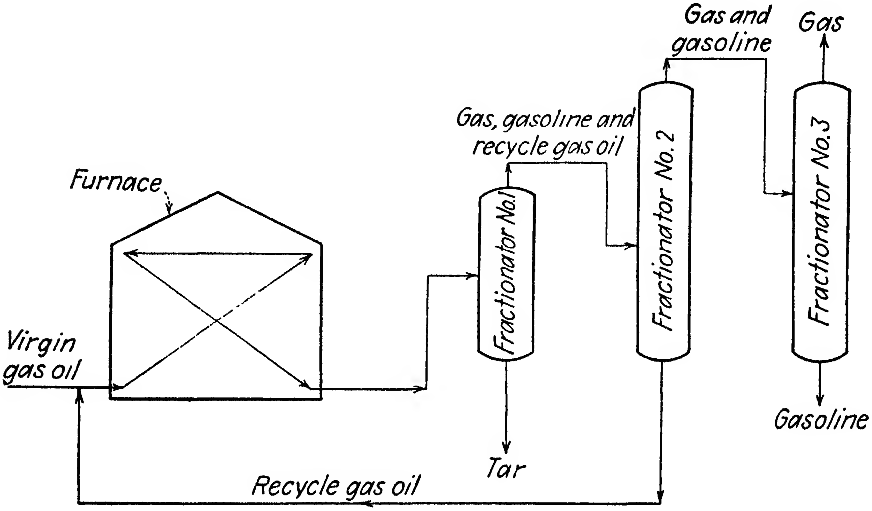

FIG. 5.5.

Example 25. Virgin gas oil is processed by cracking it in one pass (once-through) through a coil at 25 per cent by liquid-volume crack per pass. The recycle gas oil is processed in a separate coil at 12 per cent crack per pass (net) to its ultimate yields. The maximum gasoline yield from the virgin gas oil (with sharp fractionation) is 68.1 per cent by volume. The recycle gas oil contains 10 per cent by volume of gasoline. What net yield of gasoline is obtained, and what is the charge to recycle gas oil coil per 100 volumes of virgin gas oil?

Solution:

Basis: 100 gal of virgin gas oil.

Maximum ultimate yield = 68.1 gal

Once-through from virgin gas oil = 25.0 gal

Possible yield (gross) from recycle gas oil = 68.1 − 25.0 = 43.1 gal

Charge to recycle gas oil coil = C

Gasoline in the charge = $0.1C$

Since 15 per cent of the gasoline in the charge is cracked to gas and tar,

Loss of gasoline in the charge $= (0.15)(0.1C) = 0.015C$

Net gasoline (12% crack per pass) $= 0.12C$

Gross gasoline $= 0.12C + 0.015C = 43.1$ gal

$C = 319$ gal charge/100 gal of virgin gas oil

Net gasoline yield $= 25.0 + (0.12)(319) = 63.3$ gal

PROBLEMS

1. The following flue-gas analysis was obtained:

	Vol. %
CO_2	12.0
CO	0.5
O_2	2.0

What was the weight ratio of hydrogen to carbon of the fuel? What was the excess air?

2. Coal that contains 75 per cent (weight) carbon has a proximate analysis as follows:

	Wt. %
Moisture	3.5
Fixed carbon	65.0
Volatile combustible	22.5

A sample of refuse from the ashpit contained 22.0 per cent moisture, 0.0 per cent volatile combustibles, and 20.0 per cent fixed carbon. The flue-gas analysis was

	Vol. %
CO_2	15.0
O_2	4.0

What percentage of the carbon was burned? How many pounds of coal was burned per 100 moles of air?

3. The following charge to a fractionating column is separated into net overhead product that contains nothing boiling above isobutane and bottoms that contain nothing boiling below propane:

	Mole %
Ethylene	2.0
Ethane	3.0
Propylene	5.0
Propane	15.0
Isobutane	25.0
n-Butane	35.0
n-Pentane	15.0
Total	100.0

The concentration of isobutane in the overhead is 5.0 mole per cent, and the concentration of propane in the bottoms is 0.8 mole per cent. Calculate the moles of the various components in the overhead and bottoms per 100 moles of feed.

4. Nitric acid is produced by the oxidation of ammonia according to the over-all reaction

$$NH_3 + 2O_2 = HNO_3 + H_2O$$

The process, however, actually requires three steps:

$$(a)\ 4NH_3 + 5O_2 = 6H_2O + 4NO$$

$$(b)\ 2NO + O_2 = 2NO_2$$

$$(c)\ 3NO_2 + H_2O = 2HNO_3 + NO$$

In the first step as represented by Eq. (*a*), air is mixed with the ammonia and the reaction carried out over a catalyst at about 1300°F. Then the gases are cooled, and the reaction as shown by Eq. (*b*) occurs. In the third step, the products of reaction from the second step are passed into absorbers, where the NO_2 reacts with the H_2O absorbent. Part of the NO from the third step is oxidized by further contact with oxygen and converted to HNO_3 according to Eqs. (*b*) and (*c*). About 25 per cent excess air is used in the process.

Calculate the volume of NH_3 and air required to produce 10 tons per day of 23°Bé acid. Assume that 85 per cent of the NO produced in the first step is converted to nitric acid. Assume that the oxidation of ammonia in the first step is complete according to Eq. (*a*).

5. Carbon dioxide is produced by recovering CO_2 from flue gas. The flue gas is passed up through an absorber in contact with an aqueous solution of Na_2CO_3. The flue gas contains 20 per cent CO_2 by Orsat analysis. The effluent gas contains 9.0 per cent CO_2 by Orsat analysis. How many moles of flue gas is required to produce 1 ton of CO_2 if 90 per cent of the CO_2 absorbed is recovered as product?

6. Raw water that has the following analysis is to be treated with $Ca(OH)_2$ and Na_2CO_3 to provide boiler feed water. An interval treatment with sodium metaphosphate will be used.

	Grains/Gal.
HCO_3^-	7.7
SO_4^{--}	4.2
Ca^{++}	2.3
Mg^{++}	1.2
Total dissolved solids	42.0

The continuous blowdown from the boiler contains 300 grains/gal of dissolved solids. Calculate the daily requirement of each chemical that corresponds to a steam production of 300,000 lb/hr.

7. Producer gas has the following analysis:

	Vol. %
CO	27.5
CO_2	5.0
H_2	14.0
N_2	50.0
O_2	0.5
CH_4	3.0
Total	100.0

Calculate the Orsat analysis of the flue gas when this is burned with 25 per cent excess air.

8. Sulfuric acid is in some cases produced by burning pyrites (FeS_2) to form SO_2 and then SO_3. Unlike the case of the combustion of pure sulfur, the gases from the burner contain an appreciable concentration of SO_3. In the combustion of pyrites, oxygen is consumed to convert the FeS_2 to Fe_2O_3 as well as to produce SO_2 and SO_3. The reactions are as follows:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

$$4FeS_2 + 15O_2 = 2Fe_2O_3 + 8SO_3$$

In a specific case, pyrites fines that contain 46 per cent sulfur by weight are burned in a suitable burner. An Orsat analysis of the gases from the burner showed 9.0 per cent SO_2 and 6.5 per cent O_2. The cinder from the burner contains 1.5 per cent sulfur by weight, which is a result of the reaction of some of the SO_3 formed with such components in the cinder as CaO. What percentage of the sulfur in the pyrites is converted to SO_3 which leaves in the burner gases?

9. A petroleum naphtha that has a gravity of 41.0°API is charged to a cracking coil in which the naphtha is decomposed. The effluent from the coil (decomposition products) contained 86.4 gal[1] of gasoline (liquid) per 100 gal of charge. The gasoline has a gravity of 46.6°API. The effluent also contained 2.0 gal of 10°API tar per 100 gal of charge and 13.8 lb of gas of the following analysis per 100 lb of charge:

	Mole %
Methane	35.8
Ethylene	8.3
Ethane	21.9
Propylene	16.7
Propane	17.3
Total	100.0

In order to check the accuracy of the data, make a material balance on any convenient basis that shows the pounds of charge entering and the pounds of gasoline, tar, and each component in the gas leaving the coil.

10. Pure calcium carbonate is burned with hydrogen-free coke, which contains 83 per cent carbon, to produce lime. The gas from the kiln contains 26.5 per cent CO_2, 5.0 per cent O_2, and 68.5 per cent N_2. Calculate the ratio of lime produced to coke burned, the per cent excess air used in combustion, and the amount of stack gas per ton of lime.

11. Gas that may be represented by the empirical formula $C_nH_{2.2n}$ will be burned with 25 per cent excess air. Calculate the Orsat analysis of the flue gas.

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[1] When temperature is not specified for the liquid volume, it is at 60°F.

CHAPTER VI

THE ENERGY BALANCE

The energy balance is one of the five technical fundamentals of chemical engineering. It is based on the first law of thermodynamics (law of conservation of energy), which was discussed briefly in Chap. IV. It is similar to the material balance inasmuch as it deals with an account (preferably written) of energy in a process compared with an account (preferably written) of mass. Energy input is equated to energy output plus energy accumulation in the system. The best procedure for calculations is identical with that for a material balance, *viz.*:

1. Sketch a simplified flow sheet of the process.
2. Insert on the flow sheet all pertinent data.
3. Write all chemical equations of reactions involved.
4. Fix a convenient basis for calculations.

As pointed out in Chap. V, there are two types of processes or combinations of processes that the chemical engineer deals with, static and dynamic. As in the case of the material balance, an energy balance on a batch process is made over a single processing cycle, whereas the energy balance on a continuous process is made over a selected period of time when conditions are constant. Theoretically the conditions should be constant at all times at any given point in a continuous process, but this ideal is not always realized in practice.

In the discussion that follows the theory of the total energy balance and heat balance will be presented. Following this, many applications of the total energy balance and heat balance will be illustrated by examples. The examples will include the application of the material balance as well as of the energy balance.

Total Energy Balance.—In order to apply the energy balance, all forms of energy must be expressed in the same units. Table A.13 presents conversion factors for the more common expressions of energy. All the different types of energy entering a process can be equated to the different types of energy leaving the process plus accumulation in the process when all the forms of energy are expressed in the same units. The different types of energy, *viz.*, potential and kinetic, must be considered in any energy balance. For the purposes of chemical engineering it is desirable to subdivide the two types of energy into the various forms that will be commonly encountered. These are discussed below.

External potential energy is a result of the position of a mass as a whole relative to the earth. It is measured relative to some arbitrarily selected horizontal (datum) plane. The product of the distance above the datum plane and the force of gravity on the mass of each item entering, leaving, or accumulating in a process is the external potential energy of each item. The force of gravity is mg, where g is the acceleration due to gravity and m the mass. If X is the vertical distance of the mass above the datum plane, then the external potential energy relative to this plane is mgX because the force of gravity could act through the distance X. In engineering, however, the force of gravity is usually expressed in terms of pounds. Since the force of one pound is the force of gravity acting on a mass of one pound at sea level, this force is equivalent to 32.2 poundals. Thus, the expression of external potential energy in foot-pounds is numerically equivalent to mX, but it must be understood that m is numerically equal to the force involved only when the force is expressed in units of the force of gravity. It will be recalled from Chap. IV that X is commonly used to express head, or pressure. In this case the head is defined as *potential head.*

The external kinetic energy of each item of mass entering and leaving a process is a result of the motion of the mass. Accumulation of material within a process entails no significant motion, and thus only the streams entering and leaving contain external kinetic energy. If V is the velocity of an item of mass entering or leaving, its external kinetic energy is $mV^2/2g$. In this case m represents mass; therefore, if it is desired to express external kinetic energy in terms of foot-poundals, the expression becomes $mV^2/2$. Thus, external kinetic energy is expressed in foot-pounds if one-half the product of mass in pounds and velocity squared (ft/sec)^2 is divided by the acceleration of gravity, 32.2 ft/(sec)(sec). The term $V^2/2g$ is commonly called *velocity head* since it has the dimensions of feet.

Work energy appears in several ways in a process. An entering stream must be forced into a continuous process against a constant pressure P. The work done on the process in this instance is mPv, where v is the specific volume of the mass. If pressure is expressed in pounds (of force) per square foot, v in cubic feet per pound, and m in pounds, then mPv will be in foot-pounds. It is likewise true that work is done by the process in forcing an effluent stream out of the process. Thus, the net work done by the process owing to a stream entering and leaving a process is $m(P_2v_2 - P_1v_1)$. In the case of a batch process, pressure may not remain constant while an item of mass is charged and eliminated. Under such conditions the work energies are expressed as $\int P_1\,dv_1$ and $\int P_2\,dv_2$. The relationship between volume and pressure must therefore be known in order to calculate the net work done by the process owing to the admission and elimination of a given item of mass.

Work may be performed by the process itself in the form of mechanical or electrical energies. For example, the expansion of steam through a heat engine, such as a turbine, involves the forms of work discussed above, but in addition work energy is removed from the steam by the turbine. All forms of work energy that the process expends or consumes must be considered. Such forms will be denoted by w.

Heat energy Q supplied to the process must be included in the energy balance. Heat energy is commonly given in Btu, which can be converted to foot-pounds by multiplying by 778.

Internal energy U, as defined in Chap. IV, is contained by each item of mass that enters and leaves a process. The change in internal energy of each item of mass is $m(U_2 - U_1)$ or $m\ \Delta U$. This represents the summation of the changes in both internal kinetic and internal potential energies.

In addition to external potential energy, external kinetic energy, heat energy, and internal energy, chemical engineers sometimes deal with surface energy. Even so, surface energy will not be considered further in this text, for much of the study of this subject requires a more advanced knowledge than it is intended to furnish here. Likewise, no consideration will be given to electrostatic and magnetic energies.

Thus, as far as this text is intended to extend, the total energy balance may be written as in Eq. (6.1) for any given item of mass that enters and leaves a process.

$$mX_1 + \frac{mV_1^2}{2g} + mP_1v_1 + mU_1 + Q = mX_2 + \frac{mV_2^2}{2g} + mP_2v_2 + mU_2 + w \quad (6.1$$

It will be noted that by solving Eq. (6.1) for Q the terms $m(U_2 - U_1) + m(P_2v_2 - P_1v_1)$ or $m(\Delta U + \Delta Pv)$ will appear on one side of the equation. It will be observed that $\Delta U + \Delta Pv$ is merely the change in enthalpy as defined and discussed in Chap. IV. It was learned in the discussion that, since enthalpy is an integral quantity, a change in enthalpy is dependent only upon the initial and final conditions. Furthermore, the total change is equal to the sum of any series of changes whose summation is the total change. It will be recalled that enthalpy is given, never as an absolute quantity, but always as a value above some suitable datum plane. Thus, the terms $m(U_2 + P_2v_2)$ and $m(U_1 + P_1v_1)$ may be represented by enthalpy values above a common datum plane or $m\,\Delta H_2$ and $m\,\Delta H_1$, respectively. Equation (6.1) may therefore be written as Eq. (6.2).

$$mX_1 + \frac{mV_1^2}{2g} + m\,\Delta H_1 + Q = mX_2 + \frac{mV_2^2}{2g} + m\,\Delta H_2 + w \qquad (6.2)$$

Equations (6.1) and (6.2) were set up for a single item of mass, but in a total energy balance on any process Eq. (6.1) or (6.2) must be applied to every item of mass that enters and leaves the process. If Σ represents the summation of each energy item such as mX_1, $mV_1^2/2g$, etc., Eq. (6.2) will become Eq. (6.3) when applied to all items of mass that enter and leave.

$$\Sigma mX_1 + \sum \frac{mV_1^2}{2g} + \Sigma m\,\Delta H_1 + Q = \Sigma mX_2 + \sum \frac{mV_2^2}{2g} + \Sigma m\,\Delta H_2 + w \qquad (6.3)$$

Heat Balances.—In the application of energy balances it is usually inconvenient to use Eq. (6.3) as such. Its real value is to remind one of the forms of energy that should be considered for each process under study. In this way every form of energy that is important can be evaluated in any specific energy balance. There is, however, one general application of the energy balance that simplifies into what is commonly called a heat balance in chemical-engineering practice.

The chemical engineer will, in general, deal with continuous processes to a far greater extent than with batch processes. Furthermore, in the great majority of these continuous processes, the difference between the external potential and external kinetic energies of the entering and effluent streams are so small that they can be disregarded. Likewise, the only work items involved are a result of forcing the various streams into and out of the process. In such cases Eq. (6.3) reduces to Eq. (6.4).

$$Q = \Sigma m\,\Delta H_2 - \Sigma m\,\Delta H_1 \qquad (6.4)$$

Thus, the heat transferred to the process for all practical purposes is equal to the increase in enthalpy, between the streams that enter and leave the process. Inasmuch as enthalpy values are integral quantities, tables or charts are available or can be prepared (Tables A.14 and A.15 and Figs. A.9 to A.14) that give the enthalpy values for each specific type of mass as a function of pressure temperature and phase conditions. This greatly simplifies the energy balance. It must be remembered, however, that the so-called "heat balance" is valid for a continuous process only when external potential, external kinetic, and all forms of work energy except those included in enthalpy are negligible. It is valid for any batch process at constant pressure, as was shown in Chap. IV in the development of Eq. (4.3). It is not valid, however, for a batch process at constant volume if pressure is a variable. Example 26 illustrates the accuracy of the heat balance as compared with a total energy balance on a typical continuous process.

Example 26. Steam is passing into a condenser at a linear velocity of 100 ft/sec. It is at a pressure of 100 lb/sq in. abs and at a temperature of 400°F. The condensate leaves the condenser at 325°F with a linear velocity of 1 ft/sec. The difference in vertical height between the steam inlet at the top and condensate exit at the bottom is 10 ft. How much heat is given up per pound of condensate?

Solution: Table A.15 gives the enthalpy of steam at 100 lb/sq in. abs and 400°F as 1228.4 Btu/lb above water at 32°F. The enthalpy of the condensate at 325°F is given as 295.5 Btu/lb above water at 32°F. Thus, by a heat balance the heat given up was 1228.4 − 295.5, or 932.9, Btu/lb of condensate.

The external kinetic energy of 1 lb of steam as it entered the condenser was

$$\frac{mV^2}{2g} = \frac{(1)(100)^2}{(2)(32.2)} = 155 \text{ ft-lb} \qquad \text{or} \qquad \frac{155}{778} = 0.2 \text{ Btu/lb}$$

The external kinetic energy of the condensate at the exit was $[(1)(1)^2]/[(2)(32.2)(778)] = 2.0 \times 10^{-5}$, which is nil.

The external potential energy of 1 lb of entering steam relative to the exit was (1)(10) = 10 ft-lb or $^{10}/_{778} = 0.0129$ Btu/lb.

It is apparent from Example 26, therefore, that the entering steam contained 0.2129 Btu/lb more energy than indicated by the enthalpy. The energy contained by the condensate was essentially identical with its enthalpy.

Thus, the heat transferred per pound of steam should be 932.9 + 0.2, or 933.1, Btu when all figures beyond the first digit to the right of the decimal point are ignored. For all practical purposes the heat balance was as good as the total energy balance in this case, because the correction for the differences in external potential and external kinetic energies is far outside the limits of accuracy of measuring the quantity of steam to the condenser or the condensate effluent.

The heat balance is by far the most common application of the energy balance. There are two methods of application, *viz.*, the gross and the net balance. Each has its advantages.

The *gross heat balance* is used most frequently and conveniently in process-design calculations. It is based on a common datum plane. All enthalpies used in the balance are relative to the common datum plane, which, for convenience, is identical with the datum plane on which the enthalpy charts or tables are based. For example, if the enthalpy charts or tables are based on liquid at 32°F as is the case of steam tables (Tables A.14 and A.15), a gross balance would involve the accounting for enthalpy of the input streams above liquid at 32°F, enthalpy of the output streams above liquid at 32°F, heat transferred to or from the system, and the heat of reaction relative to liquid at 32°F for any chemical change that took place in the process. It is apparent that the lower the datum-plane temperature, the greater the enthalpies. Thus, by selecting a very low temperature for the datum plane the energy quantities on the input and output side of the balance can be made large. In the case of a heat balance on an operating process an "unaccounted for" difference between the energy input and output will remain fixed in Btu. Nevertheless, the unaccounted for item is almost always expressed as a percentage on the total of the energy input or output. Thus, the lower the datum-plane temperature, the greater the total of the energy input and output and the lower the percentage unaccounted for. A gross heat balance in a performance test on an operating unit can frequently be made to appear excellent on the surface, even though very poor, by selecting a low datum plane.

In the case of process designs, there is no unaccounted for item, and thus the gross balance is usually the more convenient and more easily applicable method. However, its application in performance tests may lead to erroneous conclusions inasmuch as the process may not have involved as much energy as would be shown on the input or output side of the balance. For example, consider the performance of a boiler that is charged with treated water at 270°F. It produces steam at 405 lb/sq in. gauge and 500°F. The continuous blowdown is 10 per cent, based on the treated feed water. Table A.14 shows an enthalpy for water at 270°F of 238.84 Btu/lb. The temperature of saturated steam at 420 lb/sq in. abs is 449.4°F, and the enthalpy of the blowdown at that temperature is 429.4 Btu/lb. The enthalpy of the feed water, 238.84 Btu/lb, would be used to calculate the energy input contained in the feed water. Likewise, the above enthalpies for the blowdown and steam would be used to calculate the corresponding output items. All these enthalpies are above water at 32°F. It is apparent, however, that the boiler should not be given credit for its having transferred heat to the feed water below 270°F. Consequently, the performance of the boiler should be based on heat input on the water side above water at 270°F since the boiler had nothing to do with providing heat from 32 to 270°F.

The *net heat balance* is best adapted to performance tests, for it involves only the net heat energy for which the process is accountable. Each input item is followed through the process, and the heat that is absorbed or given up is calculated. There is consequently no common datum plane. A datum plane is selected for each input item so that the enthalpy of the input item is zero. If heat is given up, the calculated heat quantity goes on the input side. If heat is absorbed, the calculated quantity of heat goes on the output side of the balance. In this way only the net heat being transferred within the process is considered. The net *energy* balance is therefore the most sensitive method for analyzing performance data on an operating process. The unaccounted for item as per cent on total input in a gross balance is frequently magnified manifold when examined on the basis of a net balance. Application of the gross- and net-heat-balance methods is illustrated in Example 27.

Example 27. A boiler with integral superheater is producing 59,000 lb/hr of steam at 411 lb/sq in. gauge. The steam from the superheater is at 690°F. The boiler room is at 94°F, and the feed water enters the boiler at 267°F. The products of combustion pass from the furnace through an air preheater to the stack at 518°F. An Orsat analysis of the gases to the stack shows 9.8 per cent CO_2, 5.9 per cent O_2, and no CO. The air for combustion contains 0.017 lb of water vapor per pound of H_2O-free air. The boiler is fired with hydrocarbon gas at the rate of 50,000 cu ft/hr S. C., which has a specific gravity relative to air of 1.12. The feed water contains 90 grains/gal of total dissolved solids. The continuous blowdown contains 433 grains/gal of total solids. The above data were taken several hours after intermittent blowdown, and thus steady conditions prevailed. Make an energy balance to account for the energy in the process.

Solution: By application of a material balance to the dissolved solids, the feed-water rate can be calculated.

Basis: 1 hr.

Let B = blowdown, in gal
F = feed water, gal

$$8.33F = 8.33B + 59{,}000$$

Also,

$$90F = 433B$$

$$F = \frac{433}{90}B = B + \frac{59{,}000}{8.33}$$

$$B = \frac{7090}{3.81} = 1860$$

$$F = 8950$$

Blowdown = 20.8% of feed water

Feed water = (8950)(8.33) = 74,550 lb/hr

Blowdown = 15,550 lb/hr

The quantity of flue gas can be calculated by material balance.

Basis: 100 moles of dry flue gas.

	Mole %	Moles C	Moles O_2
CO_2	9.8	9.8	9.8
O_2	5.9	—	5.9
N_2	84.3	—	—
	100.0	9.8	15.7

$$O_2 \text{ in air} = (84.3)\left(\frac{21.0}{79.0}\right) = \underline{22.4}$$

$$O_2 \text{ combined with } H_2 \quad = \ 6.7$$

$$H_2O \text{ formed} = (2)(6.7) = 13.4 \text{ moles}$$

$$H_2O\text{-free air to furnace} = 22.4 + 84.3 = 106.7 \text{ moles}$$

$$\text{Excess air} = \frac{(5.9)(100)}{9.8 + 6.7} = 35.7\%$$

$$H_2O \text{ in air to furnace} = \frac{(0.017)(106.7)(29.0)}{18} = 2.9 \text{ moles}$$

$$\text{Total } H_2O \text{ in flue gas} = 2.9 + 13.4 = 16.3 \text{ moles}$$

$$H/C \text{ wt. ratio} = \frac{(13.4)(2)}{(9.8)(12)} = 0.228 \text{ lb/lb}$$

From Table A.7, fuel gas has specific gravity of 1.13 at H/C weight ratio of 0.228. Thus, flue-gas analysis seems to be very good, for the specific gravity of the fuel gas was determined to be 1.12.

NOTE: It is always desirable to check the flue-gas analysis by such a method if possible. The specific gravity of gas relative to air can be determined very accurately by an Edwards balance or other methods; if there should be an appreciable discrepancy, the flue-gas analysis would be questionable.

$$\text{Mole wt. of fuel gas} = (1.12)(29.0) = 32.5$$

$$\text{Moles of C/mole of fuel gas} = \frac{(1)(32.5)}{(12)(1.228)} = 2.207$$

$$\text{Moles of fuel gas/100 moles dry flue gas} = \frac{9.8}{2.207} = 4.44$$

$$\text{Moles of fuel gas/100 moles of dry air} = \frac{4.44}{1.067} = 4.16$$

Material balance on furnace. Basis: 1 hr.

$$\text{Fuel gas} = \frac{50{,}000}{379} = 132 \text{ moles} = (132)(32.5) = 4290 \text{ lb}$$

$$\text{Dry air} = \frac{(132)(100)}{4.16} = 3170 \text{ moles} = (3170)(29.0) = 92{,}000 \text{ lb}$$

$$H_2O \text{ in air} = \frac{(3170)(2.9)}{106.7} = 86 \text{ moles} = (86)(18) = 1550 \text{ lb}$$

$$CO_2 \text{ in flue gas} = (132)(2.207) = 291.5 \text{ moles} = (291.5)(44) = 12{,}800 \text{ lb}$$

$$O_2 \text{ in flue gas} = \left(\frac{5.9}{9.8}\right)(291.5) = 175 \text{ moles} = (175)(32) = 5600 \text{ lb}$$

$$N_2 \text{ in flue gas} = \left(\frac{84.3}{9.8}\right)(291.5) = 2505 \text{ moles} = (2505)(28.2) = 70{,}700 \text{ lb}$$

$$H_2O \text{ in flue gas} = \left(\frac{16.3}{9.8}\right)(291.5) = 485 \text{ moles} = (485)(18) = 8740 \text{ lb}$$

	Lb
Input:	
Dry air	92,000
Fuel gas	4,290
H_2O in air	1,550
Total	97,840
Output:	
CO_2 in flue gas	12,800
O_2 in flue gas	5,600
N_2 in flue gas	70,700
H_2O in flue gas	8,740
Total	97,840

It was not necessary that the material balance be made, but it serves to check calculations. The air and flue gas were not measured but were calculated on the basis of stoichiometric relations and a perfect material balance. The perfect material balance, therefore, is a check, not on the data, but merely on the calculations up to this point.

Heat capacities of gases from Table A.3:

	At 518°F		At 94°F	
	Btu/(mole)(deg F)	Above 60°F, Btu/mole	Btu/(mole)(deg F)	Above 60°F, Btu/mole
CO_2	10.01	4580	8.72	296
H_2O vapor	8.20	3750	8.00	272
N_2	7.02	3210	6.96	237
O_2	7.24	3320	7.02	239
Fuel gas	.....	....	11.92	405 *

* Based on an average of C_2H_4 and C_3H_8 to correspond with specific gravity of 1.12.

From Tables A.14 and A.15,

	Btu/Lb
Steam at 426 lb/sq in. abs and 690°F	1355.2
Blowdown at saturation temperature (426 lb/sq in.)	431.0
Feed water at 267°F	235.7
Water at 60°F	28.1

Net heat of combustion of fuel gas:

From Table A.7, at 60°F, heat of combustion at 60°F = 1724 Btu/cu ft.

The heat of combustion of 1724 Btu/cu ft is relative to 60°F and will be corrected to 94°F as follows:

The oxygen used to form CO_2 and H_2O was 16.5 moles/100 moles of dry flue gas, or $16.5/4.44 = 3.72$ moles of O_2/mole of fuel gas. CO_2 formed $= 9.8/4.44 = 2.21$ moles/mole of fuel gas. H_2O formed $= 13.4/4.44 = 3.02$ moles/mole of fuel gas.

$$\text{Heat of combustion at } 94^\circ\text{F} = 1725 + \frac{+(3.72)(239) + 405 - (2.21)(296) - (3.02)(272)}{379}$$

$$= 1725 - 0.48$$

or, say, 1724.5 Btu/cu ft (at standard conditions).

Thus, it is seen that over the temperature ranges usually encountered the heat of combustion is essentially unaffected, and corrections for temperature can be disregarded under such circumstances.

Gross heat balance. Basis: 1 hr and 60°F.

	Btu
Input:	
O_2 in air = (0.21)(3160)(239)	159,000
N_2 in air = (0.79)(3160)(237)	591,000
H_2O in air = (86)(272)	23,400
Fuel gas = (132)(405)	53,000
Feed water = (74,550)(235.7 − 28.1)	15,470,000
Heat of combustion = (50,000)(1725)	86,250,000
Total	102,546,400
Output:	
CO_2 in flue gas = (291.5)(4580)	1,335,000
O_2 in flue gas = (175)(3320)	580,000
N_2 in flue gas = (2505)(3210)	8,050,000
H_2O in flue gas = (485)(3750)	1,820,000
Steam = (59,000)(1355.2 − 28.1)	78,300,000
Blowdown = (15,550)(431.0 − 28.1)	6,260,000
Total accounted for	96,345,000
Unaccounted for (6.0% on total)	6,201,400
Total	102,546,400

Net heat balance. Basis: 1 hr.

	Btu
Input:	
Heat of combustion (94°F) = (50,000)(1724.5)	86,225,000
Total	86,225,000
Output:	
CO_2 in flue gas = (291.5)(4580 − 296)	1,250,000
O_2 in flue gas = (175)(3320 − 239)	540,000
N_2 in flue gas = (2505)(3210 − 237)	7,454,000
H_2O in flue gas = (485)(3750 − 272)	1,689,600
Steam = (59,000)(1355.2 − 235.7)	66,055,000
Blowdown = (15,550)(431.0 − 235.7)	3,035,000
Total accounted for	80,023,600
Unaccounted for (7.2% on total)	6,201,400
Total	86,225,000

Thus, it is noted from Example 27 that, in the gross heat balance above 60°F, the unaccounted for item is 6.0 per cent on the total input, whereas in the net heat balance it is 7.2 per cent on total input. The difference in percentage unaccounted for between the two bases is usually about this magnitude for heat balances on combustion processes. The difference is ordinarily much greater when large heats of reaction are not involved.

The limits of tolerance in heat balances depend largely on the accuracy with which the flow rates and temperatures of streams can be measured. In general, however, if the unaccounted for item in a *net* heat balance exceeds 10 per cent on total input, it should be rejected. Actually, a good net heat balance should show no more than 5 per cent unaccounted for.

ENERGY BALANCES IN UNIT OPERATIONS

Fluid Flow.—One of the classical examples of the application of the mass balance and the total energy balance is in the unit operation, fluid flow. By means of these two simple but powerful fundamentals most of the problems of fluid flow can be solved.

One of the more important problems encountered in fluid flow is the calculation of pressure drop through a system that may include lengths of tubes or pipe of different sizes, a heater, nozzles, etc. Also, closely allied with this problem is the calculation of the power that must be provided to pump the liquid or compress the gas that is flowing.

Consider the flow of *any* fluid through the system described in Fig. 6.1. The fluid enters at *A*, passes up through the heater, and leaves the system at B. Consider a differential length dL of the tube in the section that is receiving heat from the heater. A mass m of the fluid having internal energy of U and a specific volume v enters the differential length at a linear velocity of V. The elevation of the entrance to the differential length is X. As the mass passes through the differential length, it absorbs a differential quantity of heat dq per unit mass. Thus, the conditions at the entrance and exit of the differential length are summarized as follows:

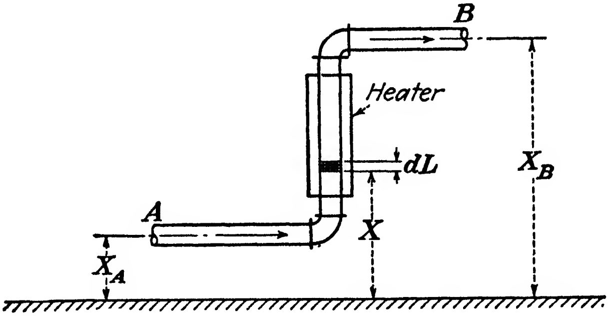

FIG. 6.1.

	Differential length dL	
	Inlet	Exit
Elevation	X	$X + dX$
Internal energy	U	$U + dU$
Specific volume	v	$v + dv$
Linear velocity	V	$V + dV$
Pressure	P	$P + dP$
Heat energy	dq	

It is apparent that the mass m which flows through any cross section of the system in Fig. 6.1 during any time θ is constant. Otherwise, there would be an accumulation or depletion of mass in the system. It follows, therefore, that

$$\frac{m}{\theta} = VS\rho = GS = G_1S_1 = G_2S_2 \qquad (6.5)$$

where S = cross-sectional area, sq ft
G = mass velocity, lb/sq ft/sec
ρ = fluid density = $1/v$ lb/cu ft

The total energy balance over the differential length dL is therefore as follows:

$$mX + mU + mPv + \frac{mV^2}{2g} + m\,dq$$
$$= m(X + dX) + m(U + dU) + m(P + dP)(v + dv) + \frac{m(V + dV)^2}{2g}$$

or

$$X + U + Pv + \frac{V^2}{2g} + dq$$
$$= X + dX + U + dU + Pv + P\,dv + v\,dP + dP\,dv + \frac{V^2 + 2V\,dV + dV\,dV}{2g}$$

Then
$$dq = dX + dU + P\,dv + v\,dP + \frac{V\,dV}{g} \tag{6.6}$$

The total amount of heat dQ absorbed by the fluid within the length dL is equal to the heat received from the heater dq plus the amount of mechanical energy transformed into heat energy owing to friction. The friction energy per unit mass is dF. Thus, by Eq. (4.27) (first law of thermodynamics),

$$dQ = dq + dF = dU + P\,dv \tag{6.7}$$

Then the substitution of Eq. (6.7) in Eq. (6.6) gives Eq. (6.8).

$$-v\,dP = dX + \frac{V\,dV}{g} + dF \tag{6.8}$$

or
$$P_1 - P_2 = \Delta P^{*} = \int_{X_1}^{X_2} \frac{dX}{v} + \int_{V_1}^{V_2} \frac{V\,dV}{gv} + \int_0^L \frac{dF}{v} \tag{6.9}$$

Equations (6.8) and (6.9) are expressions of Bernoulli's theorem. Since the specific volume v is the reciprocal of the density ρ, Eq. (6.9) may be written as

$$\Delta P = \int_{X_1}^{X_2} \rho\,dX + \int_{V_1}^{V_2} \rho\frac{V\,dV}{g} + \int_0^L \rho\,dF \tag{6.10}$$

It will be noted that F has the dimensions of length. It is frequently called the *friction head.*

If the fluid is a liquid, ρ will be essentially constant and Eq. (6.10) reduces to Eq. (6.11).

$$\Delta P = \rho(X_2 - X_1) + \frac{\rho}{2g}(V_2^2 - V_1^1) + \rho\int_0^L dF \tag{6.11}$$

---

[*] **In this specific case, in order to make ΔP positive it is commonly expressed as the initial minus the final pressure instead of the reverse.**

If the fluid is a gas, Eq. (6.10) must be used to calculate the pressure drop in the system. The relationship between ρ and X, and V and L must be known. This does not represent much difficulty in most cases, for the system can be divided into sufficiently short sections so that in effect Eq. (6.11) is applied to each section in which the density ρ can be regarded as constant at an average value. The total pressure drop is then the sum of the pressure drops for the short sections.

The friction energy is usually the most important item in Eqs. (6.10) and (6.11). It has been evaluated by the combination of theory and experimentation. There are many different types of friction loss, *i.e.*, there are many causes for the transformation of mechanical energy into heat energy. Some of these are friction due to the flow of fluids in tubes, to a sudden enlargement in the path of flow, to a sudden contraction in the path of flow, and to pipe fittings such as elbows, tees, and valves. The study of the unit operation, fluid flow, is devoted largely to the evaluation of friction losses in the various cases commonly encountered by the chemical engineer. Although it is not the purpose of this text to present a detailed treatment of any of the unit operations or chemical processes, it is desirable at this time to introduce the evaluation of friction loss due to the flow of fluids in tubes of constant cross-sectional area. This will give the student a preview of the type of studies involved in a comprehensive treatment of the flow of fluids as given by Walker, Lewis, McAdams, and Gilliland[1] or Badger and McCabe.[2]

The pressure drop due to the friction loss in the flow of fluids through tubes is expressed by the Fanning equation [Eq. (3.1)] and discussed in Examples 1 and 3 (Chap. III).

$$\Delta P_f = \int_0^L \rho \, dF = \int_0^L \frac{2fV^2\rho \, dL}{gD} \tag{3.1}$$

where ΔP_f = pressure drop due to friction, lb/sq ft
f = friction factor (dimensionless)
V = linear velocity of fluid, ft/sec
ρ = density of fluid, lb/ft
L = length of tube, ft
g = acceleration of gravity, 32.2 ft/(sec)(sec)
F = friction head, ft

---

[1] WALKER, W. H., W. K. LEWIS, W. H. MCADAMS, and E. R. GILLILAND, "Principles of Chemical Engineering," 3d ed., McGraw-Hill Book Company, Inc., New York, 1937.

[2] BADGER, W. L., and W. L. MCCABE, "Elements of Chemical Engineering," McGraw-Hill Book Company, Inc., New York, 1931.

It was learned in Example 3 that the friction factor f is a function of a dimensionless group of variables called the Reynolds number, $DV\rho/\mu$.

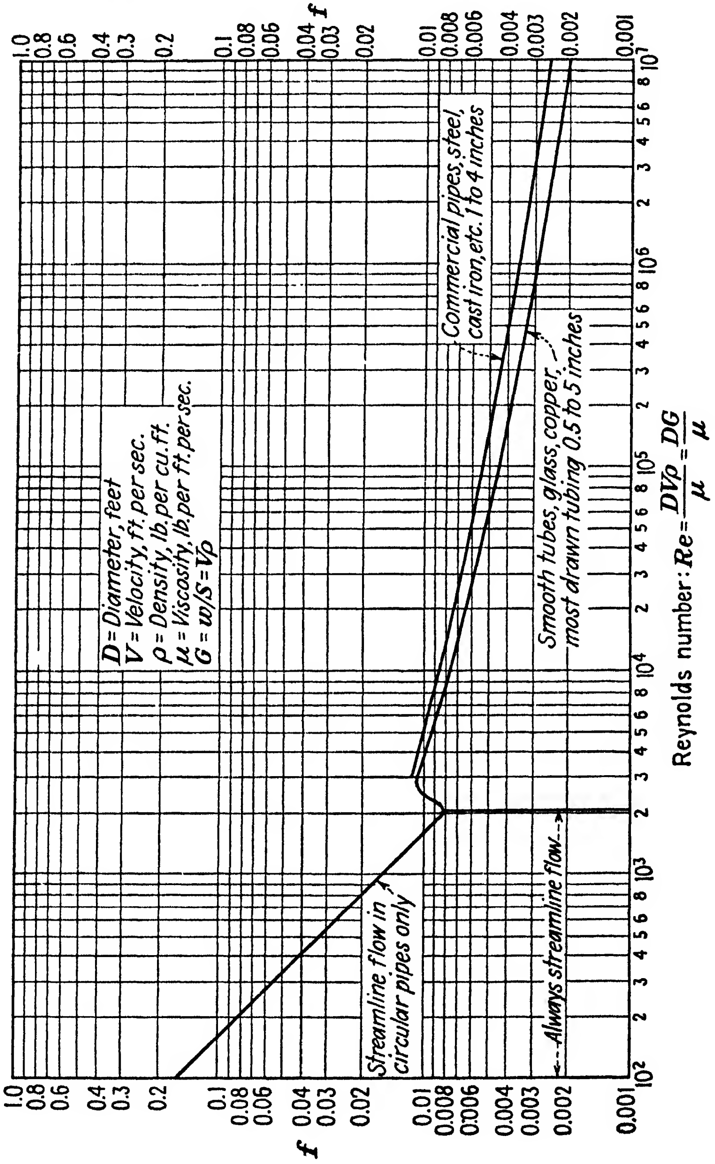

FIG. 6.2.

This function is presented graphically in Fig. 6.2. In this connection it will be noted that the mass velocity (pounds per square foot per second) G is equal to $V\rho$. The Reynolds number is therefore also expressed as DG/μ.

It is apparent that, for the flow of fluids through a tube of constant cross-sectional area S, the mass velocity G is constant since the mass flow rate w is constant. Thus, for this case Eqs. (6.10) and (6.11) reduce to Eqs. (6.12) and (6.13), respectively. For any fluid and constant cross-sectional area of flow,

$$\Delta P = \int_{X_1}^{X_2} \rho\, dX + \frac{G}{g}(V_2 - V_1) + \frac{2G}{Dg}\int_0^L fV\, dL \tag{6.12}$$

For liquids and constant cross-sectional area of flow,

$$\Delta P = \rho(X_2 - X_1) + \frac{2fGVL}{gD} \tag{6.13}$$

Equation (6.12) requires a knowledge of the relationship between ρ and X and between V and L. When there is a large variation in ρ and V from inlet to outlet, the tube length can be divided into short sections over each of which ρ and V can be regarded as constant at the arithmetic average of the values at the inlet and outlet of each section. Likewise, an average value of f is used. In this way all the integrals of Eq. (6.12) can be evaluated.

The application of the fluid-flow equations (6.10) to (6.13) is illustrated with a typical case in Example 28.

Example 28. Air at 60°F and 100 lb/sq in. abs enters a vertical Schedule 40 1-in. steel pipe at a linear velocity of 100 ft/sec. The pipe is 40 ft in length and is heated so that the air leaves at 200°F. What is the pressure drop through the pipe? Assume that the ideal-gas law applies and that the viscosity of air over the pressure range involved is the same as if it were at atmospheric pressure.

Solution: From Table A.12 the internal diameter of the pipe is found to be 1.049 in. or 0.0875 ft.

$$PMv = nRT$$

where M is molecular weight and v is specific volume in cubic feet per pound.

$$Mv_1 = \frac{(1)(10.7)(60 + 460)}{100} = 55.7 \text{ cu ft/mole}$$

$$\rho_1 = \frac{29.0}{55.7} = 0.520 \text{ lb/cu ft}$$

If P_2 is in pounds per square foot,

$$Mv_2 = \frac{(10.7)(200 + 460)}{P_2/144} = \frac{1.016 \times 10^6}{P_2}$$

$$\rho_2 = \frac{29.0P_2}{1.016 \times 10^6} = 2.86 \times 10^{-5}P_2$$

$$G = V\rho = V_1\rho_1 = (100)(0.520) = 52.0 \text{ lb/(sq ft)(sec)}$$

$$V_2 = \frac{G}{\rho_2} = \frac{52.0}{2.86 \times 10^{-5}P_2} = \frac{1.82 \times 10^6}{P_2}$$

From Fig. A.8,

$$\mu_1 = (0.018)(0.000672) = 1.21 \times 10^{-5}\ \text{lb/(ft)(sec)}$$

$$\mu_2 = (0.021)(0.000672) = 1.41 \times 10^{-5}\ \text{lb/(ft)(sec)}$$

$$\mu_{av} = \frac{1.21 + 1.41}{2} \times 10^{-5} = 1.31 \times 10^{-5}\ \text{lb/(ft)(sec)}$$

$$\frac{DG}{\mu_{av}} = \frac{(0.0875)(52.0)}{1.31 \times 10^{-5}} = 348{,}000$$

From Fig. 6.2, $f_{av} = 0.0043$

Since pipe is vertical, $X = L = 40$

Thus, from Eq. (6.12)

$$P_1 - P_2 = \int_{X_1}^{X_2} \rho\, dX + \frac{52.0}{32.2}(V_2 - 100) + \frac{(2)(52.0)(0.0043)}{(0.0875)(32.2)} \int_0^L V\, dL$$

An average value of ρ and V must be obtained to evaluate the integrals; thus, assume outlet pressure of 95 lb/sq in. abs.

Then $P_2 = (95)(144) = 13{,}680$ lb/sq ft

$$\rho_2 = (2.86 \times 10^{-5})(13{,}680) = 0.39\ \text{lb/cu ft}$$

$$V_2 = \frac{1.82 \times 10^6}{13{,}680} = 133\ \text{ft/sec}$$

$$\rho_{av} = \frac{0.52 + 0.39}{2} = 0.45\ \text{lb/cu ft}$$

$$V_{av} = \frac{100 + 133}{2} = 117\ \text{ft/sec}$$

$$14{,}400 - P_2 = (0.45)(40) + 1.61(133 - 100) + (0.158)(40)(117)$$

$$P_2 = 14{,}400 - (18 + 93 + 739) = 13{,}550\ \text{lb/sq ft}$$

Thus, the pressure drop is 6 lb/sq in. This is close enough to the assumed value so that correction of V_2, V_{av}, and ρ_{av} would have no effect.

It is noted, therefore, that pressure drop was calculated merely by the application of the material balance and energy balance. The power required for transmission of fluids can be calculated once the initial (suction) and final (discharge) pressures and the quantity of fluid to be handled per unit time are known. A material balance and an energy balance between the suction and discharge of the pump or compressor will permit the calculation of the power required. The power requirement for compressors will be considered in Chap. IX, but the power requirement for pumping liquids will be taken up at this time.

The difference in external potential energy, external kinetic energy, and internal energy between the suction and discharge of a pump is nil and may be ignored. Actually, since mechanical perfection is not realized, there is a difference in internal energy; but this is accounted for by including it in an efficiency factor (100 × work output/energy input).

The theoretical horsepower required is therefore based entirely on the entrance- and exit-work items, $P_2v_2 - P_1v_1$. The theoretical amount of work required to take a volume of liquid per unit time from the suction pressure to the discharge pressure is the theoretical power required as given by Eq. (6.14).

$$\text{Theoretical hp} = \frac{144Q\ \Delta P}{33{,}000} = 0.00436Q\ \Delta P \tag{6.14}$$

where Q = liquid flowing, cu ft/min
ΔP = discharge minus suction pressure, lb/sq in.

It must be fully understood that the suction and discharge pressures are immediately at the pump. Thus, if a pump takes suction on a reservoir of fluid at rest, as shown diagrammatically by Fig. 6.3, the pressure drop between the reservoir and the suction of the pump should be negative. This is particularly important if the liquid in the reservoir is at a pressure that corresponds to its vapor pressure at the temperature of the liquid. It is good practice to set the diameter of the suction line so that the external potential energy between the reservoir and the pump suction is 50 to 100 per cent greater than the friction loss in the suction line plus the increase in external kinetic energy between the reservoir and the pump suction. If a pump takes suction on a reservoir of fluid at rest that is at its saturation vapor pressure, the pressure at the suction of the pump must not drop below the reservoir pressure or vaporization of the liquid will occur. If vaporization takes place at the pump suction, the capacity of the pump will be reduced proportionately to the amount of vaporization, for it will be pumping vapor instead of liquid. This is perhaps the chief fault in many pump installations made by practicing engineers and chemists. There are other important factors, too, which the student of chemical engineering will learn later in his comprehensive study of the unit operations.

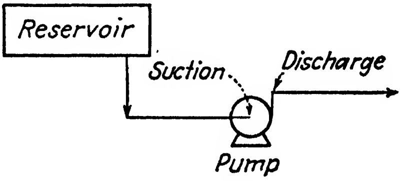

FIG. 6.3.

Evaporation.—Solutions of nonvolatile liquids or solids in volatile liquid solvents are frequently concentrated by removing the volatile solvent from the solution by vaporization. This is classified as evaporation, which is one of the unit operations of chemical engineering.

Evaporators are of many different types, though all have several essential features in common. They contain a heating surface that separates the heating medium from the boiling solution that is being concentrated. In the great majority of cases the heating medium is a condensing vapor such as steam.[1] The heating surface consists of a bundle of tubes that extends between two tube sheets. Frequently, however, the heating medium is a liquid of sufficiently high temperature to provide the necessary heat for evaporation. Figure 6.4 is a diagrammatic sketch of a standard type of vertical-tube evaporator. Although this is only one of the many types of evaporator designs, it will provide the student with a sufficiently clear conception, for the time being, of the principal design features of evaporators.

The two tube sheets are in the form of doughnuts. The steam chest is the space on the outside of the tubes. It is separated from the boiling solution by the tube walls, tube sheets, and downtake wall. The steam passes into the steam chest and condenses on the outside of the vertical tubes. The condensate drains to the bottom of the steam chest, where it is removed. A small vent is located at the top of the tube chest on the opposite side from the steam inlet. The purpose of the vent is to remove noncondensable gases, which would otherwise accumulate in the steam chest over a period of time and seriously affect the transfer of heat through the tube walls. The feed (solution to be concentrated) is admitted above the top tube sheet. The boiling solution passes up through the inside of the tubes owing to natural convection currents (difference in densities of fluids in tubes and in downtake) that are set up. The vapor disengages from the solution at the liquid level, which is maintained at a point just above the top tube sheet. The vapor passes out the top of the evaporator through the vapor line. The feed (solution to be concentrated) and the solution that has just disengaged from the vapor pass down through the central downtake and into the tubes at the bottom tube sheet. The concentrated solution is removed from the bottom of the evaporator shell.

The evaporator installation described is what is known as a single-effect. It is common practice, however, to install evaporators in groups of two, three, and four. These are called double-effect, triple-effect, and quadruple-

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[1] When water is being evaporated by use of steam, the evaporated water is distinguished from the steam by being called "vapor." Water vapor used for heating is called "steam."

effect, respectively. Badger and McCabe[1] state that as many as eight in a group have been operated successfully, but installations of more than four are not common. The advantage of multieffect installations is a saving in fuel. The vapor evaporated in one evaporator (first effect) is used as steam in the second evaporator (second effect). The vapor from the second effect is used as steam in the third effect, and so on. In this way, 1 lb of steam supplied from a boiler will evaporate roughly 1 lb of water in a single-effect, 2 lb of water in a double-effect, 3 lb of water in a triple-effect, and so on. More detailed consideration of multieffect evaporation will be delayed until Chap. VIII, but some attention will be devoted at this point to single-effect evaporators.

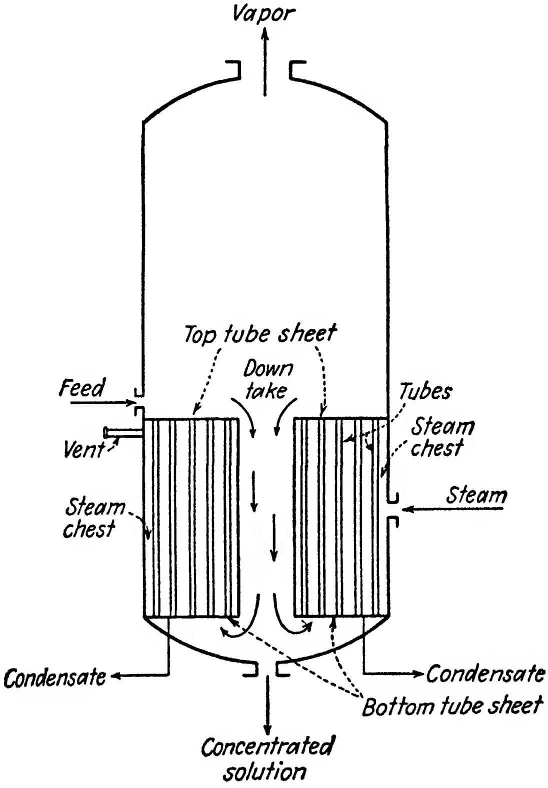

FIG. 6.4.

Evaporation offers many opportunities for application of the material balance and energy balance. Example 29 illustrates some of the advantages in connection with design and performance studies.

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[1] *Op. cit.*

Example 29. A performance test was made on a single-effect evaporator that was concentrating an aqueous solution of inorganic salts. The following data were obtained:

Concentration of salts as weight per cent:
  In feed, 12.0%
  In concentrated solution, 50%
Steam:
  25.0 lb/sq in. gauge
  300°F
Feed:
  50,000 lb/hr
  200°F
  Specific heat 0.90
Concentrated solution:
  180°F
  Specific heat 0.60
Vapor:
  180°F
  26 in. Hg vacuum relative to 30 in. barometer
Condensate from steam chest:
  39,000 lb/hr
  265°F

Make a heat balance on the evaporator to determine the accuracy of the data. Assume that the difference between the integral heats of solution for the feed and concentrated liquor is zero.

Solution: By material balance, determine vapor evaporated.

Basis: 1 hr.

$$\text{Feed} = 50{,}000 \text{ lb/hr}$$

$$\text{Salt in feed} = (0.12)(50{,}000) = 6000 \text{ lb}$$

$$\text{Water in feed} = 44{,}000 \text{ lb}$$

$$\text{Water in concentrate} = (6000)\left(\frac{0.50}{0.50}\right) = 6000 \text{ lb}$$

$$\text{Water evaporated} = 38{,}000 \text{ lb/hr}$$

Gross heat balance. Basis: 1 hr; water at 32°F.

	Btu
Input:	
Sensible heat of feed = (50,000)(0.9)(200 − 32)	7,550,000
Steam = (39,000)(1187.1)	46,300,000
Total	53,850,000
Output:	
Sensible heat of concentrate = (12,000)(180 − 32)(0.60)	1,065,000
Steam, condensate = (39,000)(233.7)	9,100,000
Vapor = (38,000)(1140.0)	43,250,000
Unaccounted for (0.81% on total)	435,000
Total input	53,850,000

Net heat balance. Basis: 1 hr.

	Btu
Input:	
Concentrate = 12,000(200 − 180)(0.60)	144,000
Steam = 39,000(1187.1 − 233.7)	37,200,000
Total input	37,344,000
Output:	
Vapor [1] = 38,000(1140.0 − 168)	36,909,000
Unaccounted for (1.17% on total)	435,000
Total output	37,344,000

[1] The heat in the vapor is taken relative to water at 200°F (temperature of the feed). This, therefore, divides the feed into water plus concentrate.

Distillation.—The unit operation distillation, or fractionation as it is frequently called, has many applications of the material balance and energy balance. In essentially all cases the energy balance reduces to a heat balance, for the differences in external potential energy and external kinetic energy between the inlet and outlet streams are quite negligible.

One of the important applications of the material balance and energy balance is in process design of fractionating columns. Example 30 illustrates the calculation of heat required by a fractionating column by means of a material balance and energy balance.

Example 30. A blend of 55 mole per cent *n*-pentane and 45 mole per cent *n*-heptane is to be fractionated at atmospheric pressure into an overhead product that contains 0.5 mole per cent *n*-heptane and a bottoms product of 3 mole per cent *n*-pentane. The feed is charged to the column as liquid at 100°F. The reflux ratio is 6 moles/mole of net overhead product. The net overhead product (distillate) is withdrawn as liquid from the reflux drum. The temperature of the reflux drum, overhead to the condenser, and bottoms from the column is 80, 105, and 200°F, respectively. How much heat must be supplied by the reboiler at the base of the column for a feed rate of 48,000 gal/day? How much heat must the overhead condenser remove? Assume that enthalpies of *n*-heptane are same as for *n*-hexane (Fig. A.9).

Solution: By material balance calculate the overhead and bottoms quantities.

Basis: 100 moles of feed.

Over-all balance:

$$\text{Feed} = \text{distillate} + \text{bottoms}$$

$$F = D + B = 100$$

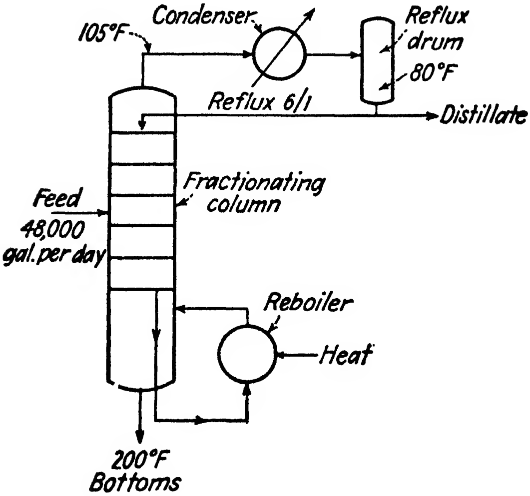
Pentane balance:

$$55.0 = 0.995D + 0.03B$$

$$D = 55.25 - 0.0302B = 100.0 - B$$

$$B = \frac{44.75}{0.9698} = 46.15$$

$$D = 53.85$$



Calculate moles of feed equivalent to 48,000 gal/day.

	Moles	Mol. wt.	Lb	Lb/gal*	Gal	Vol. %
n-C_5	55.0	72	3960	5.428	73.0	48.15
n-C_7	45.0	100	4500	5.723	78.6	51.85
Total	100.0	84.6	8460	5.58	151.6	100.00

* Table A.9.

Over-all material balance on fractionator. Basis: 1 hr.
Feed:

	Gal	Lb/gal	Lb	Mol. wt.	Moles
n-C_5	963	5.428	5,225	72	72.55
n-C_7	1,037	5.723	5,935	100	59.35
Total	2,000	5.58	11,160	84.6	131.90

Distillate = (131.9)(53.85)/100 = 71.1 moles.

	Moles	Mol. wt.	Lb
n-C_5	70.75	72	5095
n-C_7	0.35 *	100	35
Total	71.10	...	5130

* 0.5 per cent of distillate.

Bottoms = 131.9 − 71.1 = 60.8 moles.

	Moles	Mol. wt.	Lb
n-C_5	1.8 *	72	130
n-C_7	59.0	100	5900
Total	60.8	...	6030

* 3% of bottoms.

It will be noted that the pentane in the distillate plus that in the bottoms checks with the total pentane in the feed. The same, of course, is true for the heptane. This is merely a check on the calculations up to this point.

Enthalpies of streams in process. Basis: 1 hr; liquid at 32°F; enthalpy values from Figs. A.9 and A.14.

Reflux (6) × (distillate):[1]

	Lb/hr	Δh at 80°F	Btu/hr
n-C_5	30,570	25	765,000
n-C_7	210	24	5,000
	30,780	..	770,000

---

[1] The ratio of reflux to net overhead (distillate) = 6.0/1.0. Note that this applies to each component as well as the total.

Feed:

	Lb/hr	Δh at 100°F	Btu/hr
n-C_5	5,225	35	183,000
n-C_7	5,935	34	202,000
	11,160	. .	385,000

Gross overhead vapor = reflux + distillate[1] = (7)(distillate).

	Lb/hr	ΔH at 105°F	Btu/hr
n-C_5	35,665	190	6,770,000
n-C_7	245	190	46,500
	35,910	. . .	6,816,500

Bottoms:

	Lb/hr	Δh at 200°F	Btu/hr
n-C_5	130	91	12,000
n-C_7	5,900	89	525,000
	6,030	. .	537,000

Distillate:

	Lb/hr	Δh at 80°F	Btu/hr
n-C_5	5,095	25	128,000
n-C_7	35	24	Nil
	5,130	. .	128,000

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[1] Mass balance around condenser and reflux drum. Note that each component as well as total must balance.

Gross heat balance. Basis: 1 hr; liquid at 32°F.

	Btu/hr
Output:	
Bottoms	537,000
Gross overhead	6,816,500
Total output	7,353,500
Input:	
Reflux	770,000
Feed	385,000
Reboiler (by difference)	6,198,500
Total input	7,353,500

Condenser duty[1] = heat in gross overhead − heat in reflux − heat in distillate

Duty = 6,816,500 − 770,000 − 128,000 = 5,918,500 Btu/hr

The material balances and heat balance as illustrated in Example 30 are typical of those encountered in process design of distillation equipment and processes. The heat needed to carry out the distillation is obtained by difference between the known total heat output and the known items of heat input. Of course, the chemical engineer will occasionally make process designs to fit the heat-output capacity of an existing reboiler or piece of equipment that will supply the reboiler heat duty. In such cases the other streams such as reflux will be determined by difference between the total heat input and the known output items. The reflux duty is the heat energy removed from the reflux per unit time. Thus, the reflux duty is equal to the quantity of reflux multiplied by the difference between the enthalpies of the reflux at the temperature and pressure of the gross overhead and at its temperature as it leaves the reflux drum. This, of course, is predicated upon no change in enthalpy of the reflux between the reflux drum and the top of the column, which is practically always the case.

Reflux duty in Example 30 was provided by vaporizing liquid. Frequently, however, it is supplied by a nonvaporizing reflux as illustrated in Example 31. The chief advantage of this method is that the heat can be removed from a column at high temperature and used for reboiling fractionating columns which operate at lower temperature or used to preheat various lower temperature process streams. Another advantage is that the vapor rate in the column is less and a lower pressure can sometimes be maintained on a column.

Example 31. A fractionating column is being charged with hydrocarbon vapor at 760°F from a thermal cracking coil in a petroleum-refining unit. The vapor consists of

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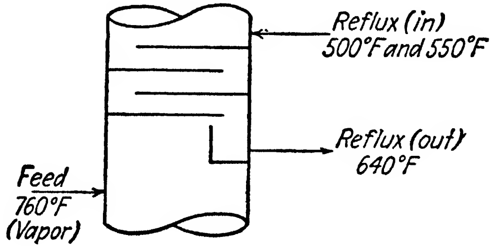
[1] "Duty" is used to designate the heat dissipated, supplied, or needed per unit time.

noncondensable gas, gasoline, and recycle gas oil (see Fig. 5.5). A vaporizing reflux is used at the top of the column, but it is desirable to remove 90,000,000 Btu/hr as intermediate reflux duty from the column at a point just above the feed by means of a nonvaporizing reflux. The temperature of the trap-out pan in the column from which the intermediate reflux would be withdrawn is 640°F. How much intermediate reflux must be recirculated if it is used to supply heat at a minimum temperature level of 500°F? How much reflux is needed if the minimum temperature level is 550°F? The enthalpies of the (liquid) reflux have been determined by the Shell Development Co. method [1] to be 367, 295, and 261 Btu/lb at 640, 550, and 500°F, respectively.

Solution:



Reflux rate:

$$\text{At } 500°\text{F minimum} = \frac{90{,}000{,}000}{367 - 261} = 849{,}000 \text{ lb/hr}$$

$$= \frac{849{,}000}{(60)(7.296)} = 1940 \text{ gal/min}$$

$$= \frac{(1940)(24)(60)}{42} = 66{,}500 \text{ bbl/day}$$

$$\text{At } 550°\text{F minimum} = \frac{90{,}000{,}000}{367 - 295} = 1{,}250{,}000 \text{ lb/hr}$$

$$= \frac{1{,}250{,}000}{(60)(7.296)} = 2850 \text{ gal/min}$$

$$= \frac{(2850)(60)(24)}{42} = 97{,}800 \text{ bbl/day}$$

It will be noted in Example 31 that the reflux duty could be used for auxiliary heating at any temperature up to 640°F merely by changing the rate of recirculation. Obviously, however, there are economic limitations on this that make it impractical to approach 640°F closely, for the recirculation rate would be infinite if all the heat were removed at 640°F.

Absorption.—The recovery of vapor by dissolving it in a selective liquid solvent is called absorption. This is another of the important unit operations of chemical engineering. It is common practice to separate one or more components of a vapor mixture by use of a solvent that has a selective

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[1] *Petroleum Refiner*, **24**, 127.

solubility for either the desired or the undesired components of the mixture. It is apparent that the objective, *viz.*, separation of the desired components from the mixture, can be attained by selectively absorbing either the desired or the undesired components. The only specific requirement is that there must be an appreciable difference between the solubilities of the desired and undesired components in the solvent.

Absorption is carried out in columns in very much the same way as fractionation. Either trays or packing may be used to obtain intimate countercurrent contacting of the vapor and solvent (absorbent). An absorption system is shown diagrammatically in Fig. 6.5.

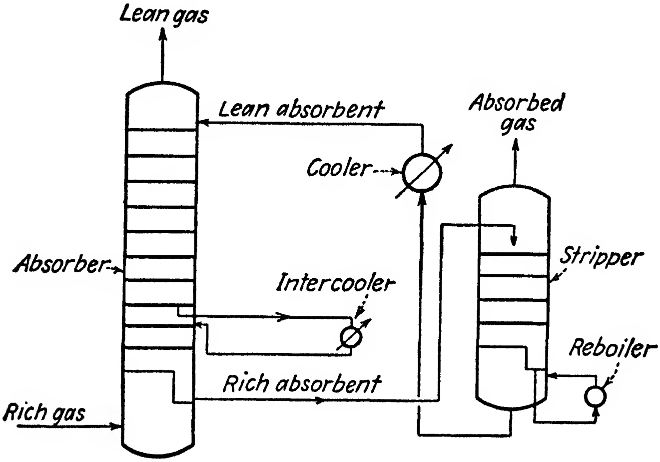

Fig. 6.5.

The rich gas, which contains the desired components, is admitted at the bottom of the absorber. The lean absorbent, which contains none or a negligible amount of the desired components, is admitted to the top of the absorber. It flows down the absorber from tray to tray or over the packing in contact with the rising gas. The lean absorbent is in contact with lean gas, and the rich absorbent is in contact with the rich gas. It will be noted in Fig. 6.5 that the liquid is trapped out of the absorber at an intermediate point, passed through an intercooler, and returned to the absorber. The reason for this is that, as the gas dissolves in the absorbent, heat is liberated owing to a latent heat effect and heat of solution. The heat of solution for nonpolar compounds such as hydrocarbons is nil, but the latent heat is important. Owing to the liberation of the latent heat and heat of solution, the temperature of the liquid rises, which in general reduces the solubility of the gases being absorbed. Thus, by removing this heat in an intercooler the absorption will be more effective. Intercoolers, however, are not always used. Each design must be considered separately to determine whether the economic benefits will justify such an installation.

The rich absorbent is sent to a stripper, where the absorbed gases are removed either by reboiling or by use of an inert vapor that is immiscible with the absorbed vapors in the liquid phase. Steam is frequently used for stripping absorbed hydrocarbon vapor from a rich absorbent, for it can be separated from the stripped gas merely by condensation.

The similarity between absorption and fractionation will be noted in Fig. 6.5. The absorber corresponds to the rectification section (above the feed point) of a fractionating column, whereas the stripper corresponds to the stripping section (below the feed point) of the fractionating column. The rectification section of a fractionating column is often called the absorption section. The reflux at the top of the rectification section corresponds to the lean absorbent in the case of absorption.

Example 32 illustrates the utility of the mass balance and energy balance on an absorber that is recovering hydrocarbon vapors. In this case the heat of solution is nil. In effect, the heat-energy exchange in absorption is identical with condensation of the absorbed vapors followed by dissolving the condensate in the absorbent. Thus, if the vapor that is absorbed could by some imaginary means be condensed from the rich gas and the condensate dissolved in the absorbent, the amount of energy transformed would be the same. This is a simplified picture upon which calculation can be based.

For a detailed treatment of absorption, the reader is referred to Sherwood.[1]

Example 32. An absorber is recovering butane and pentane from a gaseous mixture. The rich gas and lean gas are as follows:

	Moles/hr	
	Rich gas	Lean gas
Methane	852	801
Ethane	379	216
Propane	340	9
n-Butane	134	0
n-Pentane	13	0
Total	1718	1026

---

[1] SHERWOOD, T. K., "Absorption and Extraction," McGraw-Hill Book Company Inc., New York, 1937.

The lean oil used as absorbent is of such a low vapor pressure that it may be assumed that none of it is lost in the lean gas. The lean oil is at 100°F and has a gravity of 35°API. Its enthalpies at 100 and 110°F are 41.4 and 46.0 Btu/lb, respectively. The rich gas is at 100°F. The absorber operates at 225 lb/sq in. gauge. If 12,500 bbl/day of lean oil are used and the rich oil leaves the absorber at 110°F, how much heat must be removed by the intercooler?

Solution: Inasmuch as the lean gas enters and leaves the absorber at the same temperature and about the same pressure there was no change in its enthalpy. (Actually, there is usually about a 5 lb/sq in. pressure drop from the bottom to the top of an absorber to provide the driving force for the flow of gas through the absorber.) The ΔH is negligible, however, for such a slight change in pressure, as can be seen by inspecting the enthalpy values given in Figs. A.9 to A.14.

By material balance,

	Mole/hr		
	Rich gas	Lean gas	Absorbed
C_1	852	801	51
C_2	379	216	163
C_3	340	9	331
n-C_4	134	0	134
n-C_5	13	0	13
Total	1718	1026	692

Since there is no heat of solution to be accounted for (hydrocarbons are nonpolar), the only heat to be considered is that due to condensation of the absorbed vapors plus that due to heating the lean oil and condensed vapors from 100 to 110°F.

Absorbed vapors:

	Moles/hr	Mol. wt.	Lb/hr	Btu/lb			Btu/hr
				$H_{100°}^{240\text{lb}}$	$h_{110°}$	ΔH	
C_1	51	16	815	130	56	74	60,300
C_2	163	30	4,890	188	108	80	391,000
C_3	331	44	14,570	172	45	127	1,853,000
n-C_4	134	58	7,770	184	39	145	1,127,000
n-C_5	13	72	936	188	41	147	137,500
Total	692	. .	28,981	. . .	. . .	. . .	3,568,800

Lean oil

	Gal/hr	Lb/gal	Lb/hr	Btu/lb			Btu/hr
				$h_{110°}$	$h_{100°}$	Δh	
Lean oil	21,850	7.076	154,800	46.0	41.4	4.6	712,000

Net heat balance:

	Btu/hr
Input:	
Absorbed vapors	3,568,800
Total input	3,568,800
Output:	
Lean oil	712,000
Intercooler (by difference)	2,856,800
Total output	3,568,000

It will be noted that the heat of absorption in the case of Example 32 was considerable. Had it not been removed by an intercooler, it would have corresponded to a 35 to 40°F higher temperature of the rich oil. This would have affected the absorption adversely so that a greater amount of lean oil would have been necessary.

ENERGY BALANCES IN CHEMICAL PROCESSES

Combustion.—The material balance and energy balance are very informative when problems in combustion are encountered. Example 27 clearly illustrated this. There are other types of problems in combustion, however, that should be given consideration at this time—those having to do with the calculation of the theoretical flame temperature or the production of producer gas, for example.

Example 33 illustrates the calculation of the theoretical flame temperature by means of the mass balance and energy balance. The temperature of the products of combustion when fuel is burned adiabatically with air or oxygen is the theoretical flame temperature. It is dependent upon the temperature of the reactants, the relative proportion of inert gases, and the extent to which complete combustion to CO_2 and H_2O is approached. If sufficient oxygen is not supplied to convert all carbon to CO_2, the theoretical flame temperature will obviously be less than if no CO were in the products of combustion. Also, if excess oxygen is used, the theoretical flame temperature will be lower than the theoretical maximum.

Example 33. *a.* Calculate the maximum theoretical flame temperature when methane is burned with the stoichiometric amount of air (complete combustion). The reactants are in each case thoroughly mixed at 60°F.

Solution:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

$$N_2 \text{ in air} = (79/21)(2) = 7.53 \text{ moles}$$

The enthalpies in Table A.3 and the heats of combustion in Table A.5 are based on 60°F. Thus, the heat balance will not include an item due to any difference between temperature of the reactants and the base temperature (60°F), for the difference is zero. The heat of combustion will therefore be the only heat input that will show up as sensible heat of the products of combustion above 60°F. If the reactants had been at a temperature above 60°F, their sensible heat above 60°F would have represented an input item in addition to the heat of combustion.

Material balance. Basis: 1 mole of CH_4.

	Moles	
	Input	Output
CH_4	1	—
O_2	2	—
N_2	7.53	7.53
CO_2	—	1
H_2O	—	2

Gross heat balance. Basis: 60°F; 1 mole of CH_4.

	Btu
Input:	
Net heat of combustion	344,900
Output:	
Enthalpy of N_2, CO_2, and H_2O (*g*)	344,900

The enthalpies of N_2, CO_2, and H_2O in Btu per mole above T_1 °R are given by equations in Table A.3.

$$\Delta H \text{ of } CO_2 + 7.53 \quad \Delta H \text{ of } N_2 + 2 \quad \Delta H \text{ of } H_2O(g) = 344{,}900$$

where ΔH is molal enthalpy above 60°F.

For CO_2,

$$\Delta H_{60} = 6.85(T - 520) + 23.7\left[\left(\frac{T}{100}\right)^2 - \left(\frac{520}{100}\right)^2\right] - 0.254\left[\left(\frac{T}{100}\right)^3 - \left(\frac{520}{100}\right)^3\right]$$

For H_2O,

$$\Delta H_{60} = 6.89(T - 520) + 18.25\left[\left(\frac{T}{100}\right)^2 - \left(\frac{520}{100}\right)^2\right] - 0.106\left[\left(\frac{T}{100}\right)^3 - \left(\frac{520}{100}\right)^3\right]$$

For N_2,

$$\Delta H_{60} = 6.30(T - 520) + 5.05\left[\left(\frac{T}{100}\right)^2 - \left(\frac{520}{100}\right)^2\right] - 0.0355\left[\left(\frac{T}{100}\right)^3 - \left(\frac{520}{100}\right)^3\right]$$

Products of reaction:

$$\begin{aligned}\Delta H_{60} &= [6.85 + (2)(6.89) + (7.53)(6.30)(T - 520)] \\ &\quad + [23.7 + (2)(18.25) + (7.53)(5.05)]\left[\left(\frac{T}{100}\right)^2\left(\frac{520}{100}\right)^2\right] \\ &\quad - [0.254 + (2)(0.106) + (7.53)(0.0355)]\left[\left(\frac{T}{100}\right)^3 - \left(\frac{520}{100}\right)^3\right] \\ &= 68.13(T - 520) + 98.3\left[\left(\frac{T}{100}\right)^2 - \left(\frac{520}{100}\right)^2\right] - 0.734\left[\left(\frac{T}{100}\right)^3 - \left(\frac{520}{100}\right)^3\right]\end{aligned}$$

$$68.13T + 98.3\left(\frac{T}{100}\right)^2 - 0.734\left(\frac{T}{100}\right)^3 = 381{,}960$$

Solving by trial and error, assume values of T, and try them in the equations until the correct value of T is found.

$$\begin{aligned}T &= 3990°\text{R} \\ &= 3530°\text{F}\end{aligned}$$

Actually the theoretical flame temperature cannot be realized, for at such temperatures carbon dioxide dissociates into CO and O_2. Also, H_2O and CO react to form some CO_2 and H_2. Thus, the reaction of methane with oxygen as indicated in Example 33 is not exactly representative at high temperatures. Owing to the secondary reactions the total heat of combustion is not liberated until the products of combustion are cooled to a lower temperature where the secondary reactions become insignificant. The calculation of theoretical flame temperature is therefore limited by these secondary reactions, as well as other factors that need not be discussed at this time.

The application of the material balance and energy balance to the production of producer gas will now be considered. Producer gas is manufactured by passing air through a thick, incandescent bed of solid fuel. Either coal or coke is used in the industry as the solid fuel. A detailed description of the producer-gas process is given by Walker, Lewis, McAdams, and Gilliland,[1] Perry,[2] and Haslam and Russell.[3] For the present purpose it is sufficient to know merely that the air which enters the bottom of the incandescent bed of solid fuel burns carbon to CO_2. As the CO_2 passes up through the bed, much of it reacts with carbon to form CO. Also, hydrogen in the fuel reacts with oxygen to form H_2O, which reacts with carbon to form H_2 and CO. As a matter of fact, steam is commonly admitted to the incandescent bed in order to take full advantage of this reaction. The amount of steam used is about 25 per cent of the weight of carbon charged to the producer. When steam is admitted to form H_2 and CO, the gas is called water gas or blue gas.

The modern producer consists of a refractory or water-jacketed steel shell with a system for continuously or intermittently charging solid fuel at the top, a system for continuously removing ashes at the bottom,[4] a system for continuous supply of air and steam at the bottom, and a gas outlet at the top. Example 34 illustrates the utility of the material balance and energy balance on a producer.

Example 34. Producer gas of the following analysis was produced from a solid fuel:

	Vol. %
CO_2	5.0
H_2	14.0
CO	27.0
CH_4	3.0
N_2	50.5
O_2	0.5
	100.0

The proximate analysis of the coal showed 5.0 per cent moisture and 7.5 per cent ash. Its net heating value as fired was 13,900 Btu/lb. The air contained 0.013 lb of H_2O (*g*) per pound of moisture-free air and was at 90°F. The gas left the producer at 1200°F. Steam of 99.5 per cent quality[5] at 40 lb/sq in. abs was admitted at the rate of 0.35 lb/lb of coal. The coal is known to contain 77.0 per cent carbon. The tar produced was 7.5 per cent by weight of the coal. It can be represented by the formula, $(CH_2)_n$ and is 10°API. Its enthalpy as vapor at 1200°F is 705 Btu/lb above liquid at 32°F. The ash contained 8.0 per cent carbon. How much gas was produced per ton

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[1] *Op. cit.*

[2] PERRY, JOHN H., "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

[3] HASLAM, R. T., and R. P. RUSSELL, "Fuels and Their Combustion," McGraw-Hill Book Company, Inc., New York, 1925.

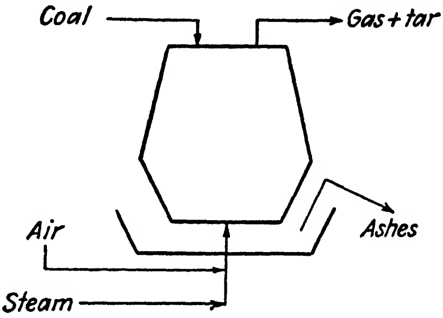
[4] If ashes are not removed continuously, a large space is provided so that removal is necessary only after long periods of operation.

[5] Quality of steam is 100 per cent minus weight per cent liquid water in it.

of coal? Make an energy balance on the producer to determine how the heating value of the coal is dissipated. What percentage of the steam including water vapor in the air and combined water in the coal was decomposed? The oxygen content of the coal can be estimated by the equation [1]

$$\frac{\text{Wt. \% carbon}}{\text{Wt. \% (oxygen + ash)}} = \frac{17{,}230}{16{,}750 - \text{Btu/lb}} - 0.98$$

Solution: By application of the material balance the amount of gas produced per ton of coal and the amount of the steam decomposed can be calculated. A balance on the ash will show how much of the carbon in the coal was transformed into gas.



Basis: 100 lb of coal as fired.

$$\text{Ash in coal} = 7.5 \text{ lb}$$

$$\text{Ashes removed} = \frac{7.5}{1.00 - 0.08} = 8.15 \text{ lb}$$

$$\text{Carbon in ashes} = 0.65 \text{ lb}$$

Carbon in tar: Such tars can be represented by the formula $(CH_2)_n$ or 0.856 lb of carbon per pound of tar.

$$\text{Carbon in tar} = (7.5)(0.856) = 6.42 \text{ lb}$$

Carbon transformed into gas: Since the carbon in the coal left the producer in the tar, gas, and ashes,

$$\text{Carbon in gas} = 77.0 - 0.65 - 6.42 = 69.93 \text{ lb}$$

$$= \frac{69.93}{12} = 5.83 \text{ moles}$$

It was shown in Example 19 (Chap. V) that nitrogen in coal can be ignored in calculations which involve a nitrogen balance. Thus, the amount of air consumed per 100 moles of producer gas can be computed by a nitrogen balance. Then, a nitrogen, oxygen, and hydrogen balance will show how much H_2O was decomposed.

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[1] HASLAM, and RUSSELL, *op. cit.*

Basis: 100 moles of dry producer gas.

	Moles	Moles		
		C	H_2	O_2
CO_2	5.0	5.0	—	5.0
H_2	14.0	—	14.0	—
CO	27.0	27.0	—	13.5
CH_4	3.0	3.0	6.0	—
O_2	0.5	—	—	0.5
N_2	50.5	—	—	—
Total	100.0	35.0	20.0	19.0
O_2 in air = $(50.5)(^{21}/_{79})$				13.4
O_2 by H_2O decomposition				5.6
H_2 by H_2O decomposition = (2)(5.6)			11.2	
H_2 from H_2 in coal			8.8	

$$\text{Coal consumed} = (100)\left(\frac{35.0}{5.83}\right) = 600 \text{ lb/100 moles of dry gas}$$

$$\text{Gas produced} = \frac{(100)(379)(2000)}{600} = 126{,}300 \text{ cu ft/ton of coal}$$

$$\text{Water decomposed} = (11.2)(18) = 202 \text{ lb/100 moles of dry producer gas}$$

or

$$^{202}/_{600} = 0.337 \text{ lb/lb of coal}$$

Inasmuch as the coal gradually passes down the bed in the producer, the moisture in the coal is evaporated and leaves with the hot gas without any opportunity to react with the incandescent coke lower in the bed. Thus, the water that was decomposed entered as steam, moisture in the air, and combined water in the coal. The combined water in the coal is a result of the oxygen in the coal, which corresponds to 2 moles of water per mole of oxygen. The oxygen content is estimated as follows:

$$\frac{\text{Wt. \% of carbon}}{\text{Wt. \% of (oxygen + ash)}} = \frac{17{,}230}{16{,}750 - \text{Btu/lb}} - 0.98$$

$$\text{Wt. \% oxygen} = \frac{77.0(16{,}750 - 13{,}900)}{17{,}230} - 0.98 - 7.5$$

$$= 12.73 - 8.48 = 4.25$$

Total water input, excluding moisture in coal. Basis: 100 moles of dry flue gas.

$$\text{Air} = 50.5 + 13.4 = 63.9 \text{ moles}$$

	Lb
H_2O in air = (0.013)(63.9)(29.0)	24.1
H_2O (as combined) = $\frac{(600)(2)(4.25)}{100}$	51.0
H_2O as steam = (0.35)(600)	210.0
Total	285.1

Steam decomposed = (202/285.1)(100) = 70.5%

Moisture in coal = (600)(0.05) = 30.0 lb

Moisture in producer gas = 30.0 + 285.1 − 202 = 113.1 lb

It is noted that the combined water as estimated was 17.9 per cent of the total H_2O available for decomposition. Even if the formula were 15 per cent in error, this would result in only a 2 per cent variation from the estimated decomposition of 70.5 per cent. The formula is within such limits of accuracy.

A gross heat balance will now be made on the producer. Basis: 100 moles of dry gas; 60°F.

The heat input will consist of the heating value of the coal, sensible heat of the air, and enthalpy of the steam above water at 60°F. Assume that the coal enters at 60°F since its effect would be small in any case. The heat output will consist of (1) the heating value of the gas, ash, and tar, (2) the sensible heat of the gas and unreacted water, (3) the enthalpy of the tar, (4) the latent heat of water that entered the producer as steam, and (5) unaccounted for.

	Btu
Input:	
Heating value of coal = (600)(13,900)	8,340,000
Sensible heat of air = (63.9)(6.99)(90–60)	13,000
Sensible heat of H_2O in air	Nil
Enthalpy of steam = $[(236.0 - 28.0) + (0.995)(933.7)](210.0)$	231,000
Total input	8,584,000
Output:	
Net heat of combustion of gas (Table A.5)	
H_2 = (14.0)(103,800)	1,455,000
CO = (27.5)(121,200)	3,330,000
CH_4 = (3.0)(344,900)	1,035,000
Sensible heat of wet gas at 1200°F	
CO_2 = (12,700)(5.0)	53,500
H_2 = (7980)(14.0)	111,700
CO = (8350)(27.0)	226,000
CH_4 = (14,200)(3.0)	42,500
N_2 = (8270)(50.5)	417,000
O_2 = (8730)(0.5)	4,300
$H_2O = (9910)\left(\frac{91.3}{18}\right)$	50,300
Heat of combustion of ash	
Carbon $= \frac{(0.65)(600)(14,090)}{100}$	55,000
Heat of combustion of tar * $= (0.075)(600)\left(\frac{145,300}{8328}\right)$	785,000
Enthalpy of tar vapor = (0.075)(600)(705)	27,200
Latent heat of water at 60°F:	
H_2O in coal and steam = (113.1 − 24.1)(1087)	96,800
Unaccounted for (10.4% on total)	894,700
	8,584,000

The unaccounted for item is slightly over 10 per cent of the net heat of combustion, which is not a satisfactory heat balance. This indicates that either the performance data or the analytical results (or both) are not as accurate as could be obtained.

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* Since the tar is a complex aromatic mixture, quite similar to petroleum fractions, the heat of combustion may be obtained from Table A.6.

Pyrolysis.—The thermal cracking of hydrocarbons as carried out in the petroleum industry (see Fig. 5.5) affords many interesting applications of the energy balance in combination with the material balance. One of the applications of the material balance was illustrated in Example 25. The heat balance is just as informative as the material balance.

When a heat balance is made on a cracking furnace, the total heat input will consist of the enthalpy of the charge, the sensible heat of the air and fuel, and the heat of combustion. The total heat output will include the sensible heat of the products of combustion, the enthalpy of the effluent from the cracking coil, and the heat of reaction due to the decomposition of hydrocarbons in the cracking coil. The latter item is commonly called the heat of cracking. It may be calculated directly if the heats of combustion of the charge and effluent are known. The heat of cracking is the difference between the heat of combustion of the effluent and the heat of combustion of the charge. This method of calculation is preferred if reliable heats of combustion and the compositions of the charge and effluent are known. Frequently, however, complex hydrocarbon mixtures are cracked, and detailed analyses of the charge and effluent are not available. In this case the heat of cracking can be estimated by means of Eq. (6.15).

$$\Delta H_c = \frac{48{,}800(M_1 - M_2)}{M_1 M_2} \tag{6.15}$$

where ΔH_c = heat of cracking, Btu/lb of charge
M_1 = molecular weight of charge
M_2 = average molecular weight of effluent

Usually sufficient data are available to estimate the average molecular weights of the charge and effluent. The heat of cracking ΔH_c as given by Eq. (6.15) is an estimate and does not justify correction when applied at different temperatures. It gives good results in practice when merely added to the total heat output. The reason for this is that the difference in sensible heat between the products and charge over a wide temperature range is relatively small compared with the heat of reaction. Thus, the heat of cracking for hydrocarbons apparently is almost constant over a wide temperature range.

Example 35. A petroleum naphtha fraction that has a gravity of 41.0°API and molecular weight of 130.0 is charged to a cracking coil at the rate of 9000 bbl [1]/day. The effluent from the coil contained 84.5 gal of gasoline (liquid) per 100 gal [1] of charge, which had a gravity of 46.6°API and a molecular weight of 115.2. Also, the effluent

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[1] Where liquid volumes such as barrels or gallons are quoted, they will always be referred to 60°F unless otherwise stated.

contained 13.1 gal of tar of 250 molecular weight and 10°API per 100 gal[1] of charge and 13.8 lb of gas of the following analysis per 100 lb of charge:

	Mole %
Methane	35.8
Ethylene	8.3
Ethane	21.9
Propylene	16.7
Propane	17.3
Total	100.0

The enthalpies, relative to liquid at 32°F, of the charge and the gasoline and tar in the coil effluent are 331, 715 and 662 Btu/lb, respectively. How much heat was transferred per hour by the cracking coil?

Solution: A material balance will be made to obtain the yield of products and average molecular weight.

	Gas			
	Moles	Mol. wt.	Lb	Wt. %
C_1	35.8	16	573	19.6
$C_{2=}$	8.3	28	232	7.9
C_2	21.9	30	656	22.4
$C_{3=}$	16.7	42	701	24.0
C_3	17.3	44	761	26.1
Total	100.0	29.23	2923	100.0

Material balance. Basis: 100 gal of charge.

	Gal	Deg API	Lb/gal	Lb	Mol. wt.	Moles
Charge	100.0	41.0	6.83	683	130	
Products						
Gasoline	84.5	46.6	6.615	559	115.2	4.85
Gas						
C_1 (683)(0.138)(0.196)				18.5		
$C_{2=}$ (683)(0.138)(0.076)				7.5		
C_2 (683)(0.138)(0.224)				21.2		
$C_{3=}$ (683)(0.138)(0.240)				22.6		
C_3 (683)(0.138)(0.260)				24.6		
				94.4	29.2	3.23
Tar	2.0	10	8.328	16.6	250	0.07
Total Products	.....	.....	.....	670.0	82.2	8.15

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[1] Where liquid volumes such as barrels or gallons are quoted, they will always be referred to 60°F unless otherwise stated.

Thus, it is noted that 13.0 lb was unaccounted for. This is 1.9 per cent on charge, which is a fairly good balance.

A heat balance will be made to determine the heat transferred by the coil. The heat balance will be based on the unaccounted for mass being included in the tar.

Enthalpy of products at 996°F (vapor) (Figs. A.9 to A.14):

Products	Lb	Btu/lb	Btu
Gasoline..............	559	715	400,000
Gas:			
C_1	18.5	860	15,900
$C_{2=}$	7.5	690	5,200
C_2	21.2	812	17,200
$C_{3=}$	22.6	730	16,500
C_3	24.6	770	19,000
Tar..................	29.6	662	19,800
Total products.....	683.0	722	493,400

Heat of cracking per pound of charge.

$$\Delta H_c = \frac{48{,}800(130 - 82.2)}{(130)(82.2)} = 218 \text{ Btu/lb}$$

Net heat balance. Basis: 1 hr.

	Btu
Output:	
Enthalpy of effluent $= \dfrac{(9000)(42)(6.83)(722 - 331)}{24}$	42,000,000
Heat of cracking $= \dfrac{(9000)(42)(6.83)(218)}{24}$	23,500,000
Total output	65,500,000
Input:	
Total heat transferred	65,500,000

It is of interest to note in Example 35 that, of the total heat transferred by the coil to the hydrocarbons, 35.9 per cent was consumed as heat of cracking. It is apparent that a process design which did not include heat of cracking might be far short of desired capacity.

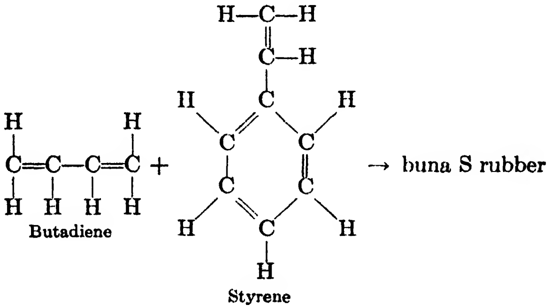
Polymerization.—Another of the important chemical processes with which the chemical engineer deals is polymerization. It will be recalled from Chap. IV that this involves the chemical reaction by complete addition of reacting molecules to produce molecules of substantially higher molecular weight. For example, the reaction of acetylene to form benzene is polymerization.

$$3C_2H_2 \rightarrow C_6H_6$$

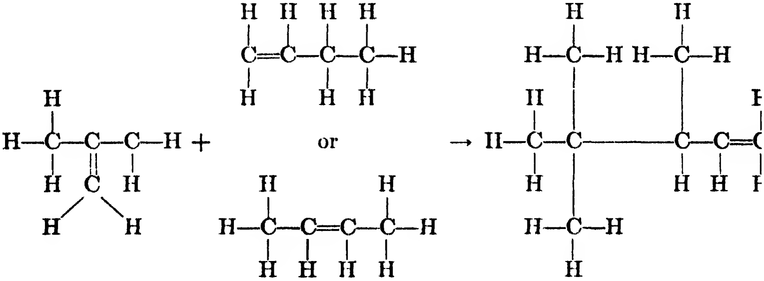
Benzene in this case is a polymer of acetylene.

In many cases the polymers attain huge molecular weights, even well over 100,000. An example of this is the production of plastics by polymerization of ethylene (C_2H_4).

Another type of polymerization that is of great importance is the reaction between two unlike molecules to form molecules seemingly of almost unlimited size. Buna S synthetic rubber is of this type. It is formed by the copolymerization of butadiene with styrene.



One of the methods of producing aviation gasoline is to copolymerize isobutylene with either of the normal butylenes to form iso-octene, which is then hydrogenated to iso-octane. The iso-octene is called a codimer because it is made up of only two molecules.



Isobutylene + n-butylenes → iso-octene

Iso-octene + hydrogen → iso-octane

The structural formula for iso-octene as shown is merely typical. The actual copolymer is a mixture of different iso-octenes.

High-quality automobile gasoline is produced by the copolymerization of the three butylenes. The copolymer is not of a high molecular weight since it is composed primarily of codimers and cotrimers. A cotrimer is made up of three of the reacting molecules.

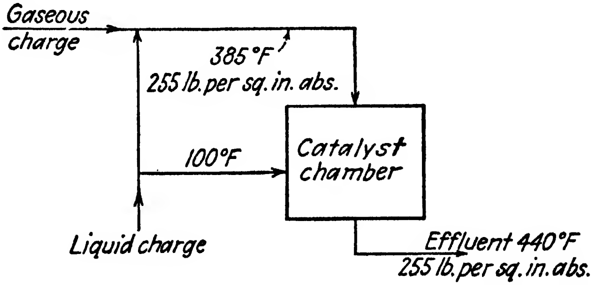
Polymerization is ordinarily an exothermic reaction, and the removal of the heat of reaction sometimes presents quite a problem to the chemical engineer inasmuch as the temperature of many of the polymerization reactions must be controlled within limits that necessitate continuous removal of the heat of reaction. Example 36 describes such a case in connection with the polymerization of butylenes and propylene.

Example 36. A process design is being made of a catalytic polymerization plant to process the following material:

	Charge, moles/hr	
	Gas	Liquid
Methane	735.0	—
Ethylene	105.0	—
Ethane	347.0	—
Propylene	380.0	—
Propane	530.0	—
Isobutane	—	165.0
Isobutylene	—	115.0
Butene-2	—	175.0
Butene-1	—	170.0
n-Butane	—	381.0
n-Pentane	—	67.0
Total	2097.0	1073.0

Automobile gasoline will be produced. The catalyst is a granular bed of solid particles. Each particle is about ⅜ in. in diameter. The gas will flow downward through the catalyst bed. In order not to injure the catalyst the temperature of the gas in the catalyst chamber will be controlled below a maximum of 440°F. This will be accomplished by injecting part of the liquid charge directly into the catalyst chamber at proper points so that the temperature of the gas in the chamber will fluctuate between 400 and 440°F. The temperature of the effluent of the chamber will be 440°F at 240 lb/sq in. gauge. The liquid charge is available at 100°F, but that portion not used for temperature control will be mixed with the gas charge and heated to 385°F at 250 lb/sq in. gauge. The effluent of the catalyst chamber will contain 6 moles of propylene plus butylenes per 100 moles of effluent exclusive of copolymer. The ratio of propylene to butylenes in the effluent will be equal to the ratio of the moles of propylene to the sum of the moles of butene-1 and butene-2 charged to the catalyst chamber. It may be assumed that the butylenes in the catalyst effluent are entirely butene-2 inasmuch as the catalyst not only promotes polymerization but also isomerizes butene-1 to butene-2. None of the ethylene reacts, but all the isobutylene is polymerized. The polymer produced has a molecular weight of 103.5 and a gravity of 61.9°API. How much polymer (barrels per day) will be produced? How much of the liquid charge will be needed for temperature control in the catalyst chamber? The enthalpy of the polymer as vapor at the operating pressure, relative to liquid at 32°F, is 350 Btu/lb at 440°F and 320 Btu/lb at 385°F.

Solution: By material balance the production of polymer and the heat of reaction can be computed. Then, by heat balance the amount of liquid for temperature control can be determined.



Material balance:

Total charge to catalyst	3170.0 moles
Total $C_{3=} + C_{4=}$ to catalyst	840.0 moles
Inert gas in charge	2330.0 moles

Since there will be 6 moles of $(C_{3=} + C_{4=})/100$ (exclusive of polymer),

$$C_{3=} + C_{4=} \text{ in effluent} = (2330)(6/94) = \qquad 148.8 \text{ moles}$$

$$\frac{C_{3=}}{C_{4=}} \text{ in effluent} = \frac{380}{175 + 170} = \qquad 1.1 \text{ moles}$$

$$C_{3=} \text{ in effluent} = \left(\frac{1.1}{1.1 + 1}\right)(148.8) = \qquad 78.0 \text{ moles}$$

$2\text{-}C_{4=}$ in effluent = 70.8 moles

$C_{3=}$ polymerized = 380.0 − 78.0 = 302.0 moles

$i\text{-}C_{4=}$ polymerized = 115.0 moles

$1\text{-}C_{4=}$ disappearance = 170.0 moles

$2\text{-}C_{4=}$ disappearance = 175 − 70.8 = 104.2 moles

Total $C_{4=}$ polymerized = 389.2 moles

Polymer from $C_{3=}$ = (302.0)(42) = 12,700 lb

Polymer from $C_{4=}$ = (389.2)(56) = 21,800 lb

Total polymer = 34,500 lb

$$\text{Total polymer} = \frac{(34{,}500)(24)}{(6.09)(42)} \quad \ldots\ldots\ldots\ldots \quad 3{,}240 \text{ bbl/day}$$

$$= \frac{34{,}500}{103.5} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 333.0 \text{ bbl/day}$$

Total charge	Moles/hr	Mol. wt.	Lb/hr
C_1	735.0	16	11,750
$C_{2=}$	105.0	28	2,940
C_2	347.0	30	10,430
$C_{3=}$	380.0	42	15,980
C_3	530.0	44	23,350
i-C_4	165.0	58	9,570
i-$C_{4=}$	115.0	56	6,450
2-$C_{4=}$	175.0	56	9,800
1-$C_{4=}$	170.0	56	9,520
n-C_4	381.0	58	22,100
n-C_5	67.0	72	4,820
Total	3,170.0	40	126,710

Total effluent	Moles/hr	Mol. wt.	Lb/hr
C_1	735.0	16	11,750
$C_{2=}$	105.0	28	2,940
C_2	347.0	30	10,430
$C_{3=}$	78.0	42	3,280
C_3	530.0	44	23,350
i-C_4	165.0	58	9,570
i-$C_{4=}$	—	56	—
2-$C_{4=}$	70.8	56	3,970
1-$C_{4=}$	—	56	—
n-C_4	381.0	58	22,100
n-C_5	67.0	72	4,820
Polymer	333.0	103.5	34,500
Total	2,811.8	45.0	126,710

Heat balance: The heat of polymerization will be calculated by Eq. (6.15). However, since those components in the charge which reacted are known, the equation will be applied to them in order to improve the accuracy of $M_1 - M_2$.

Components polymerized:

	Moles/hr	Mol. wt.	Lb/hr
$C_{3=}$	302.0	42	12,700
$C_{4=}$	389.2	56	21,800
Total	691.2	50.0	34,500

$$\Delta H = \frac{48{,}800(50.0 - 103.5)}{(50.0)(103.5)} = -504 \text{ Btu/lb}$$

Thus, the reaction is exothermic.

$$\text{Heat evolved} = (504)(34{,}500) = 17{,}400{,}000 \text{ Btu/hr}$$

The calculation could have been based on the total charge and total effluent, in which case

$$\Delta H = \frac{48{,}800(40 - 50)}{(40)(50)} = -136 \text{ Btu/lb}$$

$$\text{Heat evolved} = (136)(126{,}710) = 17{,}200{,}000 \text{ Btu/hr}$$

It will be noted, however, that the difference between M_1 and M_2 is relatively smaller in the second case, which reduces the accuracy.

Gross heat balance. Basis: 1 hr; vapor at 385°F and 265 lb/sq in. abs. Enthalpies of charge and products obtained from Figs. A.9 to A.14.

Output:
Sensible heat:

	Lb	Vapor, Btu/lb			Btu
		440°	385°	ΔH	
C_1	11,750	345	306	39	459,000
$C_{2=}$	2,940	324	296	28	82,300
C_2	10,430	376	343	33	344,000
$C_{3=}$	3,280	348	318	30	98,400
C_3	23,350	355	322	33	771,000
C_4	9,570	331	299	32	307,000
2-$C_{4=}$	3,970	348	317	31	123,000
C_4	22,100	340	308	32	707,000
C_5	4,820	331	300	31	149,600
Polymer	34,500	350	320	30	1,037,000
	126,710	. . .	. . .	. .	4,078,300

	Btu
Input:	
Heat of polymerization	17,200,000
Sensible heat (by difference)	−13,122,000
Total	4,078,000

Enthalpy difference between vapor at 385°F and 265 lb/sq in. abs and liquid at 100°F for liquid charge:

	Lb	Btu/lb			Btu
		Vapor 385°	Liquid 100°	ΔH	
Isobutane	9,570	299	36	263	2,520,000
Isobutylene	6,450	309	36	273	1,760,000
Butene-2	9,800	317	35	272	2,670,000
Butene-1	9,520	317 *	35 *	272	2,590,000
n-Butane	22,100	308	34	274	6,050,000
n-Pentane	4,820	300	35	265	1,277,000
	62,260	...	..	271	16,867,000

* Assume same as butene-2.

Thus, each pound of the liquid charge used for cooling will consume 271 Btu relative to 385°F (vapor).

$$\text{Liquid required for temperature control} = \frac{13{,}122{,}000}{271} = 48{,}400 \text{ lb/day}$$

$$= \frac{(48{,}400)(100)}{62{,}260} = 77.7\% \text{ of liquid charge}$$

If exact heat-of-reaction data were available for the polymerization reaction, they should be used. In the absence of such data, Eq. (6.15) can be used for hydrocarbons. It seems to give results that check closely with commercial operation. Its application should be confined to hydrocarbons, however, and even then it may not be valid for the production of high polymers. When the difference between M_1 and M_2 becomes greater than 100, it should be used with caution.

Alkylation.—It will be recalled from Chap. IV that the reaction between an olefin and an aromatic, naphthenic, or paraffinic hydrocarbon in which the olefin combines with the other hydrocarbon to form one molecule is called alkylation. For example, the reaction between ethylene and benzene to form ethyl benzene is an alkylation reaction, as pointed out in Chap. IV.

Alkylation has many applications of great importance to the chemical engineer. In recent years the commercialization of the alkylation of butylene with isobutane to form iso-octane has advanced rapidly. The alkylation of an olefin with an isoparaffin was thought to be impossible prior to about 1930. Even so, it was accomplished, and this reaction became one of the most important sources of high-grade aviation gasoline during the Second World War.

There are two leading processes for the alkylation of butylene with isobutane, *viz.*, an earlier development, which uses sulfuric acid as a catalyst, and a later development, which uses anhydrous HF as a catalyst. The processes are quite similar in many respects. Consequently, description here will be confined to the process which uses sulfuric acid as a catalyst. Figure 6.6 presents a simplified flow sheet of the process.

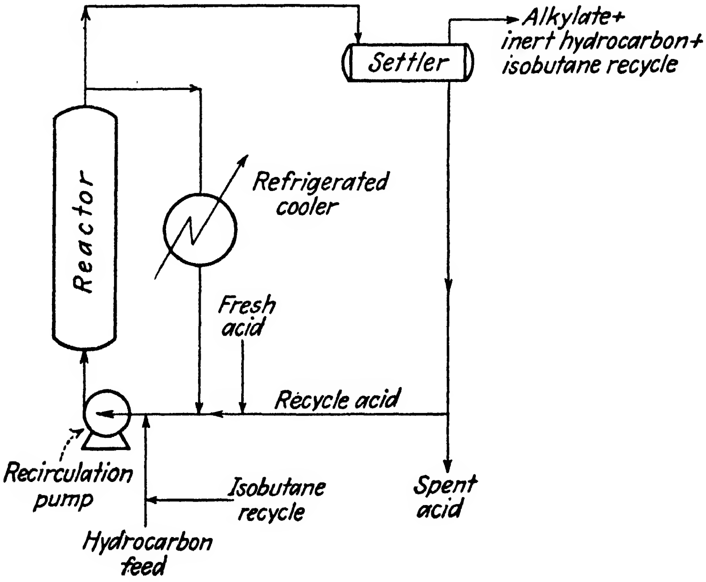


FIG. 6.6.

The alkylation reaction is carried out in an emulsion of sulfuric acid in the hydrocarbon phase. The emulsion is maintained by vigorous recirculation of the sulfuric acid and hydrocarbon phases from the reactor through a pump and back to the reactor. The pump is of a type that provides intimate mixing of the two phases. As a matter of fact, in certain designs the pump is called a mixer.

The reaction is preferably carried out at 40 to 50°F since the quality of the alkylate as an aviation gasoline is somewhat better than if a higher temperature obtains. Since the reaction is exothermic, it is necessary to provide refrigeration for the reactor. The refrigeration must be sufficient to handle the heat of alkylation plus the mechanical energy transformed into heat energy by the recirculation pump. The latter item becomes quite significant in this case although in most processes it is negligible. The chemical engineer should keep it in mind, however, in any process design he makes.

Sulfuric acid is a very good polymerization catalyst, and therefore the concentration of butylene must be nil or butylene polymer will be formed. In order to avoid this, a very high mole ratio (usually over 100/1) of isobutane to butylene is maintained in the reactor. This is called the internal ratio. In order to do this there must be an excess of isobutane in the hydrocarbon feed to the unit. Then, by distillation the excess can be separated and recycled to the reactor. Usually the mole ratio of isobutane to butylene in the combined stream of isobutane recycle and hydrocarbon feed is 4/1 to 8/1. This is called the external ratio. The higher the external ratio, the better the quality of alkylate; but improvement strikes the point of diminishing returns at about 8/1 ratio.

The refrigeration may be obtained merely by evaporation of butanes from the reactor. This is done by maintaining a vapor space at the top of the reactor or in a drum outside the reactor. The pressure in the vapor space is automatically controlled by a pressure regulator, which releases vapor from the vapor space in order to maintain the desired temperature. This type of refrigeration is called autorefrigeration. It has the advantage of eliminating a tubular cooler since the refrigerant is a part of the process stream.

Example 37. A process design of an alkylation plant is being made to process 5000 bbl/day of a hydrocarbon stream that contains the following:

	Mole %
i-C_4	32.0
$C_{4=}$	29.0
n-C_4	39.0
Total	100.0

The alkylate (predominately iso-octane) after being debutanized has a molecular weight of 114 and a gravity of 71.5°API. The design is being based on maintaining an external mole ratio of 5/1 and an internal mole ratio of 200/1 at the recirculation pump, where the combined feed and recirculated stream mix. The reactor will operate at 45°F. The acid in the emulsion corresponds to 40 volumes of 91 per cent H_2SO_4 per 100 volumes of the combined hydrocarbon feed (recycle i-C_4 + fresh feed) to the reactor. There is no butylene unreacted at the outlet of the reactor. The acid consumed is 1.2 lb/gal of alkylate produced. How much refrigeration must be provided if the heat of reaction is 320 Btu/lb of alkylate relative to 45°F, the combined hydrocarbon feed and fresh acid (96 per cent) at 70°F, and the recirculation pump expends 300 hp on the emulsion? Allow 33.3 per cent additional refrigeration to provide for flexibility of operation and radiation. How much alkylate will be produced? Assume that only the alkylation reaction takes place, *viz.*, that one mole of butylene combines with one mole of isobutane to produce iso-octanes.

Solution: A material balance will be made to itemize each input and output item, which will disclose the amount of alkylate produced. A heat balance will then be made to determine the refrigeration capacity that must be provided.

Feed:

	Moles	Mol. wt.	Lb	Lb/gal	Gal
i-C_4	32.0	58	1860	4.72	394
$C_{4=}$	29.0	56	1625	5.07 *	320
n-C_4	39.0	58	2265	4.87	465
	100.0	..	5750	4.89	1179

* Average of pounds per gallon for the three butylenes.

	Gal/hr	Lb/gal	Lb/hr	Mol. wt.	Moles/hr
i-C_4	2,920	4.72	13,800	58	238
$C_{4=}$	2,380	5.07	12,070	56	216
n-C_4	3,450	4.87	16,830	58	290
Total	8,750	4.89	42,700	57.5	744

Alkylate:

	Moles/hr	Mol. wt.	Lb/hr	Lb/gal	Gal/hr
i-C_4	216	58	12,530	4.72	2,650
$C_{4=}$	216	56	12,070	5.07	2,380
Alkylate	216	114	24,600	5.802	4,220

Thus, the alkylate production will be 4220 gal/hr or 2410 bbl/day.

	Moles/hr
i-C_4 in combined feed = (5)(216)	1080
i-C_4 in fresh feed	238
i-C_4 recycle	842

Combined hydrocarbon feed:

	Moles/hr	Mol. wt.	Lb/hr	Lb/gal	Gal/hr
i-C_4	1,080	58	62,600	4.72	13,270
$C_{4=}$	216	56	12,070	5.07	2,380
n-C_4	290	58	16,830	4.87	3,450
	1,586	..	91,500	....	19,100

Product hydrocarbons from reactor system:

	Moles/hr	Mol. wt.	Lb/hr	Lb/gal	Gal/hr
i-C_4	864	58	50,070	4.72	10,620
n-C_4	290	58	16,830	4.87	3,450
Alkylate	216	114	24,600	5.802	4,220
	1,370	...	91,500	.....	18,290

Recirculation rate:

Ratio of moles i-$C_4/C_{4=} = 200/1$

	Moles/hr
i-C_4 to pump = (200)(216)	43,200
i-C_4 in combined feed	1,080
i-C_4 recirculated	42,120

Since the hydrocarbon composition in the recirculated emulsion is identical with the hydrocarbon products eliminated from the reaction system,

$$\text{Hydrocarbons in emulsion} = \left(\frac{42{,}120}{864}\right)(1370) = 66{,}750 \text{ moles/hr}$$

$$\text{Hydrocarbons in emulsion} = \left(\frac{42{,}120}{864}\right)(91{,}500) = 4{,}455{,}000 \text{ lb/hr}$$

$$\text{Hydrocarbons in emulsion} = \left(\frac{42{,}120}{864}\right)(18{,}290) = 891{,}000 \text{ gal/hr}$$

$$\text{Acid (91\%) in emulsion} = (^{40}\!/_{60})(891{,}000) = 594{,}000 \text{ gal/hr}$$

$$\text{Acid (91\%) in emulsion} = (594{,}000)(15.2)^{*} = 9{,}020{,}000 \text{ lb/hr}$$

Total emulsion recirculated:

Lb/hr = 13,475,000

Gal/hr = 1,485,000

$$\text{Fresh acid (96\%) required} = (1.2)(4220) = 5060 \text{ lb/hr}$$

The spent acid is 91 per cent acidity. The reduction is due to absorption of water brought into the reactor with the combined hydrocarbon feed and to dissolving some hydrocarbons, which reacted with the acid. Assuming it all to be water,

$$\text{Water content} = \left(\frac{0.96 - 0.91}{0.91}\right)(5060) = 280 \text{ lb/hr}$$

Material balance on reactor. Basis: 1 hr.

	Lb/hr
Input:	
Feed	
i-C_4	13,800
$C_{4=}$	12,070
n-C_4	16,830
i-C_4 recycle	48,800
Recirculation	
$i\text{-}C_4 = \left(\frac{42{,}120}{864}\right)(50{,}070)$	2,440,000
$n\text{-}C_4 = \left(\frac{42{,}120}{864}\right)(16{,}830)$	819,000
$\text{Alkylate} = \left(\frac{42{,}120}{864}\right)(24{,}600)$	1,196,000
Acid	9,020,000
Fresh acid	5,060
Water in hydrocarbons	280
Recycle acid $= (^{40}\!/_{60})(4220)(15.2)$	42,800
Total input to reactor	13,614,640

---

[*] Pounds per gallon for 91.0 per cent H_2SO_4 (Table A.1). Actually the reduction in acidity is due primarily to reaction between the acid and hydrocarbons, but to simplify the calculations it will be assumed that the reduction in acidity is due entirely to water absorption. This assumption will have little effect on the final conclusions.

Output:	
Hydrocarbon product	
i-C_4	50,070
n-C_4	16,830
Alkylate	24,600
Acid to settler (91%)	48,140
Recirculation:	
i-C_4	2,440,000
n-C_4	819,000
Alkylate	1,196,000
Acid	9,020,000
Total output from reactor	13,614,640

Heat balance on reactor system. Basis: 1 hr; liquid at 45°F.

	Btu
Input:	
Feed	
i-C_4 = (13,800)(20 − 7)	180,000
$C_{4=}$ = (12,070)(20 − 7)	157,000
n-C_4 = (16,830)(19 − 7)	202,000
Fresh acid = (5060)(70 − 45)(0.35) *	44,000
Water in hydrocarbons = (280)(38 − 13)	7,000
Recycle i-C_4 = (48,800)(20 − 7)	634,000
Heat of reaction = (24,600)(320)	7,870,000
Recirculation pump = $\frac{(300)(33{,}000)(60)}{778}$	693,000
Total input	9,787,000
Output:	
Refrigeration (theoretical)	9,787,000

Actual refrigeration capacity to be installed should be (9,787,000)(1.33), or 13,050,000, Btu/hr, or

$$\frac{13{,}050{,}000}{(60)(200)} = 1090 \text{ tons of refrigeration}$$

* Figure A.6.

PROBLEMS

1. How much sensible heat above gas at 60°F does the following gaseous mixture contain at atmospheric pressure and 500°F? How much at 1800°F?

	Moles
CO_2	12.0
O_2	3.5
N_2	78.5
H_2O	6.0
Total	100.0

2. How much sensible heat does the following gaseous mixture at 600°F and 100 lb/sq in. abs contain above liquid at 100°F?

	Moles
Propane	40.0
n-Butane	30.0
Isobutane	20.0
n-Pentane	10.0
Total	100.0

3. The following vapor mixture at 300°F and 325 lb/sq in. abs is sent to a condenser. Part of the vapor is condensed. Both the condensate and uncondensed vapor leave the condenser at 100°F and essentially 325 lb/sq in. abs.

	Vapor entering, moles/hr	Uncondensed vapor, moles/hr
Methane	156	140
Ethane	232	150
Propylene	179	76
Propane	374	155
Isobutylene	81	21
n-Butane	106	23
Total	1128	565

If water is used as the cooling medium and is available at 80°F, how much water in gallons per minute is required if it leaves the condenser at 90°F? If 30°API virgin gas oil is the cooling medium and is available at 85°F, how much oil is needed in barrels per day if it leaves the condenser at 95°F?

4. Natural gas, which consists essentially of pure methane, is available as fuel at 60°F and 20 lb/sq in. abs. Cracked gas oil (28°API) at 300°F (liquid) is to be vaporized at 700°F and 25 lb/sq in. gauge in a furnace that contains the necessary tubes to transfer the required heat. The furnace will operate at an over-all thermal efficiency of 80.0 per cent, based on net heating value. How much fuel will be required for 10,000 bbl/day of gas oil? If 30 per cent excess air is used, the flue gases leave the furnace at 600°F, and the radiation loss from the furnace is negligible, how much fuel would be required? Air is at 100°F. The enthalpies of the gas oil are 132 Btu/lb in the liquid phase at 300°F and 483 Btu/lb in the vapor phase at 700°F and 25 lb/sq in. gauge.

5. The gas oil from the furnace in Prob. 4 is charged to a fractionating column, and a net overhead product of 30°API is removed. A bottoms product that is 10 per cent by liquid volume of the charge is eliminated from the column at 650°F. The gross overhead leaves the column at 350°F and 10 lb/sq in. gauge. The overhead condenser operates with complete condensation. The reflux drum, from which both reflux and net overhead product are removed, is at 100°F. How much reflux must be supplied? The enthalpies of the overhead are 283 Btu/lb in the vapor state at 350°F and 10 lb/sq in. gauge, and 28.5 Btu 1 lb in the liquid state at 100°F. The enthalpy of the bottoms is 337 Btu/lb in the liquid phase at 650°F.

6. A fractionating column is separating a net overhead of composition given below. The overhead condenser operates with partial condensation to provide reflux, the composition of which is also given.

	Net overhead, moles/hr	Reflux, mole %
Propane	51.8	88.0
n-Butane	2.7	12.0
Total	54.5	100.0

The reflux drum is at 115°F and 195 lb/sq in. gauge. The gross overhead to the condenser is at 127°F and 200 lb/sq in. gauge. The mole ratio of reflux to net overhead is 12/1. The composition of the liquid on the top tray of the column is as follows:

	Mole %
Propane	75.5
n-Butane	24.5

What are the compositiod and quantity per hour of vapor that passes from the second tray from the top to the top tray? The vapor is at 138°F.

7. An overhead condenser of a fractionating column is operated with complete condensation. The net overhead, which has the following analysis, is withdrawn from the reflux drum at the rate of 500 moles/hr.

	Mole %
Methane	1.2
Ethane	9.5
Propylene	1.4
Propane	80.4
Isobutane	3.5
n-Butane	4.0
Total	100.0

The mole reflux ratio is 4/1. The vapor leaves the column at 160°F and 350 lb/sq in. abs. The reflux drum is at 125°F. Water is used as cooling medium in the condenser, with inlet and outlet temperatures of 85 and 110°F, respectively. How much water in gallons per minute is needed?

8. Hydrocarbon fuel gas is being burned in a furnace with air that contains 0.01 lb of water vapor per pound of dry air. The flue gas leaves at 650°F and has the following Orsat analysis:

	Vol. %
CO_2	11.0
O_2	2.0
N_2	87.0
Total	100.0

The air enters at 100°F, and the fuel gas enters at 60°F. Assuming no radiation loss, what was the thermal efficiency, based on net heating value of the fuel gas?

CHAPTER VII

STATIC EQUILIBRIA

The objective in this chapter is to present another (the third) of the technical fundamentals of chemical engineering, *i.e.*, static equilibrium relations. When static equilibrium relations are combined with the material balance and energy balance, a very effective attack can be made on a variety of problems that the chemical engineer encounters.

This fundamental cannot be developed as fully at this time as were the material balance and the energy balance, for the text is intended primarily for the student who does not possess a knowledge of chemical-engineering thermodynamics, much of which deals with equilibria. After the student has a knowledge of thermodynamics, his perspective of the application of static equilibria will be somewhat broadened beyond the scope of this book. Even so, the philosophy can be grasped without the aid of a knowledge of thermodynamics, and in the more advanced studies, the philosophy is identical with that of the level of this book.

The application of static equilibrium relations is frequently called an equilibrium balance in chemical-engineering practice. Inasmuch as "equilibrium" signifies a balance of driving forces such as temperature, pressure, mass concentration gradients, etc., within a system, the term "equilibrium balance" is not entirely sound. Nevertheless, the term "equilibrium balance" is often used in practice and should be understood as the application of static equilibrium relations.

Equilibrium is a balance of the intensive factors of the system. It will be recalled that intensive factors do not change with the size of the system. Temperature, pressure, component concentration, etc., are intensive factors. They are referred to frequently as driving forces. A system is in equilibrium when all driving forces within the system have become balanced and there is no further tendency for change. The student, however, must not confuse stable equilibrium with unstable equilibrium. Stable equilibrium is identified by balanced driving forces such that an infinitesimal change in one of the forces will shift the equilibrium in the direction of the change in driving force. Unstable equilibrium is one which has a tendency to change but in which owing to a high resistance no change takes place. An example of unstable equilibrium is a mass on an inclined plane. The pitch of the plane can be increased gradually from the horizontal position. At first the mass will remain stationary owing to friction even though the force of gravity *tends* to make it slide down the plane. The pitch finally will reach a point where the mass begins to move. Once it is in motion, the mass will slide to the bottom of the plane, where there is no further tendency for movement. When the mass was stationary on the inclined plane, it was in a state of unstable equilibrium, for variation of the pitch of the incline had no effect at first. Once the resistance to movement was overcome, the mass moved to a state of stable equilibrium in which there was no further *tendency* for change. If the plane were polished and the same experiment repeated, it would be found that the mass would begin to move at a lower pitch than previously. This is a result of a reduction in the resistance to the change toward true or stable equilibrium.

A similar phenomenon is observed in the case of chemical reactions. For example, if oxygen and hydrogen gases are mixed at atmospheric pressure and room temperature, no apparent reaction will take place because of a resistance to the reaction. Hence, this system is in a state of unstable equilibrium, for there is considerable *tendency* for the oxygen and hydrogen to react. Furthermore, if additional oxygen, hydrogen, or water vapor is admitted to the system, no effect is observed, which is further evidence of an unstable equilibrium condition. A slight amount of energy such as an electric spark, however, will set off the reaction. This is also evidence that the system was in an unstable equilibrium state before the spark was admitted. On the other hand, if the original mixture of hydrogen and oxygen had been subjected to a temperature of 2000°C, instead of room temperature, hydrogen and oxygen would have existed in stable equilibrium with the water vapor formed by their reaction. Furthermore, the addition of hydrogen, oxygen, or water vapor to the system would result in a shift in the equilibrium concentrations, due to mass action. This is evidence of a true, or stable, state of equilibrium.

The chemical engineer deals with two types of stable equilibrium, *viz.*, static and dynamic. The static type is encountered in closed, or batch, systems, whereas the dynamic type occurs in continuous processes. An example of the dynamic type is the flow of a fluid through a tube. As long as the flow rate and characteristics of the fluid are constant, there will be a pressure gradient[1] through the tube that is in a state of equilibrium. That is, the pressure at any specific point along the tube will remain fixed, although there will be a pressure gradient from the inlet to the outlet. The pressure is therefore in a dynamic stable equilibrium. Now if there

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[1] The term "gradient" signifies variation of an intensive factor with respect to distance. Thus, pressure gradient is dP/dL, and temperature gradient is dt/dL, where L represents distance.

is a valve at the outlet of the tube and it is closed, the flow of fluid will stop and the pressure within the tube will become the same from the inlet to the valve. The system has thus been changed into a static stable equilibrium with respect to pressure. In this chapter only static stable equilibria will be considered. These will be referred to merely as static equilibria. Dynamic stable equilibria will be treated in the following chapter, for they involve rates of mass and energy transfer that will be discussed then.

Static equilibrium is independent of time. Equilibrium conditions can be determined, but in their determination no information is obtained on how long it would take for the state of equilibrium to be reached. Even so, a knowledge of static equilibrium is valuable since many chemical and physical changes occur so rapidly that, in such cases, static equilibria for all practical purposes actually prevail in continuous processes. This will be understood more fully later in the chapter when various examples are presented.

The following discussion on general principles will cover pressure, thermal, phase, diffusion, and chemical-reaction equilibria. Then, applications of these equilibrium relations in combination with the material balance and energy balance to several unit operations and chemical processes will be illustrated.

Pressure Equilibrium.—Consider two cylinders of a gas, each at identical temperature but at different pressures, connected by a tube that contains a valve. Assume also that the cylinders will be maintained under isothermal conditions. As soon as the valve is opened, however, the gas in the cylinder at the higher pressure will flow into the cylinder of lower pressure until the pressure in the two cylinders is identical. Hence, the intensive factor (driving force) pressure has become balanced between the two cylinders, and there is no further tendency for it to change. The system is in static equilibrium; for if a small amount of gas were added to one of the cylinders, the pressure in that cylinder would rise slightly and there would be a flow of gas into the other cylinder until the pressure in each was again identical.

Equilibrium pressure cannot be calculated by an average of the initial pressures, for the extensive factors (volume in this case) may be considerably different. Thus, the calculation must also consider the extensive factors. If the gas in each cylinder obeys the ideal-gas law, the equilibrium pressure can be calculated by use of that relationship,

$$P_A V_A = n_A RT \qquad \text{or} \qquad n_A = \frac{P_A V_A}{RT}$$

$$P_B V_B = n_B RT \qquad \text{or} \qquad n_B = \frac{P_B V_B}{RT}$$

where the subscripts A and B refer to the respective cylinders and initial conditions.

Then
$$P_e(V_A + V_B) = (n_A + n_B)RT$$

or
$$P_e = \frac{n_A + n_B}{V_A + V_B} RT = \frac{P_A V_A + P_B V_B}{V_A + V_B}$$

where the subscript e represents equilibrium.

This is a simple illustration of an equilibrium balance. Of course, if the gas does not obey the ideal-gas law, the equilibrium pressure can be calculated either by experimental information on P-V-T relationship for the gas or by means of correlations, as in Fig. A.29.

Another example of pressure equilibria is the balance of the force of gravity on an object that is floating in a fluid. It will be recalled from elementary physics that such an object will displace an amount of the fluid equal in mass to its own. Thus, the object having mass m_1 will displace fluid of density ρ_2 in accordance with the following:

$$\text{Force of gravity on the object} = m_1 g$$

$$\text{Force of gravity on the displaced fluid} = m_2 g = m_1 g$$

$$\text{Volume of fluid displaced} = \frac{m_1}{\rho_2}$$

Thermal Equilibrium.—If two bodies each at a different temperature are brought into contact with each other, heat will flow spontaneously from the body at the higher temperature to that at the lower temperature until the temperature of each is identical. This is a state of stable equilibrium; for if heat is transferred to one of the bodies, the equilibrium will be shifted so that heat will flow to the other until the temperatures are again identical although higher than in the first state of equilibrium. Examples 38 and 39 illustrate static thermal equilibrium relations.

Example 38. Five hundred pounds of water at 200°F is added to 100 lb of water at 150°F. Adiabatic conditions are maintained. What will be the temperature of the system when equilibrium is reached?

Solution:

Basis: 150°F.

$$\text{Heat in water at } 200° = (500)(1.0)(200 - 150) = 25{,}000 \text{ Btu}$$

$$\text{Heat in total water} = \frac{25{,}000}{600} = 41.7 \text{ Btu/lb}$$

Thus,
$$41.7 = (t - 150)(1.0)$$

$$t = 191.7\text{°F at equilibrium}$$

Example 39. Three pounds of saturated steam at 100 lb/sq in. gauge, 10 lb of ice at 32°F, and 100 lb of water at 40°F are mixed adiabatically at constant pressure. What will be the final condition of the system?

Solution: A heat balance will be made to determine the heat relative to water at 32°F.

	Btu
Heat in steam = (3)(1189.8)	3570
Heat in water = (100)(8.0)	800
Heat in ice = (10)(−143.6) *	−1436
Total	2934

$$\text{Heat} = \frac{2934}{3 + 10 + 100} = 26.0 \text{ Btu/lb}$$

* Heat of fusion of water at 32°F = 143.6 Btu/lb (Table A.14).

Thus, since the heat in the system above water at 32°F is 26.0 Btu/lb, it is apparent that water only exists and is at a temperature of 32 + 26.0 = 58.0°F.

Phase Equilibrium.—It was learned in Chap. IV that at a specific temperature two phases of a single component can exist together in equilibrium only at a specific pressure. Thus, the vapor pressure of a pure compound is a function only of temperature. This is clearly shown by the phase rule,

$$F = 2 + C - P \tag{4.18}$$

where F = degrees of freedom
C = number of components
P = number of phases

Thus, $F = 2 + 1 - 2 = 1$; and if either temperature or pressure is fixed, the system is fixed, which means that both temperature and pressure are fixed since composition is fixed owing to only one component being in the system.

In the case of two components at equilibrium in two phases, $F = 2 + 2 - 2 = 2$. Thus, in order to fix the system at equilibrium, both temperature and pressure or either temperature or pressure and the concentration of one component must be fixed. For a three-component system one additional variable (degree of freedom) must be fixed in order to fix the system at equilibrium. If both temperature and pressure together with the concentration of one of the three components are fixed, the system is completely defined. Also, if the concentrations of two of the components are fixed (the third is therefore automatically fixed), the system is completely defined if either the temperature or pressure is also fixed.

The information provided by the phase rule is very valuable but does not entirely satisfy the needs of the chemical engineer. He must know not only how many variables must be fixed but also the magnitude of those variables which were not arbitrarily fixed at given values. For example, in a single-component two-phase system at equilibrium the chemical engineer knows at once from the phase rule that the system is defined as soon as he fixes either temperature or pressure if no other restraints are imposed. Nevertheless, if he fixes the temperature, he usually must know also the magnitude of the pressure. Likewise, in a two-phase two-component system, if the concentrations of the components are fixed, the system is defined by fixing either temperature or pressure, if these are the only variables involved. The chemical engineer, however, must know the magnitude of the temperature as a function of pressure.

In most of the phase-equilibrium calculations the composition is fixed, and it is necessary to determine the value of temperature for any fixed value of pressure, or vice versa. In the case of single components it is possible to determine the relationship between temperature and vapor pressure only by experimentation. Such relationships have been determined and published for almost all the components with which the chemical engineer ordinarily deals. Thus, single-component systems usually present no difficulty in this respect. But when systems of more than one component are encountered, which is usually the case, the problem is somewhat more complicated. Actually, precise determinations of the relationship between composition, temperature, and pressure can be obtained only by experiment. Nevertheless, there are a few methods of estimating (calculating) these relationships on the basis of relationships between temperature and pressure for the pure components.

Raoult's law as presented in Chap. IV is perhaps the first widely used method for the calculation of the relationship between temperature and pressure of nonpolar solutions based on the relationships for the pure components in the solution.

$$p_i = P_i x_i \tag{4.19}$$

where p_i = absolute partial pressure of the component i in the solution
P_i = absolute vapor pressure of component i in pure state at the same temperature
x_i = mole fraction of component i in solution

The summation of the partial pressures for all the components in the system is equal to the total vapor pressure of the solution. Raoult's law checks quite well with experimental observations on nonpolar solutions at pressures not in excess of about 50 lb/sq in. gauge. At pressures above this value other methods must be used if reliable results are needed.

If Dalton's law is applied in combination with Raoult's law, a very useful relationship is obtained.

$$\pi y_i = P_i x_i \tag{4.21}$$

where y_i = mole fraction of component i in vapor
x_i = mole fraction of component i in liquid
P_i = absolute vapor pressure of component i in pure state
π = total absolute pressure of the system

or

$$\frac{y_i}{x_i} = \frac{P_i}{\pi} = K \tag{4.22}$$

where K = a constant at a given temperature and pressure

Thus, Eq. (4.22) gives a relationship for the compositions of the vapor and liquid in equilibrium with each other as a function of the pressure and temperature of the system. The relationship includes temperature inasmuch as P_i is a function only of temperature. Equation (4.22) is reasonably accurate for nonpolar solutions up to a value of π that corresponds to a reduced pressure P_r of not over 0.10 and a reduced temperature T_r of not less than 0.80.

As the value of P_r exceeds 0.10, the value of y_i/x_i departs considerably from an approximate equality with P_i/π. Nevertheless, it is found that y_i/x_i or K (phase-equilibrium constant) is still a function of the total pressure and temperature of the system over a wide range even though not equal to P_i/π. Actually, according to the phase rule the value of y_i/x_i is also a function of the composition of the system if more than two components are present. Nevertheless, experimental results on multicomponent hydrocarbon systems show that as long as the temperature is not within about 50°F of the critical temperature of the system the ratio y_i/x_i for all hydrocarbons except methane and, to some extent, ethane can be represented quite satisfactorily as a function only of the temperature and pressure of the system. The ratios of y/x for methane and, to some extent, ethane are affected considerably by the presence of hydrocarbons of high molecular weight (say over 150) or of the aromatic type. Figures A.15 to A.27 present y/x as a function only of temperature and pressure of the system. These values should be used when the value of π is above 65 lb/sq in. abs. The values of y/x for methane and ethane apply to systems that contain no component of the aromatic hydrocarbon type and no component that has a molecular weight in excess of 150. No systems will be considered in this text that do not come within these limitations. Systems outside these limitations require treatment beyond the scope of this book.

By use of Eq. (4.22) or Figs. A.15 to A.27 much information on phase equilibria valuable to the chemical engineer can be calculated. The dew point of a gas, the initial boiling point of a liquid, and the fraction of gas that will condense or the fraction of a liquid that will vaporize at a given temperature and pressure can be calculated. The *dew point* of a gas is the temperature and pressure at which condensation begins. The *initial boiling point* of a liquid is the temperature and pressure at which vaporization begins. The initial boiling point is frequently called the bubble point since it is the point at which the first minute bubble of vapor appears.

A mixture of gases is of the composition $z_1, z_2, z_3, \ldots, z_i$, where z is the mole fraction of the component corresponding to the subscript. Of course, the summation of the mole fractions is equal to unity. This gaseous mixture is cooled until an appreciable amount of it has condensed, and then the temperature and pressure are maintained constant. The vapor phase will, of course, be in equilibrium with the liquid phase.

The molal composition of the vapor phase can be expressed as in Eq. (7.1).

$$y_1 + y_2 + y_3 + \cdots + y_i = 1.00 \tag{7.1}$$

The molal composition of the liquid phase can be represented by Eq. (7.2).

$$x_1 + x_2 + x_3 + \cdots + x_i = 1.00 \tag{7.2}$$

In Eqs. (7.1) and (7.2), y and x represent the mole fractions of components in the vapor and liquid, respectively. The subscripts represent the same corresponding components.

Now if the vapor phase is separated from the liquid phase and cooled further at the same pressure, an infinitesimal amount of liquid will condense when the temperature is reduced an infinitesimal amount. Furthermore, the composition of this liquid phase will be identical with that given in Eq. (7.1), for there has been no finite change in composition of the vapor. The vapor is therefore at its *dew point*. It is apparent that when a vapor phase is in equilibrium with a liquid phase the vapor is at its dew point regardless of the amount of the liquid phase.

If the liquid phase, which was separated from the vapor phase as mentioned above, is heated at the same pressure, vaporization will occur. An infinitesimal amount of vapor will obtain, with an infinitesimal increase in temperature. The composition of this vapor phase will be identical with the composition of the vapor given by Eq. (7.2). The liquid is at its *initial boiling point*, or *bubble point*. Hence it is noted that, when a liquid phase is in equilibrium with a vapor phase, the liquid is at its initial boiling point regardless of the amount of vapor phase present.

The dew point can be calculated from Eq. (4.22) if applicable or from Figs. A.15 to A.27. If the pressure on the gas is given, temperature must be determined. The method is to assume a temperature and obtain the value of y/x for each component by means of Eq. (4.22) if applicable or from Figs. A.15 to A.27. Then the value of x for each component is computed. The summation of the calculated values of x must be unity in accordance with Eq. (7.2), or the assumed temperature was incorrect. By a trial-and-error procedure the correct temperature can be determined. There is a method of approximating the assumed temperatures after the first trial that will be described in Example 40.

The initial boiling point can be calculated by a trial-and-error procedure, also. In this case the values of x are given, and the values of y must be determined. If pressure is fixed, the procedure is to assume a temperature and obtain the values of y/x for each component by means of Eq. (4.22) if applicable or from Figs. A.15 to A.27. Then the value of y for each component is calculated. These must sum up to unity in accordance with Eq. (7.1), or the assumed temperature was incorrect and another must be assumed. There is a method of approximating the proper temperature to assume after the first trial that is described in Example 40.

Of course, if temperature is fixed in a dew-point or initial-boiling-point calculation, the procedure is to assume values of pressure until the summation of the calculated mole fractions is equal to unity. It is important to note that in a dew-point or initial-boiling-point calculation the composition of the phase in question is automatically obtained at the time the temperature (or pressure) at the dew point or initial boiling point is determined.

Example 40. Calculate the dew point at 185 lb/sq in. gauge pressure and the initial boiling point at 185 lb/sq in. gauge pressure of the following mixture:

	Mole %
Methane	5.0
Ethane	10.0
Propane	20.0
Isobutane	30.0
n-Butane	35.0
Total	100.0

Solution: The calculations can be carried out in tabular form most conveniently The mole fractions of the known mixture are set up in one column and the equilibrium constants in an adjacent column. Figures A.15 to A.22 must be used since the pressure is well over 65 lb/sq in. abs.

Dew point. Assume: 100°F.

	y = mole %	$y/x = K_{100°}^{200\text{ lb}}$	$x = y/K$
C_1	0.050	14.1	0.0035
C_2	0.100	2.75	0.0364
C_3	0.200	0.97	0.2060
i-C_4	0.300	0.465	0.6450
n-C_4	0.350	0.345	1.0150
	1.000	......	1.9059 *

* Since the K's increase with temperature in this range, the assumed temperature is too low. The next assumption will be based on a value of K for isobutane of (1.9059/1.000)(0.465) = 0.886. This is merely a convenient method for approximating the temperature that will give $\Sigma x = 1.000$. At $K = 0.886$ for isobutane the temperature is about 162°F. Thus, 160°F will be the next assumption.

	y	$K_{160°}^{200\text{ lb}}$	$y/K = x$	Corrected analysis of liquid, mole %
C_1	0.050	19.2	0.0026	0.26
C_2	0.100	4.25	0.0235	2.34
C_3	0.200	1.60	0.1250	12.43
i-C_4	0.300	0.865	0.3470	34.50
n-C_4	0.350	0.69	0.5070	50.47
	1.000	......	1.0051 *	100.00

* This is close enough so the calculated dew point is 160°F. The analysis of the liquid is corrected by the ratio of 1.00/1.0051.

Initial boiling point:

	x	Assume 60°		Assume 58° *		Corrected analysis of vapor, mole %
		$K_{60°}^{200\text{ lb}}$	$y = Kx$	$K_{58°}^{200\text{ lb}}$	Kx	
C_1	0.050	11.2	0.560	10.9	0.545	54.4
C_2	0.100	1.96	0.196	1.9	0.190	18.9
C_3	0.200	0.645	0.129	0.625	0.125	12.5
i-C_4	0.300	0.262	0.0786	0.254	0.076	7.6
n-C_4	0.350	0.194	0.0679	0.188	0.066	6.6
	1.000	......	1.0315	......	1.002	100.0

* First assumed temperature was too high. Next assumption will be based on value of K for isobutane corrected as (0.262)(1.000/1.0315) = 0.254. Temperature at $K = 0.254$ for isobutane is 58°F.

Calculation of the amount of vapor that will condense or the amount of liquid that will vaporize is based on the combination of a material balance and phase-equilibrium relation.

Let E = moles of vapor before condensation
V = moles of vapor after partial condensation
L = moles of condensate
x = mole fraction of a component in L
y = mole fraction of same component in V
z = mole fraction of same component in E

Then, by material balance,

$$E = V + L$$

and

$$Ez = Vy + Lx$$

Also,

$$Ez = VKx + Lx = Lx\left(\frac{KV}{L} + 1\right)$$

and

$$Lx = \frac{Ez}{(KV/L) + 1} \tag{7.3}$$

It is apparent that the summation of the values of Lx for all components in the system is equal to L because $\Sigma x = 1.00$. Thus, the method of calculation is by trial and error. The values of V/L are assumed until $\Sigma Lx = L$. The method is illustrated by Example 41.

Example 41. Determine the moles of vapor and liquid that will obtain if 1128 moles of the following mixture is maintained at 325 lb/sq in. abs and 100°F.

	Mole %
Methane	13.7
Ethane	20.6
Propylene	15.9
Propane	33.2
Isobutane	7.2
n-Butane	9.4
Total	100.0

Solution: The solution is most conveniently carried out in columnar form. In the first column place the moles of each component, Ez. In the second column place the values of K for each component corresponding to 100°F and 325 lb/sq in. abs. Then, assume a value for V/L, and place in the third column the values of KV/L for each component. The fourth column will have values of $(KV/L) + 1$. The fifth column Lx will be obtained by dividing the value of Ez in the first column by the corresponding values in the fourth column in accordance with Eq. (7.3). The values of Vy are obtained by subtracting the values of Lx from the corresponding values of Ez.

	Ez	$K_{100°}^{325\text{ lb}}$	$K(V/L)$ *	$(KV/L) + 1$	Lx	Vy
C_1	154.6	8.8	8.8	9.8	15.8	138.8
C_2	232.4	1.82	1.82	2.82	82.5	149.9
$C_{3=}$	179.4	0.78	0.78	1.78	100.8	78.6
C_3	374.4	0.71	0.71	1.71	219.0	155.4
i-C_4	81.2	0.35	0.35	1.35	60.2	21.0
n-C_4	106.0	0.27	0.27	1.27	83.3	22.7
	1128.0	....	....	....	561.6 †	566.4

* Assume $V/L = 1.0$.

† Check assumed V/L: $(1128 - 561.6)/561.6 = 1.01$, which is close enough.

Thus, by the use of Eq. (4.22) or Figs. A.15 to A.27, the dew point, initial boiling point, and extent of vaporization or condensation up to 500 lb/sq in. abs can be calculated. It must be kept in mind, however, that this method is valid only for nonpolar solutions and then provided that the conditions are within the limitations discussed earlier in this section. When the conditions of the system in question are outside the limits within which the methods described are reliable, it is necessary to base calculations on data that represent the specific system.

Diffusion Equilibrium.—It was learned in general chemistry that concentrations of components in a system of one phase tend to diffuse throughout the entire system so that the concentration of each component is the same throughout the system. For example, if CO_2, which has a specific gravity of $44/29 = 1.52$ relative to air at the same pressure and temperature, is admitted to a room near the floor, there will be at first a high concentration of CO_2 in the vicinity of the point at which it was admitted. The CO_2 initially will tend to flow over the floor by displacing air as a result of its greater density. Nevertheless, if considerable time is allowed to elapse, the CO_2 will diffuse throughout the entire room until its concentration is identical in every part of it. The diffusion takes place because concentration gradients represent a driving force due to molecular motion. The same thing is observed if a few crystals of NaCl are dropped into a vessel of water. At first the crystals begin to go into solution. In the immediate vicinity of the crystals the concentration of NaCl in solution is high—actually saturated at the surface of the crystals. Owing to the concentration gradient the NaCl in solution diffuses throughout the water phase. Finally all the NaCl crystals will dissolve, and the concentration in solution will become uniform throughout the liquid phase.

Thus, it is seen that concentration gradient represents an important driving force. Its importance will become even more apparent when dynamic equilibria are considered in the next chapter.

Chemical Reaction Equilibrium.—The student learned in his study of elementary chemistry that chemical reactions actually consist of a forward and a reverse reaction which take place simultaneously. Chemical reactions are reversible, and the net reaction as observed is merely the equilibrium state of the two simultaneous reactions. Before the subject of chemical reaction equilibria is discussed, however, two thermodynamic functions, *fugacity* and *activity*, will be defined and discussed. These will be found especially useful in calculations on chemical reaction equilibria.

It has been pointed out that the behavior of all vapors at low pressure is quite well represented by the ideal-gas law. But as pressure is increased, the deviation of real gases from the ideal-gas law becomes considerable and must be taken into account in chemical-engineering practice. The function fugacity is very convenient for this purpose since it is rigorously defined. There are many applications of fugacity in thermodynamics that are beyond the scope of this text. The only purpose in taking the subject up here is to facilitate calculations on chemical reaction equilibria.

In dealing with gaseous mixtures at low pressure, the partial pressure of each component, πy, is sufficiently representative of its behavior. However, as pressure is increased, partial pressure ceases to indicate the behavior of the individual components in the mixture. Thus it became necessary to define a function that could be used to represent the true behavior of components of a real gas. This was done arbitrarily but rigorously by means of the integral $\int V\,dP$.

In the case of the ideal gas under isothermal conditions,

$$PV = nRT = \text{a constant}$$

Thus,

$$\int_{P_1}^{P_2} V\,dP = nRT \int_{P_1}^{P_2} \frac{dP}{P} \qquad (7.4)$$

Or

$$\int_{P_1}^{P_2} V\,dP = nRT \ln \frac{P_2}{P_1} \qquad (7.5)$$

Unfortunately, real gases do not follow the ideal-gas law at high pressure. The relationship of Eq. (7.5) is so convenient and simple, however, that it is desirable to preserve it. In order to do this, pressure cannot be used. Instead, what might be called (although preferably not) a "corrected" pressure can be used that takes into account the deviations of real gases from ideal gases. This is the purpose for which fugacity was first introduced by G. N. Lewis,[1] as shown by Eq. (7.6),

$$\int_{P_1}^{P_2} V\,dP = nRT \ln \frac{f_2}{f_1} \tag{7.6}$$

where f_1 and f_2 are the fugacities of the gas at the beginning and at the end of compression (or expansion). Fugacity is therefore an intensive property and is expressed in the same units as pressure, such as atmospheres and pounds per square inch. It is apparent that the fugacity of an ideal gas is equal to pressure. Furthermore, it follows on the basis of experience that the fugacity of any real gas approaches an equality with pressure as pressure approaches zero. Thus, fugacity is defined so that $\int V\,dP$ is equal to $nRT \ln f_2/f_1$ and the ratio f/P approaches unity as pressure approaches zero. Fugacity is arbitrarily but rigorously defined in this way.

The fugacity of real gases must be determined by experimentation although several very useful correlations have been developed that permit its prediction within fairly narrow limits. Figures A.2 to A.4 present correlations of fugacity coefficient f/P for gases as a function of reduced temperature (absolute temperature of the system divided by the absolute critical temperature of the component) and reduced pressure (absolute pressure of the system divided by the absolute critical pressure of the component). Such correlations serve for good approximations when exact data are not available.

The fugacity of each component of a liquid phase is equal to the fugacity of the same component in the vapor phase in equilibrium with it. Likewise, the fugacity of each component of a solid phase is equal to the fugacity of the same component of the vapor or liquid in equilibrium with it.

In dealing with solutions (either gaseous or liquid) it is desirable to express fugacity so that the perfect- or ideal-solution [2] concept (see Chap. IV) can be maintained. Consequently, the utility of fugacity of a substance is enhanced somewhat in dealing with solutions if it is expressed in terms of the fugacity of this substance in some arbitrarily chosen state at the same temperature. That is, the fugacity of the substance under the conditions

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[1] LEWIS, G. N., *Proc. Am. Acad. Arts Sci.*, **37**, 49 (1901).

[2] Actually, as G. N. Lewis originally defined a perfect solution, it was based on fugacity. It was defined so that the fugacity of a component in a solution is equal to its fugacity in the pure state at the same pressure and temperature multiplied by its mole fraction in the solution. This implies additive volumes, etc., as set forth in Chap. IV.

being considered is most conveniently expressed as a ratio with the fugacity of the substance in some reference state. This is the definition of *activity.* It is used only in dealing with solutions.

$$a = \frac{\bar{f}}{f^\circ} \tag{7.7}$$

where a = activity of the substance under the given conditions
$\bar{f}$ = fugacity of the substance under the given conditions in solution
f° = fugacity of the substance in an arbitrarily chosen reference state at the same temperature

The most convenient arbitrarily chosen reference state is usually the pure substance at the same temperature and at a pressure of 1 atm. In this case it is apparent from Eq. (7.7) that the activity of a substance in the reference state is unity.

In general chemistry the law of mass action was learned. In any chemical reaction at equilibrium (static) at a fixed temperature, the product of the active masses of the reaction products divided by the product of the active masses of the unreacted reactants is a constant. The activity function introduced above is equivalent to active mass. Thus, in the general chemical reaction

$$bB + cC \cdots = mM + nN \cdots \tag{7.8}$$

the following holds true,

$$\frac{a_M^m a_N^n \cdots}{a_B^b a_C^c \cdots} = K_a \tag{7.9}$$

where a represents the activity of each component in the reaction and the subscripts refer to the specific component. The reaction equilibrium constant K_a is a function only of temperature provided that the pressure in the reference state is the same for each component.

When the chemical reaction as indicated by Eq. (7.8) takes place in the gas phase under conditions under which the ideal-gas law applies, the activities in Eq. (7.9) become equivalent to the corresponding partial pressures. Since $a = \bar{f}/f^\circ$ and $f^\circ = p^\circ = 1$ for a gas when the reference state is 1 atm, it follows that when $\bar{f} = \bar{p}$ the activity is equivalent to $\bar{p}$, the partial pressure of the component in the gas phase. Thus,

$$\frac{(y_M\pi)^m(y_N\pi)^n \cdots}{(y_B\pi)^b(y_C\pi)^c \cdots} = K_{p^\circ} \tag{7.10}$$

where $y\pi = \bar{p}$, the partial pressure of a component in solution
π = total pressure, atm

and the subscripts refer to the specific component in Eq. (7.8). It must be emphasized that K_{p° is a function only of temperature provided that conditions are such that the gas behaves in accordance with the ideal-gas law. Otherwise, it is also a function of pressure. It should be noted that the value of K_{p° in Eq. (7.10) is dependent upon the units used for π. It is common practice to express π in terms of atmospheres, and this will be done throughout this text.

If the chemical reaction takes place at high pressure so that the ideal-gas law is not applicable, the law of perfect solutions can usually be applied with reasonable accuracy. In this case

$$\bar{f}_i = f_i y_i \tag{7.11}$$

where $\bar{f}_i$ = fugacity of any component in solution (gaseous)
f_i = fugacity of the component in pure state
y_i = mole fraction of the component in solution (gaseous)

Since f° may be selected as 1 atm, Eqs. (7.9) and (7.11) will be reduced to Eq. (7.12).

$$\frac{(y_M f_M)^m (y_N f_N)^n \cdots}{(y_B f_B)^b (y_C f_C)^c \cdots} = K_f \tag{7.12}$$

The reaction equilibrium constant K_f is a function *only of temperature* when f° is unity. The product $(y_i f_i)$ of Eq. (7.12) is as defined by Eq. (7.11). The student must not confuse *reaction equilibrium constant* and *equilibrium concentrations*. Although K_f is not affected by pressure (when $f^\circ = 1.0$), the conversion of reactants or the concentration of products at equilibrium is very much affected by pressure in many cases. The numerical value of K_f is dependent upon the units used to express f. Atmospheres are commonly used in such calculations and are used throughout this text.

The scope of treatment of chemical reaction equilibria will be limited in this text to processes that come within the limits of Eq. (7.10) or (7.12) (*i.e.*, vapor-phase reactions). In his more advanced study of chemical engineering the student will deal comprehensively and extensively with chemical reaction equilibria including liquid-phase reactions, which are not treated here. For a more advanced treatment the reader is referred to Dodge.[1]

The reaction equilibrium constant K_{p° is dependent only on temperature if the gas is under conditions under which it behaves as an ideal gas. Likewise, K_f is dependent only on temperature if the reference state of each component is at unit fugacity ($f^\circ = 1.0$). The relationship with

---

[1] DODGE, B. F., "Chemical Engineering Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1944.

temperature can be rigorously defined, as the student will learn in his more advanced study of the subject. For the purpose at this time, however, it will suffice to know that the reaction equilibrium constants can be correlated over a narrow temperature range sufficiently accurately for chemical-engineering calculations by the following empirical equation,

$$\ln K = \frac{A}{T} + B \tag{7.13}$$

where A and B = constants[1]
T = absolute temperature
$K = K_{p^\circ} = K_f$

Example 42. The reaction equilibrium constant K_{p° for the formation of water vapor at 3600°R is 3300. How much steam will dissociate into hydrogen and oxygen at equilibrium at 3600°R and 1 atm? At 10 atm and 3600°R? Assume the ideal-gas law. The equation on which K_{p° is based is $H_2 + \frac{1}{2}O_2 = H_2O$.

Solution: The application of the material balance is essential to the solution of a problem of this type.

The equilibrium constant K_{p° was given as 3300 for the following reaction:

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

Thus, since it is desired to calculate the extent of dissociation of steam, the reaction pertinent to the solution of this problem is

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

The equilibrium constant as given is

$$K_{p^\circ} = \frac{y_{H_2O}\pi}{(y_{H_2}\pi)(y_{O_2}\pi)^{1/2}}$$

whereas the equilibrium constant desired is

$$K'_{p^\circ} = \frac{(y_{H_2}\pi)(y_{O_2}\pi)^{1/2}}{y_{H_2O}\pi}$$

Thus,
$$K'_{p^\circ} = \frac{1}{K_{p^\circ}} = \frac{1}{3300} = 3.03 \times 10^{-4}$$

Basis: 100 moles of H_2O initially.

Let x = moles of H_2O dissociated

Then, from the chemical equation,

Moles of H_2 = x
Moles of O_2 = $\frac{1}{2}x$
Moles of H_2O = $100 - x$

---

[1] Actually A is not constant, but this method of correlating reaction equilibrium constants with temperature is used widely and is sufficiently reliable for most chemical-engineering calculations.

By material balance,

$$\text{Total moles} = 100 + 0.5x$$

$$y_{H_2} = \frac{x}{100 + 0.5x} \qquad y_{O_2} = \frac{0.5x}{100 + 0.5x} \qquad y_{H_2O} = \frac{100 - x}{100 + 0.5x}$$

At 1 atm, $\pi = 1.0$.

Then,

$$\frac{\left(\frac{x}{100 + 0.5x}\right)\left(\frac{0.5x}{100 + 0.5x}\right)^{1/2}}{\left(\frac{100 - x}{100 + 0.5x}\right)} = \left(\frac{x}{100 - x}\right)\left(\frac{0.5x}{100 + 0.5x}\right)^{1/2} = 3.03 \times 10^{-4}$$

This equation is most easily solved by trial and error. Assume values of x, and plot them against $[x/(100 - x)][0.5x/(100 + 0.5x)]^{1/2}$.

$$x = 0.57 \text{ or } 0.57 \text{ mole \% dissociated}$$

At 10 atm,

$$\frac{(y_{H_2})(y_{O_2})^{1/2}(10)^{1/2}}{y_{H_2O}} = 3.03 \times 10^{-4}$$

or

$$\frac{(y_{H_2})(y_{O_2})^{1/2}}{y_{H_2O}} = 0.96 \times 10^{-4}$$

Thus, based on the above material balance,

$$\left(\frac{x}{100 - x}\right)\left(\frac{0.5x}{100 + 0.5x}\right)^{1/2} = 0.96 \times 10^{-4}$$

Solving by trial and error,

$$x = 0.27 \text{ or } 0.27 \text{ mole \% dissociated}$$

Hence, it is noted that an increase of 9 atm in pressure reduced the amount of H_2O dissociated from 0.57 to 0.27 per cent.

In Example 42 the dissociation of steam at 3600°R and 10 atm was calculated on the basis of the ideal-gas law. In this specific case, since the dissociation was so slight, the use of fugacity instead of pressure would have no appreciable effect.

There will be problems later that will involve the use of fugacity. Thus, an example that illustrates the mechanical manipulations in the estimation of fugacity will be given at this point.

Example 43. Determine the fugacity of the following mixture of gas at 600°F and 1500 lb/sq in. abs. Assume that the law of perfect solution applies [see Eq. (7.11)].

	Moles
Hydrogen	20
Methane	30
Ethane	30
Steam (H_2O)	20
Total	100

Solution: Since the law of the perfect solution applies, the fugacity of each component in the mixture is directly proportional to its mole fraction in the solution and its fugacity in the pure state at the same pressure and temperature.

$$\bar{f}_i = y_i f_i \qquad \text{and} \qquad \Sigma \bar{f}_i = \bar{f}$$

Fugacity of pure components:

	Deg R			Lb/sq in. abs		
	T_c*	T	T_r†	P_c*	P	P_r†
H_2	60	1060	17.7	188	1500	7.97
C_1	344	1060	3.08	673	1500	2.23
C_2	549	1060	1.93	712	1500	2.10
H_2O	1165	1060	0.91	3200	1500	0.47

* Table A.8.

† $T_r = T/T_c$; $P_r = P/P_c$.

The reduced temperature and reduced pressure of each component having been evaluated in the pure state at the conditions of the system, the fugacity coefficients f/P for each may be obtained from Figs A.2 to A.4.

	f/P	P	f	y	$y\bar{f}$
H_2	1.05	1500	1575	0.20	315
C_1	1.02	1500	1530	0.30	459
C_2	0.94	1500	1410	0.30	423
H_2O	0.76	1500	1140	0.20	228
	....	....	....	1.00	1425

Thus, the fugacity of the solution $= \Sigma y_i f_i = 1425$ lb/sq in.

In problems which deal with chemical reaction equilibria a fairly good approximation of conversion can frequently be obtained by assuming the ideal-gas law even in a pressure range where the deviation is large. Even so, the student should estimate fugacities and approach a solution from that point unless he has evidence that it will have little bearing on his final conclusion.

The fugacities of the pure components are used in Eq. (7.12) instead of the fugacity of the gaseous solution, whereas the total pressure π of the gaseous solution is used in Eq. (7.10). The reason for this distinction is apparent from the values of f/P as estimated in Example 43. The deviation of each component from the ideal-gas law is not the same and will have its individual effect on the chemical equilibrium.

The student must understand that the application of static equilibrium relations to chemical reactions is predicated upon the assumption that sufficient time elapses for the equilibrium to be reached. That is, the variable time is not considered, though it will be in the next chapter.

EQUILIBRIUM RELATIONS IN UNIT OPERATIONS

Distillation.—Equilibrium relations are indispensable in the chemical-engineering practice of distillation. Usually in the process design of distillation columns the analyses of the charge and desired products are given. The chemical engineer must set the conditions under which the column will operate. If the distillate is to be removed as a liquid, the column must operate at a sufficiently high pressure so that the distillate (and reflux) can be condensed by use of cooling water (or other mediums) available. For instance, if cooling water of 90°F minimum is available, it is apparent that the column pressure must be set so that the initial boiling point (temperature) of the reflux (and distillate if removed as a liquid) will be above 90°F. Usually the initial-boiling-point temperature should be at least 10°F above the temperature of the cooling medium.

The pressure is fixed at the reflux drum on the basis of these limitations, but this automatically fixes the pressure on the column since it will usually be designed for about 10 lb/sq in. higher pressure than the reflux drum (*i.e.*, an allowance of 10 lb/sq in. pressure drop from the column through the condenser to the reflux drum will be made).

When the column pressure is fixed, the bottom temperature is automatically fixed; for its composition was originally specified, and it is in equilibrium with vapor (Fig. 7.1). Likewise, the top temperature of the column is fixed if the distillate is withdrawn as a liquid, for the reflux and gross overhead will be the same composition as the distillate.

If the distillate is withdrawn as a vapor, the reflux will be produced by partial condensation of the gross overhead. Thus, the reflux will be in equilibrium with the distillate (vapor) and will have a composition that corresponds with the dew point of the distillate. Since its composition will differ from the distillate, it is apparent that the composition of the gross overhead will depend on the reflux ratio (moles of reflux per mole of distillate). Likewise, the tower-top temperature will be a function of the reflux ratio.

It will be noted that by phase equilibrium balance the temperature of the reflux drum, tower top, and bottoms may be calculated once the composition of distillate and bottoms, the pressures of the reflux drum and the column, and the reflux ratio are known.

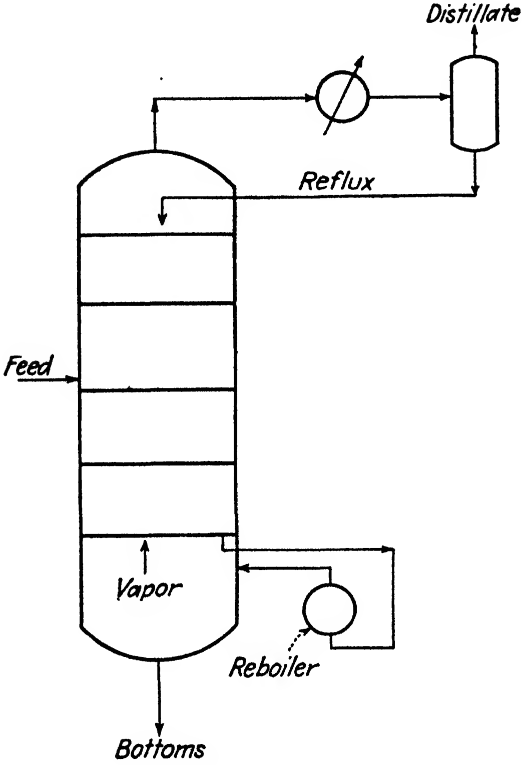


FIG. 7.1.

Example 44. A fractionating column is being designed to make the following separation:

	Moles/hr		
	Charge	Distillate	Bottoms
Propane........	54	51.8	2.2
n-Butane.......	377	2.7	374.3
n-Pentane......	60	....	60.0
Total........	491	54.5	436.5

The column will operate at 200 lb/sq in. gauge, with 5 lb/sq in. pressure drop between the column and reflux drum. The distillate will be withdrawn from the reflux drum as a gas. The reflux ratio will be 12/1. Calculate the reflux-drum temperature, the tower-top temperature, and the bottoms temperature.

Solution: Since the distillate is withdrawn as a gas, the composition of reflux in equilibrium with the distillate will be identical with the dew-point liquid composition. The pressure on the reflux drum will be 215 − 5 = 210 lb/sq in. abs. Thus, the dew point of the distillate at 210 lb/sq in. abs will be calculated first from phase equilibria relations.

	Distillate		Assume reflux drum at 115°		
	Moles/hr	y	$K^{210\text{ lb}}_{115°}$	$x = y/K$	Moles/hr
C_3	51.8	0.950	1.08	0.880	575.5
n-C_4	2.7	0.050	0.417	0.120	78.5
	54.5	1.000	.....	1.000	654.0

Thus, the reflux is in equilibrium with the distillate at 115°F.

The composition of the gross overhead will be computed by material balance and its dew point determined from phase equilibria relations.

	Moles/hr			Gross overhead y	Assume column top at 127°		
	Reflux	Distillate	Gross overhead		$K^{215\text{ lb}}_{127°}$	$x = y/K$	Liquid mole %
C_3	575.5	51.8	627.3	0.885	1.17	0.755	75.5
n-C_4	78.5	2.7	81.2	0.115	0.47	0.245	24.5
	654.0	54.5	708.5	1.000	....	1.000	100.0

Thus, the top temperature is 127°F, and the analysis of the liquid on the top tray is as given in the last column of figures to the right. Instead of reducing the moles per hour of gross overhead to mole fraction, the computation of dew point could have been made directly. The summation of (moles/hr)/K in this case must be equal to the summation of the moles per hour used as y. The student must not confuse (moles/hr)/K with the moles/hr of liquid passing from the top tray to the tray below, for (moles/hr)/K is merely *proportional* to the molal analysis.

The bottoms temperature and analysis of vapor to the bottom tray is determined next by equilibrium relations.

	Bottoms x	Assume vapor from reboiler at 220°F		
		$K_{220^\circ}^{215\text{ lb}}$	$y = Kx$	Mole %
C_3	0.005	2.25	0.011	1.1
C_4	0.857	1.07	0.917	91.7
C_5	0.138	0.52	0.072	7.2
	1.000	....	1.000	100.0

The temperature of the reboiler outlet and bottoms is therefore 220°F. Actually, there is a pressure drop from the bottom to the top of the column, but this will be only about 3 or 4 lb/sq in. It is therefore permissible to make calculations within the column on the basis that the pressure is constant over the column.

After the temperatures of all streams entering and leaving a fractionating column have been determined by equilibrium relations, the heat requirements can be determined by an over-all material and energy (heat) balance.

Example 45. As an extension of Example 44, determine the amount of heat required for reboiler duty and the amount of heat that must be removed by the overhead condenser. The charge will enter the column as liquid at 100°F.

Solution: An over-all material balance and heat balance will be made.

Material balance:

	Moles/hr	Mol. wt.	Lb/hr
Input:			
Charge			
C_3	54	44	2,380
n-C_4	377	58	21,850
n-C_5	60	72	4,320
Reflux			
C_3	575.5	44	25,300
n-C_4	78.5	58	4,600
Total input	1,145.0		58,450
Output:			
Gross overhead *			
C_3	627.3	44	27,580
n-C_4	81.2	58	4,760
Bottoms			
C_3	2.2	44	100
n-C_4	374.3	58	21,690
n-C_5	60.0	72	4,320
Total output	1,145.0	. .	58,450

* Total of reflux and net overhead (distillate).

Net heat balance:

	Lb/hr	Btu/lb			Btu/hr
		Vapor at 127°	Liquid at 100°	ΔH	
Input:					
Net overhead					
C_3	2,280	184	38	146	330,000
n-C_4	160	190	34	156	20,000
	2,440	...	..	...	350,000
	Lb/hr	Btu/lb			Btu/hr
		Vapor at 127°	Liquid at 115°	ΔH	
Reflux					
C_3	25,300	184	48	136	3,440,000
n-C_4	4,600	190	42	148	680,000
	29,900	...	..	...	4,120,000
	Lb/hr	Btu/lb			Btu/hr
		Liquid at 220°	Liquid at 100°	ΔH	
Bottoms					
C_3	100	164	38	126	10,000
n-C_4	21,690	103	34	69	1,500,000
n-C_5	4,320	104	35	69	300,000
	26,110	...	..	...	1,810,000
Total input	......	...	..	...	6,280,000
Output:					
Reboiler duty	......	...	..	...	6,280,000

Thus, the reboiler duty was obtained directly by the over-all heat balance. The overhead condenser duty can be determined now.

	Lb/hr	Btu/lb			Btu/hr
		Vapor at 127°	Vapor at 115°	ΔH	
Net overhead:					
C_3	2,280	184	178	6	13,700
$n\text{-}C_4$	160	190	187	3	500
	2,440	. . .	. .	. . .	14,200
	Lb/hr	Btu/lb			Btu/hr
		Vapor at 127°	Liquid at 115°	ΔH	
Reflux:					
C_3	25,300	184	48	136	3,440,000
$n\text{-}C_4$	4,600	190	42	148	680,000
	29,900	. . .	. . .	. . .	4,120,000
Total condenser duty	. . . . . .	. . .	. . .	. . .	4,134,000

In this case the reflux duty was essentially the entire condenser duty, but this is not always true.

Thus far only miscible liquids have been considered in distillation. In the distillation of organic compounds of high boiling point, steam is frequently used so that the distillation can be carried out at lower temperature. This is called steam distillation. Water is essentially immiscible with a great many organic compounds. Thus, some discussion at this time on phase equilibria which involves immiscible liquids is desirable.

When two liquid phases are present, each exerts the same vapor pressure as if it existed alone. Thus, if a water and a hydrocarbon phase exist together in a system, the vapor pressure within the system is the sum of the vapor pressure of the water and hydrocarbon phases. For example, if water and *n*-hexane liquid phases are in equilibrium with a vapor phase of these components at 200°F, the vapor pressure of the water phase will be 11.5 lb/sq in. abs and the vapor pressure of the *n*-hexane will be 30 lb/sq in. abs. The total pressure on the system will be 41.5 lb/sq in. abs. This is true provided that the total pressure is not so high that there is appreciable deviation from the ideal-gas law. Strictly speaking, the fugacity of the vapor phase is equal to the fugacity of the liquid phases. But since steam distillation is carried out so that temperature can be maintained low, it is most economical to conduct the distillation at low pressure, where the ideal-gas law is applicable. Thus, the solution of steam-distillation problems may be based on partial pressures with desired accuracy. In many steam distillations there is no water phase present, but the total pressure on the system is made up of the steam plus the vapor pressure of the immiscible liquid. Thus, from Dalton's law,

$$y_s = \frac{p_s}{\pi} \tag{7.14}$$

and

$$y_{im} = \frac{p_{im}}{\pi} \tag{7.15}$$

where y_s = mole fraction of steam
y_{im} = mole fraction of immiscible liquid in vapor
p_s = partial pressure of steam
p_{im} = partial pressure of immiscible liquid
π = total pressure on the system

Since the partial pressure of the immiscible liquid is a function only of its temperature, the amount of steam required for its distillation can best be calculated by presentation of Eq. (7.14) in a different form. Since

$$\pi = p_s + p_{im}$$

$$y_s = \frac{\pi - p_{im}}{\pi} \tag{7.16}$$

The moles of steam required per mole of immiscible liquid vaporized is therefore

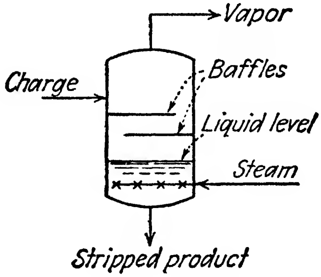
$$\frac{y_s}{y_{im}} = \frac{\pi - p_{im}}{p_{im}} \tag{7.17}$$

or

$$N_s = \frac{N_{im}(\pi - p_{im})}{p_{im}} \tag{7.18}$$

where N represents the number of moles.

Example 46. A 10°API oil of 500 molecular weight is being withdrawn from the bottom of a still, where it is being stripped with steam at atmospheric pressure. The charge to this still contains 1 per cent by liquid volume of a light hydrocarbon, which may be assumed to be *n*-heptane. The stripped product contains 0.1 per cent by liquid volume of the light hydrocarbon. The steam is admitted through a spider, which is located below the surface of the liquid. The vapor pressure of the liquid phase in the still is entirely the result of the light hydrocarbon. The distillation is carried out at 450°F. How much steam in pounds per hour is required if 2000 bbl/day of stripped product is eliminated?



Solution: It is necessary to determine how much light hydrocarbon must be vaporized and removed. A material balance will show this.

	Bbl/day	Gal/hr	Lb/gal	Lb/hr	Mol. wt.	Moles/hr
Product	2,000	3,500.0	8.33	29,200	500	58.4
n-Heptane	– 2	– 3.5	5.723	– 20	100	– 0.7
Heavy component	1,998	3,496.5	.....	29,180	...	58.2

$$n\text{-Heptane in charge} = \left(\tfrac{1}{99}\right)(3496.5) = 35.3 \text{ gal/hr}$$

$$= \frac{(35.3)(5.723)}{100} = 2.02 \text{ moles/hr}$$

$$n\text{-Heptane vaporized} = 2.02 - 0.2 = 1.82 \text{ moles/hr}$$

$$\text{Vapor pressure of } n\text{-heptane at 450°F} = 235 \text{ lb/sq in. abs}$$

$$\text{Vapor pressure of liquid in still} = \left(\frac{0.2}{58.4}\right)(235) = 0.84 \text{ lb/sq in. abs}$$

$$\text{Partial pressure of steam in still} = 14.7 - 0.84$$

$$= 13.86 \text{ lb/sq in. abs}$$

$$\text{Steam required } N_s = (1.82)\left(\frac{13.86}{0.84}\right) = 30.0 \text{ moles/hr}$$

$$= (30.0)(18) = 540 \text{ lb/hr}$$

Occasionally steam distillation of certain organic materials presents the complication that the organic material and water are partly miscible with each other. That is, the organic material will dissolve to a certain extent in any water phase that may be present and water will dissolve to a certain extent in the organic liquid. The partial pressure of each component is the same in each of the liquid phases, for the two phases are in phase equilibrium with each other and with the vapor phase. There is only one vapor phase. Consequently, the equality of the partial pressures must exist. It follows, therefore, that in such cases Raoult's law or the law of the perfect solution cannot possibly apply to both liquid phases owing to the fact that the mole fraction of each component is not the same in each of the liquid phases. Thus, in order to solve problems that involve partly miscible liquids, experimental data are required that give the composition of vapor phase and coexisting liquid phase as a function of temperature and pressure for the two different solutions (*i.e.*, solution of component A in B and solution of component B in A). With such data available, calculations can be made in the way described for immiscible liquids except that only the partial pressure of the organic material in the liquid phase (either of the two liquid phases) is used as p_{im} in Eq. (7.18).

Absorption.—Process design and performance calculations on absorbers involve the application of equilibrium relations similar in many respects to those in distillation. Even so, some of the applications are slightly different.

Example 47. An absorber is being designed to recover butane and higher boiling components from a rich gas. The designed separation of the rich gas is shown as follows:

	Moles/hr	
	Rich gas	Lean gas
C_1	852	801
C_2	379	216
C_3	506	9
i-C_4	57	—
n-C_4	77	—
n-C_5	13	—
Total	1884	1026

The composition of lean gas, however, does not include any loss of lean oil owing to vaporization of it on the top tray of the absorber. The design lean oil rate is 12,500 bbl/day. It has a gravity and molecular weight of 62.0°API and 105, respectively. The volatility characteristics of the lean oil may be assumed to be identical with those of *n*-octane. The top temperature of the absorber will be 120°F. How much lean oil will be lost in the lean gas if the absorber operates at 225 lb/sq in. gauge?

Solution:

	Moles/hr	y*	$y/x = K^{240\text{ lb}}_{120°}$	y/K
Lean gas:				
C_1	801	$801/G$	13.2	$6.14/G$
C_2	216	$216/G$	2.72	$78.5/G$
C_3	9	$9/G$	1.01	$8.9/G$
Lean oil	V	V/G	0.0088	$113.7V/G$
	G	1.000	1.000	$\frac{148.8 + 113.7V}{G} = 1.000$

* It will be apparent from these calculations that it is not necessary to convert moles per hour of lean gas to mole fractions. The calculations can be made direct.

But $G = 1026 + V$

Then,
$$1026 + V = 148.8 + 113.7V$$
$$V = 7.8 \text{ moles/hr}$$
$$= \frac{(7.8)(105)}{6.087} = 135 \text{ gal/hr}$$

Such a loss is rather high from an economic standpoint. Thus, a lean oil of less volatility should be used.

Materials Handling.—The unit operation, materials handling, offers many opportunities for applications of chemical-engineering fundamentals. In particular, this operation is of very great importance in the petroleum industry. Specifically, the blending and storage of petroleum products is encountered frequently enough by a large company to occupy the attention of a staff of chemical engineers.

The demand for petroleum products fluctuates seasonally. The demand for gasoline is normally at a minimum during the winter months, then rises during the spring, and reaches a maximum during the summer, followed by a decline in the autumn months. The demands for domestic fuel oils and kerosene, on the other hand, reach a minimum during the summer and a maximum in the winter months. To add to the complications the chemical engineer in the petroleum industry must take into account that in the northern part of the United States some of the bulk-storage plants which supply many of the market areas become inaccessible because of ice. It is essential, therefore, that the inventories of all products, particularly domestic fuel oil, at such plants be sufficient to meet the heavy demand during the coldest weather.

The fluctuations in demand are so great that it is not economical to install sufficient refining capacity to handle the maxima. It is far more economical to design refinery capacity so that the average demand can be met and to install sufficient storage to care for the fluctuations.

Not only is it necessary for the chemical engineer in the petroleum industry to see that sufficient storage is provided for seasonal fluctuations in demand for gasoline, but also he must make certain that there is sufficient storage capacity and of the proper type to permit seasonal balancing of the properties of the gasoline. Example 48 is a very much simplified illustration of the seasonal balancing of gasoline.

Example 48. A petroleum refinery is being operated to produce gasoline at the average rate of 11,850 bbl/day. The gasoline as produced is 61.0°API, 105 molecular weight, and has a true vapor pressure at 100°F of 12.57 lb/sq in. abs. Vapor pressure of gasoline, however, is specified in terms of Reid vapor pressure (RVP), which is determined at 100°F in a bomb that permits some vaporization of the gasoline. Thus the Reid vapor pressure is lower than the true vapor pressure except in the case of a pure component, for partial vaporization of a pure component does not change the composition of the unvaporized portion. The true vapor pressure for average gasoline at five different Reid vapor pressures is as follows:

RVP, lb/sq in. abs	9.0	10.0	11.0	12.0	13.0
True vapor pressure, lb/sq in. abs	10.40	11.46	12.52	13.57	14.60

The refinery ships its gasoline as soon as produced, but the shipments must meet a specified vapor pressure for each month of the year as follows:

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
RVP	13	13	12	11	10	9	9	9	10	11	12	13

This necessitates the removal of normal butane from the average gasoline produced during periods when the specified vapor pressure of shipments is less than that of average gasoline (12.57 lb/sq in. true vapor pressure). The normal butane is stored in pressure storage tanks and blended into average gasoline produced when the specified vapor pressure of shipments is above that of average gasoline production. Thus there is no net production of normal butane during the period of a year.

Calculate the minimum storage capacity required for normal butane.

Solution: The solution of this problem is obtained by material balances combined with phase equilibria relations (Raoult's law). The first step in the solution is to determine the amounts of normal butane that must be added or removed from a given volume of average gasoline to obtain gasolines of the five different Reid vapor pressures specified. This can be done most conveniently by setting up an equation in terms of P, the true vapor pressure of specification gasoline, and X, the gallons of normal butane that must be added to 100 gal of average gasoline to obtain the vapor pressure P.

Basis: 100 gal of average gasoline.

	Gal	Lb/gal	Lb	Mol. wt.	Moles	Mole fract	True vapor pressure	Partial pressure
Av. gasoline...	100	6.12	612.0	105	5.83	$5.83/N$	12.57	$73.25/N$
n-C_4..........	X	4.87	$4.87X$	58	$0.048X$	$0.084X/N$	52.0	$4.37X/N$
	$100 + X$				N	1.000	P	$\frac{73.25 + 4.37X}{N}$

But

$$N = 5.83 + 0.084X$$

Thus

$$\frac{73.25 + 4.37X}{5.83 + 0.084X} = P$$

Or

$$X = \frac{73.25 - 5.83P}{0.084P - 4.37}$$

RVP	P	X
13	14.60	3.76
12	13.57	1.81
11	12.52	−0.07
10	11.46	−1.86
9	10.40	−3.59

Based on the above values of X (gallons of n-C_4 to be added to 100 gal of average gasoline to meet specifications), the amount of n-C_4 can be calculated that must be added to or removed from average gasoline during each month to meet specifications.

The amount of n-C_4 that must be removed represents the amount that must be stored.

	Av. gasoline produced, bbl	Shipments			n-C_4 inventory end of month, bbl
		RVP	Barrels n-C_4 added	Total bbl	
Jan.	367,000	13.0	13,800	380,800	19,090
Feb.	331,000	13.0	12,450	344,450	6,640
Mar.	367,000	12.0	6,640	373,640	0
Apr.	355,000	11.0	−250	354,750	250
May	367,000	10.0	− 6,830	360,170	7,080
June	355,000	9.0	−12,750	342,250	19,830
July	367,000	9.0	−13,200	353,800	33,030
Aug.	367,000	9.0	—13,200	353,800	46,230
Sept.	355,000	10.0	− 6,600	348,400	52,830
Oct.	367,000	11.0	−260	366,740	53,090
Nov.	355,000	12.0	6,400	361,400	46,690
Dec.	367,000	13.0	13,800	380,800	32,890
	4,330,000		0	4,330,000	

Thus a minimum storage capacity for normal butane of 53,090 bbl must be available.

This is a rather simplified example of a storage and blending program for a petroleum refinery. Frequently, the program will also involve storage of volatile stocks for blending into the gasoline that will be consumed during cold weather, to improve starting quality. Then, too, a storage program will almost always include balancing of the octane number (detonating quality) of the gasoline over the year. The refinery that operates without close attention to its storage program will sooner or later come face to face with an unbalanced condition for gasoline, vapor pressure, volatility, and octane number that will be costly to overcome. If the program is followed carefully by frequent projections a year in advance, serious difficulties can be foreseen months ahead and action taken to avoid them in an economical way. Thus, by the application of the simple fundamentals of chemical engineering, the material balance and equilibrium relations, intelligent storage and blending programs can be set up and followed.

EQUILIBRIUM RELATIONS IN CHEMICAL PROCESSES

Sulfuric Acid Manufacture.—In the platinum contact process for the manufacture of sulfuric acid, sulfur dioxide is converted to sulfur trioxide at atmospheric pressure according to the following reaction:

$$SO_2 + \tfrac{1}{2}O_2 = SO_3$$

The reaction-equilibrium constant [see Eq. (7.10)] is therefore

$$K_{p^\circ} = K_f = \frac{(y_{SO_3}\pi)}{(y_{SO_2}\pi)\sqrt{y_{O_2}\pi}} = \frac{y_{SO_3}}{y_{SO^2}\sqrt{y_{O_2}\pi}} \qquad (7.19)$$

where y represents the mole fraction of a component in the gas, π is the pressure in atmospheres on the system, and the subscripts refer to the specific component. The reaction is exothermic and therefore is affected adversely by increase in temperature. Also, it is apparent that it is facilitated by increase in pressure or concentration of SO_2.

The reaction equilibrium constant K_{p° is given as a function of temperature by Badger and Baker [1] as

$$\log K_{p^\circ} = \frac{8775}{T} - 4.46 \qquad (7.20)$$

where log = logarithm to base 10

T = deg R

The commercial processes are conducted in the temperature range of 750 to 850°F. Conversion obtained in commercial plants is almost equivalent to the thermodynamic equilibrium given by Eq. (7.20).

Example 49. Gases from the sulfur burner that pass to the platinum catalyst chamber of a contact sulfuric acid plant have been found from analysis to contain 8 per cent SO_2. The reaction is carried out at 840°F and atmospheric pressure. Assuming that static equilibrium is reached, what percentage of the SO_2 is converted, and what is the complete analysis of the gases from the catalyst chamber?

Solution: The solution is obtained by use of a material balance and equilibrium relations.

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[1] BADGER, W. L., and E. M. BAKER, "Inorganic Chemical Technology," 1st ed., p. 68, McGraw-Hill Book Company, Inc., New York, 1928.

Basis: 100 moles of gas to catalyst.

$$\text{SO}_2 \text{ in exit gas} = 8.0 \text{ moles}$$

$$\text{O}_2 \text{ in exit gas} = N_0 \text{ moles}$$

$$N_2 \text{ in exit gas} = N_n \text{ moles}$$

$$\text{Oxygen to burner} = 8.0 + N_0$$

$$\text{N}_2 \text{ to burner} = (8.0 + N_0)(^{79}/_{21}) = N_n$$

$$N_0 = 13.0$$

$$N_n = 79.0$$

Actually the above result should be apparent merely by inspection, *i.e.*, the sum of $SO_2 + O_2$ per 100 moles of burner gas must be equal to 21.0.

$$\log K_{p^\circ} = \frac{8775}{840 + 460} - 4.46 = 2.29$$

$$K_{p^\circ} = 195 = \frac{y_{\text{SO}_3}}{y_{\text{SO}_2}\sqrt{y_{\text{O}_2}}}$$

Basis: 100 moles of burner gas.

Let x = moles of SO_2 converted

$$N_{\text{SO}_3} = x$$

$$N_{\text{SO}_2} = 8.0 - x$$

$$N_{\text{O}_2} = 13.0 - \frac{x}{2}$$

$$N_{\text{N}_2} = 79$$

$$\text{Total gas at equilibrium} = 79 + x + 8.0 - x + 13.0 - 0.5x$$

$$= 100 - 0.5x$$

$$y_{\text{SO}_3} = \frac{x}{100 - 0.5x}$$

$$y_{\text{SO}_2} = \frac{8.0 - x}{100 - 0.5x}$$

$$y_{\text{O}_2} = \frac{13.0 - 0.5x}{100 - 0.5x}$$

$$\frac{x}{8.0 - x} = 195\sqrt{\frac{13.0 - 0.5x}{100 - 0.5x}}$$

Solving the equation by trial and error,

$$x = 7.87$$

Exit gas analysis:

	Moles	Mole %
SO_3	7.87	8.19
SO_2	0.13	0.13
O_2	9.06	9.43
N_2	79.00	82.25
Total	96.06	100.00

$$\% \ SO_2 \text{ converted} = 100.0\left(1 - \frac{0.13}{8.0}\right)$$
$$= 98.38\%$$

The conversion of SO_2 to SO_3 in Example 49 is typical of commercial operation. Thus, in this case the static equilibrium balance (rate of reaction not considered) and dynamic equilibrium balance (based on rate of reaction) give essentially the same result because the rate of reaction is so high. This happens only when the rate of reaction is such that static equilibrium is attained for all practical purposes.

Fixation of Nitrogen.—The greatest source of NH_3 is the fixation of nitrogen from the atmosphere. Nitrogen and hydrogen are reacted together at high pressure over a catalyst according to the reaction

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3(g) \qquad \Delta H_{60} = -19{,}800 \text{ Btu}$$

which is highly exothermic. Thus, the temperature of the reaction must be controlled by removing the heat of reaction. The reaction-equilibrium constant [see Eq. (7.12)] for the reaction as given above is

$$K_f = \frac{(yf)_{NH_3}}{(yf)_{N_2}^{1/2}(yf)_{H_2}^{3/2}} \tag{7.21}$$

Obviously, if the reaction equilibrium constant K_f were for the reaction

$$N_2 + 3H_2 = 2NH_3$$

it would be the square of the value given by Eq. (7.21). It is important, therefore, to be sure that any reaction equilibrium constant taken from the literature is for the reaction specifically as written for the calculations. Otherwise, the proper adjustment must be made.

The variation with temperature of the reaction equilibrium constant of Eq. (7.21) has been developed from the work of Larson and Dodge,[1]

$$\log_{10} K_f = \frac{4880}{T} - 5.883 \tag{7.22}$$

where T = deg R

There are a number of catalytic processes for the production of ammonia by the fixation of nitrogen. Several different catalysts are used successfully. Iron is ordinarily employed, promoted by different metallic oxides. The pressures used on the catalyst chambers vary from 100 to at least 1000 atm. The temperature varies from 750 to 1200°F, although it is reported that activity of the catalyst is reduced somewhat at temperatures above 950°F. There has been considerable development of processes for NH_3 production in the last few years, but information on this development has not been released as yet. For a more detailed description of the various processes in commercial use, at least up to the time of the Second World War, the reader is referred to Shreve[2] and Curtis.[3]

Example 50. A stoichiometric mixture of N_2 and H_2 is processed over doubly promoted catalyst at 800°F and 300 atmospheres absolute pressure. Assuming that the rate of reaction is sufficiently high that static reaction equilibrium is reached, how much NH_3 is produced per 100 moles of reactants?

Solution:

Basis: 100 moles of reactants.

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3$$

Reactants:

	Moles
N_2	25.0
H_2	75.0
	100.0

From Eq. (7.22),

$$\log_{10} K_f = \frac{4880}{800 + 460} - 5.883 = -2.013$$

$$K_f = 0.00097$$

Thus

$$\frac{(yf)_{NH_3}}{(yf)_{N_2}^{1/2}(yf)_{H_2}^{3/2}} = 0.0097$$

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[1] Larson, A. T., and R. L. Dodge, *J. Am. Chem. Soc.*, **45**, 2918 (1923).

[2] Shreve, R. N., "The Chemical Process Industries," p. 393, McGraw-Hill Book Company, Inc., New York, 1945.

[3] Curtis, H. A., "Fixed Nitrogen," Chemical Catalog Company, Inc., New York, 1932.

In order to calculate the conversion the fugacity of N_2, H_2, and NH_3 in the pure state must be determined.

	N_2	H_2	NH_3
T_c, deg R	227	60	730
T_r *	5.55	21.0	1.73
P_c, atm	33.5	12.8	111.5
P_r *	8.92	23.4	2.69

* $T_r = 1260/T_c$; $P_r = 300/P_c$.

From Figures A.2 to A.4,

	N_2	H_2	NH_3
f/P	1.17	1.11	0.89
f	355	333	267

The fugacity of each component having been calculated, the conversion can be calculated by mass balance.

Let x = moles of NH_3 formed

Then in the equilibrium gas,

$$N_2 = 25 - 0.5x$$

$$H_2 = 75 - 1.5x$$

$$NH_3 = x$$

$$\text{Total equilibrium gas} = 100 - x$$

$$y_{N_2} = \frac{25 - 0.5x}{100 - x}$$

$$y_{H_2} = \frac{75 - 1.5x}{100 - x}$$

$$y_{NH_3} = \frac{x}{100 - x}$$

$$0.0097 = \frac{\left(\frac{x}{100 - x}\right)(267)}{\left[\left(\frac{25 - 0.5x}{100 - x}\right)(355)\right]^{1/2}\left[\left(\frac{75 - 1.5x}{100 - x}\right)(333)\right]^{3/2}}$$

$$4.20 = \frac{x(100 - x)}{(25 - 0.5x)^{1/2}(75 - 1.5x)^{3/2}}$$

Solving this equation by trial and error,

$$x = 30.3$$

The effect of pressure on the production of ammonia is rather large. For instance, if in Example 50 the pressure had been 100 atm, the production of NH_3 would have been about 17 moles/100 moles of reactants.

Methanol Synthesis.—One of the more important organic chemical processes is the synthesis of methyl alcohol (CH_3OH) from carbon monoxide and hydrogen. Prior to this process the only important source of methyl alcohol was the destructive distillation of wood. Thus, methyl alcohol was called "wood alcohol."

The methyl alcohol process employs a catalyst, usually copper mixed with oxides of aluminum, chromium, manganese, or zinc. The reactants in the process must not come into contact with hot iron. Thus, the reactor is usually copper-lined. The reactor is maintained at 300 atm and 575 to 675°F. The methyl alcohol (methanol) in the products of reaction from the reactor is condensed at high pressure (3500 to 4000 lb/sq in.), and the uncondensed gases are returned to the reactor.

The reaction is written as follows:

$$CO + 2H_2 = CH_3OH(g) \qquad \Delta H_{60} = -43{,}100 \text{ Btu}$$

The reaction is therefore quite exothermic, and a means for removing the heat of reaction from the catalyst chamber must be provided.

The reaction equilibrium constant for the reaction as written as is follows:

$$K_f = \frac{(yf)_{CH_3OH}}{(yf)_{CO}(yf)^2_{H_2}} \tag{7.23}$$

The variation of K_f with temperature is given by Eq. (7.24), which is based on the work of Newton and Dodge [1] and Perry,[2]

$$\log_{10} K_f = \frac{8700}{T} - 12.00 \tag{7.24}$$

where T is expressed in degrees Rankine.

Example 51. A gas mixture which consists of 30 mole per cent CO, 60 per cent H_2, and the balance inert is processed over a suitable catalyst at 300 atm pressure and 580°F according to the reaction

$$CO + 2H_2 = CH_3OH$$

How many moles of methanol is produced per 100 moles of reactants? Assume that static equilibrium is reached in the reactor.

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[1] NEWTON, R. H., and B. F. DODGE, *J. Am. Chem. Soc.*, **56**, 1287 (1934).

[2] PERRY, J. H., "Chemical Engineers' Handbook," 2d ed., p. 749, McGraw-Hill Book Company, Inc., 1941.

Solution:

Basis: 100 moles of reactants.

$$\log_{10} K_f = {}^{8700}\!/_{1040} - 12.00 = -3.65$$

$$K_f = 0.000225$$

Calculation of fugacity of components:

	CO	H_2	CH_3OH
T_c	242	60	923
T_r *	4.3	17.3	1.13
P_c	34.6	12.8	78.7
P_r *	8.62	23.4	3.81
f/P	1.15	1.15	0.42
f	345	345	126

* $1040/T_c$; $300/P_c$.

$$K_f = \frac{(126y)_{CH_3OH}}{(345y)_{CO}(345y)^2_{H_2}} = 0.000225$$

$$\frac{y_{CH_3OH}}{(y_{CO})(y)^2_{H_2}} = 51.7$$

Let x = moles of CH_3OH produced. Then, in reactor effluent,

$$CH_3OH = x$$

$$CO = 30 - x$$

$$H_2 = 60 - 2x$$

$$\text{Inerts} = 10$$

$$\text{Total} = 100.0 - 2x$$

Mole fractions:

$$CH_3OH = \frac{x}{100 - 2x}$$

$$CO = \frac{30 - x}{100 - 2x}$$

$$H_2 = \frac{60 - 2x}{100 - 2x}$$

Then

$$\frac{\dfrac{x}{100 - 2x}}{\left(\dfrac{30 - x}{100 - 2x}\right)\left(\dfrac{60 - 2x}{100 - 2x}\right)^2} = 51.7$$

$$\frac{x(100 - 2x)^2}{(30 - x)(60 - 2x)^2} = 51.7$$

Solving by trial and error,

$$x = 23.2$$

Thus, about 77 per cent of the CO is converted to CH_3OH. This is higher than obtained in industry owing to the fact that the rate of reaction is not high enough to permit attainment of static equilibrium under the most economic processing rate.

Isobutane Manufacture.—The chemical process isomerization has made rapid progress during the past few years, particularly in the petroleum industry. This process supplies a large portion of the isobutane needed in the alkylation plants that produce high-quality alkylate for the best-grade aviation gasoline.

There are several good processes for the isomerization of *n*-butane to isobutane. Some of these carry out the isomerization reaction in the vapor phase, whereas others conduct the reaction in the liquid phase. All the processes that have been successful commercially utilize aluminum chloride as a catalyst in one way or another, with anhydrous HCl as a promoter.

The temperature of the reaction in the different processes varies from 170 to 200°F. The pressure on the reactor varies from 150 lb/sq in. to 300 lb/sq in. gauge. The vapor-phase processes use the lower pressure.

The $AlCl_3$ catalyst in the liquid-phase processes is usually dissolved in a molten salt such as antimony chloride.[1] The $AlCl_3$ catalyst in the vapor-phase processes is usually a liquid hydrocarbon complex. Thus, in either case conditions are very favorable for intimate contact between the *n*-butane charge and the catalyst. The chemical reaction is as follows:

$$n\text{-}C_4H_{10}(l) = i\text{-}C_4H_{10}(l)$$

or

$$n\text{-}C_4H_{10}(g) = i\text{-}C_4H_{10}(g)$$

The reaction equilibrium constant for reaction in the vapor phase is given by Eq. (7.25).

$$K_f = \frac{(yf_v)_{i\text{-}C_4}}{(yf_v)_{n\text{-}C_4}} \tag{7.25}$$

Since only reactions in the vapor phase will be considered at this time, the reaction equilibrium constant for the reaction in the liquid phase will not be given here. The student will learn in his more advanced training in chemical engineering that the equilibrium constant for the liquid-phase reaction is related directly to the equilibrium constant of the vapor-phase reaction.

The variation with temperature of the reaction equilibrium constant in the vapor phase [Eq. (7.25)] is given by Eq. (7.26),[2]

$$\log_{10} K_f = \frac{908}{T} - 0.925$$

where T = deg R

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[1] McAllister, S. H., W. E. Ross, H. E. Randlett, and G. J. Carlson, *Trans. Am. Inst. Chem. Engrs.*, **42**, 33 (1946).

[2] Pines, H., B. Kutinskas, L. S. Kassel, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **67**, 631 (1945).

Example 52. A vapor mixture that consists of 95.0 mole per cent *n*-butane and 5.0 mole per cent isobutane is contacted at 180°F and 10 atm pressure by an active isomerization catalyst until static equilibrium is reached. What percentage of the *n*-butane is converted to isobutane?

Solution:

Basis: 100 moles of reactants.

	Moles
n-C_4	95.0
i-C_4	5.0
Total	100.0

$$\log_{10} K_f = {}^{908}\!/_{640} - 0.925 = 0.495$$

$$K_f = 3.125$$

Calculation of fugacities of components:

	n-C_4	i-C_4
T_c, deg R	766	733
T_r	0.835	0.873
P_c, atm	36.0	37.0
P_r	0.278	0.270
f/P	0.80	0.84
f	8.0	8.4

$$K_f = \frac{(yf)_{i\text{-}C_4}}{(yf)_{n\text{-}C_4}} = \frac{(y_{i\text{-}C_4})(8.4)}{(y_{n\text{-}C_4})(8.0)} = \frac{1.05y_{i\text{-}C_4}}{y_{n\text{-}C_4}}$$

Let x = moles of n-C_4 converted

Then, in the equilibrium mixture,

	Moles	y
n-C_4	$95.0 - x$	$0.95 - 0.01x$
i-C_4	$5.0 + x$	$0.05 + 0.01x$
Total	100.0	1.00

$$K_f = \frac{(1.05)(0.05 + 0.01x)}{0.95 - 0.01x} = 3.125$$

$$x = 69.7$$

Thus, $$\frac{(69.7)(100)}{95.0} = 73.5\% \text{ of } n\text{-}C_4 \text{ converted}$$

Conc. of i-C_4 in equilibrium mixture = 69.7 + 5.0 = 74.7 mole %

If in Example 52 the reactants had consisted of 100.0 per cent n-C_4, the conversion of n-C_4 to i-C_4 would have been 74.7 moles instead of 69.7. It is apparent, therefore, that the performance of a commercial unit will be more favorable the nearer 100 per cent the concentration of n-butane is in the charge to the catalyst. This is actually even more important than would be indicated by Example 52, for in the commercial units it is not feasible to allow sufficient time in the reactor to attain static equilibrium. The isobutane content of the reactor effluent in commercial units is more nearly 40.0 to 45.0 mole per cent owing to the fact that the reaction rate is not high enough to permit static equilibrium with the most economical operating conditions. Thus, a 5 per cent concentration of isobutane in the charge would have a somewhat greater effect on conversion.

CONCLUSIONS

It has been seen that the application of static equilibrium relations broadens the scope of problems which can be handled by the chemical engineer, particularly when combined with the material balance and energy balance.

It must be emphasized again, however, that the application of static equilibrium relations is predicated upon the assumption that the rates of energy and mass transfer are sufficiently high so that the variable, time, can be eliminated from consideration in the calculations. This is not usually true, and the chemical engineer must therefore recognize this in his application of fundamentals. Even so, equilibrium relations will show how far a reaction (either chemical or physical) can go. This is particularly valuable information when the performance of processes and process equipment is being scrutinized to determine whether or not improvement can be made. Obviously, if static equilibrium has been attained in a chemical reaction, for example, it would be a waste of time to attempt to improve conversion under existing operating conditions. Such information is exceptionally enlightening if further research is being considered for improving product yields.

Dynamic equilibrium, which is covered in the following chapter, takes into account the time variable or rates of transfer of mass and energy. Nevertheless, it is related directly to static equilibrium, for the latter is the ultimate extent of the reaction (either physical or chemical) in any event.

PROBLEMS

1. Calculate the analysis of the vapor in equilibrium with the following liquid at 500 lb/sq in. abs:

	Mole %
Methane	5.0
Ethylene	10.0
Ethane	15.0
Propylene	30.0
Propane	40.0
Total	100.0

2. Calculate the analysis of liquid in equilibrium with the following vapor at 150°F:

	Mole %
Ethane	10.0
Propane	25.0
Isobutane	30.0
n-Butane	25.0
Isopentane	10.0
Total	100.0

3. Calculate the amount of each component that will vaporize when the following liquid is heated to 200°F at 200 lb/sq in. abs:

	Moles
Propane	28
Isobutane	701
n-Butane	888
Isopentane	344
n-Pentane	39
Total	2000

4. Calculate the amount of the following vapor that is condensed when cooled to 50°F and 200 lb/sq in. abs:

	Moles
Ethane	100
Propane	350
Isobutane	400
n-Butane	450
Isopentane	50
Total	1350

5. Calculate the amount of liquid, its analysis, and the analysis of uncondensed vapor when the vapor of Prob. 4 is cooled to 150°F at 200 lb/sq in. abs.

6. The reaction equilibrium constants for the following reaction at 840°F and 660°F are 50.0 and 66.9, respectively:

$$H_2 + I_2 = 2HI$$

Calculate the amount of HI that will dissociate at 700°F and atmospheric pressure.

7. Calculate the amount of HI that would be present at equilibrium if 3 moles of hydrogen and 1 mole of iodine were brought to 800°F and atmospheric pressure.

What would be the equilibrium concentrations if 1 mole of hydrogen and 3 moles of HI were brought to the same conditions?

8. The reaction equilibrium constant for the dissociation of nitrogen tetroxide at 75°F and 1 atm is 0.14 according to the reaction

$$N_2O_4 = 2NO_2$$

How much is dissociated at 0.10 atm and 75°F? How much at 5 atm and 75°F?

9. Carbon dioxide is 40 per cent dissociated at 5450°F and 1 atm. Calculate the reaction equilibrium constant according to the reactions

$$2CO_2 = 2CO + O_2$$

$$CO_2 = CO + \frac{1}{2}O_2$$

$$CO + \frac{1}{2}O_2 = CO_2$$

Assuming the ideal-gas law applies, how much is dissociated at 5450°F and 10 atm?

10. The reaction equilibrium constant K_f for production of methyl alcohol from carbon monoxide and hydrogen at 650°F is 6.90×10^{-5} according to the reaction

$$CO + 2H_2 = CH_3OH$$

How much methyl alcohol is formed from a mixture of 40 per cent CO and 60 per cent H_2 at 400 atm and 650°F?

11. A depropanizer is to be designed to produce the following products:

	Moles/hr		
	Feed	Net overhead	Bottoms
Methane	2.3	2.3	—
Ethane	7.1	7.1	—
Propane	27.0	24.9	2.1
Isobutane	22.0	—	22.0
n-Butane	28.3	—	28.3
Isopentane	14.9	—	14.9
n-Pentane	11.4	—	11.4
n-Hexane	9.9	—	9.9
C_{7+}	8.9	—	8.9
Total	131.8	34.3	97.5

The net overhead will be removed as a gas from the reflux drum, which will operate at 100°F. Assume that the fractionating column will operate with negligible pressure drop to the reflux drum.

The molal reflux ratio will be 8/1, and the feed will be charged to the column as 100 per cent liquid at 160°F. Calculate the amount of heat that must be supplied to the reboiler and the amount that must be removed by the overhead condenser. Also calculate the amount of vapor produced in the reboiler and the amount of liquid that flows from the top plate of the column to the second plate from the top.

The C_{7+} fraction has a molecular weight of 113, and a gravity of 69.2°API. Its volatility may be taken as that of normal heptane and its enthalpies may be assumed to be the same as for normal hexane.

12. Calculate the moles of liquid and its composition when the following mixture is maintained at 100°F and 500 lb/sq in.

	Moles
Methane	32.4
Ethane	27.0
Propane	32.8
Isobutane	47.1
n-Butane	60.7
Total	200.0

13. The chemical reaction equilibrium constant for the reaction

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3$$

is given as follows:

$$\log_{10} K_f = \frac{4880}{T} - 5.883$$

How much NH_3 would be formed from a mixture of 20 moles of N_2, 60 moles of H_2, and 20 moles of inert gas at a pressure of 400 atm and a temperature of 850°F if the reaction time is sufficiently long to allow static equilibrium to be reached?

14. The reaction equilibrium constant for the vapor-phase reaction of ethylene with water to form ethyl alcohol is given by the following equation,

$$\log_{10} K_f = \frac{3835}{T} - 6.24 \qquad (T = {}^\circ R)$$

for the reaction

$$C_2H_4 + H_2O\ (g) = C_2H_5OH\ (g)$$

The critical temperature and pressure of ethyl alcohol average 469°F and 63.1 atm, respectively.

Calculate the amount of ethyl alcohol formed at equilibrium if a mixture of 60 moles of ethylene and 40 moles of water vapor is reacted at 650°F and 50 atm.

15. Calculate the analysis of the liquid in equilibrium with the following vapor at 100 lb/sq in. abs:

	Mole %
Ethane	10.0
Propane	25.0
Isobutane	30.0
n-Butane	25.0
Isopentane	10.0
Total	100.0

16. Calculate the amount of each component of the following liquid that will vaporize when heated to 300°F at 200 lb/sq in. abs:

	Moles
Propane	280
Isobutane	7,010
n-Butane	8,880
Isopentane	3,440
n-Pentane	390
Total	20,000

17. A fractionating column is operating at a pressure of 200 lb/sq in. abs. The pressure drop to the reflux drum is negligible. A reflux ratio of 6/1 is used. Calculate the temperature of the gross overhead leaving the column. The net overhead that is removed as a gas from the reflux drum is as follows:

	Moles/hr
Ethane	11.0
Propane	35.0
Isobutane	5.5
Total	51.5

CHAPTER VIII

DYNAMIC EQUILIBRIA

Thus far three of the technical fundamentals of chemical engineering have been treated. These are the material balance, the energy balance, and static equilibria. It has been noted that these fundamentals are applied with no regard for time as a variable except in the case of fluid flow when it is necessary to take kinetic energy into account in an energy balance. This is the only exception, however. In general, it may be concluded that those fundamentals provide no information in regard to the size of equipment, for size is directly related to the processing of a given amount of material within certain time limits.

It is apparent that the size of equipment for processing 10,000 units of material per day would be larger and would have a greater capacity than equipment for processing 1000 units per day. Thus, in order to determine the size of equipment for a given job or the maximum capacity of existing equipment, the chemical engineer must deal with the transfer and transformation of mass and energy per unit time. Time as a variable is essential in the determination of size and capacity of processing equipment.

Actually, rates of transfer and transformation of mass and energy enter as an essential variable in all dynamic equilibria. It was learned in the previous chapter that in a static system all driving forces will eventually become balanced so that at true equilibrium the net driving forces are each zero. Furthermore, it was learned that the final static equilibrium state could be calculated from static equilibrium relations. In a continuous system a dynamic equilibrium is reached, but the driving forces *may not* be zero. For example, consider the flow of a gas through a tube. If the static pressure at the outlet of the tube is maintained constant and the rate of flow of the gas is constant, the pressure at any point in the conduit will soon reach a constant value. Nevertheless, the pressure from the inlet to the outlet will decrease. Thus the driving force (pressure in this case) is not zero within the conduit, but even so a state of equilibrium (dynamic) exists. If the rate of flow of the gas is changed to another constant value, the pressure gradient from the inlet to the outlet will likewise change. Nevertheless, it will reach a dynamic equilibrium (or steady state, as it is frequently called) so that the pressure at any given point in the conduit is constant but different from the value prior to the change in flow rate. It is apparent, therefore, that the state of dynamic equilibrium is dependent upon the *rate* of flow of the gas.

As another example of dynamic equilibrium, consider the flow of a liquid through a tube that has a valve at the outlet and that is surrounded by saturated steam at atmospheric pressure. Assume that the liquid enters the tube at 100°F. If the valve at the outlet is closed and the flow stopped, the temperature of the liquid will eventually increase to 212°F, which is the temperature of the condensing steam. The thermal equilibrium state is static in this case, and the driving force (temperature) is zero. However, if the valve is opened and the flow of liquid is held constant at a fixed *rate*, the temperature at any given point in the liquid within the heated conduit will reach a constant value. The temperature gradient of the liquid lengthwise of the tube will therefore vary from 100°F at the inlet to the outlet temperature, which can never exceed 212°F, the static-equilibrium temperature. Thus, a dynamic equilibrium state exists, the exact nature of which is dependent among other things upon the *rate* of flow of the fluid.

Calculation of states of dynamic equilibria is usually of greatest importance to the chemical engineer. Nevertheless, states of static equilibria must be evaluated frequently in order to define the states of dynamic equilibria, for in any specific case the extent to which the driving forces are different from those in the state of static equilibrium determines the rate at which the static equilibrium condition is approached.

It is the purpose of this chapter to introduce the student to the application of rate equations (whether analytical or graphical) in process-design and process-performance calculations that deal with the size and capacity of process equipment. In such an introductory treatment it should be understood that it will not be desirable to deal thoroughly with any specific unit operation or chemical process. The sole objective is to convey a philosophy or viewpoint that will be useful in the student's later study and practice of chemical engineering. Detailed treatment of rates of mass and energy transfer and transformation constitutes a major part of the study of unit operations and chemical processes.

The following will take up the fundamental rate equation and the film concept, which are of a general nature. Then the utilization of rates of transfer and transformation of mass and energy in conjunction with the material balance, the energy balance, and static equilibria in the unit operations and chemical processes will be presented.

Fundamental Rate Equation.—It was learned in elementary physics that the rate of flow of electricity (amperage) is directly proportional to the electromotive force (voltage) and inversely proportional to the resistance. Actually this is merely a specific application of a more general law, which states that the rate at which a state of static equilibrium is approached at any instant is directly proportional to the driving force and inversely proportional to the resistance.

$$\frac{dQ}{d\theta} = C\frac{\Delta F}{R'} \tag{8.1}$$

where Q = quantity of mass or energy transferred
θ = time corresponding to Q
C = a constant
ΔF = difference in driving forces
R' = resistance to the transfer

Equation (8.1) is applicable directly to the flow of electricity, but it can be extended for applications in chemical engineering. The transfer of mass and energy in chemical engineering is ordinarily carried out through an area perpendicular to the direction of transfer. Thus, the rate of transfer in this case is directly proportional to the area through which the transfer is being made.

$$\frac{dQ}{d\theta} = C\frac{\Delta FA}{R} \tag{8.2}$$

where A = area perpendicular to direction of transfer
R = resistance to the transfer per unit area

Equation (8.2) will be found generally applicable to all chemical-engineering processes, although in specific cases it will be impossible to determine the actual area.

Although Eqs. (8.1) and (8.2) may not be entirely rigorous in certain cases, in general they are sufficiently representative of the various rates with which the chemical engineer deals. Usually the chemical engineer need not know the rate of mass or energy transfer within an accuracy greater than ±10 per cent. Often he will have to deal with rates that cannot be predicted more accurately than ±25 per cent. Even so, if he knows the limits of accuracy, he can make allowance in the form of a safety factor in the size of equipment or capacity of existing equipment to make certain that the predicted process performance will be attained. This does not mean that the chemical engineer does not desire precise information. On the contrary, he would like to have as reliable a basis as possible for his process-design and process-performance calculations. Nevertheless, he is ordinarily employed by organizations that require results within a short time. Consequently, the methods used to determine rates of mass and energy transfer must be sufficiently free of complications so that they will produce results rapidly. From the standpoint of the practicing chemical engineer, except in rather rare instances, a simple method that permits prediction of rates within ±10 per cent is far to be preferred to a complicated method that is reliable within ±1 per cent. Perhaps one of the chief reasons for this is that process equipment is seldom operated at exactly the capacity for which it was designed. As a matter of fact, most businessmen seem disappointed if the new plant does not perform continuously at a rate somewhat above that for which it was designed. Consequently, an additional allowance of 10 or even 25 per cent to compensate for the limits of error in the rates that are used in the design ordinarily is not bad economy.

The student may be disillusioned at this point, particularly since his previous training in the sciences, such as mathematics, is likely to have accustomed him to meeting the requirement of exact answers. But the practice of chemical engineering is always in connection with the fulfillment of the needs and wants of human beings, which are by no means exact. The chemical engineer can usually predict (calculate) the size or capacity of process equipment far more accurately than the human wants and needs that the equipment is to satisfy.

In any event, the calculation of rates of transfer of mass and energy has not been developed to the same high degree of accuracy as the material balance, energy balance, and static equilibrium relations. Many of the methods for predicting rates are predicated upon purely empirical correlations. The student must therefore develop judgment to guide him in the use of data and methods of calculation in his chemical-engineering practice. This will be invaluable to him throughout his career. Furthermore, the practicing chemical engineer must always review his calculations from the standpoint of required limits of error. Sometimes a relatively small tolerance in the limits of error can be permitted. In such cases the solution may have to be approached from several independent bases.

The Film Concept.—In the great majority of cases involving the transfer of mass and energy in chemical-engineering operations, mass and energy are transferred either to or from a body of fluid in a state of agitation through a more or less stagnant film of the fluid. A clear understanding of this can be obtained by consideration of the mechanics of fluid flow.

Consider the flow of a fluid through a tube. At low flow rates each particle of the fluid follows a straight-line path parallel to the tube wall. There is therefore no mixing effect in the stream of fluid. As the flow rate is increased, however, a critical velocity is reached at which the various particles of fluid cease to follow straight-line paths. Eddy currents form, and the entire stream is in a state of turbulence, although its net motion is still forward through the tube. The stream of fluid in this case is in a state of agitation. There are thus two types of fluid flow. The flow in which each particle follows a straight-line path parallel to the tube is called *streamline flow* or *viscous flow*. The type in which the particles enter into the formation of eddy currents is called *turbulent flow*. The linear velocity of the fluid at which the type of flow changes from streamline to turbulent flow is called the *critical velocity.*

By experimentation numerous investigators have shown that the type of flow which will occur is a function of the dimensionless group $DV\rho/\mu$, where D is the diameter of the tube, V the average linear velocity of flow through the tube, ρ the density of the fluid, and μ the viscosity of the fluid. This group is called the Reynolds number after Osborne Reynolds, who first pointed out its significance. Below a value of 2000 (consistent units) for the Reynolds number, streamline flow will prevail. Above a value of about 3000, turbulent flow will obtain. At intermediate values, the flow will be unstable since it passes through a transition between streamline and turbulent flows. By reference to Fig. 6.2 it will be noted that the change from streamline to turbulent flow has a pronounced effect on the friction factor. Also, the region of transition is clearly shown by the friction-factor curves.

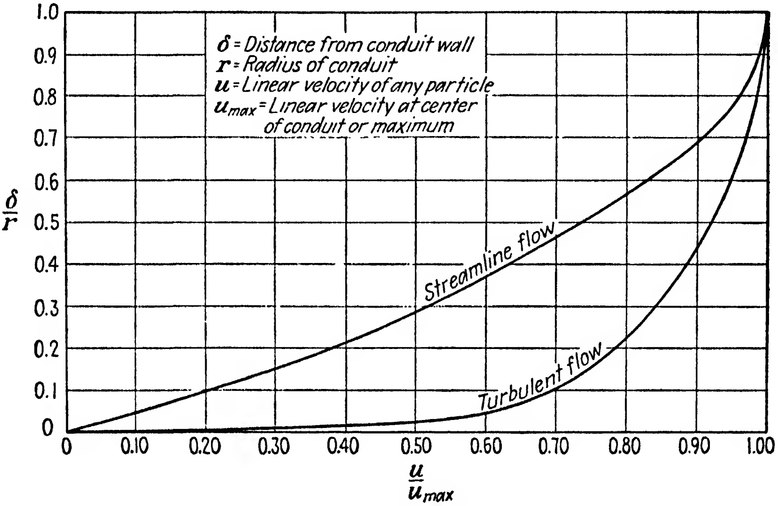

FIG. 8.1.

The linear-velocity distribution over a cross section of the stream perpendicular to the direction of flow is of great significance in connection with the film concept. Figure 8.1 shows the linear velocity of any particle of fluid as a fraction of the maximum linear velocity vs. the distance from the tube wall expressed as a fraction of the radius of the tube. It will be noted that both in streamline and in turbulent flow the velocity increases from zero at the wall of the tube to a maximum at its center. In particular, it will be seen that the velocity-distribution curve for turbulent flow becomes tangent to the tube wall, and at the wall the linear velocity is zero.

Inasmuch as the velocity at the wall is zero and increases rapidly as the distance from the conduit wall is increased from zero, there is a slight distance in which the linear velocity of the fluid is below the critical velocity. Within this slight distance the fluid must therefore be flowing in streamline motion. Beyond this streamline film of fluid the flow is turbulent. Furthermore, the higher the velocity of flow of the main body of fluid, the thinner the streamline film becomes. Several investigators[1] have explored the velocity distribution within streams of fluid in turbulent flow and have demonstrated conclusively the existence of streamline films at the tube wall. This is a most important phenomenon, for it is the basis for practically all the developments in chemical engineering that involve the rate of transfer of mass and energy from one phase or body to another. It is therefore essential that the student have a complete understanding of this before he proceeds further.

An example of the use of the film concept in the transfer of energy is an extension of the example discussed earlier in the chapter. A liquid is flowing in turbulent motion through a horizontal tube surrounded by saturated steam at atmospheric pressure. The liquid enters the tube at 100°F and receives heat from the steam by a mechanism that involves two fluid films and the tube wall. First, steam will condense on the wall of the tube, and a condensate film[2] will form. Further condensation of steam will occur on the surface of the condensate film; for as the condensate flows from the tube, it will be replaced at once by additional condensation. Thus, the latent heat of the steam is transferred through the condensate film. Then the heat flows through the tube wall. At the inside of the wall the heat is transferred to the streamline film of the liquid. Since there is no mixing effect within this film, the heat is conducted from molecule to molecule until the border area between the film and the turbulent body of fluid is reached. At this point the heat is transferred to the turbulent part of the stream and owing to the mixing that exists is very rapidly dissipated throughout the turbulent body of the stream of liquid.

As an example of the film concept in the transfer of mass, consider a body of stagnant water over which moisture-free air is passed in turbulent flow. Assume that the concentration of water vapor in the air is less than that at the surface of the water. Hence there is a mass concentration gradient of water vapor from the surface of the liquid to the main body of the air stream, which will result in evaporation of the liquid water. Actually this mass (moisture) concentration gradient can be represented by the

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[1] LANGMUIR, I., *Phys. Rev.*, **34**, 421 (1912); PANNELL, J., *Brit. Aeronaut. Research Comm. Rept.*, *Mem.* 243, June, 1916, H. M. Stationery Office, London, England.

[2] Under certain conditions steam will condense in the form of drops rather than as a film; but dropwise condensation is not considered here.

partial pressure of water vapor, as is apparent from Dalton's law. In any event, at the surface of the stagnant water a streamline film of air exists. Thus, for the water to evaporate, the water vapor must diffuse through the air film until it reaches the turbulent body of air, where it is picked up rapidly and mixed throughout the turbulent portion of the air stream. This transfer of mass can continue so long as the partial pressure of water vapor in the turbulent body is less than the partial pressure of water vapor at the very surface of the stagnant water. Figure 8.2 presents a graphical representation of the mass concentration gradient that exists in such cases.

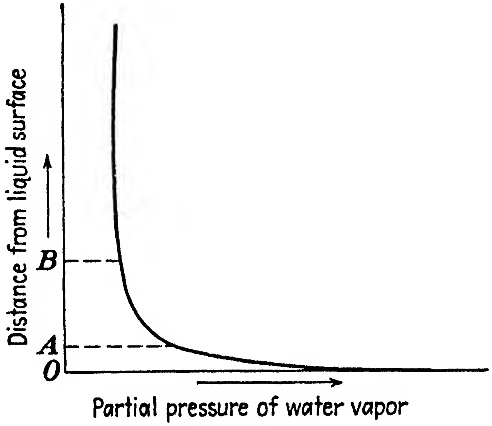

FIG. 8.2.

The distance *OA* from the surface of the water represents the streamline air film. The distance *AB* represents an intermediate or transition thickness between the film and the turbulent body of the air stream.

The velocity at which a vapor (gas) diffuses through another vapor is proportional to the sum of the reciprocals of the density of the two vapors and inversely proportional to the cross-sectional area of the two types of molecules. Thus, hydrogen has the highest diffusional velocity of any gas. It actually diffuses through steel. This represents a serious problem in the synthesis of ammonia. It is clear, too, on the basis of these facts why it is so difficult to eliminate a chemical fog by absorbing its particles in a solvent. Such particles have a very large cross-sectional area compared with the molecules of the gas that carries the fog particles. Thus, their diffusional velocity is very low compared with that of the gas molecules. Consequently, the molecules form a film on the surface of the solvent, which prevents the fog particles from reaching the solvent owing to their relatively negligible diffusional velocity.

The important objective in dealing with the rates of transfer of mass and energy through films is the quantitative evaluation of the effect of those variables in a unit operation or chemical process which can be controlled and which affect the thickness of the films. It is by no means necessary to be able to calculate the thickness of these films in order to use the film concept effectively. It is merely necessary to be able to predict the effect of the controllable process variables on the rates of mass and energy transfer. A major portion of the study of unit operations is devoted to this feature. The student should, therefore, develop the habit of interpreting transfer rates by means of the film concept even though a quantitative determination of the film thicknesses will not be necessary. This concept will be particularly useful in the interpretation of results on heat transfer, absorption, distillation, drying, chemical reaction, dynamic equilibria, etc.

DYNAMIC EQUILIBRIA IN UNIT OPERATIONS

Heat Transfer.—There are three general methods by which heat is transferred. These are conduction, convection, and radiation. Conduction involves the transfer of heat energy from molecule to molecule with no significant net movement of the molecules within the body of the material. Convection consists in the transfer of heat energy within a body of a liquid or gas by means of a mass movement or agitation of the fluid. In this way heat is conducted from one molecule to another, but the molecules are moving throughout the fluid so that the heat energy may be carried from one part of the body of fluid to another part by the actual movement of a large aggregate of the molecules of the fluid. Thus, the transfer of heat by both conduction and convection is done by means of material contact. Radiation, on the other hand, is the emission of radiant energy from one body to another without material contact. It will proceed in a total vacuum, whereas neither conduction nor convection could function under such conditions. The exact mechanism by which radiant energy is emitted is not understood, but this does not preclude an understanding of the laws that govern the rate of radiation from one body to another.

The attack on all heat-transfer problems is based on Eq. (8.2). In this case A is the area through which the heat is transferred, the driving force is temperature difference, and the rate $dQ/d\theta$ is the heat transferred per unit time. If a state of dynamic equilibrium (commonly called steady state) has been reached, the rate of heat transfer is constant and $dQ/d\theta = Q/\theta$. Only the steady state will be considered in this text. The general equation for heat transfer is therefore as follows,

$$\frac{Q}{\theta} = UA\,\Delta t \tag{8.3}$$

where Q = heat transferred, Btu
θ = time, hrs
Δt = temperature difference, deg F
U = over-all heat-transfer coefficient, Btu/(sq ft) (deg F) (hr)

The study of heat transmission involves essentially the development and utilization of methods of predicting (calculating) the heat-transfer coefficient for different methods of transferring heat.

It will be noted that the over-all heat-transfer coefficient U has the dimensions in English units of Btu per deg F per square foot per hour. It is really the reciprocal of resistance used in Eq. (8.2). Furthermore, the over-all coefficient U is usually made up of several coefficients. To illustrate this, consider the example discussed under The Film Concept earlier in the chapter. Heat was transferred through a condensate film on the outside surface of the tube, then through the tube wall, and finally through the streamline film inside the tube to the turbulent body of the stream. In this case the over-all heat-transfer coefficient U is made up of three independent coefficients, for any one could be varied independently of the other two. The flow of heat in this case is through a series of resistances.

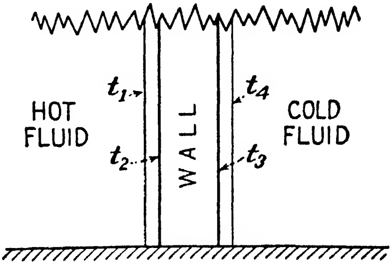

FIG. 8.3.

In order to establish the relationship between the over-all coefficient U and the individual coefficients of heat transfer in a series, consider a vertical wall (Fig. 8.3) through which heat is being transferred from a hot turbulent fluid on one side to a cold turbulent fluid on the other side. The individual coefficients will be represented by h_1, h_w, and h_2 for the film on the hot side, the wall, and the film on the cold side, respectively. The temperature of the turbulent body of hot fluid is t_1, the temperature of the wall surface on the hot side is t_2, the temperature of the wall surface on the cold side is t_3, and the temperature of the turbulent body of cold fluid is t_4. It will be assumed that these temperatures are constant over the respective surfaces represented so that there will be no longitudinal flow of heat. The various areas are parallel and equal, and the flow will be only in a direction perpendicular to the wall. By heat balance it is apparent that heat transferred through a given area of the hot film will be identical with the quantity of heat transferred through the corresponding area of the wall and the corresponding area of the cold film.

Thus
$$\frac{Q}{\theta} = h_1A(t_1 - t_2) = h_wA(t_2 - t_3) = h_2A(t_3 - t_4) \tag{8.4}$$

Also,
$$\frac{Q}{\theta} = UA(t_1 - t_4)$$

and
$$t_1 - t_2 = \frac{Q}{\theta A h_1} \qquad t_2 - t_3 = \frac{Q}{\theta A h_w} \qquad t_3 - t_4 = \frac{Q}{\theta A h_2}$$

but
$$t_1 - t_4 = \frac{Q}{\theta A h_1} + \frac{Q}{\theta A h_w} + \frac{Q}{\theta A h_2} = \frac{Q}{\theta A U}$$

or
$$\frac{1}{U} = \frac{1}{h_1} + \frac{1}{h_w} + \frac{1}{h_2} \tag{8.5}$$

and
$$U = \frac{1}{(1/h_1) + (1/h_w) + (1/h_2)} \tag{8.6}$$

It was pointed out earlier that U corresponds to the reciprocal of resistance in Eq. (8.2). Thus, $1/U$ corresponds to the over-all resistance, and Eq. (8.5) shows that the over-all resistance is equal to the sum of the individual resistances in the series. It was learned in elementary physics that the total resistance in an electric circuit is the sum of the component resistances. Hence, the same principle is valid for thermal resistances.

It should be noted that if the individual coefficients of a series are known the temperature drop through each component of the series can be calculated by the same type of method used to develop the relationship between U and the individual coefficients.

The heat-transfer coefficient, which corresponds to the *conduction* of heat through any material, is related to a property of the material. For instance, when a state of dynamic equilibrium has been reached (steady state) in the conduction of heat through a given material, the rate of heat transfer is represented by Eq. (8.7),

$$\frac{Q}{\theta} = \frac{kA\,\Delta t}{L} \tag{8.7}$$

where k = thermal conductivity, Btu/(deg F)(ft)(hr)
A = cross-sectional area, sq ft
Δt = temperature drop, deg F
L = thickness or distance of heat flow, ft

Thermal conductivity is a property of the specific material and is a function only of temperature for solids and liquids. Pressure has a slight effect on the thermal conductivity of gases at very high pressure. Otherwise, it also is a function only of temperature for gases.

Table A.10 presents thermal conductivities for a number of different materials. For a more complete presentation of data the student is referred to the "International Critical Tables,"[1] McAdams,[2] and Perry.[3]

Comparison of Eq. (8.7) with (8.4) shows that the coefficient of heat transfer for conduction is

$$h = \frac{k}{L} \tag{8.8}$$

Example 53. What are the over-all heat-transfer coefficient and temperature drop through each thickness of the following series of materials on a flat wall if the over-all temperature drop is 150°F?

1.0 in. of steel plate ($k = 26$)

2.0 in. of brick ($k = 0.60$)

0.5 in. of asbestos packing ($k = 0.05$)

0.5 in. of wool felt ($k = 0.03$)

Solution:

	L(ft.)	k	$1/h = L/k$	Δt *
Steel plate	$\frac{1}{12}$	26	0.0032	0.2
Brick	$\frac{1}{6}$	0.60	0.278	16.7
Asbestos	$\frac{1}{24}$	0.05	0.8325	49.9
Wool felt	$\frac{1}{24}$	0.03	1.39	83.3
			2.5037	150.0

$$U = \frac{1}{2.5037} = 0.4 \text{ Btu/(deg F)(sq ft)(hr)}$$

* Since $1/h$ represents the resistance of each thickness of material to heat flow, the corresponding Δt can be obtained directly as the fraction of the total resistance multiplied by the total Δt. This is apparent from the derivation of Eq. (8.5).

In the event that the thickness of material through which heat is conducted is circular in its form, as in pipe insulation, there is a question immediately as to what area should be used to express the coefficient of heat

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[1] "International Critical Tables," McGraw-Hill Book Company, Inc., New York, 1929.

[2] McAdams, W. H., "Heat Transmission," 2d ed., McGraw-Hill Book Company, Inc., New York, 1942.

[3] Perry, J. H., "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

transfer. The problem is represented by Fig. 8.4. The thickness of material through which heat is to be conducted is $r_2 - r_1$, and the length of the hollow cylinder is N. It is apparent that if heat is transferred from the inside to the outside, the area through which the heat will pass will vary from $2\pi r_1 N$ to $2\pi r_2 N$. Or, if only a unit length is considered, N will be unity and the area will vary from $2\pi r_1$ to $2\pi r_2$. Thus, in the application of Eq. (8.7) to this case the area A is a variable with temperature drop.

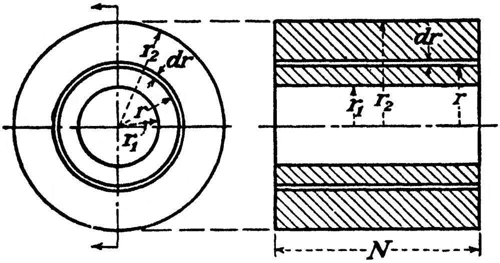

FIG. 8.4.

Temperature drop will not be linear with r, for A is not constant. Consider the area that corresponds to any radius r. Then,

$$A = 2\pi r$$

and

$$dL = dr$$

Thus

$$\frac{Q}{\theta} = \frac{-kA\,dt}{dr} = \frac{-2\pi kr\,dt}{dr} \tag{8.9}$$

The negative sign occurs because t_2 is less than t_1.

It would be convenient if the average area A_{av} could be used so that the simplicity of Eq. (8.7) could be retained. Thus,

$$\frac{Q}{\theta} = \frac{kA_{av}\,\Delta t}{r_2 - r_1} = \frac{-2\pi kr\,dt}{dr} \tag{8.10}$$

and

$$\int_{r_1}^{r_2} \frac{dr}{r} = \int_{t_1}^{t_2} \frac{-2\pi(r_2 - r_1)\,dt}{A_{av}\,\Delta t}$$

$$\ln\frac{r_2}{r_1} = \frac{2\pi(r_2 - r_1)(t_1 - t_2)}{A_{av}\,\Delta t}$$

but

$$\Delta t = t_1 - t_2{}^{*}$$

and thus

$$A_{av} = \frac{2\pi(r_2 - r_1)}{\ln(r_2/r_1)} = \frac{A_2 - A_1}{\ln(A_2/A_1)} \tag{8.11}$$

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* Δt is usually chosen so that it is positive.

Thus, it is seen that, if an average area is used as defined by Eq. (8.11) in terms of the outside and inside areas, Eq. (8.7) can be used directly. This average is commonly called the log-mean area.

In case the ratio, A_2/A_1, is less than 2, an arithmetic mean area will be within 4 per cent of the log-mean average. This is usually sufficiently accurate for the purpose. Thus, in this case,

$$A_{av} = \frac{A_2 + A_1}{2} \tag{8.12}$$

It is common practice to express the film heat-transfer coefficients on the basis of the area of the respective films. It is apparent therefore that in the case of pipe which is covered with a significant thickness of insulation the area of the film inside the pipe will be substantially less than the log-mean area of the insulation, which in turn will be substantially less than the area of the film on the outside surface of the insulation. Consequently, it is necessary to correct the various film coefficients and wall coefficients to a common area in arriving at an over-all heat-transfer coefficient. This is done by multiplying each coefficient to be corrected by the ratio of the area on which it is based to the area used as a basis for the over-all coefficient. Thus if the outside area of the insulation is used as a basis, the coefficient for the film inside the pipe should be multiplied by the ratio of the inside pipe diameter to the diameter of the outside of the insulation. Likewise, the coefficient for the insulation should be multiplied by the ratio of its log-mean diameter to the diameter of the outside surface of the insulation.

Example 54. How much heat is lost per hour from a rotary kiln, 30 ft in length by 3 ft in inside diameter (I.D.). The kiln is covered with insulating brick [k = 0.05 Btu/(deg F)(ft)(hr)] of 2.0 ft in thickness, and the temperature of the outside surface of the brick is 500°F less than the inside surface of the brick.

Solution:

$$\frac{Q}{\theta} = \frac{kA_{av}\,\Delta t}{L}$$

Since $A_2/A_1 = D_2/D_1 = (3 + 4)/3 = 2.33$, the log-mean average will be used.

$$D_{av} = \frac{7 - 3}{\ln 7/3} = \frac{4}{0.846} = 4.73$$

$$A_{av} = N\pi D_{av} = (30\pi)(4.73) = 445 \text{ sq ft}$$

$$\frac{Q}{\theta} = \frac{(0.05)(445)(500)}{2.0} = 55{,}600 \text{ Btu/hr}$$

Convection heat transmission is somewhat more complicated than steady-state conduction of heat. There are several different methods of transferring heat by convection. These might be outlined briefly as follows:

1. Transfer to or from fluids flowing in turbulent or streamline motion
    - *a.* Inside of tubes
    - *b.* Outside and parallel to tubes
    - *c.* Outside and perpendicular to tubes
    - *d.* Parallel to a plane
2. Transfer by natural convection to or from fluids
    - *a.* Outside vertical tubes
    - *b.* Outside horizontal tubes
    - *c.* Adjacent to vertical and horizontal planes
3. Transfer by condensing vapors
    - *a.* Outside and inside vertical tubes
    - *b.* Outside and inside horizontal tubes
    - *c.* On a vertical or inclined wall
4. Transfer to boiling liquids
    - *a.* Outside and inside of horizontal tubes
    - *b.* Outside and inside of vertical tubes
    - *c.* Adjacent to horizontal and vertical planes

In any advanced study of heat transmission, attention will be concentrated on methods of predicting coefficients of heat transfer for these specific cases. As far as the scope of this text is concerned, however, it is the purpose merely to acquaint the student with the use of heat-transfer rates.

A very common example of convection heat transmission is the transfer of heat from one fluid to another. This is frequently done by passing one of the fluids through one or several parallel tubes while the other fluid flows around these tubes parallel to them. If the two fluids flow in the same direction (*i.e.*, if the hot fluid and cold fluid enter at the same end of the heat exchanger so that heat is flowing from the highest temperature on the hot fluid side to the lowest temperature on the cold fluid side), the flow arrangement is called parallel flow (Fig. 8.5). If, however, the hot fluid enters the heat exchanger at the same end as the cold fluid leaves, the flow arrangement is called *countercurrent flow* (Fig. 8.6). The temperature of the hot fluid is denoted by t', whereas the temperature of the cold fluid is denoted by t. Subscripts 1 and 2 represent inlet and outlet.

It will be noted that with countercurrent flow the maximum average Δt can be obtained, *i.e.*, a higher exit temperature of the cold fluid can be obtained by transferring heat from the highest temperature of the hot fluid to the highest temperature of the cold fluid. The chief reason for this is that heat will flow most effectively from the lowest temperature of the hot fluid if the temperature of the cold fluid is at its lowest level (inlet temperature).

It is apparent from both Figs. 8.5 and 8.6 that the Δt varies with tube length or heat-transfer area. Thus far, Eqs. (8.3) and (8.7) have been applied only to cases which involved a constant Δt over the entire heat-transfer area. In order to apply Eq. (8.3) to cases of variable Δt an average, Δt_{av}, must be used. Furthermore, it would be very convenient to define Δt_{av} in terms of the terminal Δt's. This can be done by application of the material balance, energy balance, and equation for rate of energy transfer.

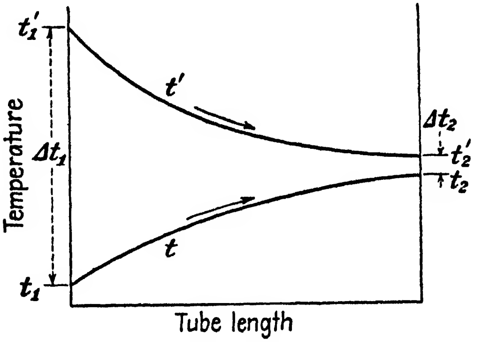


FIG. 8.5.

In the case of steady-state (dynamic-equilibrium) transfer of heat [Eq. (8.3)] as illustrated by either Fig. 8.5 or 8.6 the amount of heat transferred through an infinitesimal area dA is as given by Eq. (8.13a).

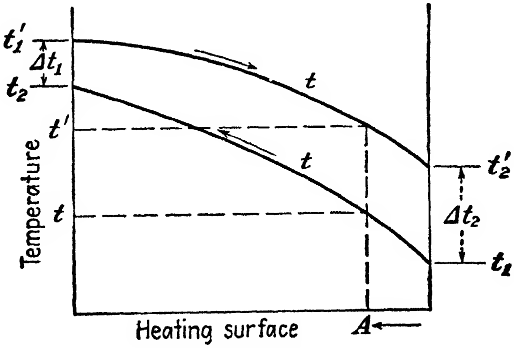


FIG. 8.6.

Let q = quantity of heat transferred per unit time through the area that extends from the inlet to any point within the exchanger.

Then,
$$dq = U\,\Delta t\,dA \tag{8.13a}$$

Note that q is identical with Q/θ when the area extends from inlet to outlet.

Let c' = heat capacity of hot fluid, Btu/lb
c = heat capacity of cold fluid, Btu/lb
W' = rate of flow of hot fluid, lb/hr
W = rate of flow of cold fluid, lb/hr

Then, by material balance and heat balance,

$$dq = cW\,dt = -c'W'\,dt'\ * \qquad (8.13b)$$

Although c and c' do not remain constant with change in temperature, they do not vary greatly and for the purpose here it may be assumed that an average value may be used which may be regarded as a constant. Therefore, if A is zero at the outlet of the hot fluid, by heat balance

$$q = c'W't'_1 - c'W't' \qquad (8.14)$$

and

$$q = cWt_2 - cWt \qquad (8.15)$$

Thus, q is a straight-line function of t and of t' as indicated in Fig. 8.7.

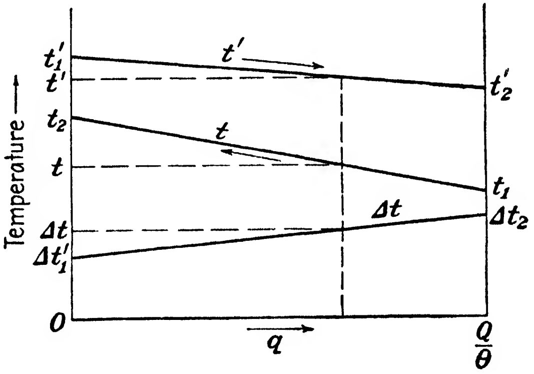


FIG. 8.7.

Of course, q is identical with Q/θ when the area extends from the inlet to the outlet of the hot fluid. Thus,

$$\frac{Q}{\theta} = c'W't'_1 - c'W't'_2 \qquad (8.16)$$

and

$$\frac{Q}{\theta} = cWt_2 - cWt_1 \qquad (8.17)$$

---

* The proper sign for this side of the equation will depend on whether parallel (+) or countercurrent (−) flow is used. To simplify the presentation, countercurrent flow (see Fig. 8.6) will be assumed, and therefore the sign will be negative.

From Eqs. (8.14) and (8.15),

$$t' = \frac{c'W't'_1 - q}{c'W'} \tag{8.18}$$

and

$$t = \frac{cWt_1 - q}{cW} \tag{8.19}$$

But

$$\Delta t = t' - t$$

where Δt is the temperature drop from the hot fluid to the cold fluid at any point in the exchanger. Therefore,

$$\Delta t = \frac{c'W't'_1 - q}{c'W'} - \frac{cWt_1 - q}{cW} \tag{8.20}$$

It is apparent from Eq. (8.20) that Δt is also a straight-line function of q (Fig. 8.7) the slope of which is

$$\frac{d\,\Delta t}{dq} = \frac{1}{cW} - \frac{1}{c'W'} \tag{8.21}$$

or, from Eqs. (8.15) and (8.16),

$$\frac{1}{c'W'} = \frac{t'_1 - t'_2}{Q/\theta}$$

and

$$\frac{1}{cW} = \frac{t_2 - t_1}{Q/\theta}$$

or

$$\frac{d\,\Delta t}{dq} = \frac{t_2 - t_1 - t'_1 + t'_2}{Q/\theta} \tag{8.22}$$

and, from Eqs. (8.12) and (8.22),

$$dq = \frac{Q}{\theta}\left[\frac{d\,\Delta t}{(t_2 - t'_1) - (t_1 - t'_2)}\right] = U\,\Delta t\,dA \tag{8.23}$$

Assuming that U is constant over the entire heating surface and noting in Fig. 8.6 that $t'_1 - t_2 = \Delta t_1$ and $t'_2 - t_1 = \Delta t_2$, Eq. (8.23) can be rearranged and integrated,

$$\frac{Q}{\theta(\Delta t_2 - \Delta t_1)} \int_{\Delta t_1}^{\Delta t_2} \frac{d\,\Delta t}{\Delta t} = U \int_0^A dA$$

or

$$\frac{Q}{\theta} = UA\left(\frac{\Delta t_2 - \Delta t_1}{\ln \Delta t_2/\Delta t_1}\right) \tag{8.24}$$

But
$$\frac{Q}{\theta} = UA\,\Delta t_{av} \tag{8.25}$$

Thus.
$$\Delta t_{av} = \frac{\Delta t_2 - \Delta t_1}{\ln(\Delta t_2/\Delta t_1)} \tag{8.26}$$

It is seen, therefore, that again an important average turns out to be a log-mean average just as in the case of Eq. (8.11). It is predicated upon uniform cross-sectional area of heat flow, true countercurrent or true parallel flow, and adiabatic conditions, as well as the limitations mentioned during the development. It is valid, therefore, to retain the simple type of equation [Eq. (8.3)] provided that an average Δt is used as defined by Eq. (8.26) and provided that the conditions on which the development was based prevail. If the ratio of the terminal Δt's is not over 2.0, the arithmetic mean Δt,

$$\Delta t_{av} = \frac{\Delta t_1 + \Delta t_2}{2} \tag{8.27}$$

will be within 4 per cent of the log-mean value.

In the derivation of Eq. (8.26) it was assumed that average heat capacities may be used. Usually the heat capacity approaches a linear relationship with temperature, and thus an arithmetic mean value of c and c' is sufficiently accurate, particularly since the variation with temperature is usually relatively small. Also, in this connection it was assumed that the over-all heat-transfer coefficient U is constant over the entire heating surface. For the purpose of this text, deviations from this premise will not be considered, but the student will learn in his more advanced studies that U is not always constant, although it can be dealt with effectively.

Example 55. In Example 45 calculate the heat-transfer area required in the overhead condenser and the reboiler if the over-all heat-transfer coefficients are 85 and 45 Btu/(deg F)(sq ft)(hr), respectively. Cooling water is available at 85°F and will leave the overhead condenser at 105°F. The reboiler heating medium is a 30°API hydrocarbon oil. Its specific heat at any temperature may be determined from the relationship

$$c_p = \frac{(t + 670)(2.10 - \text{sp. gr.})}{2030} \tag{8.28}$$

where c_p = specific heat
t = deg F
sp. gr. = specific gravity of the oil at 60°F

The heating medium is available at 400°F and at a rate of 200 bbl/hr.

Solution: First, the surface for the overhead condenser will be determined on the basis of the duty as calculated in Example 42.

$$\frac{Q}{\theta} = 4{,}134{,}200 = 85A\,\Delta t_{av}$$

Although the overhead vapor enters the condenser at 127°F and is condensed at 115°F, very little of the heat is removed in cooling the vapor from 127 to 115°F. Essentially all the heat is latent heat of vaporization, and therefore the condensate side will be assumed constant at 115°F. The log mean Δt is valid in this case, for the temperature on both the hot and the cold side is a straight-line function of the heat transferred.

Condensate side	115	115
Water side	85 →	105
Δt	30	10

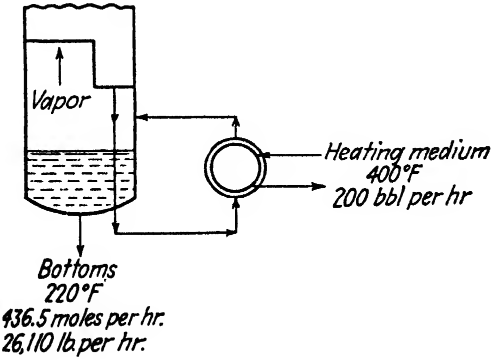
$$\frac{\Delta t_1}{\Delta t_2} = \frac{30}{10} = 3.0 \text{ (thus use log mean)}$$

$$\Delta t_{av} = \frac{30 - 10}{\ln 3} = 18.2°\text{F}$$

Thus,

$$A = \frac{4{,}134{,}200}{(85)(18.2)} = 2670 \text{ sq ft}$$

The surface for the reboiler will now be calculated, based on the duty calculated in Example 42. It will first be necessary to calculate the temperature of the material from the bottom tray. This will be done by material balance, heat balance, and static equilibrium relations. Of course, the temperature of the liquid from the bottom tray could be calculated directly by means of static equilibrium relations if the liquid analysis were known. This is not known, but the analyses of the two streams that make up the liquid from the bottom tray are known (vapor to the bottom tray and the bottoms).



The quantity of the bottoms per unit time is known, but the quantity of vapor to the bottom tray per unit time is not known, although it can be calculated by trial and error so that a heat balance around the reboiler is obtained.

Liquid to reboiler from bottom tray = vapor from reboiler plus bottoms

Assume quantity of vapor from reboiler, the analysis of which was calculated in Example 44. Then calculate the analysis of liquid to reboiler by material balance and its temperature by static equilibrium relations. If the correct quantity was assumed, a heat balance will be obtained around the reboiler. If not, another assumption must be made.

Assume: Vapor from reboiler = 896 moles/hr.

	Vapor to bottom tray			Assume liquid at 215°F			
	Mole %	Moles/hr	Lb/hr	Moles/hr *	x	$K^{215°}_{215\text{ lb}}$	$(x)(K)$
C_3	1.1	9.9	440	12.1	0.009	2.21	0.020
n-C_4	91.7	821.6	47,600	1,195.9	0.898	1.04	0.933
n-C_5	7.2	64.5	4,650	124.5	0.093	0.50	0.047
	100.0	896.0	52,690	1,332.5	1.000		1.000

* Vapor + bottoms.

Thus, the reboiler inlet temperature = 215°F for this quantity of vapor. Check assumed quantity of vapor by heat balance.

	Bottoms, lb/hr	Btu/lb			Btu/hr
		Liquid 220°	Liquid 215°	Δh	
C_3	100	163	160	3	300
n-C_4	21,690	103	100	3	70,000
n-C_5	4,320	104	101	3	10,000
	26,110				80,300

	Vapor, lb/hr	Btu/lb			Btu/hr
		Vapor 220°	Liquid 215°	Δh	
C_3	440	333	160	73	32,000
n-C_4	47,600	217	100	117	5,565,000
n-C_5	4,650	227	101	126	586,000
	52,690				6,183,000
	To heat bottoms from 215 to 220°				80,300
Total heat from reboiler					6,263,300

Thus, the assumed quantity of vapor was essentially correct since the calculated reboiler duty for this quantity is only 17,300 Btu/hr less than the correct reboiler duty as calculated in Example 45 by over-all heat balance.

Now the reboiler heating surface can be calculated.

Since the quantity of heating medium is 200 bbl/hr, its outlet temperature can be calculated by heat balance.

$$\text{Heating medium} = (200)(42)(7.296) = 62{,}400 \text{ lb/hr}$$

$$\frac{Q}{\theta} = 6{,}280{,}000 = 62{,}400(400 - t_2)c_p$$

At 400°F,

$$c_p = \frac{(400 + 670)(2.10 - 0.876)}{2030} = 0.645$$

Assume exit temperature = 300°F.

At 300°F,

$$c_p = \frac{(300 + 670)(2.10 - 0.876)}{2030} = 0.585$$

$$\text{Av. } c_p = 0.615 \qquad \text{or} \qquad t_2 = 400 - \frac{100.7}{0.615} = 236°\text{F}$$

Assume exit temperature = 225°F since 300° was too high.

At 225°F,

$$c_p = \frac{(225 + 670)(2.10 - 0.876)}{2030} = 0.54$$

$$\text{Av. } c_p = 0.592 \qquad \text{or} \qquad t_2 = 400 - \frac{100.7}{0.592} = 230°\text{F}$$

Thus, the assumed temperature of 225°F was close enough for the purpose of calculating the average c, and the true outlet temperature is 230°F. The log mean Δt will be used even though it is not strictly valid, for the temperature on the cold side is not exactly a straight-line function of the heat transferred. Even so, it is not far from a straight-line function.

$$\begin{array}{lrcr}
\text{Hot side} & 230 & \leftarrow & 400 \\
\text{Cold side} & 215 & \rightarrow & 220 \\
\hline
 & 15 & & 180
\end{array}$$

$$\Delta t_{av} = \frac{180 - 15}{\ln 180/15} = 66.4°\text{F}$$

$$\text{Area} = \frac{6{,}280{,}000}{(45)(66.4)} = 2100 \text{ sq ft}$$

Radiation of heat energy occurs with solids, liquids, and certain gases. The radiant heat energy received by a body may be absorbed, reflected, or transmitted unchanged through the body. If all the radiant heat energy received by a body is absorbed, the latter is called a *black body.* The amount of the radiant heat energy emitted by a body divided by the amount that would be emitted if the body were a black body is called the emissivity of the body. Thus, the emissivity of a black body is 1.0.

The rate at which heat energy is radiated from a black body is given by the Stefan-Boltzmann law,

$$E_B = 0.173 \left(\frac{T}{100}\right)^4 \tag{8.29}$$

where E_B is the Btu per hour per square foot radiated by a black body and T is the absolute temperature in degrees Rankine. All bodies radiate energy at a rate proportional to the fourth power of the absolute temperature of the body. Thus, the net heat transferred from a hot body to a cold body is the difference between the radiant energy absorbed by the cold body from the hot body and the radiant energy absorbed by the hot body from the cold body. It is seen, therefore, that in radiation heat is actually transferred in both directions. Furthermore, when a body is receiving heat by conduction or convection in addition to radiation, the rates of heat transfer by radiation and conduction or convection are additive.

The net heat transferred by radiation is given by Eq. (8.30),

$$\frac{Q}{\theta} = 0.173A \left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right] F_A F_E \tag{8.30}$$

where F_A = a shape factor
F_E = an emissivity factor

The factor F_A is dependent upon the physical arrangement and shape of the two radiating bodies. For instance, the value of F_A in the case of radiation between two parallel planes is different from the value for two perpendicular planes. The area A is related directly to F_A. The factor F_E is dependent upon the emissivities of the two radiating bodies and the physical arrangement and shapes of the two radiating surfaces.

Since the study of radiant heat transfer is too complicated for treatment in this text, no further consideration will be given to it. It will suffice to know that the rates of radiant heat transfer can be calculated on the basis of Eq. (8.30). Values of F_A and F_E have been worked out for several different arrangements frequently encountered in practice.

Evaporation.—Single-effect evaporators were considered in Chap. V, but more attention will be devoted at this point to multieffect evaporators. Figure 8.8 presents a diagrammatic sketch of a single-effect, a double-effect, and a triple-effect evaporator. The flow arrangement as shown for the double- and triple-effect evaporators is called "forward feed," *i.e.*, the feed is sent to the first effect and the liquor flows from this effect through the succeeding effects so that it becomes progressively more concentrated from the first to the last effect. If the flow had been in the opposite direction, the arrangement would be what is called "backward feed." The ensuing discussion will be based on Fig. 8.8, or forward feed.

With steam available at a given pressure and cooling water available at a given temperature the total temperature drop through any evaporator is fixed by the difference between the temperature at which the steam will

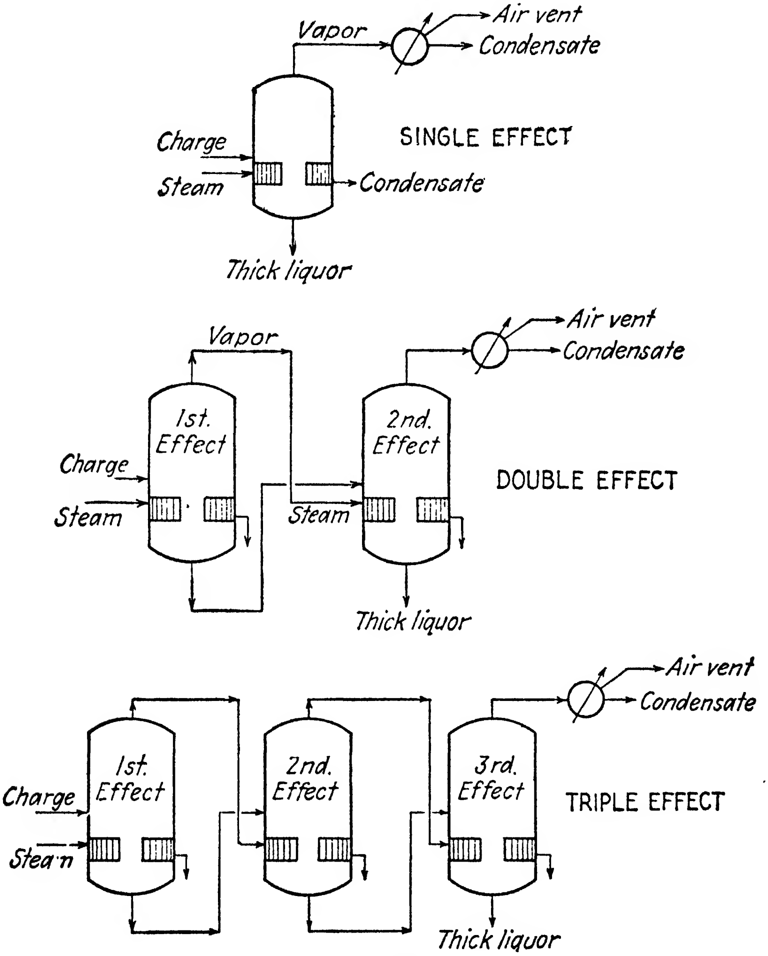


Fig. 8.8.

condense and the temperature of the condensate from the condenser. For example, assume that water is being charged to an evaporator and that the absolute pressure at the condenser is 4.0 in. of mercury. Assume that the steam is available at 35 lb/sq in. gauge with 19°F superheat. Thus, the steam temperature is 300°F; and since it condenses at saturation temperature, condensation takes place at 281°F. The latent heat of condensation is 923 Btu/lb, and the sensible heat owing to the superheat is

10.6 Btu/lb. All the sensible heat as well as the latent heat is transferred through the condensate film on the heating surface. Hence, the temperature drop from the surface of the condensate film through the tube wall and the film of boiling liquid is the difference between the saturation temperature of the steam and the temperature of the boiling liquid. The effect of the superheat is merely a slight increase in the coefficient of heat transfer, which the student will learn in his more advanced study of unit operations. For the purpose here, however, the effect on the coefficient of heat transfer will be disregarded, for it has little bearing on the final results.

The temperature of the boiling liquid is controlled by the pressure that is maintained on the evaporator. Actually evaporators are designed so that the pressure drop from the evaporator to the condenser is very small. Consequently, it may be assumed that the pressure on the evaporator is identical with that of the condenser. The temperature of the boiling liquid, which corresponds to 4 in. of mercury, is 126°F, and the temperature drop is 281 − 126 or 155°F.

In the case of a single-effect evaporator it is apparent that the surface required will be

$$A = \frac{Q/\theta}{\Delta t U} = \frac{Q/\theta}{155U} \tag{8.31a}$$

On the other hand, it will be noted from Fig. 8.8 that if a double-effect evaporator is to be used the temperature drop from the saturation temperature of the steam to the temperature of condensation in the condenser will be divided between the two effects. If the saturation temperatures of the vapor from the first effect is represented by t_1, the temperature drop in that effect will be $281 - t_1$. Also, the vapor from the first effect will condense on the heating surface of the second effect at essentially t_1, for evaporators are designed so that the pressure drop is negligible. Thus, the temperature drop in the second effect will be $t_1 - 126$, and the heating surface of each effect will be

$$A_1 = \frac{Q_1/\theta}{U_1(281 - t_1)} \tag{8.31b}$$

and

$$A_2 = \frac{Q_2/\theta}{U_2(t_1 - 126)} \tag{8.31c}$$

where the subscripts refer to the two effects.

By heat balance it follows that if the water is charged to the first effect at its boiling point the heat transferred in the first effect will be used entirely to supply latent heat of evaporation. Also, since the latent heat of evaporation will be removed in the second effect, it is apparent that

Q_1 is equivalent to Q_2. Thus, if U_1 is the same as U_2, it follows directly from Eqs. (8.31*b*) and (8.31*c*) that

$$\frac{A_1}{A_2} = \frac{t_1 - 126}{281 - t_1}$$

or that the ratio of the areas is inversely as the ratio of temperature drops. If the areas are made the same, the temperature drops will be equal. Consequently, the total area $A_1 + A_2$ will be twice the area required for a single effect, for the temperature drop for the transfer of the total amount of heat $Q_1 + Q_2$ will be half the total that would obtain in a single-effect evaporator.

The same type of analysis for a triple-effect evaporator will show that the total area will be three times the area of a single-effect evaporator when the total temperature drop from the condensing steam to the condenser is divided into equal temperature drops over the three effects. Thus, it is apparent that the advantage of multieffect evaporators is merely an economy of steam for evaporation, which justifies the installation of the additional heating surface.

The example that was used in the above discussion is valid when the evaporator is charged with pure water. This is not usually the case, however. Evaporation is ordinarily employed to concentrate aqueous solutions that contain nonvolatile components. In this case the elevation of boiling point of the solution becomes quite important, particularly for multieffect evaporators.

Assume that a salt solution is charged to the evaporator in the example discussed above. Let e represent the elevation in boiling point in each effect, with subscripts to indicate the different effects. In the case of a single effect, Eq. (8.31*a*) will then be changed to

$$A = \frac{Q/\theta}{U(155 - e)}$$

For a double-effect evaporator, Eqs. (8.31*b*) and (8.31*c*) will be changed respectively to

$$A_1 = \frac{Q_1/\theta}{U_1(281 - t_1 - e_1)}$$

and

$$A_2 = \frac{Q_2/\theta}{U_2(t_1 - e_2 - 126)}$$

The total available temperature drop is the sum of Δt_1 and Δt_2, or

$$\begin{aligned}\Delta t &= 281 - t_1 - e_1 + t_1 - e_2 - 126 \\ &= 281 - 126 - e_1 - e_2\end{aligned}$$

Thus, the boiling-point elevation in each effect represents a reduction in the total available Δt.

With the same amount of heat transferred in each effect and if U_1 and U_2 are identical, then

$$\frac{A_1}{A_2} = \frac{t_1 - e_2 - 126}{281 - t_1 - e_1}$$

Also, if A_1 and A_2 are the same, it is apparent that the net total available Δt will be divided equally between the different effects as was the case in the example that involved no boiling-point elevation. It will be noted, too, that the boiling-point elevation in the second effect of the double-effect evaporator is identical with the boiling-point elevation if a single-effect evaporator were used. Thus, the net available Δt for a single-effect evaporator would be $281 - 126 - e_2$ compared with the total net available for a double-effect evaporator of $281 - 126 - e_1 - e_2$. It is seen, therefore, that the double-effect evaporator would have more than twice the surface required for a single-effect evaporator owing to the boiling-point elevation in the first effect.

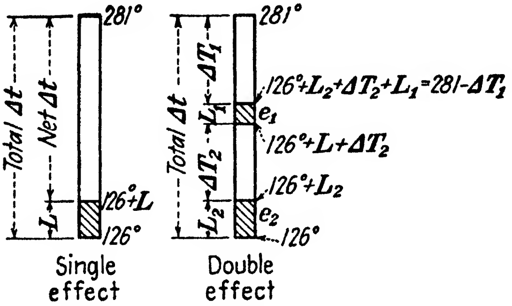


FIG. 8.9.

The effect of boiling-point elevation can also be presented graphically as in Fig. 8.9, where the shaded areas represent the boiling-point elevations. Note that e for the single effect is identical with e_2 for the double effect.

There are many factors involved in the study of evaporation that will not be considered in this text. The chemical-engineering student will eventually study evaporation in detail in his future work in the unit operations. If a more detailed discussion of evaporation should be wanted at this time, the student is referred to Badger and McCabe.[1]

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[1] BADGER, W. L., and W. L. MCCABE, "Elements of Chemical Engineering," 1st ed., p. 160, McGraw-Hill Book Company, Inc., New York, 1931.

Example 56. Caustic soda is produced at a rate of 98 tons/day by electrolysis of an aqueous solution of NaCl. About 40 per cent of the NaCl is decomposed, and the solution of NaOH with the remaining NaCl is withdrawn from the electrolytic cells. It is concentrated in a triple-effect evaporator to 30 per cent by weight NaOH in solution. The 30 per cent solution is then concentrated in a double-effect evaporator to 42 per cent by weight NaOH. The pressure on the second effect is 4.0 in. of mercury absolute. The charge to the double-effect is saturated with NaCl. How much heating surface is required by the double-effect evaporator? What is the steam consumption by the double-effect if the steam is available at 37 lb/sq in. abs? How much NaCl is crystallized out of solution in the double-effect? The amount of evaporation in each effect per pound of saturated steam to the first effect is as follows:

	1st	2d
Double.	0.7	1.0

The average heat transferred per pound of water evaporated including heat of solution, sensible heat of charge, heat of crystallization, and latent heat is 1250 Btu. The over-all heat-transfer coefficient is 500 Btu/(deg F)(sq ft)(hr) in each effect, and the surface in each effect is the same. Assume that the heat transferred in each effect is the same. The NaCl content and boiling-point elevation may be obtained from the following tabulation:

% NaOH	Lb/1000 lb NaOH		Deg F increase in boiling point *
	NaCl	H_2O	
30.0	200	2100	40.8
40.0	105	1380	59.0
50.0	80	920	88.5

* Relative to water at the same vapor pressure.

Forward-feed arrangement will be used.

Solution:

Basis: 1 day.

$$\text{NaOH in solution} = (98)(2000) = 196{,}000 \text{ lb}$$

Solution to first effect at 30% NaOH:

$$\text{Charge} = \frac{196{,}000}{0.3} = 653{,}000 \text{ lb}$$

$$\text{NaCl at 200 lb/1000 lb of NaOH} = (200)(196) = 39{,}200 \text{ lb}$$

$$H_2O = 653{,}000 - 196{,}000 - 39{,}200 = 417{,}800 \text{ lb}$$

Solution from second effect at 42 per cent NaOH:

$$\text{Thick liquor} = \frac{196{,}000}{0.42} = 466{,}000 \text{ lb}$$

$$\text{NaCl at 100 lb/1000 lb of NaOH} = (196)(100) = 19{,}600 \text{ lb}$$

$$H_2O \text{ in solution} = 466{,}000 - 196{,}000 - 19{,}600 = 250{,}400 \text{ lb}$$

Thus,

19,600 lb of NaCl crystallized

167,400 lb of H_2O evaporated

$$\text{Steam required} = \frac{167{,}400}{1.7} = 98{,}700 \text{ lb}$$

$$\text{Evaporated in 1st effect} = \left(\frac{0.7}{0.7 + 1.0}\right)(167{,}400) = 69{,}200 \text{ lb}$$

$$\text{Evaporated in 2d effect} = 167{,}400 - 69{,}200 = 98{,}200 \text{ lb}$$

$$H_2O \text{ from 1st effect} = 417{,}000 - 69{,}200 = 347{,}800 \text{ lb}$$

$$\text{Lb of } H_2O\text{/1000 lb of NaOH} = \frac{347{,}800}{196} = 1775$$

or from tabulation the solution is 34 per cent NaOH.

NaCl/1000 lb of NaOH = 145 lb in solution from 1st effect

	Deg F
Boiling-point elevation at 34% NaOH	47
Boiling-point elevation at 42% NaOH	63.5
Total boiling-point elevations	110.5

Estimation of total net available Δt:

	Deg F
Temperature of steam to 1st effect	262.6
Temperature of condensation in condenser	125.4
Total Δt	137.2
Total of boiling-point elevations	110.5
Total net Δt	26.7

The heat-transfer coefficient, the quantity of heat, and the heating surface are the same in each effect. Thus, the net Δt in each effect must be the same, *viz.*, the total net Δt must be divided equally between the two effects.

Thus,

$$\Delta t_1 = \Delta t_2 = \frac{26.7}{2} = 13.35°\text{F}$$

and

$$A_1 + A_2 = \frac{(167{,}400)(1250)}{(13.35)(500)(24)} = 1307 \text{ sq ft}$$

Humidification.—The problem of removal of moisture from and addition of moisture to air is frequently encountered by the chemical engineer in process calculations. In order to facilitate such calculations a simple method of determining the moisture content of air as well as other related information is needed. Such a method was developed by Grosvenor [1] and will be described briefly at this time. Before proceeding with the details of the description, however, several terms will be defined.

Humidity is the pounds of water vapor per pound of moisture-free air under any given conditions.

Percentage humidity is the moisture content of air under any specific conditions as a percentage of the maximum amount of moisture the air can carry under those conditions.

Relative humidity is the partial pressure of water vapor in the air under existing conditions, expressed as a percentage of the partial pressure of water vapor when saturated at the dry-bulb temperature.

Saturated air contains the maximum amount of moisture that air can carry under the existing conditions.

Dew point is the temperature at which air with a given moisture content is saturated (in a state of static equilibrium with liquid water). The partial pressure of moisture in the air is equal to the partial pressure of liquid water at the dew point.

Wet-bulb temperature is the temperature that corresponds to dynamic equilibrium when a large amount of unsaturated air comes in contact with a small amount of liquid water under adiabatic conditions. The wet-bulb temperature is therefore higher than the dew point (static-equilibrium temperature) but lower than the temperature of unsaturated air.

Humid heat is the heat in Btu required to raise the temperature of one pound of dry air plus the moisture it contains 1°F. Thus, if 0.24 is the specific heat of dry air and 0.48 the specific heat of water vapor, the humid heat is given by Eq. (8.32),

$$S = 0.24 + 0.48H \tag{8.32}$$

where S = humid heat, Btu/lb of dry air
H = humidity, lb of H_2O/lb of dry air

Humid volume is the total volume in cubic feet of one pound of air and the moisture it contains at the existing conditions.

Saturated volume is the total volume in cubic feet of one pound of dry air plus the volume of water vapor necessary to saturate it at the existing conditions.

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[1] Grosvenor, W. M., *Trans. Am. Inst. Chem. Engrs.*, **1** (1908).

The most convenient and simplest method for determination of the moisture content of air is the determination of the wet-bulb and dry-bulb temperature. This is usually done by means of a sling psychrometer, which consists of two thermometers attached to a metal frame that can be rotated rapidly about a pivot at one end of the frame. The bulb of one of the thermometers is wet by means of a piece of cloth that encloses the bulb and that is dipped in water. The water reaches the thermometer bulb by capillary action, and evaporation takes place owing to the large volume of air that passes over the bulb when the psychrometer is being rotated rapidly. The wet-bulb temperature corresponds to a dynamic equilibrium between the rate of diffusion of water vapor through the air film that surrounds the water and the rate of heat transfer from the air through the air film to the water. The significance of the wet- and dry-bulb temperature will become apparent from the discussion below.

The water in the cloth that surrounds the wet bulb must diffuse through an air film that surrounds the cloth. After a state of dynamic equilibrium is reached, an infinitesimal amount of water dW diffuses through the air film into the main body of air in $d\theta$ hr. Likewise, the amount of heat dQ is transferred through the same air film in $d\theta$ hr to supply the heat for evaporation. If r_w is the latent heat of evaporation in Btu per pound at the temperature of the water (wet-bulb temperature), then $r_w\, dW/d\theta$ is the Btu consumed per hour for evaporation, which is equal to $dQ/d\theta$ Btu/hr supplied as sensible heat of the air. Thus,

$$\frac{r_w\, dW}{d\theta} = \frac{dQ}{d\theta} \tag{8.33}$$

Also, the rate of heat transfer is given by Eq. (8.34),

$$\frac{dQ}{d\theta} = hA(t_a - t_w) \tag{8.34}$$

where h = coefficient of heat transfer for the air film
A = area through which heat is flowing
t_a = temperature of main body of air
t_w = temperature of water in the cloth, or the wet-bulb temperature

Based on the general equation [Eq. (8.2)], the rate of diffusion may be expressed as in Eq. (8.35),

$$\frac{dW}{d\theta} = k_g A(p_w - p_a) \tag{8.35}$$

where k_g = mass-transfer coefficient for the water through the air film, lb/(hr)(sq ft)(atm)
p_a = partial pressure of water vapor in main body of air, atm
p_w = partial pressure of liquid water in the cloth, atm
A = surface through which both diffusion and heat transfer occur

The similarity of Eq. (8.35) to Eq. (8.34) will be noted. The film mass-transfer coefficient k_g compares with the film heat-transfer coefficient except that the former involves mass transfer and the latter heat transfer. The driving force for mass transfer is the difference in partial pressures of water vapor at the water surface and in the main body of the air.

Equation (8.35) can be expressed in terms of humidity difference rather than partial-pressure difference.

$$H_a = \frac{(p_a)(18)}{(1 - p_a)(29)} \tag{8.36}$$

and

$$H_w = \frac{(p_w)(18)}{(1 - p_w)(29)} \tag{8.37}$$

In all cases of humidity that will be encountered the value of p_a and p_w will be very small compared with atmospheric pressure. Thus, Eqs. (8.36) and (8.37) can be simplified.

$$H_a = (p_a)(18/29) \tag{8.36a}$$

$$H_w = (p_w)(18/29) \tag{8.37a}$$

and Eq. (8.35) can be expressed as

$$\frac{dW}{d\theta} = (k_gA)\left(\frac{29}{18}\right)(H_w - H_a)$$

or

$$\frac{dW}{d\theta} = (k_g'A)(H_w - H_a) \tag{8.38}$$

where $k_g' = \dfrac{29k_g}{18}$

Then, by Eq. (8.33), (8.34), and (8.38) the following equation is obtained:

$$H_w - H_a = \frac{h}{k_g'r_w}(t_a - t_w) \tag{8.39}$$

Since h and k_g' represent heat-transfer and mass-transfer coefficients, respectively, for the same air film, it is apparent that if the film thickness increases or decreases both h and k_g' will be affected in the same proportion. Thus, the ratio of h/k_g' is a constant; and since r_w is a function only of t_w, Eq. (8.39) may be represented as follows,

$$H_w - H_a = \frac{k^\circ}{r_w}(t_a - t_w) \tag{8.40}$$

where k° = a constant = h/k_a

It is seen, therefore, that the wet-bulb temperature t_w is a function only of the temperature and humidity of the main body of air. The values of H_w and r_w are a function only of t_w, for the vapor pressure of liquid water is a function only of its temperature.

Equation (8.40) was developed on the basis that a state of dynamic equilibrium exists. Actually, this only partly fulfills the needs of the chemical engineer. It is desirable to know the path that unsaturated air will follow upon being cooled adiabatically by water. On the basis of 1 lb of dry air, when unsaturated air comes in contact with water that is at the wet-bulb temperature, dH lb of water is evaporated at the expense of a loss in sensible heat of the air. The reduction in temperature of the air is dt. Thus, the amount of sensible heat given up by the air is equal to the latent heat of evaporation at the wet-bulb temperature t_w, plus the amount of heat required to bring the evaporated water to the temperature of the cooled air t, or

$$dQ = dH[r_w + 0.48(t - t_w)] \tag{8.41}$$

where t is the temperature to which the air is cooled and 0.48 is the specific heat of the water vapor. Likewise, the loss of sensible heat of the air is that which is given up by 1 lb of dry air plus the moisture it originally contained, or

$$dQ = -(0.24 + 0.48H)\,dt \tag{8.42}$$

Thus, Eqs. (8.41) and (8.42) may be equated, or

$$dH[r_w + 0.48(t - t_w)] = -(0.24 + 0.48H)\,dt \tag{8.43}$$

By rearranging the variables and integrating from the initial conditions of H_1 and t_1 to the final conditions H_w and t_w when the air reaches the wet-bulb temperature, Eqs. (8.44) and (8.45) can be obtained.

$$\int_{H_1}^{H_w} \frac{dH}{0.24 + 0.48H} = -\int_{t_1}^{t_w} \frac{dt}{r_w + 0.48(t - t_w)} \tag{8.44}$$

or

$$\frac{0.24 + 0.48H_w}{0.24 + 0.48H_1} = \frac{r_w + 0.48(t_1 - t_w)}{r_w} \tag{8.45}$$

Thus, Eq. (8.45) can be applied to air that initially has a moisture content of H_1 at temperature t_1. Adiabatic cooling paths can be calculated, therefore, for different moisture contents of air at a specific temperature.

Figure A.28 presents a humidity chart based on the equations that were developed earlier. All the information needed by the chemical engineer in calculations on humidification can be obtained from the chart. The humidity is given as ordinates, whereas the dry-bulb temperature is given as abscissas.

Assume that air at 90°F dry-bulb temperature has a wet-bulb temperature of 75°F. In order to determine its humidity locate the point on the wet-bulb and dew-point curve (100 per cent relative humidity) that corresponds to 75°F. This is at a humidity H of 0.0187 lb/lb of dry air. Follow the wet-bulb line (adiabatic cooling curve) until it reaches the dry-bulb temperature of 90°F. This corresponds to a humidity H_1 of 0.0153 lb of water vapor per pound of dry air. This is the humidity of air that has the given wet-bulb and dry-bulb temperatures. Note that the point is on the 50 per cent relative humidity curve. Also, the humid volume is 14.2 cu ft/lb of dry air, which is obtained by interpolating between the saturated-volume curve and the curve for dry air. Interpolation is made for 50 per cent relative humidity. Follow the humidity line of 0.0153 lb/lb to the dew-point curve. The dew point of the air is 69°F. Follow the dry-bulb-temperature line to the wet-bulb curve. The humidity of the air would have to be 0.031 lb/lb to be saturated at the dry-bulb temperature of 90°F. The humid heat in Btu per degree Fahrenheit per pound of dry air is given as a function of humidity. For 0.0153 lb of water vapor per pound of dry air the humid heat is 0.247. The latent heat of the water vapor is given as a function of the dry-bulb temperature in Btu per pound of water vapor.

The student should make certain that he understands fully the use of Fig. A.28 and its significance. It will be used frequently in his advanced study of several of the unit operations and chemical processes.

Example 57. Cooling water is supplied to a large process unit by recirculating the hot water from the unit through a forced-draft cooling tower. The tower is so constructed that the hot water is distributed at the top and drains to the basin at the bottom. The air is supplied at the bottom by suitable fans and passes upward in countercurrent contact with the water. The cooled water in the basin is returned to the process unit. Fresh water from wells is added to the basin to make up the loss due to evaporation in the tower and to maintain a maximum dissolved-solids concentration in the water to the process unit of 600 grains/gal. The maximum solids concentration is maintained in order that the rate of solids deposition on condenser and cooler surfaces in the process unit can be tolerated. The dissolved-solids concentration of the well water is 28 grains/gal. A performance test was made on the cooling tower with the following results:

Temperature, deg F	To tower	From tower
Air:		
Dry bulb...........	83.0	90.0
Wet bulb...........	75.0	90.0
Water............ ...	106	81

Hot water to tower 6500 gal/min corrected to 60°F.

Fans operated at maximum capacity.

Calculate the quantity of moisture-free air and humid air that was delivered to the cooling tower. Calculate the heat duty of the cooling tower. Calculate the amount of make-up water required.

Solution: The hot water from the process unit is identical with the flow rate of cold water. Therefore

$$\text{Present heat duty} = (6500)(8.33)(106 - 81) = 81{,}200{,}000 \text{ Btu/hr}$$

Determine humid volume of air per unit time to tower by heat and material balance.

Let A = lb/hr of dry air to tower

From Fig. A.28,

$$H_1 = 0.01685 \text{ lb/lb of dry air}$$

$$H_2 = 0.029 \text{ lb/lb of dry air}$$

$$H_2 - H_1 = 0.001215 \text{ lb/lb of dry air (evaporated)}$$

$$\text{Water evaporated} = 0.01215A \text{ lb/hr}$$

$$\text{Cooled water to basin} = (6500)(8.33)(60) - 0.01215A$$

$$= 3{,}250{,}000 - 0.01215A$$

By net heat balance,

Heat given up by cooled water = heat picked up by fresh air to tower + heat picked up in evaporated water

Heat given up by cooled water = $(3{,}250{,}000 - 0.01215A)(106 - 81) = 81{,}200{,}000 - 0.3125A$

Heat to fresh air = $[0.24 + (0.48)(0.01685)][88 - 83A] = 1.243A$

Heat picked up by evaporated water = latent heat at 106°F − sensible heat of vapor to 88°F = $[1033.0 - 0.48(106 - 88)][0.01215A] = 12.45A$

Thus,

$$81{,}200{,}000 - 0.3125A = 1.243A + 12.45$$

$$A = \frac{81.200{,}000}{14.00} = 5{,}800{,}000 \text{ lb/hr}$$

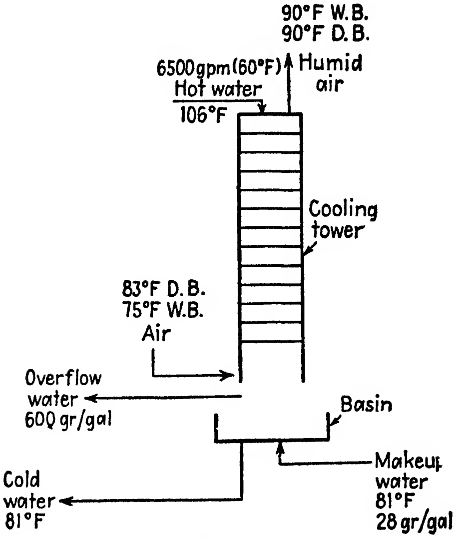

Fig. 8.10.

Make-up water required:

$$\text{Water evaporated} = \frac{70{,}500}{8.33} = 8460 \text{ gal/hr}$$

By material balances on the solids and water

Let M = gal/hr of make-up water
S = gal/hr of hot water to the sewer

Then $$28M = 600S$$

Also, $$M = S + 8460 = 21.4S$$

$$S = 4150 \text{ gal/hr to sewer}$$

$$M = 88{,}800 \text{ gal/hr of make-up}$$

DYNAMIC EQUILIBRIA IN CHEMICAL PROCESSES

When chemical reaction equilibria (static) were discussed in Chap. VII, it was mentioned on several occasions that the calculation of static equilibria provides no information whatever in regard to the time required for any chemical reaction to reach equilibrium. Since the size of equipment required to carry out any specific chemical reaction is dependent upon the reaction rate, this subject will be considered at this point. The discussion will be devoted primarily to homogeneous (single-phase) chemical reactions in order to simplify the presentation as far as possible.

Unfortunately, the fundamentals surrounding the rates of chemical reactions have not been developed to the same extent as for other phases of chemical engineering. Nevertheless, there is much work being done in this field at present. It is probable that the greatest future progress in chemical-engineering development will be in connection with chemical-reaction rates. Aside from the law of mass action, there are no fundamental generalizations at present that enable the chemical engineer to establish sound theoretical relationships for the rate of specific chemical reactions. Thus, it has become common practice to develop an empirical correlation for each specific chemical reaction, valid only for the conditions under which the correlation was developed. The chemical engineer must have some such relationships that permit him to determine the size of process equipment required to carry out chemical reactions. Even though present development in this field leaves much to be desired, the student should have at least an elementary knowledge of some of the present concepts related to chemical-reaction rates. Such concepts will be of assistance in the development of reaction-rate equations, even though empirical in nature. The field of chemical-reaction kinetics is very involved and complicated. Furthermore, the chemical kineticist is usually forced to resort to simplifying assumptions and unfounded theories, owing to the lack of fundamental generalizations. Thus, the final results of a sound mathematical treatment of the chemical-reaction kinetics of a specific reaction usually do not provide the chemical engineer with anything reliable for his purposes. Except in the case of research the chemical engineer is usually concerned with chemical-reaction kinetics only insofar as it is able to provide him with a reliable basis for calculating the type and size of equipment required to carry out a given chemical reaction. This, of course, is owing to the fact that he is concerned primarily with the determination of the proper size of process equipment to carry out a specific chemical reaction or the determination of the capacity of existing equipment for a given extent of chemical reaction within a fixed period of time. If a sound approach to the relationship between extent of reaction and reaction period (time during which the reaction proceeds) cannot be obtained by theoretical means, the chemical engineer is forced to resort to the use of empirical correlations based on a large number of experimental data.

The following presentation will take up first the development of a fundamental reaction-rate equation for isolated[1] homogeneous chemical reactions. Then reaction-rate equations for batch processes and a system of classifying chemical reactions will be discussed. Finally, reaction-rate equations for continuous processes will be presented.

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[1] An isolated reaction is one that takes place to the exclusion of all other reactions.

Fundamental Reaction-rate Equation.—For any general isolated homogeneous chemical reaction[1]

$$eE + fF + gG = \text{products} \tag{8.46}$$

e moles of E, f moles of F, and g moles of G react to give the products of reaction. Equation (8.46) specifies the stoichiometric number of each type molecule that must disappear per molecule of any of the species that disappears. Thus, in order to set up a mathematical expression for the rate of reaction the disappearance of any one of the type molecules in the equation may be used as a basis. The appearance of any one of the product molecules could be used as a basis if desired.

In order to simplify the presentation, however, the disappearance of E will be arbitrarily selected as the basis. At any time θ let N_E represent the number of moles of E present. Consequently, $-dN_E/d\theta$ represents the instantaneous rate at which moles of E are disappearing. In this case, as θ increases, N_E decreases; thus $dN_E/d\theta$ is inherently negative. The number of moles of any component available for reaction is proportional to the number of moles of the component present, which in turn is proportional to the rate of disappearance in moles per unit time. Thus, the rate at which E disappears is proportional to the number of moles of E present (N_E). The general reaction [Eq. (8.46)] may therefore be written as

$$1E + (e - 1)E + fF + gG = \text{products} \tag{8.47}$$

For 1 molecule of E to react, it must have a simultaneous collision with $e - 1$ molecules of E, f molecules of F, and g molecules of G. The rate of disappearance of 1 molecule of E is proportional to the number of such collisions per unit time, which in turn is proportional to the concentration of *each* reacting molecule, in other words, to the product of the concentrations of the other molecules that react with the 1 molecule of E. This applies to each molecule that appears in the chemical equation [Eq. (8.47)], even though there are several of a given species. That is, if 2 molecules of a given species M should appear in the chemical equation as reacting with 1 molecule of E, the concentration of that species will appear as $(C_M)(C_M)$, in other words, will be raised to the power of 2. Thus, the rate of disappearance of E can be expressed as

$$-\frac{dN_E}{d\theta} = kN_E C_E^{e-1} C_F^f C_G^g \tag{8.48}$$

where C represents the concentration in moles per unit volume of the species indicated by the subscript and k is the reaction velocity constant, which is

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[1] That is, this and only this reaction takes place.

primarily a function of temperature although affected to some extent by pressure. Equation (8.48) is developed by Sherwood and Reed;[1] the reader is referred to their treatment for further details.

Equation (8.48) is fundamental in its application to homogeneous chemical reactions. It is valid for either batch-process or continuous-process chemical reactions under any conditions. It can be simplified somewhat, however, if applied to batch-process chemical reactions in which the volume of the system is constant.

The reaction velocity constant k varies with temperature in much the same way as the reaction equilibrium constant. It can be represented with reasonable accuracy over a considerable temperature range by the equation

$$\log k = \frac{A}{RT} + B \tag{8.49}$$

where A and B are constants that must be determined experimentally and R is the gas constant. The similarity between Eqs. (8.49) and (7.13) is apparent. Actually, A is not constant but is sufficiently nearly so for the reaction rate constant to be expressed quite satisfactorily over fairly wide ranges of temperature by Eq. (8.49). The constant A is called the *energy of activation.* Theoretically it is the amount of energy required to activate one mole of reactants sufficiently above the average energy level for reaction to proceed.

Reaction velocity constants are also affected by catalysts, and in practice this must be taken into consideration. However, this subject is much too complicated for discussion here and will be given no further consideration than this mere mention.

Batch-process Reactions.—Chemical reactions are frequently carried out within closed vessels, particularly in experimental work designed to determine the rate of reaction of specific reactions. Thus, the volume is maintained constant throughout the reaction. In this case the number of moles of E [Eq. (8.46)] can be expressed as

$$N_E = C_E V_R \tag{8.50}$$

where V_R is the volume of the reactor. Also,

$$dN_E = V_R\, dC_E \tag{8.51}$$

Thus, Eq. (8.48) reduces to Eq. (8.52).

$$-\frac{dC_E}{d\theta} = kC_E^e C_F^f C_G^g \tag{8.52}$$

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[1] SHERWOOD, T. K., and C. E. REED, "Applied Mathematics in Chemical Engineering," p. 54, McGraw-Hill Book Company, Inc., New York, 1939.

This equation is applicable only to isolated chemical reactions at *constant volume.*

A scheme of classifying chemical reactions has been devised by use of Eqs. (8.48) and (8.52). The scheme is based on theoretical isolated chemical reactions. If only one molecule reacts to produce reaction products, the reaction is called a *first-order,* or *unimolecular,* reaction. If two molecules react, the reaction is called a *second-order,* or *bimolecular,* reaction. If three molecules react, it is a *third-order,* or *termolecular,* reaction. There are no known reactions of higher order than termolecular and relatively few first order. Most reactions are second order. Actually, if a reaction follows the theoretical relationship for a specific order, it is classified accordingly, regardless of the number of molecules reacting. Consequently, if the reaction rate of any chemical reaction is proportional to the concentration of one of the reactants, it is classified as a first-order reaction with respect to that reactant. If the reaction rate is proportional to the product of the concentrations of two of the reactants or the square of the concentration of one of the reactants, the reaction is second order. If the reaction rate is proportional to the concentration of reactant A and the square of the concentration of reactant B, the reaction may be classified as (1) third order with respect to A and B, (2) first order with respect to A, or (3) second order with respect to B.

If the coefficient e in Eq. (8.46) is unity and all other coefficients are zero, the reaction is of first order and Eq. (8.52) reduces to Eq. (8.53).

$$-\frac{dC_E}{d\theta} = kC_E \tag{8.53}$$

This equation presents the instantaneous rate of reaction for a batch-process (constant-volume) first-order reaction. By rearranging the variables it can be integrated between the limits of zero to θ time and C_{E_1} to C_{E_2} concentration of E,

$$\int_{C_{E_1}}^{C_{E_2}} -\frac{dC_E}{C_E} = \int_0^\theta k\,d\theta$$

or

$$\ln\frac{C_{E_1}}{C_{E_2}} = k\theta \tag{8.54}$$

Thus, Eq. (8.54) is applicable to batch-process chemical reactions of the first order where C_{E_1} is the moles of E per unit volume at zero time and C_{E_2} is the concentration of E at time θ.

If the coefficient e in Eq. (8.46) is equal to 2 and all other coefficients are 0 the reaction is second order and Eq. (8.52) reduces to

$$-\frac{dC_E}{d\theta} = kC_E^2 \qquad (8.55)$$

which presents the instantaneous rate of reaction. It can be integrated between the limits of 0 to θ time and C_{E_1} to C_{E_2} concentration of E as follows:

$$\int_{C_{E_1}}^{C_{E_2}} -\frac{dC_E}{C_E^2} = \int_0^\theta k\,d\theta$$

or

$$\frac{C_{E_1} - C_{E_2}}{C_{E_1}C_{E_2}} = k\theta \qquad (8.56)$$

This equation therefore represents a second-order reaction in a batch process at constant volume in which two molecules of the same component are reacting. In the more general-type second-order reaction the coefficients e and f of Eq. (8.46) are each unity and all others zero. Thus,

$$-\frac{dC_E}{d\theta} = -\frac{dC_F}{d\theta} = \frac{dx}{d\theta} = kC_EC_F \qquad (8.57)$$

where x = moles of E or F per unit volume that has disappeared in time θ. If C_{E_1} and C_{F_1} represent the initial concentrations of E and F, then

$$\frac{dx}{d\theta} = k(C_{E_1} - x)(C_{F_1} - x)$$

or

$$\int_0^x \frac{dx}{(C_{E_1} - x)(C_{F_1} - x)} = \int_0^\theta k\,d\theta$$

and

$$\frac{1}{C_{F_1} - C_{E_1}} \ln \frac{C_{E_1}(C_{F_1} - x)}{C_{F_1}(C_{E_1} - x)} = k\theta \qquad (8.58)$$

Equation (8.58) can also be presented as

$$\frac{1}{C_{F_2} - C_{E_2}} \ln \frac{C_{F_2}C_{E_1}}{C_{E_2}C_{F_1}} = k\theta \qquad (8.59)$$

In this case C_{E_2} and C_{F_2} represent the concentrations of E and F at time θ, and C_{E_1} and C_{F_1} represent the concentrations of E and F at zero time. Equation (8.58) or (8.59) may be used directly for study of a second-order batch-process reaction (constant volume) in which two different kinds of molecules react.

There are three different possible types of third-order reactions. (1) Coefficient e in Eq. (8.46) is equal to 3, and all other coefficients are zero. (2) Coefficients e is equal to 2, coefficient f is unity, and all others are zero. (3) Coefficients e, f, and g are each unity, and all others zero. The instantaneous rates of reaction for the three types are given by Eqs. (8.60), (8.61), and (8.62), respectively.

$$\frac{dx}{d\theta} = k_x C_E^3 \tag{8.60}$$

$$\frac{dx}{d\theta} = k_x C_E^2 C_F \tag{8.61}$$

$$\frac{dx}{d\theta} = k_x C_E C_F C_G \tag{8.62}$$

The integrated forms of the third-order reaction equations will not be presented here since there will be no occasion for their application in this text.

In addition to first-, second-, and third-order reactions there are reactions in which the rate is constant, independent of concentration of reactants. The rate of reaction may be controlled by the rate of diffusion or some other factor. Such reactions are of zero order. The rate may be expressed as in Eq. (8.63).

$$-\frac{dC_E}{d\theta} = k \tag{8.63}$$

Perhaps the greatest use the chemical engineer has for the rate equations of batch-process chemical reactions is in his study of experimental data to determine an equation that will provide him with a basis for calculating the required size of process equipment. The most convenient way to describe a chemical reaction is to establish the reaction order (even though empirical) and corresponding reaction velocity constant. Once these are known, they can be applied to any type of process, batch or continuous.

Example 58. A chemical compound is being decomposed in a bomb. Assume that the reaction rate follows a first-order reaction. If one-half is decomposed in 20 min, how much time is required to decompose 90 per cent?

Solution: Since the reaction is being carried out in a closed vessel (batch process),

$$\ln \frac{C_1}{C_2} = k\theta$$

Then, at 50 per cent decomposition, $C_1/C_2 = 2.0$,

and $$k = \frac{1}{\theta} \ln 2 = \frac{\ln 2}{20} = 0.0347$$

In this case, k has the dimensions of $(\text{minutes})^{-1}$. Then, at 90 per cent decomposition, $C_1/C_2 = 10$,

and
$$\theta = \frac{\ln 10}{0.0347} = \frac{2.3}{0.0347} = 66.5 \text{ min}$$

Example 59. A certain chemical reaction is being carried out in a bomb in accordance with the equation

$$4A = B + 6C$$

According to the chemical equation it might be suspected that the reaction would be of the fourth order. The experimental results show the following relationship between per cent of A that disappeared vs. reaction period.

% Disappeared	Min
0	0
21.5	20
45.2	50
61.8	80
70.0	100

Determine the reaction velocity constant.

Solution: Although the over-all chemical reaction indicates that a fourth-order reaction might occur, if the results are plotted on semilogarithmic paper it will be found that a straight line will correlate the data as logarithm of percentage of undecomposed reactant vs. time. Thus, this indicates that the reaction is of the first order instead of the fourth. The value of k is calculated as follows:

θ, min	0	20	50	80	100
% disappearance	0	21.5	45.2	61.8	70
% unreacted	100	78.5	54.8	38.2	30
C_1/C_2	1.0	1.274	1.825	2.62	3.33
$\ln(C_1/C_2)$	0	0.24	0.601	0.963	1.203
$k = (1/\theta) \ln(C_1/C_2)$	.....	0.01203	0.01203	0.01203	0.01203

Thus, it is seen that the reaction rate fits the first-order equation and $k = 0.01203$ per minute. This example emphasizes the fact that the reaction mechanism cannot be identified by the chemical equation since the latter merely shows the over-all reaction.

Thus far the discussion has been confined to isolated chemical reactions. The student must realize, however, that, in general, chemical reactions are far more complex than these. Since all chemical reactions may be regarded as reversible, it is at once apparent that the reverse reaction will have the effect of reducing the net forward reaction velocity of any specific reaction. Another complication is that reactions frequently take place in steps such as

$$(1)\ A + B = C$$

$$(2)\ A + C = D$$

It is noted that A and B react to give C and upon the formation of C reaction 2 takes place to give D. If reaction 1 is slow compared with reaction 2, it will control the rate of the over-all reaction, which is

$$2A + B = D$$

Owing to reverse reactions, side reactions, and consecutive reactions, a reaction will sometimes follow the equation of one reaction order but after it has proceeded for a while will gradually change so that it follows the equation of an entirely different reaction order. Furthermore, owing to the different simultaneous reactions that occur the net effect on the over-all reaction may not be represented by any of the standard type of reactions over any of the range of reaction. Such complications, however, are often very helpful in determining the exact reaction mechanism.

More often than not, the chemical engineer will find that an empirical equation will best suit his purposes, for his problem usually involves merely the determination of the velocity of the over-all reaction. For this purpose, most over-all batch-process reactions can be described for all practical purposes by the empirical Eq. (8.64), which is an extension of Eq. (8.52),

$$-\frac{dC_E}{d\theta} = kC_E^q C_F^r C_G^s \tag{8.64}$$

where C represents the concentrations of the reactants indicated by subscripts at any time θ and q, r, and s are constants that must be determined experimentally. Usually the chemical engineer will be interested in the reaction rate over only a short range of concentrations, in which case Eq. (8.64) meets his needs fairly well. Empirical equations will be given no further consideration in this text.

Continuous-process Reactions.—Experimental data on rates of chemical reactions are usually obtained by conducting the reactions in bombs so that the volume of the system is fixed. Thus, Eqs. (8.52) to (8.64) for batch-process chemical reactions are of considerable importance to the chemical engineer primarily for the purpose of analyzing experimental results. Nevertheless, some of these equations are applicable to continuous-process chemical reactions provided that there is no change in volume between the charge to the reaction zone and the products from the reaction zone. In such cases, Eqs. (8.50) and (8.51) are valid, and in turn Eqs. (8.52), (8.53), (8.55), (8.57), etc., are likewise valid. This condition is fulfilled in isothermal vapor-phase reactions if the moles of reaction products is equal to the moles of reactants consumed provided that there is no significant pressure drop between the inlet and outlet of the reaction zone. Also, the condition is usually fulfilled for all practical purposes in the case of liquid-phase reactions even though there may be a substantial change in the moles of reaction products relative to the moles of reactants.

There are two general methods used to carry out chemical reactions in continuous processes. In the first method, the reactants flow continuously from inlet to outlet through an elongated reaction zone so that agitation may occur within any stream front, but there is no agitation between stream fronts. In other words, agitation will occur predominantly within the stream front perpendicularly to the direction of flow, but there will be no short circuiting of material from one point within the reaction zone to another point downstream. This condition is met very well by the flow of fluid through a tube as shown by Fig. 8.11. In the case of streamline flow there will, of course, be no agitation within the stream front, but with turbulent flow agitation will exist. In each case, however, the flow will be uniform from points A to B, with no short circuiting of any particle of fluid between these points.

FIG. 8.11.

In the second method, the reaction zone is in a state of agitation such that the concentration of reactants throughout the entire zone is essentially constant. This is sometimes done as shown in Fig. 8.12. An internal recycle is carried out by returning reactor effluent to the inlet of the reactor at a very high rate relative to the feed rate.

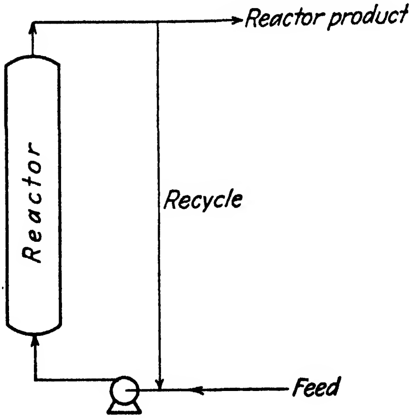

FIG. 8.12.

Thus, the two methods represent the extreme cases. In the first, the concentration of reaction products increases gradually from that of the feed to that of the effluent so that the change in concentrations is entirely a result of reaction. In the second, an essentially constant concentration of reaction products is maintained within the reaction zone equivalent to the reactor effluent so that the concentrations at any point in the reactor are a result of agitation as well as reaction. Of course, combinations of the two methods are frequently used. For example, several reactors of the type in Fig. 8.12 may be operated in series. As the number approaches infinity, the process approaches a once-through operation (first method). Also, the ratio of the reactor effluent rate of recycle to the fresh feed rate may be reduced from a high to a low value. As this is reduced, the process approaches a once-through operation. If the student has an understanding of the two extreme methods (once-through and recycle operations), he will be able to deal adequately with their combinations.

Now that the two extreme methods of conducting chemical reactions in continuous processes have been described, the calculation of rates of reaction in once-through constant-volume continuous processes will be discussed. It is apparent that in a constant-volume once-through operation a given volume of charge reacts as it passes through the reaction zone so that the concentration of reactants decreases with time just as though this same volume were retained in a bomb. The process can be visualized by considering the given volume of charge as a cylinder of fixed volume that passes through the reaction zone (Fig. 8.13). Reaction proceeds within the fixed volume in exactly the same way as if the volume were retained in a bomb. The time during which the fixed volume resides in the reaction zone is called the *residence time*. It corresponds to the time of reaction, or reaction period, in a batch process. Thus, Eqs. (8.52) to (8.64) for batch-process chemical reactions are applicable directly to *constant-volume* chemical reactions in a once-through continuous process. Further discussion of their application is not necessary owing to the pronounced similarity between a batch process and a once-through continuous process.

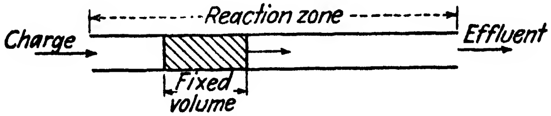

FIG. 8.13.

The recycle continuous process, on the other hand, presents certain complications so that none of the integrated equations for batch-process chemical reactions are applicable. Since the concentrations of reactants and reaction products are essentially constant throughout the reactor, it is apparent that Eqs. (8.54), (8.56), (8.58), and (8.59) may not be used. The differential equations, however, from which the integrated equations were derived are quite valid for this case and can be used to develop other integrated equations that apply to constant-volume recycle continuous processes.

MacMullin and Weber[1] have presented a rather complete treatment of the theory that surrounds chemical-reaction rates in recycle continuous

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[1] MACMULLIN, R. B., and M. WEBER, JR., *Trans. Am. Inst. Chem. Engrs.*, **31**, 409 (1935).

processes *at constant volume.* They derived equations that relate the concentration of unreacted reactants in the reactor effluent with residence time and other pertinent variables. Their derivation is based on a dynamic equilibrium between the feed rate, rate of product elimination, and reaction rate.

For an isolated first-order reaction the rate of reaction at constant volume for a recycle continuous process is represented by Eq. (8.53).

$$-\frac{dC_E}{d\theta} = kC_E \tag{8.53}$$

Let V_R = volume of reactor
C_0 = moles of reactant per unit volume of feed
C_E = moles of reactant per unit volume in reactor effluent
N = moles of reactant in reactor
F = volume of feed per unit time

From Eq. (8.50),

$$N = C_E V_R$$

$$dN = V_R\,dC_E$$

and Eq. (8.53) reduces to

$$-\frac{dN}{d\theta} = kC_E V_R \tag{8.65}$$

The value of N is a constant when dynamic equilibrium is reached. It is a balance between feed rate, reaction rate, and rate of product elimination.

By reaction rate,

$$\frac{dN}{d\theta} = -kC_E V_R$$

By feed rate,

$$\frac{dN}{d\theta} = C_0 F \tag{8.66}$$

By product elimination, at constant volume, F = product-elimination rate, and

$$\frac{dN}{d\theta} = -C_E F \tag{8.67}$$

Thus, the total effect of the three rates of change is

$$\frac{dN}{d\theta} = -kC_E V_R + C_0 F - C_E F \tag{8.68}$$

But since N is a constant in the steady state,

$$C_0 F = kC_E V_R + C_E F \tag{8.69}$$

But V_R/F = residence time θ. Therefore

$$C_E = \frac{C_0}{1 + k\theta} \tag{8.70}$$

Eq. (8.70) is applicable to first-order chemical reactions at constant volume in a recycle continuous process with one reactor. If two such reactors are operated in series, C_E becomes C_0 for the second reactor and

$$C_2 = \frac{C_E}{1 + k\theta_2} = \frac{C_0}{(1 + k\theta_1)(1 + k\theta_2)} \tag{8.71}$$

where the subscripts 1 and 2 refer to the first and second reactors, respectively. In the event that the residence time is the same in each reactor, the following general equation is obtained,

$$C_n = \frac{C_0}{(1 + k\theta)^n} \tag{8.72}$$

where n = number of such reactors in series.

Example 60. Experimental data were obtained in a constant-volume bomb at 150°F on the isomerization of n-butane by catalytic action of $AlCl_3$. The data are as follows:

i-C_4, mole %	n-C_4, mole %	Time, min
0	100.0	0
20.0	80.0	240
43.0	57.0	600
56.0	44.0	900

What theoretical residence time must be provided in the reactor of a commercial unit that will operate as a recycle continuous process if the reactor effluent contains 45 mole per cent isobutane? The charge will consist of 95.0 per cent n-butane and 5.0 per cent isobutane.

Solution: It would be expected that this reaction is of the first order. By plotting the logarithm of mole per cent n-butane vs. time it is found that a straight line is obtained which indicates that the reaction is of first order.

The reaction rate constant can be calculated by means of Eq. (8.54).

$$\ln \frac{100.0}{44.0} = 900k$$

$$k = \frac{0.82}{900} = 0.000912/\text{min}$$

Now, by means of Eq. (8.70),

$$\theta = \frac{95.0 - 55.0}{(55.0)(9.12 \times 10^{-4})} = 798 \text{ min}$$

Thus, a residence time of 13.3 hr is required in this case. The probability is that by increasing the amount of catalyst a more favorable reaction velocity constant could be obtained and somewhat shorter residence time used.

For an isolated second-order reaction of the type $2E$ = products the rate of reaction at constant volume for a recycle continuous process is represented by Eq. (8.55).

$$-\frac{dC_E}{d\theta} = kC_E^2 \tag{8.55}$$

Since

$$dN = V_R\, dC_E$$

$$-\frac{dN}{d\theta} = kC_E^2V_R \tag{8.73}$$

The dynamic equilibrium is a balance between feed rate, rate of reaction, and rate of product elimination.

By reaction, $$\frac{dN}{d\theta} = -kC_E^2V_R$$

By feed rate, $$\frac{dN}{d\theta} = C_0F$$

By product elimination, $$\frac{dN}{d\theta} = -C_EF$$

Thus, $$\frac{dN}{d\theta} = 0 = -kC_E^2V_R + C_0F - C_EF \tag{8.74}$$

Also, since $V_R/F = \theta$,

$$\theta = \frac{C_0 - C_E}{kC_E^2} \tag{8.75}$$

Equation (8.75) is applicable to a second-order reaction of the type

(1) $2E$ = products

or

(2) $E + F$ = products

where moles of E equals moles of F at constant volume in a recycle continuous process with one reactor. If more than one reactor is used in series, the equations become involved so that they will not be presented here.

The student should be able to develop the necessary equation for a given case by the same procedure employed in the derivation of Eq. (8.72).

In the case of an isolated second-order reaction of the type

$$E + F = \text{products}$$

at constant volume for a recycle continuous process, the rate of reaction is given by equation

$$-\frac{dC_E}{d\theta} = kC_EC_F \tag{8.57}$$

By the procedure used in the development of Eqs. (8.70) and (8.75), the following relationship is obtained,

$$\theta = \frac{C_{E_0} - C_E}{kC_EC_F} \tag{8.76}$$

where C_{E_0} is the moles of E per unit volume in the feed. Equation (8.76) is therefore applicable to the general-type second-order reaction at constant volume in a recycle continuous process.

It might at first appear that there should be few occasions for use of the recycle continuous process owing to the fact that longer residence time is required relative to the once-through continuous process. Nevertheless, the recycle method is used quite frequently. Often it has many advantages that more than compensate for the longer residence time. It is especially well adapted for removal or supply of heat of reaction so that isothermal conditions can be maintained in the reactor. Also, in the case of surface reactions, which are frequently encountered with catalysts, the reaction rate may be controlled by the diffusion of reactants to the catalyst surface or diffusion of products away from the surface. In such a case the film through which diffusion takes place will be reduced in thickness as the velocity of the reactor contents is increased over the catalyst surface. Likewise, the diffusion rate will be increased. In order to obtain a desired velocity over the catalyst surface it is frequently necessary to use the recycle method, for the once-through method may entail a reactor of such dimensions as are not feasible.

It should not be assumed that all rate equations for chemical reactions with which the chemical engineer deals involve merely the rate of mass transfer. Very frequently the chemical engineer is more concerned with the quality of the product than with the rate of disappearance of reactants. For example, in the process for alkylation of isobutane with butylenes the reaction rate is so high that the rate of disappearance of the butylenes is not important. On the other hand, the octane number (detonation quality) of the alkylate is affected considerably by residence time and those variables which affect residence time such as ratio of isobutane to butylene. Thus, in this case the residence time is established on the basis of quality of the alkylate rather than the rate of butylene disappearance. The size of a reactor (or the residence time) is established on the basis of an economic balance, with quality rather than rate of butylene disappearance as the determining factor.

Thus far only chemical reactions at constant volume have been considered. These, of course, are of great importance to the chemical engineer, but reactions are often encountered in continuous processes that are not at constant volume. Such reactions are usually conducted in the vapor phase in continuous processes and involve a significant change in the moles of product relative to reactants as a result of the reaction. Thus, the treatment of such reactions must be based on Eq. (8.48), for Eq. (8.50) is valid only when volume is fixed.

Benton,[1] Sherwood and Reed,[2] and Perry [3] have discussed the subject of reaction velocity in constant-pressure continuous processes; the reader is referred to their treatments for greater detail. Of course, a constant-pressure process may also be one of constant volume. However, if the chemical reaction is carried out in the vapor phase and there is a significant change in the number of moles owing to chemical reaction, the process is not one of constant volume. The change in concentrations of the reactants will be affected by the change in volume as well as the rate of their disappearance. Thus, instead of dealing in terms of concentrations, the problem must be attacked on the basis of actual moles flowing.

Consider a first-order reaction in a once-through continuous process in which there is a significant change in volume as the stream passes through the reaction zone.

Let V_0 = volume [4] of charge to the reactor/unit time
V = volume [4] of stream in reactor/unit time at time θ
N_{E_0} = moles of reactant E in charge to reactor/unit time
N_E = moles of reactant E/unit time after time θ in the reactor

Assume that

$$\frac{V_0 - V}{N_{E_0} - N_E} = \text{a constant} = \alpha$$

Then,

$$V = V_0 - \alpha(N_{E_0} - N_E)$$

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[1] BENTON, *J. Am. Chem. Soc.*, **53**, 2984 (1931).

[2] *Op. cit.*

[3] *Op. cit.*, p. 684.

[4] Existing conditions.

Equation (8.48) for a first-order reaction reduces to

$$-\frac{dN_E}{d\theta} = kN_E \tag{8.77}$$

But

$$d\theta = \frac{dV_R}{V} = \frac{dV_R}{V_0 - \alpha(N_{E_0} - N_E)} \tag{8.78}$$

where V_R is the volume of the reactor and V is the instantaneous volume of the stream flowing at any point in the reactor.

Then,

$$\frac{dN_E[V_0 - \alpha(N_{E_0} - N_E)]}{N_E} = k\,dV_R \tag{8.79}$$

Equation (8.79) can be integrated into the following:

$$\alpha(N_{E_0} - N_E) + (V_0 - \alpha N_{E_0}) \ln \frac{N_{E_0}}{N_E} = kV_R \tag{8.80}$$

Equation (8.80) is therefore applicable to a first-order chemical reaction in a once-through continuous process whether or not the volume of the stream per unit time remains constant as the reaction proceeds.

Example 61. A first-order reaction is to be carried out in a once-through continuous process. The flow rates, extent of reaction, and reaction velocity constant are as follows:

Charge rate to reactor = 5000 cu ft/hr [1]
Reactant in the charge = 100 moles/hr
Effluent from reactor = 8000 cu ft/hr [1]
Reactant in effluent = 50 moles/hr
Reaction velocity constant = 1.5/hr

Calculate the size reactor required.

Solution: Since there was a large change in volume at existing conditions, it will be necessary to use Eq. (8.80).

$$\alpha = \frac{V_0 - V}{N_{E_0} - N_E} = \frac{5000 - 8000}{100 - 50} = -60$$

$$\alpha(N_{E_0} - N_E) + (V_0 - \alpha N_{E_0})\ln \frac{N_{E_0}}{N_E} = kV_R$$

or

$$-60(100 - 50) + [5000 + (60)(100)]\ln {}^{100}\!/_{50} = 1.5V_R$$

$$V_R = 3070 \text{ cu ft}$$

An approximation of the reactor volume required can be obtained by using an arithmetic average flow rate in the proper first-order reaction equation for constant volume. Thus, in the case of Example 60 the average

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[1] Volumes correspond to existing conditions.

flow rate would be $(5000 + 8000)/2 = 6500$ cu ft/hr. Then Eq. (8.54) may be applied after it is revised slightly.

$$\ln \frac{C_{E_0}}{C_E} = k\theta \tag{8.54}$$

But since $C = N/V$ and $\theta = V_R/V$,

$$V \ln \frac{N_{E_0}}{N_E} = kV_R \tag{8.81}$$

The average flow rate of 6500 cu ft/hr can be substituted for V in Eq. (8.81) together with the values for the other variables. Thus,

$$V_R = \frac{6500 \ln 100/50}{1.5} = 3000 \text{ cu ft}$$

In the case of this first-order reaction the approximate method gives fairly good results because the reactor volume is directly proportional to the average volume used. It should not be assumed, however, that this method is always so reliable.

For a second-order reaction of the type $2E$ = products a reasonably simple equation can be developed that is applicable whether or not there is a change in volumetric flow rate as the stream proceeds through the reactor. Equation (8.48) for the type of reaction under consideration reduces to

$$-\frac{dN_E}{d\theta} = \frac{kN_E^2}{V} \tag{8.82}$$

But since

$$V = V_0 - \alpha(N_{E_0} - N_E)$$

and

$$d\theta = \frac{dV_R}{V}$$

$$-\frac{[V_0 - \alpha(N_{E_0} - N_E)]^2 \, dN_E}{N_E^2} = k \, dV_R \tag{8.83}$$

Equation (8.83) is integrated into the following:

$$\frac{(V_0 - \alpha N_{E_0})^2(N_{E_0} - N_E)}{N_{E_0}N_E} + 2\alpha(V_0 - \alpha N_{E_0}) \ln \frac{N_{E_0}}{N_E} + \alpha^2(N_{E_0} - N_E) = kV_R \tag{8.84}$$

Equation (8.84) is therefore applicable to second-order reactions of the type $2E$ = products that are conducted in once-through continuous processes whether or not the volumetric flow rate is constant as the stream passes through the reactor.

Example 62. A second-order reaction is to be carried out in a once-through continuous process. The flow rates and extent of reaction are identical with those given in Example 61. The reaction velocity constant is 0.9×10^{-2} cu ft/(sec)(mole).[1] Calculate the size reactor required.

Solution: Since all other rates are expressed in terms of hours, the reaction velocity constant will be put on the same basis.

$$k = (0.9 \times 10^{-2})(3600) = 32.4 \text{ cu ft/(hr)(mole)}$$

Equation (8.84) can now be used to determine V_R.

$$\frac{(V_0 - \alpha N_{E_0})^2(N_{E_0} - N_E)}{N_{E_0}N_E} + 2\alpha(V_0 - \alpha N_{E_0}) \ln \frac{N_{E_0}}{N_E} + \alpha^2(N_{E_0} - N_E) = kV_R$$

$$\frac{[5000 + (60)(100)]^2(50)}{(100)(50)} - 120[5000 + (60)(100)] \ln \frac{100}{50} + (60)^2(50) = 32.4V_R$$

or

$$V_R = 14{,}650 \text{ cu ft}$$

The approximate method will now be applied to show its accuracy relative to the more exact method used in Example 62. Equation (8.56) will be used in the approximation.

$$\frac{C_{E_0} - C_E}{C_{E_0}C_E} = k\theta \tag{8.56}$$

Since $C = N/V$ and $\theta = V_R/V$, Eq. (8.56) reduces to

$$\frac{V^2(N_{E_0} - N_E)}{N_{E_0}N_E} = kV_R \tag{8.85}$$

An average value of $(5000 + 8000)/2$, or 6500, can be substituted for V in Eq. (8.85) with proper values for the other variables.

$$V_R = \frac{(6500)^2(50)}{(100)(50)(32.4)} = 13{,}050 \text{ cu ft}$$

Thus, it is seen that the approximate method in this case gave a value of V_R of 89.0 per cent of the value obtained by use of the more exact method in Example 62. The chief reason for the poorer agreement than was obtained in the case of Example 61 is that the reactor volume is directly proportional to the square of the volumetric flow rate. Any error in the average used for V is therefore magnified. Even so, the agreement is not

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[1] Note that the dimensions of the reaction velocity constant must be consistent with the equation in which it is used.

at all bad when it is considered that there is a 60 per cent increase in volumetric flow rate between the inlet and the outlet of the reactor.

Recycle continuous processes that involve chemical reactions with variable volumetric flow rate are fortunately in a small minority. Even so, they can be attacked in the same way as in the case of reactions at constant volumetric flow rate by use of the differential equations that express the instantaneous rates of reaction. In most cases, perhaps, it will be found that the change in volumetric flow rate is not so great but that the approximate method gives sufficiently reliable results. If the change in volume is no greater than 40 per cent of the initial volume, the approximate method will usually suffice for most purposes. The equations for constant volumetric flow rates for chemical reactions in recycle continuous processes can be modified by the substitution of V_R/V for θ and N/V for C. The value of V should be an arithmetic average of the volumetric flow rates of the charge and product eliminated.

Conclusions.—It is desirable to emphasize again that, whenever the chemical engineer is faced with the task of specifying the size of equipment to handle a given processing job or the determination of the capacity of existing process equipment, he must in the final analysis use a suitable *rate equation.* A complete understanding of this is the most important point to be derived from this chapter. In his advanced studies of chemical engineering the student will concentrate upon the prediction of rates of transfer and transformation of mass and energy based chiefly on sound mathematical approaches. It will be found very helpful, however, if he has developed the essential philosophy of analyzing his technical problems in terms of the material balance, energy balance, equilibrium relations, and rates of transfer and transformation of mass and energy.

Of course, the final solution of chemical-engineering problems in practice must usually be based on the economic picture. This is the foundation upon which all processing must be established if the owners intend to stay in business.

PROBLEMS

1. A furnace wall is made up of a layer of 4.5 in. of firebrick, 4.5 in. of insulating brick, and 4.5 in. of building brick, the thermal conductivities of which are 0.85, 0.15, and 0.40 Btu/(ft)(deg F)(hr). The inside surface temperature of the firebrick is at 2000°F, and the outside surface temperature of the building brick is 100°F. How much heat is lost per 1000 sq ft of the wall? What is the temperature of the inside and outside surfaces of the insulating brick?

2. A 1500-ft 6-in. steam main (Schedule 40, Table A.12) is to be installed to supply saturated steam at 385 lb/sq in. gauge to various process units in a manufacturing department. The film coefficient for the steam condensate is 2000 Btu/(deg F)(sq ft)(hr). A 4-in. thickness of insulation (85 per cent magnesia) of 0.043 Btu/(deg F)(ft)(hr) thermal conductivity will be used. The pipe line will be unprotected from the weather, and the air film coefficient of heat transfer will be 2.5 Btu/(sq ft)(deg F)(hr). How much steam condensate should steam trap capacity be installed to handle per hour if the minimum air temperature is 0°F?

3. A double-pipe heat exchanger is used to cool hot oil (35°API) with water. The water passes through the annular space and the hot oil through the inner tube. The inner tube is a 2-in. standard pipe 15 ft in length. Countercurrent flow is used. The film coefficients of heat transfer for the water and oil are 400 and 45 Btu/(deg F)(sq ft)(hr), respectively. The water enters at 100°F and leaves at 130°F. What are the rates of flow of oil and water in gallons per hour?

4. What would be the minimum temperature to which the oil in Prob. 3 could be cooled with parallel flow if the same water rates are used and the heat-transfer coefficients are the same?

5. A fractionating column is to make the following separation:

	Moles/hr		
	Feed	Net overhead	Bottoms
Propane	7.3	7.3	.....
Isobutane	25.7	25.7	.....
n-Butane	189.0	113.0	76.0
Isopentane	29.0	.....	29.0
n-Pentane	56.0	.....	56.0
n-Hexane	44.2	.....	44.2
Total	351.2	146.0	205.2

The column will operate at a pressure of 100 lb/sq in. abs with a reflux ratio of 6/1. The pressure drop between the column and reflux drum is nil. The net overhead will be withdrawn as liquid from the reflux drum. Feed will be charged as liquid at 90°F.

a. Calculate the duty for the overhead condenser.

b. Calculate the duty for the reboiler.

c. With cooling water available at 80°F, how much heating surface is required for the overhead condenser? The over-all heat-transfer coefficient is 90 Btu/(deg F)(sq ft)(hr), and the rise in temperature of the water is 20°F. How much cooling water in gallons per minute is required?

d. The reboiler heating medium is saturated steam at 250 lb/sq in. abs. If the over-all heat-transfer coefficient is 85 Btu/(deg F)(sq ft)(hr), how much heating surface is needed? How much steam is required?

6. A double-effect evaporator is used to concentrate 6000 lb/hr of an aqueous salt solution from 10 to 30 per cent. Forward feed is used. Steam at 30 lb/sq in. abs is supplied to the steam basket of the first effect. The condenser maintains a pressure of 1.5 lb/sq in. abs on the second effect. The feed enters at 100°F. The specific heats of feed and thick liquor (product) are 0.92 and 0.75, respectively, and may be assumed to be linear with salt concentration. The boiling-point elevation in the first effect is 8°F and in the second effect is 12°F. The heat-transfer coefficients in the first and second effects are 275 and 175, respectively. The heating surface in the second effect is twice that of the first effect. Calculate

a. Pounds of steam required per hour
b. Evaporation in each effect
c. Vapor pressure and temperature in each effect
d. Heating surface in each effect

7. What is the absolute humidity of air that has wet-bulb and dry-bulb temperatures of 80 and 100°F, respectively? What is the dew point?

8. Air is available for a drier at 145°F, 40 per cent absolute humidity and atmospheric pressure.

a. What is the dew point of the air?

b. What is the partial pressure (pounds per square inch absolute) of water vapor in the air?

c. The air is passed through a drier and is cooled adiabatically to 125°F owing to evaporation of water. How much water was evaporated per 1000 cu ft of initial air?

d. What is the maximum humidity the air could attain by adiabatic drying, and what would be the final temperature?

9. A cooling tower is performing as indicated:

Water to the tower—5000 gal/min
Temperature of entering water, 115°F
Temperature of effluent water, 90°F
Temperature of entering air, 88°F
Temperature of effluent air, 110°F

The wet-bulb temperature of the entering air is 75°F. The effluent air has a wet-bulb temperature of 109.5°F. How many cubic feet per minute of air is supplied to the tower?

10. Experimental work was carried out in bombs on the gaseous-phase reaction, $A \rightarrow B + 2C$, which showed that the reaction rate was in accordance with what would be expected based on the chemical equation. It was found that 50 per cent of A had reacted after 25 min at 750°F. Assuming that the order of the reaction does not change with higher conversion of A, how much reactor volume should be provided to carry out the reaction in a once-through continuous operation with 70 per cent conversion? The charge rate will be 300 moles/hr. The charge will consist of 90 per cent A and 10 per cent inerts on a mole basis. The reaction is to be maintained at 750°F and 25 atm.

11. Cumene (isopropyl benzene) was maintained for 1.2 sec at 1290°F with 63 per cent decomposition. For every 100 moles of cumene decomposed, 15 moles of benzene, 30 moles of styrene, 30 moles of methyl styrene, and 25 moles of miscellaneous compounds were formed. What reactor volume should be provided to produce 1 ton/day of styrene (C_8H_8) by continuous once-through operation at 1290°F and 1 atm with 60 per cent cumene decomposition? The reaction is of the first order.

12. Monochlorobenzene is hydrolyzed in an autoclave at 675°F and 100 atm in the presence of caustic soda and cuprous chloride. The reaction data follow the first-order reaction equation. The reaction velocity constant is 0.010 per min. How much reaction time must be allowed to obtain conversions of (*a*) 50 per cent? (*b*) 95 per cent? (*c*) 99 per cent?

13. The reaction $A + B \rightarrow 3C + 2D$ is carried out in a bomb in the laboratory at 400°F, and 10 atm. The data show that 25 per cent of A had reacted after 20 min, 50 per cent had reacted after 48.2 min, and 75 per cent had reacted after 96.0 min.

Assuming no deviation from the ideal-gas law, calculate the volume of a continuous once-through reactor to react 100 moles of *A* with 100 moles of *B* per hour at 400°F and 50 atm with 65 per cent conversion.

14. The liquid-phase reaction $A + B \rightarrow C$ was studied in laboratory bombs at 200°F and 10 atm. The reaction velocity constant was found to be 0.85×10^3 cu ft/(mole)(hr). It is desired to carry out this reaction on a commercial unit with continuous recycle operation. The fresh feed will contain 20 per cent *A*, 70 per cent *B*, and 10 per cent inerts on a mole basis. The volumetric ratio of recycle to fresh feed will be 100/1. What is the size of the reactor required to handle 100 moles/hr of fresh feed if 75 per cent of *A* is reacted? Conditions will be 200°F and sufficiently high pressure to maintain liquid phase only in the reactor. The charge may be regarded as a perfect solution. The molal volumes of *A*, *B*, and the inerts under the conditions of the reactor are 2.0, 2.1, and 2.3 cu ft/mole, respectively. Assume no change in volume owing to the reaction.

CHAPTER IX

THE ECONOMIC BALANCE

The fifth and last technical fundamental of chemical engineering is the economic balance. Chemical-engineering economics deals primarily with the determination of the point of maximum profit per unit time to do a given job. Essentially, everything the chemical engineer does must be reduced eventually to a profit-and-loss basis. The economic balance, therefore, is at all times the guide of the practicing chemical engineer. An employer is always vitally interested in any well-supported proposal that shows how the earnings of the enterprise can be increased.

In most of the large companies the board of directors who are responsible for appropriation of funds will usually be interested merely in the answer to the following questions:

1. What do you want to do?
2. How much does it cost?
3. When will we get our money back?

If the proposal is attractive from an economic standpoint, the board will then be interested in a more detailed description of it. Thus, the chemical engineer should determine as soon as possible the economic feasibility of any project on which he works. His results should be reduced to a profit-and-loss basis so that he can be sure his efforts are being directed toward a worth-while end.

The philosophy in some foreign countries is quite different from that in this country inasmuch as processes are frequently developed for the sole purpose of making the country self-sufficient with respect to the product that the process will provide. Such developments were carried out before the Second World War despite the fact that the cost of the new process was substantially greater than the cost of the product if purchased from other countries. Such a controlled economy results in a higher cost. The system in this country is in general based on obtaining products at the lowest available cost even though from a foreign country. Thus, the chemical engineer who practices in this country must work toward production at competitive costs or his proposals will not fit in with the economic system. Of course, in the case of war the philosophy of self-sufficiency may become necessary.

The success of the chemical engineer is directly related to his economic contributions to the enterprise. The chemical engineer who merely follows instructions will not be very successful. On the other hand, the chemical engineer will attain success who frequently effects a significant reduction in cost of production, makes a new design at lower cost, obtains an increase in production at a profit, leads the way to an increase in the yield of the more valuable products, shows how to produce a new product at a profit, makes a profitable trade, or obtains a valuable patent.

It is impossible to cover all the various aspects of chemical-engineering economics in a single chapter. It will be feasible merely to introduce the philosophy of the economic balance and show by a few examples how it can be applied to the unit operations and chemical processes. For a broader treatment of chemical-engineering economics the reader is referred to Tyler.[1]

Possibilities for Economic Contributions.—The chemical engineer in practice should familiarize himself with the economic status of the enterprise with which he is connected. This will enable him to determine the most likely possibilities for increasing the earnings of the business. If he has a knowledge of the processing costs of the manufacturing plant, he will be in a position to determine which costs to reduce to obtain a large annual saving to the company. When attention is concentrated on reducing a small cost (dollars per year), the achievement is often relatively unimportant even though a substantial percentage reduction is realized. Instead, if attention is directed toward reducing a large cost, the saving may be considerable even though only a small percentage reduction in cost is effected. Consequently, it is usually preferable to direct attention toward the reduction of the larger manufacturing costs.

If fuel is expensive, the average chemical engineer can usually make attractive economic contributions by improving combustion efficiency. On the other hand, if fuel is relatively inexpensive, the probability is that a large saving in fuel cost could not be obtained in this way.

In the event that consideration is being given to marketing a new product or increasing production for an existing market, an accurate estimate of the market potential is essential. The chemical engineer must have a reliable estimate of how much can be sold and the corresponding price before an economic appraisal can be made. If the amount of products to be sold is reduced, a rather accurate estimate of the effect can usually be made; but when the volume of products is increased, it is not always possible to predict the effect as accurately as desired. A slight increase in the supply may "break" the market and result in a loss. If the sales demand is supplied by manufacturing a portion and purchasing the remainder from other

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[1] TYLER, CHAPLIN, "Chemical Engineering Economics," 2d ed., McGraw-Hill Book Company, Inc., New York, 1938.

manufacturers, the effect of an increase in production is to replace the supply at highest cost. This almost always is the cost of the portion purchased from other manufacturers. The saving is therefore the difference between the cost of producing the additional amount of product and the cost of purchasing that amount from other manufacturers. This is a frequent case in the petroleum industry.

If there is a large supply of raw material at low cost, the situation presents an opportunity for large economic returns. A process for converting low-value raw material into products of high value is what is needed. The persons who can show how this can be done will have made an important economic contribution to their company. Frequently such a process constitutes an invention, and a patent on the invention is a valuable asset of the company.

Basis of Economic Balances.—The fundamental basis for all economic balances is maximum profit per unit time. Industry and business operate on a basis of earnings per unit time. Consequently, any economic appraisal must be on that basis. When an economic balance deals with reduction in manufacturing costs, the balance must be made so that profit or net earnings per unit time is the maximum. In the event that production per unit time is fixed (fixed gross income) as a result of a fixed market, the economic balance may be based on the minimum cost of production per unit time or per unit of production. This is valid, however, only when the gross income or its equivalent is fixed. If production is not limited by the market, the point of maximum profit will not necessarily be at the point of minimum unit cost of production. For example, a manufacturing plant can produce 100,000 units of production per day at a cost of $1 per unit but can produce 150,000 units per day at a cost of $1.10 per unit. The last increment of 50,000 units therefore costs $65,000, or $1.30 per unit. Assume that the volume of the market is sufficiently great so that the increase in production can be absorbed without any change in sale price. In this case it is apparent that, as long as the price f.o.b. the manufacturing plant is above $1.30 per unit, the earnings will be greater at the higher production rate even though the unit cost of production is higher.

The chemical engineer who is engaged in technical service in a manufacturing plant will occasionally encounter cases in which one department will lose money by carrying out a certain operation but the enterprise as a whole will realize a significant increase in profit per unit time. In such a case the operation should be conducted so that the enterprise as a whole realizes maximum profit per unit time. Usually a department head will appreciate this fully and will be quite willing to accept the loss so that the firm can obtain the increase in earnings. The economic balance, however, must be well founded and fully supported by evidence before the department head will be willing to direct the operations of his department along the lines indicated by the economic balance. He must have a good argument to justify operating so that a loss to his department is incurred.

The same principle is frequently encountered in the operation of a given production unit. In order that the production unit may operate at maximum profit to the enterprise, it is often necessary to operate a single piece of equipment in the production unit well below its maximum efficiency. For example, it may be necessary to operate a furnace so that the fuel consumed per unit of production is considerably higher than would be the case if the production rate were reduced. But at the higher rate the earnings per unit time of the enterprise is a maximum.

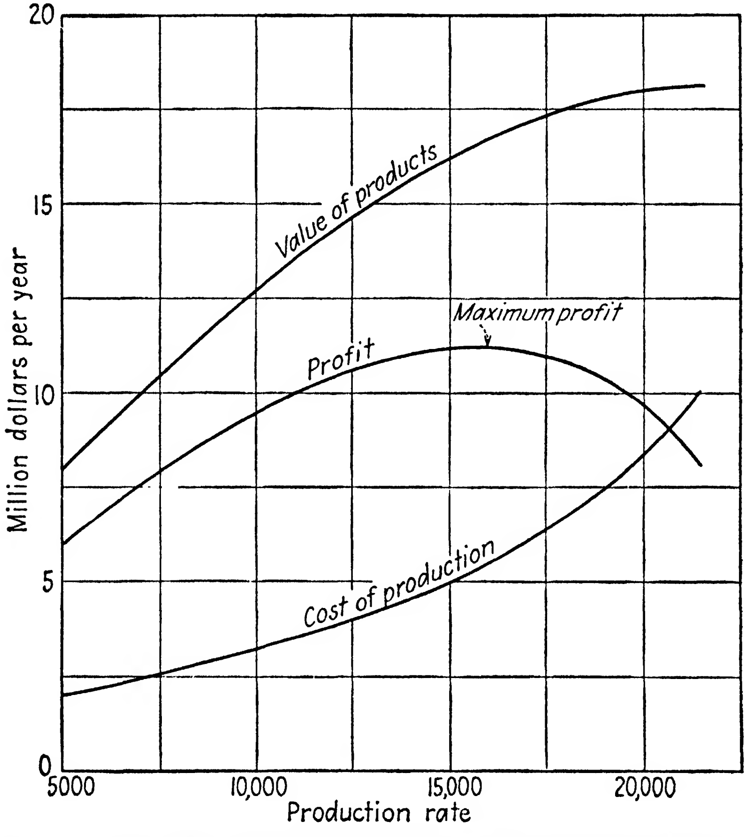

FIG. 9.1.—Graphical representation of relation between profit and production.

Thus, the economic balance will consist of a balance between costs and income per unit time so that the difference between them is a maximum. This is shown graphically by Fig. 9.1. If production rate (gross income) is fixed or does not enter into the economic calculations, the balance may be made between the various costs so that the total cost per unit time or per unit of production is a minimum.

Another procedure very often used in an economic balance is based on *incremental costs.* This involves merely the calculation of changes in costs and changes in income that are a result of a change in a primary variable. In the example described above the incremental method was used. The change in cost for the increase in production of 50,000 units per day was $65,000. The primary variable in this case is the rate of production.

If consideration is being given to the installation of a new process in a manufacturing plant, it is usually much simpler to appraise it on the basis of differences or increments. A base case is established that represents the current situation. Then the effect of the new process in terms of production and costs is calculated. Often the effect on production includes a reduction in production of certain materials and an increase in the production of others. If the net changes in production and costs are known, the economic balance can be made as a predicted difference in net earnings of the enterprise relative to the base case, or existing situation.

There are several terms commonly used in chemical-engineering economics that should be defined and discussed before proceeding with applications of the economic balance. *Fixed charges* or *fixed costs* are those which are not affected by changes in production rate. For example, the depreciation charges on an investment are fixed per unit time regardless of the use to which the process or equipment is put. Also, a large portion of overhead charges is fixed, for the salaries of most of the keymen in the management will not be affected by changes in processing or in raw materials. For the purpose of economic balances it is almost always essential that the fixed costs be separated from the *variable costs.* The variable costs will be affected by changes in processes or changes in equipment. A good example of a variable cost is fuel consumed by a boiler. The rate of fuel consumption is directly related to the rate of steam generation. Thus, the fixed and variable costs should be segregated in order to make a sound economic appraisal. The chemical engineer must exercise caution when obtaining cost figures from accounting or bookkeeping records. Such costs frequently include cost items that are not pertinent to the economic balance and that must therefore be eliminated from the cost figures used in the balance.

In economic balances involving new investments the fixed costs that are a result of the new investment must be considered. On the other hand, the fixed charges on existing investments usually are not pertinent, for they will be constant per unit time and therefore will not affect the final conclusion. In other words, after an investment is made the fixed charges continue, regardless of how the investment is used.

The most important factor concerning the possibility of making an investment is the length of time for the investment to pay for itself. This is commonly called the *pay-off time* or the *time for amortization.* The maximum length of time that will be considered for amortizing an investment depends to a large extent on what the project is. In the case of ocean cargo vessels it is not uncommon for them to be amortized over a period of 20 years. On the other hand, a maximum time of 4 years for amortization of process equipment is not unusual. One of the chief reasons for this is that process equipment becomes obsolete at a rapid rate because of research and development that provide substantially more economical processes.

Although the board of directors of a corporation may not consider an investment in process equipment unless it will amortize itself within 4 years, after an investment is made the amortization may be at a somewhat lower rate than 25 per cent per year. Usually such rates are fixed at maximum values by the government in connection with corporation income taxes.

THE ECONOMIC BALANCE IN UNIT OPERATIONS

Owing to the fact that this text is written primarily for the student who has not had a course in unit operations, the presentation here will of necessity be limited to only a few of the unit operations. Even so, the philosophy of the economic balance in unit operations can be learned. This is of the greatest importance, for the applications to those unit operations not covered here will become more or less apparent as the student progresses with his more advanced study of chemical engineering. Those variables which affect the size and capacity of process equipment will be found to be the key to economic balances in the unit operations.

Fluid Flow.—Compression of gas is one of two widely used methods to transfer gas at low pressure to a higher pressure. In Chap. VI the calculation of the power required for pumping liquids was discussed. At this time the calculation of power required for the compression of gas will be considered. The subject was deferred to this point in the text because it involves in effect an economic balance.

Gas compressors are of two general types, *viz.*, reciprocating and centrifugal. Only the reciprocating type of compressor will be considered in this text. The reader is referred to Kearton [1] for a treatment of centrifugal compressors, which are of more recent development.

Reciprocating compressors are designed with one to nine compression cylinders. Usually, however, the number of compression stages is one to six. Each cylinder is jacketed so that cooling water can be circulated

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[1] KEARTON, W. J., "Turbo-blowers and Compressors," Sir Isaac Pitman & Sons, Ltd., London, 1926.

around the cylinders to maintain the cylinder walls at a lower temperature. This does not have much effect on the temperature of the gas, for the rate of heat transfer from the gas to the cylinder walls is rather low. Thus, gas compression is carried out under essentially adiabatic conditions. With adiabatic compression the temperature of the gas increases during compression because the work done on the gas is converted into internal energy. Consequently, in the case of more than one compression stage the gas is passed through intercoolers located between the stages. In this way the gas is cooled to its initial temperature before going to the next compression stage. This reduces the power required for compression, as will be seen later.

In order to determine the amount of power required for adiabatic compression of gas it is necessary first to calculate an equation for the path of the gas during adiabatic compression. Then the power required for compression can be calculated by considering the complete compression cycle. Such calculations are made below on the basis of compressing an ideal gas.

The heat capacities at constant volume and constant pressure were defined in Chap. IV as follows:

$$C_v = \frac{dU}{dT} \tag{4.35}$$

$$C_p = \frac{dH}{dT} = \frac{dU}{dT} + \frac{P\,dV}{dT} \tag{4.36}$$

For one mole of the ideal gas at constant pressure,

$$PV = RT$$

and

$$\frac{P\,dV}{dT} = R$$

or, from Eq. (4.36),

$$C_p = \frac{dU}{dT} + R \tag{9.1}$$

and from Eqs. (4.35) and (9.1) Eq. (4.38) is obtained. This equation was presented in Chap. IV without the supporting proof of its validity.

$$C_p - C_v = R \tag{4.38}$$

Writing Eq. (4.27) in differential form,

$$dQ = dU + P\,dV \tag{9.2}$$

But, from Eq. (4.35),

$$dU = C_v\,dT$$

and

$$dQ = C_v\,dT + P\,dV \tag{9.3}$$

By the ideal-gas law,

$$d(PV) = R\,dT = P\,dV + V\,dP \tag{9.4}$$

or

$$dT = \frac{P\,dV}{R} + \frac{V\,dP}{R} \tag{9.5}$$

By substituting Eq. (9.5) in Eq. (9.3),

$$dQ = \frac{C_vP\,dV}{R} + \frac{C_vV\,dP}{R} + P\,dV \tag{9.6}$$

or

$$dQ = P\,dV\left(\frac{C_v}{R} + 1\right) + \frac{C_vV\,dP}{R} \tag{9.7}$$

By substituting $C_p - R$ for C_v [Eq. (4.38)],

$$dQ = P\,dV\left(\frac{C_p}{R}\right) + \frac{C_vV\,dP}{R} \tag{9.8}$$

The ratios of P/R and V/R can then be eliminated by means of the ideal-gas law.

$$dQ = C_pT\frac{dV}{V} + C_vT\frac{dP}{P} \tag{9.9}$$

For adiabatic compression and expansion,

$$dQ = 0$$

and Eq. (9.9) reduces to

$$C_p\frac{dV}{V} + C_v\frac{dP}{P} = 0 \tag{9.10}$$

If

$$\frac{C_p}{C_v} = \gamma \text{ (a constant)} \tag{9.11}$$

then

$$\gamma\frac{dV}{V} + \frac{dP}{P} = 0 \tag{9.12}$$

which can be integrated as follows,

$$\gamma \ln V + \ln P + K = 0 \tag{9.13}$$

where K is the constant of integration; or Eq. (9.8) can be written as

$$PV^\gamma = P_1V_1^\gamma = P_2V_2^\gamma = K' \tag{9.14}$$

where K' is a constant.

Equation (9.14) is therefore the equation of the path of an ideal gas when expanded or compressed under adiabatic conditions. This, of course, is predicated upon the assumption that C_p/C_v or γ is a constant. This is not quite true but for the purpose is sufficiently representative of the facts over pressure ranges normally encountered in compressors.

The work of adiabatic compression (or expansion) may now be calculated for an ideal gas by means of Eq. (9.14),

$$W = -\int_{V_1}^{V_2} P\,dV \tag{9.15}$$

where W is the work done on the gas.

Since $$PV^\gamma = P_1V_1^\gamma,$$

$$W = -P_1V_1^\gamma \int_{V_1}^{V_2} \frac{dV}{V^\gamma} \tag{9.16}$$

The integrated form of Eq. (9.16) is

$$W = \frac{P_1V_1^\gamma}{1-\gamma}\left(V_1^{1-\gamma} - V_2^{1-\gamma}\right) \tag{9.17}$$

or $$W = \frac{P_1V_1}{1-\gamma} - \frac{P_1V_1^\gamma V_2^{1-\gamma}}{1-\gamma} \tag{9.18}$$

But since $P_1V_1^\gamma = P_2V_2^\gamma$,

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \tag{9.19}$$

Since V_2 is unknown, it can be eliminated by means of Eq. (9.14).

$$V_2 = V_1\left(\frac{P_2}{P_1}\right)^{-\frac{1}{\gamma}} \tag{9.20}$$

or $$W = \frac{P_2V_1\left(\frac{P_2}{P_1}\right)^{-\frac{1}{\gamma}} - P_1V_1}{\gamma - 1} \tag{9.21}$$

and $$W = \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] \tag{9.22}$$

Equation (9.22) gives the theoretical amount of work done on the system in adiabatic compression (or expansion) of a perfect gas from P_1 and V_1 to P_2 and V_2.

The relationship between initial temperature and final temperature for adiabatic compression of an ideal gas can be developed by means of Eq. (9.20) and the ideal-gas law. The relationship is given by Eq. (9.23).

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \tag{9.23}$$

Compressors.—The compression of gas by compressors involves a cycle that consists of (1) drawing the low-pressure gas into the cylinder, (2) adiabatically compressing to the exhaust pressure, and (3) rejecting the compressed gas from the cylinder. Figure 9.2 illustrates the cycle. When the gas at pressure P_1 is drawn into the cylinder during the suction stroke (A to B), work is done by the gas on the piston equal to P_1V_1. Then, in the compression stroke (B to C) work is done on the gas in amount given by Eq. (9.22). Finally work is done on the gas in the exhaust stroke (C to D) equal to P_2V_2. Thus, the total work done on the gas in the cycle is given by Eq. (9.24).

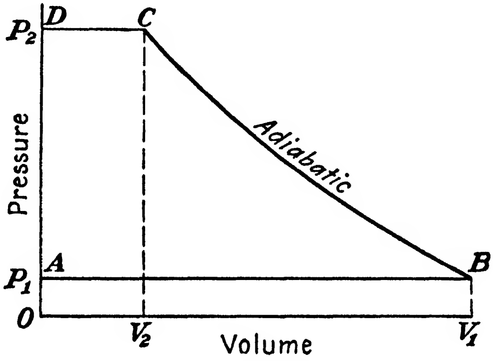

FIG. 9.2.—Single-stage adiabatic compression.

$$W_{\text{cycle}} = P_2V_2 - P_1V_1 + \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] \tag{9.24}$$

But, from Eqs. (9.19) and (9.22),

$$P_2V_2 - P_1V_1 = P_1V_1\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] \tag{9.25}$$

Then,

$$W_{\text{cycle}} = \frac{\gamma P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] \tag{9.26}$$

Equation (9.26) represents the theoretical work done by a single-stage compressor on an ideal gas when compressed adiabatically from P_1 and V_1 to P_2 and V_2.

It is apparent that if the temperature were maintained constant (isothermal) V_2 would be smaller than in the case of adiabatic compression. Thus, the amount of work done on the gas would be less with isothermal compression than with adiabatic compression. Owing to this fact, less work of compression is required if a gas is compressed in stages and cooled to the initial temperature between stages. Essentially this is an approach toward isothermal compression. An infinite number of stages is equivalent to isothermal compression. The number of stages, however, for any given amount of compression is limited by economic and physical considerations. Even so, the design of any multistage compressor is based on an economic balance, one factor of which is the amount of energy required for compression. The question, therefore, arises as to what the exhaust pressure should be from each stage.

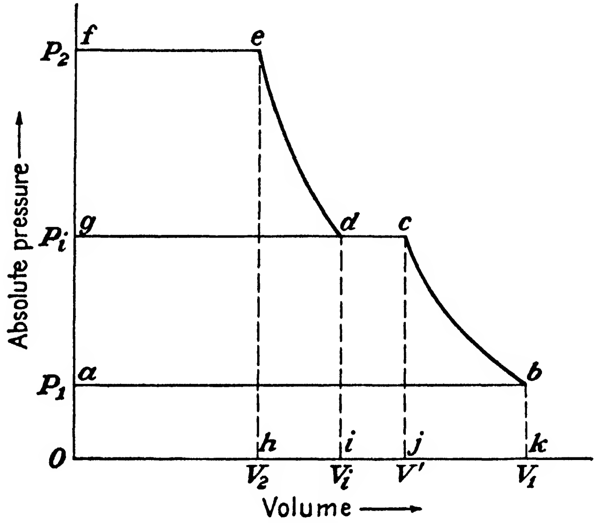

FIG. 9.3.—Two-stage adiabatic compression with cooling between stages.

Consider the design of a two-stage compressor. Figure 9.3 illustrates the complete cycle. In the first stage the intake, or suction, stroke is from *a* to *b*, which results in work being done by the gas on the piston equal to P_1V_1. Then adiabatic compression in the first stage is carried out from *b* to *c*, which involves work on the gas equal to the area *jkbc*. Next, the gas is exhausted from the first stage at P_i. This requires work on the gas of P_iV'. The net work done on the gas in the first stage is therefore equal to the area *abcg*, or, according to Eq. (9.26),

$$W_1 = \frac{\gamma P_1 V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] \tag{9.27}$$

where W_1 is the total work done on the gas in the first cycle.

The gas from the first stage is then passed through an intercooler, which reduces the temperature to its initial value. From the intercooler it is drawn into the cylinder of the second stage on the suction stroke g to d. Note that the volume of the gas was reduced from V' to V_i as a result of the reduction in temperature to the initial value. The work done by the gas on the piston of the second stage is therefore P_iV_i. Adiabatic compression is then carried out from d to e, which results in work being done on the gas equal to the area *dehi*. The gas is finally exhausted from the cylinder by doing work on the gas equal to P_2V_2. The net work done by the gas in the second stage according to Eq. (9.26) is

$$W_2 = \frac{\gamma P_1 V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_i}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] \tag{9.28}$$

where W_2 is the total work done on the gas in the second cycle. But since the temperature of the gas entering the second stage is identical with that entering the first stage and no condensation occurs between stages,

$$P_iV_i = P_1V_1 = RT_1 \tag{9.29}$$

Then, the total work done by the gas in both stages is

$$W = W_1 + W_2 = \frac{\gamma P_1 V_1}{\gamma - 1}\left[\left(\frac{P_i}{P_1}\right)^{\frac{\gamma-1}{\gamma}} + \left(\frac{P_2}{P_i}\right)^{\frac{\gamma-1}{\gamma}} - 2\right] \tag{9.30}$$

The value of P_i should be set so that the total work is the minimum. Since for any specific case P_i and W are the only variables in Eq. (9.30),

$$\frac{dW}{dP_i} = 0 = \left(P_1^{\frac{1-\gamma}{\gamma}}\right)\left(\frac{\gamma - 1}{\gamma}\right)P_i^{\frac{-1}{\gamma}} + \left(P_2^{\frac{\gamma-1}{\gamma}}\right)\left(\frac{1 - \gamma}{\gamma}\right)P_i^{\frac{1-2\gamma}{\gamma}} \tag{9.31}$$

which reduces to

$$P_i = \sqrt{P_1P_2} \tag{9.32}$$

or

$$\frac{P_i}{P_1} = \frac{P_2}{P_i} \tag{9.33}$$

Thus, for a two-stage compressor the most economical intermediate pressure based only on minimum energy required for compression is the square root of the product of the initial and final pressures. In other words, the ratio of the exhaust to the suction pressure of each stage is the same. By substitution of $\sqrt{P_1P_2}$ for P_i in Eqs. (9.19) and (9.20) it will be found that the minimum work of compression corresponds to $W_1 = W_2$. It can be shown that the ratio of the exhaust to suction pressure is the same (at minimum work) for each stage, regardless of the number of stages. This corresponds to the same amount of work done in each stage. In practice, the economic balance must also consider other factors such as mechanical limitations. Fortunately, however, it is most economical also from the standpoint of the mechanical design to do the same amount of work in each stage. For a more complete treatment of the theory of multistage compression the reader is referred to Dodge.[1]

It must be kept in mind that Eqs. (9.22) to (9.33) were predicated upon the compression of an ideal gas. Actually, rather large deviations from the ideal gas are frequently encountered in the compression of real gases. Although this subject is outside the scope of this text, it should be mentioned that the deviation can be dealt with by use of reduced equations of state such as are shown in Fig. A.29 or Figs. A.2 to A.4. For a treatment of this subject the reader is referred to York.[2]

Example 63. Carbon dioxide gas saturated with water vapor at 2.5 lb/sq in. gauge pressure and 100°F is to be compressed adiabatically in two stages to a final pressure of 287 lb/sq in. gauge. The gas will be cooled to its initial temperature after the first stage. The value of γ may be taken as 1.29 for CO_2 and H_2O vapor or mixtures thereof. Calculate the interstage pressure that should be used to give the total minimum work. Assume that the ideal-gas law applies and that no H_2O condenses in the cylinders.

Solution: Since the gas is saturated with water vapor at 100°F and 2.5 lb/sq in. gauge pressure, it is apparent that some of the H_2O will condense out of the gas in the interstage cooler. The partial pressure of H_2O at 100°F is 0.9487 or, say, 0.95 lb/sq in. abs (Table A.14). Since the amount of CO_2 will be the same for each stage, it will serve as a good basis for calculations.

Basis: 1.0 lb of CO_2.

$$\frac{\text{Lb of } H_2O}{\text{Lb of } CO_2} = \frac{(\text{partial pressure of } H_2O)(M_{H_2O})}{(\text{partial pressure of } CO_2)(M_{CO_2})}$$

To first stage,

$$\text{Lb of } H_2O = \frac{(0.95)(18)(1.0)}{(17.2 - 0.95)(44)} = 0.0239$$

To second stage,

$$\text{Lb of } H_2O = \frac{(0.95)(18)(1.0)}{(P_i - 0.95)(44)} = \frac{0.389}{P_i - 0.95}$$

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[1] DODGE, B. F., "Chemical Engineering Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1944.

[2] YORK, R., *Ind. Eng. Chem.*, **34**, 535 (1942).

To first stage,

$$V_{CO_2} = \frac{(1)(379)(560)(14.7)}{(44)(520)(17.2)} = 7.93 \text{ cu ft}$$

$$V_{H_2O} = \frac{(0.0239)(379)(560)(14.7)}{(18)(520)(17.2)} = 0.464 \text{ cu ft}$$

$$V_1 = 7.93 + 0.464 = 8.394 \text{ cu ft}$$

From Eq. (9.27),

$$W_1 = \frac{\gamma P_1 V_1}{\gamma - 1}\left[\left(\frac{P_i}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

$$W_1' = \frac{(1.29)(17.2)(8.394)}{1.29 - 1.00}\left[\left(\frac{P_i}{17.2}\right)^{\frac{0.29}{1.29}} - 1\right]$$

$$= 339P_i^{0.225} - 642$$

where $W_1' = W_1/144$

To second stage,

$$V_{CO_2} = \frac{(7.93)(17.2)}{P_i} = \frac{136.2}{P_i}$$

$$V_{H_2O} = \left[\frac{(379)(560)(14.7)}{(520)(18)P_i}\right]\left(\frac{0.389}{P_i - 0.95}\right) = \frac{129.7}{P_i(P_i - 0.95)}$$

$$V_i = \frac{136.2}{P_i} + \frac{129.7}{P_i(P_i - 0.95)} = \frac{(136.2)(P_i - 0.95) + 129.7}{P_i(P_i - 0.95)}$$

From Eq. (9.28),

$$W_2' = \frac{\gamma P_i V_i}{\gamma - 1}\left[\left(\frac{P_2}{P_i}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

$$= \frac{(1.29)[(136.2)(P_i - 0.95) + 129.7]}{(1.29 - 1.00)(P_i - 0.95)}\left[\left(\frac{301.7}{P_1}\right)^{0.225} - 1\right]$$

$$= \frac{(605)(P_i - 0.95) + 576}{P_i - 0.95}\left(\frac{3.62}{P_i^{0.225}} - 1\right)$$

where $W_2' = W_2/144$

$$W' = W_1' + W_2' = 339P_i^{0.225} - 642 + \left[\frac{(605)(P_i - 0.95) + 576}{P_i - 0.95}\right]\left(\frac{3.62}{P_i^{0.225}} - 1\right)$$

This equation can best be solved by assuming values of P_i and calculating W. The value of P_i that corresponds to the minimum value of W is the correct one to use. As

a guide for the values of P to assume, $\sqrt{(17.2)(301.7)} = 72$ would be the optimum interstage pressure if there were no condensation in the intercooler.

P_i	W
40	492
60	483
65	481
68	481
75	482
100	486

From the tabulation of P_i vs. W it appears that minimum work of compression occurs between 65 and 68 lb/sq in. abs.

It will be noted, in Example 63, that in this case the interstage pressure could be varied over a considerable range without departing appreciably from the minimum work of compression. In other words, the optimum interstage pressure based on no condensation in the intercooler would be quite close to the exact minimum. It will be seen also from Example 63 that the amount of work done by the gas in each stage is identical just as in the case of no condensation.

In Example 63 the value of γ for CO_2 was taken as identical with that of H_2O vapor. The problem becomes more complicated, however, when condensation occurs if the value of γ for each component of the gas mixture is not identical. The criterion is identical work performed in each stage.

Example 64. Flue gas, saturated with benzene vapor at 70°F, is compressed adiabatically in two stages from an original absolute pressure corresponding to 30 in. of mercury to an absolute pressure equivalent to 300 in. of mercury. The gas is cooled between stages to 70°F. The value of γ for flue gas (free of benzene) is 1.385 and for benzene vapor is 1.10.

a. What value of γ should be used in calculating the work in each stage if no benzene is condensed on the cylinder walls?

b. What is the theoretical horsepower of the compressor at 240 cu ft/min of gas to the first stage? Assume that the ideal-gas law is valid.

Solution: The interstage pressure should be set so that the work done by the gas in each stage is identical. It will be necessary to arrive at the proper interstage pressure by trial and error.

Basis: 1 mole of dry flue gas.

Vapor pressure of benzene at 70°F = 3.12 in. of mercury (Fig. A.1)

a. To first stage:

$$\text{Moles of benzene} = \frac{3.12}{30.0 - 3.12} = 0.116$$

$$\text{Moles of flue gas} = 1.000$$

$$\text{Total moles} = 1.116$$

$$\gamma = \frac{C_p}{C_v} \quad \text{and} \quad C_p - C_v = R = 1.99 \text{ Btu/(mole)(deg F)}$$

For flue gas,

$$\frac{C_p}{C_v} = 1.385$$

$$C_p = 1.99 + C_v = 1.385C_v$$

$$C_v = 5.17 \qquad C_p = 7.16$$

For benzene,

$$C_p = 1.99 + C_v = 1.10C_v$$

$$C_v = 19.9 \qquad C_p = 21.89$$

For gaseous mixture,

$$C_v = \left(\frac{1}{1.116}\right)(5.17) + \left(\frac{0.116}{1.116}\right)(19.9) = 6.70$$

$$C_p = 6.70 + 1.99 = 8.69$$

$$\gamma = \frac{8.69}{6.70} = 1.30$$

To second stage: As a first approximation of P_i, assume that $\sqrt{P_1P_2} = P_i = \sqrt{(30)(300)} = 95$ in. of mercury.

$$\text{Moles of benzene} = \frac{3.12}{95.00 - 3.12} = 0.034 \text{ mole}$$

$$\text{Moles of flue gas} = 1.00 \text{ moles}$$

$$\text{Total gaseous mixture} = 1.034 \text{ moles}$$

For gaseous mixture,

$$C_v = \left(\frac{1}{1.034}\right)(5.17) + \left(\frac{0.034}{1.034}\right)(19.9) = 5.655$$

$$C_p = 5.655 + 1.99 = 7.645$$

$$\gamma = \frac{C_p}{C_v} = \frac{7.645}{5.655} = 1.35$$

b. Work done in each stage:

To first stage, $$(1.116)(379)\left(\frac{530}{520}\right)\left(\frac{29.9}{30.0}\right) = 430 \text{ cu ft}$$

$$W_1 = \frac{\gamma P_1 V_1}{\gamma - 1}\left[\left(\frac{P_i}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

$$P_1 = \left(\frac{30.0}{29.9}\right)(14.7)(144) = 2125 \text{ lb/sq ft abs}$$

$$W_1 = \left[\frac{(1.30)(2125)(430)}{1.30 - 1.00}\right]\left[\left(\frac{95}{30}\right)^{0.231} - 1\right]$$

$$= 1{,}210{,}000 \text{ ft-lb}$$

To second stage, $(1.034)(379)\left(\frac{530}{520}\right)\left(\frac{29.9}{95}\right) = 126 \text{ cu ft}$

$$W_2 = \frac{\gamma P_1 V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_i}\right)^{\frac{\gamma - 1}{\gamma}} - 1\right]$$

$$P_i = \left(\frac{95.0}{29.9}\right)(14.7)(144) = 6730 \text{ lb/sq ft abs}$$

$$W_2 = \left[\frac{(1.35)(6730)(126)}{1.35 - 1.00}\right]\left[\left(\frac{300}{95}\right)^{0.259} - 1\right]$$

$$= 1{,}135{,}000 \text{ ft-lb}$$

It is apparent that the assumed value of P_i (corresponding to 95 in. of mercury) is very close to the optimum but is slightly high. The correction of the first approximation of P_i can be done without considering the slight change in extent of benzene condensed in the interstage cooler.

$$P_1 = 2125 \text{ lb/sq ft abs}$$

$$P_2 = (^{300}/_{30})(2125) = 21{,}250 \text{ lb/sq ft abs}$$

$$W_1 = \left[\frac{(1.30)(2125)(430)}{1.30 - 1.00}\right]\left[\left(\frac{P_i}{2125}\right)^{0.231} - 1\right]$$

$$= 668{,}000 P_i^{0.231} - 3{,}960{,}000$$

$$W_2 = \left[\frac{(1.35)(P_i)(126)}{1.35 - 1.00}\right]\left[\left(\frac{21{,}250}{P_i}\right)^{0.259} - 1\right]$$

$$= 6450 P_i^{0.741} - 486 P_i$$

But $W_1 = W_2$, or

$$665{,}000 P_i^{0.231} - 3{,}960{,}000 = 6450 P_i^{0.741} - 486 P_i$$

Solving by trial and error,

$$P_i = 6590 \text{ lb/sq in. abs}$$

which corresponds to 94 in. of mercury. At this point,

$$W_1 = W_2 = 1{,}145{,}000 \text{ ft-lb}$$

$$\text{Theoretical hp} = \frac{(2)(1{,}145{,}000)(240)}{(430)(33{,}000)} = 38.7$$

Optimum Pipe Diameter.—Another type of economic balance encountered in fluid flow is the determination of the most economical diameter of pipe to use in a pipe line. In such cases, if the quantity to be handled is fixed (which is usually the situation), the economic balance reduces to a balance of pumping or compressing costs against the fixed (investment, etc.) costs. The optimum diameter corresponds to the minimum cost per unit time.

Example 65. Oxygen is to be compressed adiabatically by a single-stage compressor and delivered through a pipe line to another department. The gas is at 20 atm pressure, and it must be delivered to the other department at 80 atm. The pipe line will have an equivalent length of 1000 ft and will not be insulated. Thus, it may be assumed that the gas will flow under isothermal conditions. The temperature in the pipe line will be 20°C, and the viscosity will be 0.021 centipoise.

The oxygen will be delivered at the rate of 3600 lb/hr. The compressor and drive have an over-all mechanical efficiency of 70 per cent. Power costs are $0.03 per kilowatt-hour.

The pressure-volume relationship for oxygen at 20°C over the pressure range involved is represented by the following equation,

$$Pv = 26{,}450$$

where P = pressure, lb/sq ft
v = specific volume, cu ft/lb

The molal volume of oxygen at 1 atm and 20°C is 24.4 l.

Double extra-heavy wrought pipe will be used for the line; the cost is as follows:

Nominal diam., in.	Actual, i.d., in.	Cost per ft
1½	1.100	$0.65
2	1.503	0.91
2½	1.771	1.37
3	2.300	1.86
3½	2.728	2.30
4	3.152	2.76

Compressors cost $100 per horsepower (installed) in the probable horsepower range that will be required.

Depreciation and other fixed costs of the compressor and pipe line are 15% per year based on 365 days/year and 24 hr/day.

Neglecting any changes in velocity heads between the suction and discharge of the compressor and assuming no change in external potential heads between the inlet and outlet of the pipe line, calculate

1. The size of pipe that should be used.
2. The cost of the pipe line and compressor.
3. The power required.

Solution: Since the quantity of oxygen to be transferred is fixed, the optimum pipe diameter will correspond to a balance of the operating costs to give minimum cost per unit time. The total operating cost will be composed of fixed costs plus the cost of power. The cost of power will depend upon the pressure to which it is desirable to compress the oxygen. The desirable pressure will be equal to the pressure drop through the pipe line plus 80 atm. The pressure drop through the pipe line can be calculated by Eqs. (6.8) and (3.1).

$$-dP = \frac{V\,dV}{vg} + \frac{2fV^2\rho\,dL}{gD}$$

where P = pressure, lb/sq ft
V = linear velocity, ft/sec
v = specific volume, cu ft/lb
g = acceleration of gravity, ft/sec^2
f = friction factor (Fig. 6.2)
ρ = density = $1/v$, lb/cu ft
L = length of pipe, ft
D = diameter of pipe, ft

$$\text{Mass velocity} = G = \frac{60}{\pi D^2/4} = \frac{240}{\pi D^2}\text{ lb/sq ft/min}$$

$$= \frac{240}{(60)(\pi D^2)} = \frac{1.275}{D^2}\text{ lb/sq ft/sec}$$

But $G = V\rho = V/v$.

Since mass velocity is constant,

$$dV = G\,dv$$

and

$$\frac{V\,dV}{vg} = \frac{G\,dV}{g} = \frac{G^2\,dv}{32.2}$$

$$\frac{G^2\,dv}{32.2} = \frac{(1.275/D^2)^2\,dv}{32.2} = \frac{0.0505\,dv}{D^4}$$

But, from the statement of the problem,

$$v = \frac{26{,}450}{P}$$

or

$$dv = \frac{-26{,}450\,dP}{P^2}$$

Then,

$$\frac{0.0505\,dv}{D^4} = \frac{-(26{,}450)(0.0505)\,dP}{D^4P^2} = \frac{-1335\,dP}{D^4P^2}$$

Thus,

$$-\int_{P_2}^{P_3} dP = -\int_{P_2}^{P_3}\frac{1335\,dP}{D^4P^2} + \int_0^{1000}\frac{2fVG\,dL}{32.2D}$$

or

$$P_2 - P_3 = \frac{1335}{D^4}\left(\frac{1}{P_2} - \frac{1}{P_3}\right) + \int_0^{1000}\frac{2fVG\,dL}{32.2D}$$

Since $G = 1.275/D^2$,

$$\int_0^{1000}\frac{(2fV)(1.275)}{32.2D^3}\,dL = \int_0^{1000}\frac{0.0791fV}{D^3}\,dL$$

In order to evaluate this integral, average values of f and V must be used.

Since $V = Gv$,

$$V_{\text{av}} = Gv_{\text{av}}$$

An atmospheric pressure and 20°C,

$$\text{Cu ft/mole} = \left(\frac{1}{\text{g-mole}}\right)\left(\frac{\text{cu ft}}{1}\right)\left(\frac{\text{g-mole}}{\text{lb-mole}}\right)$$

$$= (24.4)\left(\frac{1}{28{,}300}\right)(453.6) = 392$$

At 80 atm and 20°C,

$$v_3 = \frac{(392)(1)}{(32)(80)} = 0.153 \text{ cu ft/lb}$$

Assuming 5 atm pressure drop,

$$v_3 = \frac{(392)(1)}{(32)(85)} = 0.145 \text{ cu ft/lb}$$

The arithmetic average is

$$v_{\text{av}} = \frac{0.153 + 0.145}{2} = 0.149 \text{ cu ft/lb}$$

and

$$V_{\text{av}} = 0.149G = \frac{(0.149)(1.275)}{D^2}$$

$$= \frac{0.190}{D^2}$$

Then,

$$\int_0^{1000} \frac{(0.0791)(f)(0.190)}{D^5}\, dL = \frac{15.03f}{D^5}$$

And since $P_3 = (80)(14.7)(144) = 169{,}500$ lb/sq ft,

$$(P_2 - 169{,}500) + \frac{1335}{D^4}\left(\frac{1}{169.000} - \frac{1}{P_2}\right) = \frac{15.03f}{D^5}$$

It is apparent that the term

$$\frac{1335}{D}\left(\frac{1}{169{,}500} - \frac{1}{P_2}\right)$$

is negligible and will therefore be dropped.
Thus,

$$(a) \qquad P_2 = 169{,}500 + \frac{15.03f}{D^5}$$

The friction factor f is a function of the Reynolds number (Fig. 6.2).

$$(b) \qquad \frac{DG}{\mu} = \frac{(D)(1.275/D^2)}{(0.000672)(0.021)} = \frac{90{,}300}{D}$$

By assuming values of D the Reynolds number can be calculated by Eq. (*b*), and the value of f can be obtained from Fig. 6.2. Then P_2 can be calculated for the assumed value of D by means of Eq. (a). The horsepower required for compression can then be calculated as follows:

$$W = \frac{\gamma P_1 V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

$$C_p = 7.02 \text{ (Table A.3)}$$

$$Cv = 7.02 - 1.99 = 5.03$$

$$\gamma = \frac{7.02}{5.03} = 1.40$$

$$P_1 = (20)(14.7)(144) = 42{,}350 \text{ lb/sq ft}$$

$$V_1 = 60v_1 = \frac{(60)(26{,}450)}{42{,}350}$$

$$= 37.5 \text{ cu ft/min}$$

$$\text{Hp} = \frac{W}{(33{,}000)(0.7)} = \frac{W}{23{,}100}$$

$$= \frac{(1.40)(37.5)(42{,}350)}{(0.4)(23{,}100)}\left[\left(\frac{P_2}{42{,}350}\right)^{0.286} - 1\right]$$

$$= 11.45P_2^{0.286} - 241 \tag{c}$$

Cost of operation: When values of D are assumed, this automatically fixes the investment cost for the pipe line. Then the horsepower required for compression is calculated by Eq. (c), which permits the calculation of the investment cost of the compressor as well as power cost. The fixed charges per year are then calculated by taking 15 per cent of the investment costs of the pipe line and compressor. Thus, by assuming values of D and calculating the fixed costs and power costs, the total operating cost can be obtained as a function of D. The proper value of D to select is that which corresponds to the minimum total costs per unit time.

Nominal dia., in.	D	DG/u	f	P_2	Hp	Investment	
						Pipe line	Compressor
1½	0.0916	9.85×10^5	0.0037	178,280	123	\$ 650	\$12,300
2	0.125	7.22×10^5	0.0038	171,370	120	910	12,000
2½	0.1475	6.12×10^5	0.0039	170,338	119	1,370	11,900
3	0.1920	4.70×10^5	0.0040	169,730	119	1,860	11,900
3½	0.227	3.98×10^5	0.0041	169,603	119	2,300	11,900

Nominal dia., in.	Total investment	Fixed cost per year	Cost of power * per year	Total operating cost per year
1½	$12,950	$1,943	$24,100	$26,043
2	12,910	1,937	23,500	25,437
2½	13,270	1,990	23,300	25,290
3	13,760	2,065	23,300	25,365
3½	14,200	2,130	23,300	25,430

* Power cost = (365)(24)(0.746)(0.03)(hp.) = (196)(hp.).

From the above tabulation it is noted that the minimum total operating cost with a 2½-in. pipe line is a result of a balance between cost of power and fixed costs.

Heat Transfer.—There are many different economic balances in the field of heat transmission. Here again, as in essentially all applications in the unit operations, the economic balance usually reduces to a balance of costs to give the minimum operating cost.

One of the more common economic balances in heat transfer is the determination of the optimum thickness of insulation for hot (or cold) surface. This is a balance between reduction in the cost of the heat being lost and the cost of the insulation. The investment cost of insulation is made up of the cost of labor for installing it and the cost of the material itself. The investment cost is charged off at a constant rate over the life of the insulation. The life of the insulation will depend primarily upon the type of service to which it is put and may range from 1 to 10 years.

A number of papers have been published on optimum insulation thickness. McMillan[1] reduced the economic balance for optimum insulation thickness to a graphical solution, which was reproduced by Perry.[2] An example on optimum insulation thickness that involves the detailed calculations will help the student to grasp the philosophy of application of the economic balance.

Example 66. A flat vertical surface is at a temperature of 500°F, and the resistance to heat flow to the surface is nil. The surface is insulated with 1 in. of insulation, but it is thought that considerable heat is being lost from the surface of the insulation to the atmosphere, which averages about 70°F. The insulation has a thermal conductivity of 0.040 Btu/(deg F)(ft)(hr). The heat-transfer coefficient for the air film at the surface

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[1] McMillan, Fuels Steam Power, *Trans. Am. Soc. Mech. Engrs.*, **51,** 349 (1929).

[2] Perry, J. H., "Chemical Engineers' Handbook," p. 996, 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

of the insulation is 4.0 Btu/(deg F)(sq ft)(hr) and may be assumed to be constant for any thickness of insulation.[1]

If insulation costs \$0.40 per square foot per inch of thickness installed and heat loss is at a cost of \$0.50 per 1,000,000 Btu, what should the thickness of insulation be if the insulation is amortized in 4 years? The thickness should be based on operation 24 hr/day for 365 days/year. Insulation is available as boards of 1-in. thickness.

Solution:

Basis: 100 sq ft of surface.

The heat loss is:

$$\begin{aligned}\text{Btu/hr} &= UA\,\Delta t\\ &= (100)(500-70)U\\ &= 43{,}000U\end{aligned}$$

$$U = \frac{1}{(1/4.0) + [L/(12)(0.04)]} = \frac{1}{0.25 + 2.08L}$$

where L is the thickness of insulation in inches.

$$\text{Heat loss} = \frac{43{,}000}{0.25 + 2.08L}\ \text{Btu/hr}$$

or

$$\begin{aligned}\text{Heat loss} &= \frac{(43{,}000)(24)(365)}{1{,}000{,}000(0.25 + 2.08L)}\\ &= \frac{376}{0.25 + 2.08L}\ (1{,}000{,}000)\ \text{Btu/year}\end{aligned}$$

$$\text{Cost of heat loss} = \frac{188}{0.25 + 2.08L}\ \text{dollars/year}$$

Since the insulation thickness will be made up by installing layers of 1-in. thickness,

$$\begin{aligned}\text{Investment cost for insulation} &= (100)(0.40)L\\ &= 40L\end{aligned}$$

Since the insulation is amortized over a period of 4 years,

$$\begin{aligned}\text{Annual cost of insulation} &= \frac{40L}{4}\\ &= 10L\end{aligned}$$

The total annual cost of heat loss plus insulation is therefore

$$C = \frac{188}{0.25 + 2.08L} + 10L$$

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[1] This assumption is not quite valid, for radiation and natural convection increase with the surface temperature. But since these factors are beyond the scope of this text, the assumption is made merely to simplify the presentation.

The minimum cost can be determined by assuming thicknesses of 1-in. increments and calculating the value of C.

L, In.	C, Dollars/(Year)(100 Sq Ft)
1	90.60
2	62.60
3	59.00
4	61.90
5	67.65

Thus, minimum cost is obtained with a 3-in. thickness of insulation.

Another type of economic balance in the field of heat transmission is the determination of the optimum time for cleaning heat exchangers, condensers, etc. This is usually a balance between costs of heat loss and cost of cleaning such that the minimum total cost is realized. Sometimes, however, process factors of great importance enter into the balance. For example, an overhead condenser for a fractionating column may become fouled so that sufficient reflux cannot be obtained to give the desired fractionation. In such a case the loss sustained by the reduction in effectiveness of fractionation must be considered in the balance.

Actually, an economic balance should be made in an original design to determine the size of heat exchanger, condenser, etc., to be installed. Such a balance must be predicated upon an estimated rate of fouling of the heat-transfer surface. This will usually result in a surface area sufficiently large so that the heat exchanger need not be cleaned until the entire manufacturing unit is shut down for routine inspection and cleaning. If sufficient heating surface was not installed and the production capacity of the entire manufacturing unit is limited by a fouled heat exchanger, it is usually quite profitable to install additional heating surface. The amount of additional surface should be determined by economic balance.

Materials Handling.—The philosophy of the economic balance is very important in the unit operation, materials handling. The optimum amount of storage and the optimum method of transportation of both raw materials and finished products should be arrived at by economic balance.

For example, a company may have plants at two different locations that manufacture the same product. In such cases the question arises as to which market should be supplied by each plant. The optimum is a balance of manufacturing cost and transportation cost for each plant. Frequently the manufacturing cost at one plant will be somewhat less than at the other owing to various conditions that prevail. Thus, if transportation rates are the same from each plant, the plant that has the lower manufacturing cost should supply the market beyond the equidistant locus between the two plants. In effect, the division of the market should be based on the locus of identical total cost for each plant. All this, of course, is predicated upon the assumption that each plant has sufficient production capacity to handle the economical portion of the market.

Another type of economic balance involved in the question of transportation is that which applies when a company is handling part of its transportation through its own facilities and the remainder by means of other conveyances. The question that presents itself under such conditions is what trips should be handled by company-owned facilities and which should be handled by other conveyances. For example, a petroleum company may transport a large part of its crude oil by company-owned barges and the remainder to be moved by barges may be handled under contract by a transportation company. Since the company-owned barges can make any of the regular trips the company chooses to have made, it is desirable that they be used to maintain the total transportation cost at the minimum.

Example 67. A petroleum refinery is obtaining about half its crude oil supply by barging it from six different terminals. The petroleum company owns a fleet of barges and tugs, but only about 75 per cent of the total amount of oil to be barged can be handled by the company-owned barges. The remainder is barged to the refinery by a transportation company. The petroleum company has a contract with the transportation company that permits the former to nominate all trips that the transportation company is to make. The contract includes the rates that the transportation company will charge for deliveries from each of the six terminals. The rates are as follows:

Terminal	Per Bbl
A	$0.0600
B	0.1750
C	0.1700
D	0.1950
E	0.0150
F	0.0125

The company-owned barges are in units of three for each tug. Each barge has a capacity of approximately 8000 bbl, but the exact load depends upon the depth of the canals and rivers traveled in getting to and from each terminal. The incremental cost of operating a unit of three barges and a tug is $100 per day. The average load carried and the average time required for the company-owned barges to make a round trip to each terminal, which includes time en route, docking, loading, and unloading, is as follows:

Terminal	Days	Bbl/trip
A	9.63	25,000
B	21.74	24,500
C	19.94	23,500
D	18.39	24,000
E	2.94	25,500
F	2.36	25,500

Devise a table that shows in the order of their economic attractiveness the trips that should be made with the company-owned barges.

Solution: The incremental cost to the petroleum company for transporting its crude oil by barges is that of the transportation company. In other words, any change in the quantity of crude oil being barged will result in an increase or decrease in the amount transported by the transportation company.

The best schedule for the petroleum company to follow with its barges is the trips which show the greatest saving in transportation cost over that which would be charged by the transportation company. Thus, the desired table of relative economic attractiveness for trips with company-owned barges can be calculated on the basis of the incremental costs.

Terminal	Bbl/trip	Days/trip	Bbl/day	Incremental cost/bbl	Per day
A	25,000	9.63	2,600	$0.0600	$156.20
B	24,500	21.74	1,130	0.1750	197.70
C	23,500	19.94	1,180	0.1700	200.50
D	24,000	18.39	1,305	0.1950	254.50
E	25,500	2.94	8,680	0.0150	130.30
F	25,500	2.36	10,800	0.0125	135.00

The above shows the earnings of the company-owned barges at the incremental barging rates. The difference between these figures and the incremental cost of operating the company-owned barges is the saving that is made by the company by using its own barges on the trip.

Terminal	Incremental cost/day	Cost/day of company barges	Saving/ day
D	$254.50	$100.00	$154.50
C	200.50	100.00	100.50
B	197.70	100.00	97.70
A	156.20	100.00	56.20
F	135.00	100.00	35.00
E	130.00	100.00	30.30

From the above table it is apparent that trips with company-owned barges should be given preference in the order of *D*, *C*, *B*, *A*, *F*, and *E*.

THE ECONOMIC BALANCE IN CHEMICAL PROCESSES

Usually economic balances dealing with chemical processes are of greater importance than those on the unit operations, for with the former there is greater chance of economic contributions. As a matter of fact, when a design of a new manufacturing unit is being made, it is ordinarily of great economic importance to get the unit into production as soon as possible, for the earnings by which the unit was justified are usually quite large. Thus, it is questionable economy to delay the installation of a unit in order to make detailed economic balances during its design. It is usually preferable to allow liberal safety factors. For this reason, economic balances that involve the unit operations are made in a general form so that optimum size of equipment can be specified quickly. An example of this already cited is the chart prepared by McMillan for quick determination of optimum insulation thickness.

Combustion.—The feature of greatest economic importance in the combustion of a fuel is the cost of heat utilized for the desired purpose. One fuel may have a substantially higher heating value than another, but the one that provides the more useful heat per dollar is preferred from an economic standpoint, other factors being equal.

There are other things, also, to be considered in the evaluation of fuels. One of these is the cost of handling. For example, a heavy fuel oil that becomes plastic at moderate temperatures (such as 40 to 60°F) would cost more to handle in cold climates than a fuel oil that remains fluid at −20°F. Special provision for heating the oil of high "pour point" must be provided in the cold climate so that it will not solidify in the lines and burners. Another factor of great importance is the ash in the fuel. Some ash has a bad effect on refractory brickwork of furnaces. It reacts chemically with the refractory and produces a product of relatively low melting point. The result is that the refractory bricks rapidly disintegrate, or "corrode." This entails high maintenance cost on the furnaces, which is directly chargeable against the fuel with the offending ash. Still another factor is the sulfur content of fuels. The sulfur burns to SO_2, a large part of which will oxidize to SO_3 if in contact with any rust (iron oxide). In this case it is essential that the flue gases be maintained at a sufficiently high temperature to prevent the SO_3 and H_2O in them from combining and condensing so that they come in contact with any steelwork, including the smokestack. The minimum temperature that must be maintained can be calculated on the basis of the partial pressures of the SO_3 and H_2O in the flue gases. This sometimes results in poorer fuel economy in order to maintain the necessary temperature of the flue gases. There are several more factors like these that are discussed fully by Haslam and Russell.[1]

The value of fuel varies rather widely over the United States. In the Great Lakes region and in the east coast region fuel is expensive. In the

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[1] HASLAM, R. T., and R. P. RUSSELL, "Fuels and Their Combustion," McGraw-Hill Book Company, Inc., New York, 1925.

Southwest, however, it is fairly inexpensive, although its value will probably increase with time. Until about 1940 it was relatively common to see petroleum companies burning huge quantities of fuel gas at torches in order to dispose of it. It was a by-product from their processes that could not be utilized with immediate profit. In such cases it is apparent that fuel is valueless and the chemical engineer can gain nothing by improving the thermal efficiency of furnaces, for this would result merely in more fuel to burn at the torches. This situation has been corrected, however, by installing processes to utilize or conserve the gas.

If fuel is valuable, a large economic contribution can usually be effected by the chemical engineer in maintaining proper combustion conditions. This is illustrated by Example 68. Of equal importance is the selection of the most economical fuel to use.

Example 68. A manufacturing plant is being designed for location where no existing manufacturing facilities exist. The steam demand will be supplied by a boilerhouse, which will be installed at the time of the manufacturing facilities. Fuel of 12,500 Btu/lb net heating value will be available at $4.50 per ton delivered at the boilerhouse. The cost of steam will consist of fixed charges plus variable cost. The annual fixed charges, which include amortization of investment, overhead, labor, and maintenance, will be $24.82 per rated boiler horsepower.[1] The variable cost will consist entirely of fuel used to generate steam. The boilers being considered are guaranteed to perform as follows:

% of Rated Boiler Hp	Thermal Efficiency
100	76.0
180	74.9
200	74.2
220	73.2
240	71.8
260	70.1
280	67.9
300	65.0

The thermal efficiency is 100 times the fraction of the net heating value of the coal that is transferred for the evaporation of water into steam.

What would be the most economical percentage of rated boiler horsepower to operate the boilers if they are operated 365 days/year and 24 hr/day? What should it be if they are operated 40 hr/week and 50 weeks/year?

Solution: The pertinent item is the cost of steam. It is apparent that the manufacturing departments wish to obtain their steam demands at minimum cost. The demands

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[1] A boiler horsepower is equivalent to the evaporation of 34.5 lb of water per hour from and at 212°F or 33,475 Btu/hr. Rated boiler horsepower is based on the amount of steam the boiler was designed to produce. The steam production rate can be increased above the rated capacity at the expense of thermal efficiency. It is common practice, therefore, to quote the actual performance of a boiler in terms of percentage of its rated capacity.

are fixed on a time basis. Thus, the objective is to obtain steam at minimum cost per unit quantity.

Basis: 1000 boiler hp-hr.

$$\text{Cost of steam} = \frac{\text{fixed cost} + \text{variable cost}}{\text{boiler hp-hr}}$$

Let E = thermal efficiency
R = % of rated boiler hp

Fixed cost:

$$\text{At 365 days/yr and 24 hr/day} = \frac{(24.82)(1000)(100)}{(365)(24)(R)} = \frac{283.5}{R}$$

$$\text{At 40 hr/week and 50 weeks/year} = \frac{(24.82)(1000)(100)}{(50)(40)(R)} = \frac{1240}{R}$$

Variable cost:

$$\text{Coal cost} = \frac{(33{,}475)(1000)(100)(4.50)}{(E)(12{,}500)(2000)} = \frac{603}{E}$$

Total costs:

$$\text{At 365 days/year and 24 hr/day} = \frac{283.5}{R} + \frac{603}{E}$$

$$\text{At 40 hr/week and 50 weeks/year} = \frac{1240}{R} + \frac{603}{E}$$

The total costs can be calculated for each value of R and E as guaranteed.

R	E	365 days/year and 24 hr/day			40 hr/week and 50 weeks/yr	
		$603/E$	$283.5/R$	Total	$1240/R$	Total
100	76.0	7.93	2.835	10.765	12.40	20.33
180	74.9	8.05	1.575	9.625	6.89	14.95
200	74.2	8.12	1.418	9.538	6.20	14.32
220	73.2	8.23	1.287	9.517	5.63	13.86
240	71.8	8.39	1.180	9.570	5.16	13.55
260	70.1	8.60	1.090	9.690	4.77	13.37
280	67.9	8.88	1.013	......	4.43	13.31
300	65.0	9.27	0.945	......	4.13	13.50

Thus, the most economical rated boiler horsepower for operation of the boilers is 220 per cent if operated 365 days/year and 24 hr/day or 280% if operated 40 hr/week and 50 weeks/year.

The situation of Example 67 did not require that existing facilities be considered in the economic balance. Often, the installation of new facilities is merely an expansion of existing facilities. In such a case the optimum operation of existing facilities will depend upon the economics of the new facilities.

Electrolysis.—Many important industrial chemicals are produced by electrolysis. The major supply of caustic soda is by the electrolysis of common salt (NaCl). Also, oxygen and hydrogen of high purity are produced by the electrolysis of water.

In the production of caustic soda the salt and water are ionized so that Na^+, Cl^-, H^+, and OH^- ions are present. The electrolysis is carried out in cells each of which is divided into an anode and a cathode compartment by a porous diaphragm. The NaCl solution is charged to the anode compartment and caustic soda solution withdrawn from the cathode section. Liquid must therefore pass through the diaphragm. The Na^+ migrates to the cathode and there takes on an electron to form free sodium, which immediately reacts with water to form hydrogen and caustic soda. Thus, at the cathode

$$2Na^+ + 2\ominus \rightarrow 2Na$$

$$2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$$

In like manner the Cl^- migrates to the anode and gives up an electron so that chlorine is liberated. Thus, at the anode

$$2Cl^- \rightarrow Cl_2\uparrow + 2\ominus$$

Theoretically the amount of electricity required to decompose one gram equivalent of a compound is 96,500 coulombs. Hence 96,500 coulombs is theoretically required to decompose one gram-mole of NaCl or 4.38×10^7 coulombs is required for one pound-mole of NaCl. Actually, however, slightly more electricity is required. The *current efficiency* is 100 times the ratio of the desired product produced to the amount that theoretically should be produced. Usually in an electrolytic process various secondary reactions occur. Some will occur at the anode, whereas others will occur at the cathode. The extent of such reactions will not necessarily be the same at each electrode, and thus the current efficiency at the anode will usually be different from that at the cathode. Consequently, the current efficiency for caustic soda (cathode) production will probably be different from the current efficiency for chlorine production.

The *current density* is the number of amperes per square foot perpendicular to the direction of flow of electricity. It is frequently expressed as amperes per square foot of diaphragm surface.

The electric energy required to decompose a compound is the product of the coulombs and voltage. Since a coulomb is an ampere-second, the product is watt-seconds. Theoretically the electric energy required to decompose one gram-equivalent is 96,500 multiplied by the voltage.

Example 69. Hydrogen and oxygen gases are to be produced by the electrolysis of dilute NaOH solution in a number of diaphragm cells. The electrolyte is fed separately to each cell, and the gas streams from the cells are collected in separate O_2 and H_2 manifolds. The gases are purified by passing them through hot tubes. The current flows through all the cells in series. The following performance data are typical:

Current density, amp/sq ft of diaphragm	10	25	50	100	200	500
Voltage/cell	1.8	2.1	2.4	2.9	3.5	4.8
H_2 current eff.	98.5	98.4	98.2	97.2	96.0	92.0
O_2 current eff.	92.2	92.1	89.9	89.4	88.3	84.8

The total investment cost of the cells is $7.50 per square foot of diaphragm, and the total annual fixed charges are 40 per cent of the investment cost. The cells operate 10 hr/day for 300 days/year. The labor is $10 per day, and incidental costs are $1 per day. The cost of electric power is $0.030 per kilowatt-hour.

a. The manufacturing department requires 10,000 cu ft/day of dry H_2 gas at 760 mm and 20°C. How many square feet of diaphragm surface should be installed? What is the cost of H_2?

b. After the cells are installed and in operation, it is found that any excess H_2 can be sold for $0.005 per cubic foot and all the oxygen can be sold at $0.006 per cubic foot. How much H_2 and O_2 is it profitable to sell if the 10,000 cu ft/day of H_2 required by the manufacturing department is credited to the cell room at the price calculated in p rt *a*?

Solution:

Basis: 1 day.

(*a*)

$$H_2 \text{ production} = \frac{(10{,}000)(273)}{(359)(293)} = 25.9 \text{ moles}$$

$$\text{Equivalents of } H_2 = (2)(25.9) = 51.8 \text{ lb-equivalent}$$

$$\text{Electricity} = (51.8)(4.38 \times 10^7)$$

$$= 2.27 \times 10^9 \text{ coulombs/day (theoretical)}$$

$$= \frac{2.27 \times 10^9}{(10)(3600)} = 63{,}000 \text{ amp (theoretical)}$$

Volts	Density	Actual		Kw	Electricity/day	Diaphragm, sq ft	Fixed cost/day	Total cost/day †
		Watts/sq ft	Amp *					
1.8	10	18	64,000	1,152	\$34.50	6,400	\$64.00	\$109.50
2.1	25	52.5	64,100	1,347	40.40	2,560	25.60	77.00
2.4	50	120	64,400	1,545	46.40	1,290	12.90	70.30
2.9	100	290	64,900	1,883	56.50	650	6.50	74.00
3.5	200	700	65,600	2,295	68.90	328	3.28	83.18
4.8	500	2,400	68,500	3,290	98.70	137	1.37	111.07

* Actual amp = theoretical amp (63,200)/(H_2 eff./100).

† Includes electricity + fixed + labor + incidental.

The minimum cost of the hydrogen is therefore \$7.03 per 1000 cu ft. Total diaphragm surface required is 1290 sq ft.

b. Proper solution to this part must be based on profit per unit time.

Let D = current density, amp/sq ft
E_H = H_2 current efficiency
E_0 = O_2 current efficiency
V = voltage/cell

$$\text{Moles of } H_2 \text{ produced} = \frac{(1290)(D)(36{,}000)(E_H)}{(4.38 \times 10^7)(2)(100)} = 5.3 \times 10^{-3} DE_H$$

$$\text{Cu ft of } H_2 \text{ at } 20°\text{C and 760 mm} = \frac{(5.3 \times 10^{-3} DE_H)(359)(293)}{273} = 2.04 DE_H$$

Theoretically only ½ mole of oxygen is obtained per mole of H_2. Thus,

$$\text{Cu ft of } O_2 \text{ at } 20°\text{C and 760 mm} = 1.02 DE_0$$

Profit = income − cost per unit time

$$\text{Income} = 70.30 + 5(0.00204 DE_H - 10.0) + (6)(0.00102 DE_0)$$

$$\text{Cost} = \frac{(1290)(D)(V)(10)(0.03)}{1000} + 12.90 + 11.00$$

$$\text{Profit} = 0.0102 DE_H + 0.00612 DE_0 - 0.387 VD - 3.60$$

D	E_H	E_0	Profit/day
50	98.2	89.9	\$27.55
100	97.2	89.4	38.20
200	96.0	88.3	29.40

The most profit is with a current density of 100 amp/sq ft. Therefore,

$$H_2 \text{ to be sold} = 2.04E_H D - 10{,}000 = 9600 \text{ cu ft/day}$$

$$O_2 \text{ to be sold} = 1.02E_0 D = 9100 \text{ cu ft/day}$$

Processing Petroleum.—This involves many different chemical processes. There are certain principles in the economic appraisal of such processes and the economic evaluation of petroleum and its products that are generally applicable in the petroleum-refining industry. Rather than confining the discussion of economic balances on refining of petroleum to a given type of process, those principles which are more generally applicable will be discussed.

The cost of petroleum products is made up chiefly of the cost of raw material, cost of manufacturing, taxes, and cost for amortization of investment. The cost of raw material (crude oil) is by far the largest of these. Since many different kinds of crude oil are available at almost as many different prices, it is most important that the refinery process the crude oil that provides the greatest profit per unit time. The value of a given crude oil will depend upon the processes available in the refinery for refining it.

Crude oil yields a multitude of products, but gasoline is the one of greatest volume and of greatest profit to the petroleum industry. Crude oil can be processed directly to ultimate yields (gasoline, fuel gas, and black fuel oil), or it can be processed so that domestic fuel oil, kerosene, solvents, paraffin, asphalt, and a great many other products are obtained. Furthermore, it is entirely feasible from a process standpoint to convert crude oil into gas, gasoline, and petroleum coke. Likewise, such products as kerosene, domestic fuel oil, and paraffin can be processed to ultimate yields or to gas, gasoline, and coke.

The value of any crude oil will depend upon the value of the products that can be obtained from it per unit time. If a refinery has a greater capacity for producing than the market demands, a convenient method of evaluating crude oils is on the basis of ultimate yields.

The cost of gasoline of a given quality is equal to the cost of the crude oil minus the value of the black fuel oil minus the value of fuel gas plus the processing cost. Thus, if

G = cost of gasoline, dollars/gal
Y_g = yield of gasoline, vol. per cent

F = value of black fuel oil, dollars/gal
Y_{fo} = yield of black fuel oil, Vol. per cent
F_g = value of fuel gas, dollars/gal equivalent fuel oil [1]
Y_{fg} = yield of fuel gas, vol. per cent equivalent fuel oil [1]
C = cost of crude oil, dollars/gal
P = processing cost, dollars/100 gal of crude

Then
$$G = \frac{100C - Y_{fo}F - Y_{fg}F_g + P}{Y_g} \tag{9.34}$$

The cost of gasoline of desired quality should be the minimum. The crude oils should therefore be selected for processing on this basis.

If a refinery has a large source of crude oil of a given kind that can be processed at a profit, it is convenient to use it as a reference with which all other crudes are compared. For example, C represents the cost of the reference crude oil for a refinery that is considering the purchase of another crude oil, A. It is essential, therefore, that the cost of gasoline from A be not greater than the cost from the reference crude oil. Otherwise, it would be preferable from an economic standpoint to continue processing the reference crude oil. Thus, the value or maximum amount that can be paid for crude oil A is given by Eq. (9.35), which corresponds to the same unit cost of gasoline from crude oil A as from the reference crude oil.

$$\frac{100C - Y_{fo}F - Y_{fg}F_g + P}{Y_g} = \frac{100A - (Y_{fo}F)_A - (Y_{fg}F_g)_A + P_A}{(Y_g)_A}$$

or

$$A = \left[\frac{(Y_g)_A}{Y_g}\right]\left(\frac{100C - Y_{fo}F - Y_{fg}F_g + P}{100}\right) + \frac{(Y_{fo}F)_A + (Y_{fg}F_g)_A - P_A}{100} \tag{9.35}$$

The value of intermediate as well as finished products can be determined in the same way as the value of the crude oil. In other words, this is the

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[1] Fuel gas can be expressed in terms of equivalent volume of black fuel oil on a basis of net heating value.

the value based on replacing the incremental crude oil with the intermediate or finished product for gasoline production. The incremental crude oil is the one that results in the highest cost for gasoline, and the amount processed can be reduced or increased as the situation demands. It is the "come-and-go," therefore, that is used to keep production in balance with the market demand.

Example 70. A petroleum refinery is producing a domestic fuel oil that could be processed to gasoline, black fuel oil, and fuel gas with the following yields:

	Vol. %	Deg API
Domestic fuel oil	100.0	34.0
Products:		
Gasoline	62.0	58.0
Black fuel oil	30.7	10.5

The incremental crude oil of the refinery can be processed to ultimate yields as follows:

	Vol. %	Deg API
Crude oil	100.0	35.0
Products:		
Gasoline	69.0	59.0
Black fuel oil	22.7	10.5

The quality of the gasoline in each case is the same.

The cost for processing incremental crude to its ultimate yields is $0.28 per 100 gal, and the cost of processing the domestic fuel oil to its ultimate yields is $0.32 per 100 gal. The cost of incremental crude oil delivered to the refinery is $1.42 per barrel (42 gal) The value of black fuel oil is $0.95 per barrel, and the value of fuel gas on a heating value basis is $0.15 per 100 lb.

What is the value of the domestic fuel oil as replacement for crude oil in gasoline production? The refinery has an excess capacity for producing all the products marketed.

Solution: The yields as given do not include the gas, which must be calculated by material balance.

	Gal	Deg API	Lb/gal	Lb
Crude oil	100.0	35.0	7.076	707.6
Products:				
Gasoline	69.0	59.0	6.184	427.0
Black fuel oil	22.7	10.5	8.299	188.6
Gas (by diff.)	.....	....	.....	92.0
Total products	.....	....	.....	707.6
Domestic fuel oil	100.0	34.0	7.119	711.9
Products:				
Gasoline	62.0	58.0	6.216	385.7
Black fuel oil	30.7	10.5	8.299	255.0
Gas (by diff.)	.....	....	.....	71.2
Total products	.....	....	.....	711.9

Next, the cost of gasoline from the incremental crude will be calculated.

$$G = \frac{100C - 22.7F - 0.92F_g + 0.28}{69.0}$$

$$= 1.45C - 0.329F - 0.0134F_g + 0.00405$$

where C = cost of crude oil, dollars/gal
F = value of black fuel oil, dollars/gal
F_g = value of fuel gas, dollars/100 lb
G = cost of gasoline, dollars/gal

The next step is to compute the cost of gasoline from domestic fuel oil.

$$G = \frac{100D - 30.7F - 0.712F_g + 0.32}{62.0}$$

$$= 1.615D - 0.495F - 0.0115F_g + 0.00516$$

where D = value of domestic fuel oil, dollars/gal

Since the cost of gasoline from domestic fuel oil must not exceed that of gasoline from incremental crude oil,

$$1.615D - 0.495F - 0.0115F_g + 0.00516 = 1.45C - 0.329F - 0.0134F_g + 0.00405$$

and $$D = 0.897C + 0.103F - 0.0012F_g - 0.00069$$

Thus, the above equation gives the value of domestic fuel oil on the basis of replacement of crude oil for gasoline production. On the basis of values of C, F, and F_g quoted in the statement of the problem,

$$D = (0.897)(0.0338) + (0.103)(0.0226) - (0.0012)(0.15) - 0.00069$$

$$= \$0.0317/\text{gal}$$

Therefore, unless the refinery can sell the domestic fuel oil at a price greater than $0.0317 per gal, it would be more economical to process it to its ultimate yields and replace incremental crude oil.

In the event that there were any finishing costs, such as chemical treatment, for the domestic fuel oil to make it acceptable for marketing, these costs would have to be added to the value of D to obtain the value of the finished domestic fuel oil below which it would be uneconomical to sell.

Thus far the only situations considered are those which involve excess producing capacity for all products marketed. If a refinery is unable to produce a sufficient quantity of a given product to supply the market, the additional quantity required is usually purchased from other refiners. This must therefore be considered in any economic balance that involves a change in the production rate of the product. Ordinarily the price that must be paid for purchases from other refiners is above the value of the product on a crude replacement basis for gasoline production. In other words, if the product were processed to its ultimate yields, its value based on incremental crude would be less than the price paid to the other refiners. Hence, any change in processing such as another crude oil that would increase the production of the product that the refinery cannot supply completely would result in a reduction of outside purchases. This would effect a reduction in the cost of supplying the market with this product that should be credited to the new crude oil (or whatever the change is) in its evaluation.

A sound basis for evaluating a new raw material or a new process is to set up a base case that represents the current operations and then determine the change in each item that affects the economic situation. The changes in the pertinent items should be calculated relative to the base case. In this way the increase or decrease in profit per unit time can be determined. This is the "incremental method" described earlier. It is fundamental and is applicable to any change in processing whatever.

Example 71. The incremental crude oil that a refinery is processing costs $1.16 per barrel, and the market for black fuel oil is strong at $0.80 per barrel. The value of fuel gas is $0.30 per barrel of equivalent 8°API fuel oil on a net heating-value basis. The ultimate yields from the incremental crude oil are as follows:

	Vol. %	Deg API
Gasoline	67.1	
Black fuel oil	23.6	8.0
Gas (equivalent 8°API oil)	11.8	

There is insufficient producing capacity to meet the gasoline demand. Consequently consideration is being given to increasing the gasoline production by increasing the degrees API gravity of the black fuel oil, which will permit more crude oil to be processed. This effect is a result of elimination of heavy gas oil in the black fuel oil, which will be replaced with higher quality raw material from the increase in crude oil processed.

The change in crude oil charge rate and the change in yields vs. the degrees API gravity of the black oil are estimated to be as follows:

Black fuel oil, deg API	Relative crude rate *	Change in yields, vol. %		
		Gasoline	Black fuel oil	Gas †
8.0	1.00	0	0	0
10.0	1.05	−1.3	1.8	−0.5
12.0	1.08	−2.9	3.9	−1.0
14.0	1.09	−4.5	6.0	−1.5

* Ratio of crude charge rate to charge rate at 8°API black fuel oil.

† Equivalent of 8°API fuel oil on heating-value basis.

The processing cost will remain constant on a daily basis except for fuel consumption, which will be 7.5 per cent by volume of crude oil expressed as equivalent 8°API fuel oil on a heating-value basis. The refinery is purchasing gasoline from other refiners at 5.75 cents per gallon to satisfy that part of the demand which cannot be produced by the refinery. What is the optimum degrees API black fuel oil to maintain?

Solution:

Basis: Time required to process 100 bbl of crude oil with 8°API black oil elimination.

The first step is to determine the yields and volume of products at each degree API of black fuel oil.

Deg API	Crude, bbl	Gasoline		Black fuel oil		Gas equivalent	
		Vol. %	Bbl	Vol. %	Bbl	Vol. %	Bbl
8	100	67.1	67.1	23.6	23.6	11.8	11.8
10	105	65.8	69.0	25.4	26.6	11.3	11.9
12	108	64.2	69.3	27.5	29.7	10.8	11.65
14	109	62.6	68.3	29.6	32.3	10.3	11.23

Since the processing cost (excluding fuel) on a daily basis is constant, it can be disregarded.

The next step is to calculate the difference between cost of crude oil plus fuel consumed and realization on products for each degree API.

	Bbl	Per bbl	
At 8°API:			
Costs			
Crude oil	100	$1.16	$116.00
Gas for fuel	7.5	0.30	2.25
Total	......	......	$118.25
Realization			
Gasoline	67.1	2.415	162.00
Black fuel oil	23.6	0.80	18.90
Gas (equivalent)	11.8	0.30	3.54
Total	......	......	184.44
Difference	......	......	66.19
At 10°API:			
Costs			
Crude oil	105.0	1.16	121.70
Gas for fuel (equivalent)	7.86	0.30	2.36
Total	......	......	124.06
Realization			
Gasoline	69.0	2.415	166.70
Black fuel oil	26.6	0.80	21.25
Gas (equivalent)	11.9	0.30	3.57
Total	......	......	191.52
Difference	......	......	67.46
At 12°API:			
Costs			
Crude oil	108.0	1.16	125.30
Gas for fuel (equivalent)	8.1	0.30	2.43
Total	......	......	127.73
Realization			
Gasoline	69.3	2.415	167.50
Black fuel oil	29.7	0.80	23.75
Gas (equivalent)	11.65	0.30	3.50
Total	......	......	194.75
Difference	......	......	67.02
At 14°API:			
Costs			
Crude oil	109	1.16	126.50
Gas for fuel (equivalent)	8.16	0.30	2.45
Total	......	......	128.95
Realization			
Gasoline	68.3	2.415	165.00
Black fuel oil	32.3	0.80	25.85
Gas (equivalent)	11.23	0.30	3.37
Total	......	......	194.22
Difference	......	......	65.27

It is noted that the maximum difference between costs and realization occurred at 10°API. By plotting this difference vs. degrees API it appears that the optimum gravity is between 10.5 and 11°API.

CONCLUSION

The economic balance is the guide of the chemical engineer in practice. Everything the chemical engineer does must be reduced eventually to a profit-and-loss basis. If the results cannot stand this test, they will have little application.

The fundamental basis of the economic balance is maximum profit or earnings per unit time. When gross income is fixed per unit time, the economic balance may be made on the basis of minimum cost per unit time or per unit product. The latter usually holds true for economic balances on the unit operations and frequently is involved for economic balances on chemical processes. It is therefore a good policy always to examine an economic situation critically to determine whether the balance may be made on the basis of minimum cost or whether it must be based on maximum profit per unit time.

PROBLEMS

1. Gas of the composition given below is to be compressed from 15 lb/sq in. abs to 210 lb/sq in. abs by a two-stage compressor.

	Mole %
H_2S	0.56
CO_2	0.66
N_2	2.59
Methane	57.43
Ethane	16.02
Propane	12.00
Isobutane	1.09
n-Butane	5.73
Isopentane	0.88
n-Pentane	1.70
n-Hexane	1.34
Total	100.00

The temperature of the gas to the first stage is 90°F, and the effluent from each stage will be cooled to this temperature. Assuming the ideal-gas law, 85 per cent efficiency of the compressor, and 95 per cent efficiency of the motor, what is the minimum horsepower required for the motor to compress 30,000,000 cu ft/day (S.C.)?

Assuming an over-all heat-transfer coefficient of 50 Btu/(deg F)(sq ft)(hr) for both the intercooler and the aftercooler, how much heat-transfer surface will be required for each service? The water temperature is 78°F, and a 22° rise is used. How much water in gallons per minute is required? The relationship between temperature and pressure in adiabatic compression is as follows:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

2. A manufacturer has a contract with a purchaser to supply f.o.b. its plant one of its salt products at 5 cents per pound on a moisture-free basis but containing 3 per cent by weight of moisture. The contract calls for adjusting the price to be paid if the moisture content is greater than 3 per cent. The purchaser will not pay for any water in excess of 3 per cent and will be reimbursed for freight on this excess water. The freight rate is 18 cents per 100 lb on the wet basis.

The purchaser received a shipment of 54,000 lb (wet basis) that contained 6.4 per cent by weight moisture. How much should he pay for the shipment?

3. A plant purchases coal at $4 per ton delivered to the plant site that has a net heating value of 13,000 Btu/lb and 8.0 per cent ash by weight. The handling cost of the coal is $0.50 per ton, and the cost of disposing of the refuse is $0.90 per ton.

Based on these data, set up an equation which relates the value of any coal with its ash content and net heating value so that payment can be made for coal of different ash content and heating value which is fair to both supplier and purchaser.

What price should be paid for coal of 14,500 Btu/lb and 5 per cent ash?

4. A boiler plant burns coal of 12,500 Btu/lb heating value that costs $4/ton delivered at the boilerhouse. The boilerhouse is equipped with four B. and W. boilers, each rated at 250 boiler horsepower. The total annual fixed charges are $24,820. A series of boiler tests has been conducted that showed the following thermal efficiency from coal pile to the steam as supplied to the manufacturing departments:

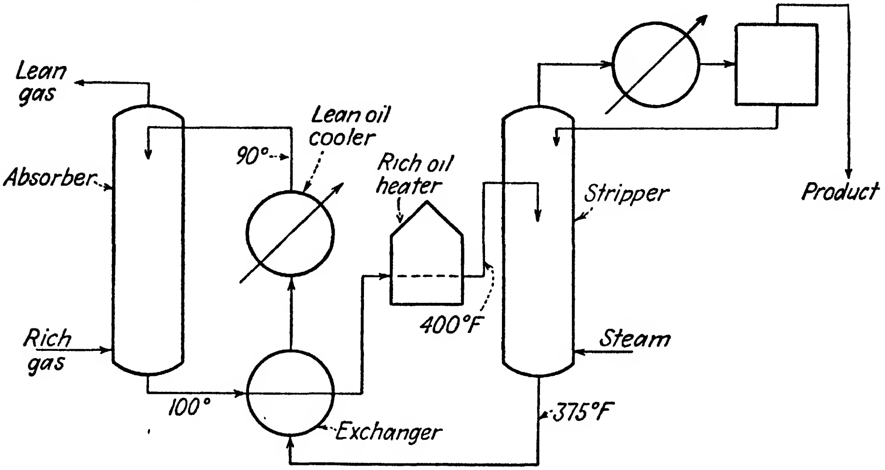
% of Rated Boiler Hp	% Over-all Efficiency
100	76.0
180	74.9
200	74.2
220	73.2
240	71.8
260	70.1
280	67.9
300	65.0

The manufacturing departments are to be expanded so that the steam requirements will be equivalent to 4400 boiler horsepower. The annual fixed charges for the new boilers will be $15 per rated boiler horsepower, and they are guaranteed to give the following performance:

% of Rated Boiler Hp	% Over-all Efficiency
100	78.0
180	76.0
200	75.0
220	74.0
240	72.5
260	71.5
280	68.2
300	65.2

How much new boiler capacity should be installed if the plant operates 365 days/year and 24 hr/day?

5. The setup of a certain absorption process consists of an absorber, a stripper, a lean-oil-to-rich-oil heat exchanger, a lean-oil cooler, and a rich-oil heater as shown by the following flow diagram:



The rich oil is heated from 100 to 400°F (*l*) by means of heat exchange with the hot lean oil (375°F) and a direct-fired heater. The lean oil (virgin) from the stripper is cooled from 375 to 90°F by heat exchange with the cold rich oil and finally heat exchange with cooling water. The lean-oil (35°API) rate is 500 gal/min, and the rich-oil (45°API) rate is 595 gal/min referred to 60°F.

The incremental investment cost for the heater is $1400 per 1,000,000 Btu per hour transferred, whereas the incremental investment costs of exchangers and water coolers are $3.25 per square foot and $3.85 per square foot of heat-transfer surface, respectively. The incremental investment cost for cooling-tower capacity may be taken as $4.50 per gallon per minute of water to the tower, which includes water pumps. This is based on water to the tower at 100°F and water from the tower at 80°F.

The over-all coefficients of heat transfer for the lean-oil–rich-oil exchanger and lean-oil cooler are 65 Btu/(deg F)(sq ft)(hr) and 75 Btu/(deg F)(sq ft)(hr), respectively. The annual fixed charges are at the same rate for each different type of equipment, *viz.*, 20 per cent on investment cost. Assume that the sum of the variable costs on a basis of unit time is not affected significantly by variation in the ratio of heating surfaces of the exchanger and lean-oil cooler.

a. How much surface should be installed in the lean-oil–rich-oil exchanger?

b. How much surface should be installed in the lean-oil cooler?

c. How much rich-oil heater capacity in Btu per hour transferred should be installed?

CHAPTER X

PRESENTATION OF TECHNICAL RESULTS

The practicing chemical engineer is faced continually with the necessity of selling the product of his professional services. If he is unable to sell the results of his efforts, his success as a chemical engineer is limited even though he may have excellent technical training. As stated in Chap. II, an employer hires chemical engineers because he expects to make a profit on their services—not because he is interested in chemical engineering. Thus, the chemical engineer not only must obtain valuable technical results but also must be able to sell them. Otherwise, they are of little value.

The sale of most commodities perhaps is based primarily on appeal to emotions. Technical results, however, are sold on the basis of logic, with essentially no appeal to the emotions. The means by which technical results are sold is the technical report, both oral and written. Whether the report is oral or written, the chemical engineer must be able to express his thoughts clearly and concisely. Thoughts must be clear so that others can understand them. They must be concise in order to induce people to take the time to listen to them or to read them. Thus, the reporting of technical results is an integral part of chemical-engineering practice in which the chemical engineer must be highly proficient before he can attain success in his profession.

Unfortunately, the inexperienced engineer is usually insufficiently impressed with the great importance of the reporting of technical results. This causes him endless trouble until he becomes convinced of its importance and develops ability at it. For this reason alone a chapter at this time on the reporting of technical results seems justified. It would be difficult to overemphasize the importance of the subject.

The inexperienced engineer is usually rather weak in the presentation of technical results. Surprising as it may seem, however, this weakness is generally a result of his engineering rather than of his English. The weakness is so common and so general among recent graduates that many large organizations start their inexperienced technical employees with a course of instruction in report writing in which experienced engineers provide instruction.

Ability at presentation of technical results comes only by practice. Furthermore, if the desired goal is attained, the chemical engineer must go about this phase of his practice with even greater effort than in the case of the work that the report is intended to cover. He must strive continually for improvement. If a high standard of quality is set and if the engineer will not compromise for anything less, proficiency at reporting of technical results can be developed rapidly. Such an attitude or frame of mind cannot exist, however, until the individual becomes fully convinced of the great importance of this phase of his practice.

Inasmuch as the weakness of the inexperienced engineer in the presentation of technical results is due chiefly to his engineering rather than to his English, it is desirable to treat this phase of the subject along with the technical phases of chemical engineering. It is the primary purpose of this chapter, therefore, to discuss the engineering aspects of the reporting of technical data and results. The following presentation deals almost entirely with the written report. Nevertheless, it must be understood that the principles that pertain to the written report apply equally well to the oral report.

First, the more common types of written report are mentioned and described briefly in a general way. This procedure will give the student an insight into what he will be faced with in practice with regard to reports. Second, the essential requirements of reports are discussed. This section deals with what the readers demand of the writer in the preparation of his reports. The writer of a report must take cognizance of these essential requirements, or his reports will not be read by those whom he wants most to influence. Third, the preparation of the formal report is taken up. This section deals with a recommended procedure to be followed in the preparation of formal reports. The formal report is the most difficult to prepare because it involves all the fundamental features of the informal report in addition to others. Finally, a typical form of each type of written report is described in considerable detail.

TYPES OF WRITTEN REPORTS

There are three different types of written reports, *viz.*, *stereotype*, *informal*, and *formal*. The stereotype report is fixed in its form, subject matter, and scope. This type is used to report on a specific operation that is repeated frequently. For example, the stereotype report is used widely to report the results of experiments carried out by students in chemistry, physics, and chemical-engineering laboratories. The experiments are of such a nature that the results and conclusions can be reported by means of a fixed form. Such forms may even be supplied to the student so that the task is reduced merely to filling in the form.

In industry the stereotype report is used frequently to present periodically the results of a repeated performance. For example, daily reports on the performance of specific manufacturing operations are usually presented on a fixed form. This form of presentation is feasible because the subject matter and its scope are essentially the same day after day. Thus, the items of interest to readers can be classified and segregated into a fixed form, or stereotype. Such forms are printed so that the preparation of the report involves merely filling in the form, with occasional remarks on items of unusual significance.

The inexperienced engineer has no difficulty with the stereotype report because the items in which the reader is interested have been segregated. Furthermore, the reader becomes fully acquainted with the form and can get from it almost instantly the information in which he is interested. The reader needs only occasional assistance from the writer in the interpretation of the results presented. Thus, the stereotype report does not require the writer to exercise his judgment in its preparation.

The informal report includes letters and memorandums. The subject matter and scope of such reports are not limited. Because the presentation depends almost entirely on the judgment of the writer, the beginner has trouble with the informal report. The letter is directed to an individual and is therefore more personal than reports of other types. Also, it is frequently an answer to another letter that asks specific questions. In this respect the subject matter may be limited. Even so, the limitations do not compare with the limitations in a stereotype report. There is ordinarily great latitude in the subject matter of the letter, which requires the judgment of the writer. The memorandum, on the other hand, is impersonal because it is directed to no one in particular. It might be classified as a short formal report; but, because of its brevity, many of the features of the formal report are not encountered.

The formal report is longer than the informal report and serves a much broader purpose. The subject matter is not limited, nor is the scope, except in a very general way. Also, it is detailed yet meets the requirements of those not interested in the details. Thus, in its preparation the formal report presents the greatest difficulties to the beginner. It includes all the principles of the informal report as well as some features peculiar only to the formal report. Consequently, the person who masters the formal report will have no difficulty whatever with the other types of written report. For this reason, the remainder of the discussion in the chapter deals primarily with the formal report.

ESSENTIAL REQUIREMENTS OF A REPORT

The essential requirements of the report are based on the fact that it must fulfill in every respect the desires and demands of the readers it is intended to serve. Courtesy to the readers is, therefore, of paramount importance. Nelson [1] describes the technical report as a specialized form of exposition and compares it to a world's fair at which there are many displays of general interest. He illustrates three of the essential requirements of the technical report by drawing an analogy with a display of electric-light bulbs. The *first requirement* is that the crowd must recognize at once that the display is of electric bulbs. The *second requirement* is that the purpose of the display must be made evident to the crowd very quickly in order to hold their interest. Otherwise they will become confused and will pass on to something they can understand. The display must be organized so that the desired purpose is attained. It may be a history of the development of the electric light, a classification of filaments, or something else just as specific. Whatever the purpose, however, it must be made clear to the crowd at the outset in order to avoid confusion. The *third requirement* is that the display must be provided with proper and adequate signs or labels so that the crowd can follow step by step through the display in its logical order. The signs therefore guide and assist the crowd in grasping the significance of the display. Furthermore, there must be no missing steps in the display without proper explanation, or the crowd will become confused.

In many respects the technical report is quite similar to a display at a fair. There are certain dominating reactions that every reader has when he begins to read a report. Immediately he wants to know *what* the report deals with, as well as its scope. Hence the writer must satisfy this desire by stating very early in the report the subject matter and its breadth. Next, the reader wants to know *why* the writer wishes to tell him about it. The writer must therefore state his objective or purpose. Finally, the reader wants to conserve his energies. He is naturally mentally lazy. The writer can assist him by stating in advance *how* the former has presented the subject matter. The reader can then orient his mind to receive the message the writer has for him. In the event the report involves people, the reader also wants to know at once *who* they are, *when* and *where* they became involved, and *how* they were involved.

The technical report consists of a logical, simple, and systematic presentation of thoughts directed toward a specific and common objective or purpose. No other thoughts have a place in the report. Furthermore, the

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[1] NELSON, J. RALEIGH, "Writing the Technical Report," McGraw-Hill Book Company, Inc., New York, 1940.

report must be courteous to the readers by satisfying their desires and demands of the report. It will be noted from the foregoing discussion that most of the desires and demands of the readers can be cared for by proper replies to questions suggested by the following six words:

What	Who
Why	When
How	Where

Perhaps it was Kipling who first pointed out the importance of these words in "The Elephant's Child."

> I keep six honest serving men,
> They taught me all I knew.
> Their names are What and Why and When
> And How and Where and Who.

The value of the technical report depends entirely on how well it serves the needs of its readers. Everything about the report should be evaluated on that basis. Its form, length, subject matter, scope, and all other features should be predicated upon fulfilling the desires and needs of the readers in the most effective way. The use to which the report will be put is of far greater importance than the contents. If the information contained in the report is not used, it is of little value and the writer of the report has wasted his time.

The report must be honest. If it contains a hidden purpose or any subterfuge whatever, the readers will become suspicious and the primary purpose of the report will be lost. The reader will not tolerate propaganda. Logic is essential, and it must be directed toward one purpose. The report must be tactful. Of course, the writer will be faced with the necessity of presenting technical results that may be at odds with certain personal prejudices of some of the readers. This difficulty can be obviated effectively, however, if the writer refrains from positive or dogmatic statements. Dogmatism usually irritates most readers. Thus, the writer should express himself in such a way that he does not give the reader an impression of egotism. The reader may be impressed with facts, but he will become irritated if the writer attempts in any manner to impress him with his own cleverness or attempts to claim credit for accomplishments. Credit will be given to those who deserve it provided that they are not too eager to claim the credit.

The human mind absorbs information by a process of repetition. The difference between individuals is that some require a greater amount of repetition to learn than others. This fact is quite important to the writer when he outlines his plan of presentation of technical results. Before he begins to prepare his plan of presentation, the writer must get clearly in mind *what* he wants to present, *why* he wants to present it, *who* can use it, *how* it can be used, and *how* it can be presented most effectively.

Since readers learn by repetition, the plan of a successful patent attorney in Chicago is very effective. This attorney was frequently faced in court trials with the presentation of highly technical information to a judge who had no technical background whatever. In order to win the case it was essential that the information be understood by the judge. In order to accomplish this objective, the following plan was used with his expert witnesses:

1. Tell the judge what you plan to tell him.
2. Then tell him.
3. Finally, tell him what you told him.

Thus, when the expert witness told the judge what he planned to discuss, the judge focused his mind on the specific subject. The expert witness could then proceed with his testimony in such a way that the judge could absorb the information presented. Finally, the expert witness reduced the information to certain pertinent facts so that the judge would not forget them.

The procedure is similar in the preparation of the technical report. In the beginning of the report the reader must be told what the writer plans to discuss. This step involves a brief description of the subject matter and its scope. Then, too, the purpose or objective of the writer must be made clear to the reader. Also, the writer should state how he will present his discussion. These three features serve to introduce the report to its readers or to tell them what is in store.

Then the writer can proceed with his presentation. He must make certain, however, that his presentation is consistent in every respect with the plan of presentation he informed the reader he would use. Otherwise the reader who has anticipated one plan of presentation will become confused by another.

After having presented the subject matter, the writer should give a résumé of his conclusions and recommendations for the benefit of the reader. He should clearly define the important facts that have been presented. Then he should tell the reader what should be done and why such action should be taken. Finally, he should tell the reader what the results of such action would be.

Throughout the preparation of the technical report the writer should forget himself and think only of the subject matter and of the reader, of whom, therefore, he must have a fairly accurate gauge. In all cases, however, it may be assumed safely that readers are mentally lazy. Thus, any feature of a report that will conserve their energies is desirable. In this connection the writer should never assume that the readers remember any particular feature of a project which may have been discussed or reported at an earlier date. The written report is a permanent record of the project. It may be used years later when the writer himself may have forgotten most of its details.

The writer of a technical report can also be sure that readers will tolerate no confusion. They must never become doubtful as to what the writer is discussing, why he is discussing it, and what plan of presentation he is using. They will rebel before they are forced into mental gymnastics. If there is any discontinuity of thought without proper explanation, the average reader will lay aside the report until he has more time to study it. Once the report has been set aside, the chances are slight that he will ever have time to study the results more intensively than in his first attempt. The writer has, therefore, failed to sell the products of his efforts in this case. On the other hand, superfluous comments detract from a report. Consequently, the writer must have a fairly accurate concept of the background and experience of the readers. When in doubt, however, the writer should assume that the reader will need additional explanatory comments.

The essential requirements of the technical report may be summarized as follows:

1. At the outset the writer must inform the reader *what* he plans to present.
2. The writer must advise the reader *why* he wishes to present it.
3. The writer must make clear to the reader *how* he will present his message.
4. If people are involved, the writer must state early in the report *who* they are, *when* they became involved, and *where* they became involved.
5. The report must be honest.
6. The report must be tactful.
7. The report must be logical.
8. The reader must never become confused.

PREPARATION OF THE FORMAL REPORT

The previous section discussed rather generally the essential requirements of the technical report. A recommended procedure for the preparation of the technical report will now be presented.

There are only four steps or phases in the preparation of the technical report,[1] (1) an analysis of the data and results, (2) the development of a plan of presentation, (3) writing the first draft, and (4) correcting the first draft. Each of the four steps in its logical sequence is essential.

Analysis of Data and Results.—The first step or phase in the procedure, analysis of data and results, is the most time-consuming of the four phases.

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[1] *Ibid.*

Furthermore, it requires the greatest technical knowledge and ability. Frequently the chemical engineer is able to carry out the analysis of the data and results during the time when the technical results are being obtained. This situation is particularly true of research and development work. Where feasible, it is the best plan, for an analysis of data frequently indicates the necessity for further investigation of other features not yet studied.

Analysis of data involves checking of their accuracy and reliability by means of fundamentals. For example, chemical-engineering data should be able to withstand the test of a material balance and of an energy balance. Then, too, they should be consistent with other well-established results from the standpoint of static and dynamic equilibria. If there is anything inconsistent, the reason for it should be determined in order to establish the probable accuracy.

After the accuracy of the data is defined, the results should be classified and segregated. Conclusions should be reached as to the significance of the results. The writer should then develop a clear conception of how the results can be used and who can use them. He must check his conclusions from every possible viewpoint to make certain that they are sound. There is nothing quite so detrimental to the writer's professional standing than to have a reader show that certain conclusions and recommendations are fundamentally unsound.

The inexperienced engineer is prone to begin the writing of his report after an incomplete or superficial analysis of the technical results. Unfortunately, in such cases the writer has no clear understanding of his subject. His mind is confused on the significance of the results. His conclusions and recommendations are likely to be unsound technically and therefore invalid. Furthermore, since he does not have a thorough understanding of the subject matter, he does not have a clear conception of how the results can be used or who can use them. Thus, his mind is confused on the purpose, or objective, of the report. In such a state of confusion, he will not be able to develop a logical and systematic plan of presentation. Report writing is difficult under such conditions, for the thoughts of the writer do not come freely. When a person has trouble with reporting of technical results, the cause is frequently due to his being unfamiliar with the subject matter and how it can be used.

After the writer has made a thorough analysis of the technical results, he should get clearly in mind the subject matter, the readers who can use the results, and the purpose of the report. Unless he takes these steps, he will not be able to transmit his thoughts logically and concisely, without confusion to the readers.

Development of Plan of Presentation.—The second phase of the procedure for preparing the technical report is the development of a simple, systematic, logical plan of presentation, directed throughout the report toward a single objective. This phase is perhaps the one most often neglected or even ignored by the inexperienced engineer. It usually consumes as much time as the third and fourth phases combined. Nevertheless, it is an essential step in the procedure.

Since the value of the technical report depends entirely on how well it meets the requirements of those it is intended to serve, no effort should be spared to make it the best that could possibly be prepared. If the subject matter is presented in a slovenly and illogical fashion, the readers will invariably assume that the work which preceded the report and the results are slipshod. After thousands of dollars have been spent on an investigation, the results should not be presented in a "10-cent" report. The report should represent in every respect the effort, thought, and precision involved in the results it presents.

The desired plan of presentation can be developed first by writing a theme sentence that defines the subject (what) and the purpose (why). For example, "The data on catalyst life show conclusively that it would be profitable to carry out the reaction at a higher temperature than currently used." This example pertains to a report that will present data on catalyst life. The purpose of presenting the data apparently is to effect changes in operation, with a reduction in cost of production. The theme sentence will force the writer to clarify his mind from details so that he can appraise the results as a whole.

After a theme sentence has been prepared, the writer should prepare an outline (or the equivalent) of the report. This will be an invaluable guide to him during the actual writing of the report. It will prevent his becoming uncertain while writing as to what should be said and why it should be said. The writer must have a clear conception of the whole, or he will become confused by the details.

The exact manner in which the final plan of presentation is prepared varies with different experienced writers. It depends considerably on personal preference. Even so, the different detailed procedures have two fundamental features in common. (1) Set down on paper each item to be covered in the report. It is not necessary at this point that the items be classified. The important objective is to get every item on paper that might come within the scope of the report. Hence, it is preferable to include items that later will be rejected rather than to omit an item that should be covered. (2) Fit each item into a simple, systematic, logical plan of presentation consistent with the purpose. This entails rejection of those items which do not come strictly within the scope of the report.

There are at least three different schemes used by experienced engineers in the development of the plan of presentation. Nelson[1] recommends the use of small cards so that only one item is written on each card. Items which do not come within the scope of the report can be rejected by eliminating the card on which it is written. Also, the items can be classified into their logical place in the presentation merely by arranging the cards. Another scheme used by many capable writers is to write on separate sheets of paper a complete discussion of each item to be covered. Then the various sheets of paper are glued together into a continuous sheet of written subject matter, which constitutes the first draft of the report. This scheme has its advantages in that the writer can get on paper the detailed discussion of each item when it is clear in his mind. Also, when he prepares the continuous sheet of subject matter, he can eliminate those items which do not come within the scope of the report. The third scheme that often is used is the preparation of a brief outline of the report. This scheme is not as convenient as that recommended by Nelson,[1] for new outlines must be prepared in order to rearrange and reclassify the items. Even so, many engineers find that they get a better appraisal of the relative importance of the various items by preparing new outlines than by rearranging cards. As stated, however, the scheme used is a matter of personal preference, which each individual must determine for himself. In any event, the following discussion refers specifically to the preparation of outlines but is equally applicable to the other schemes mentioned.

After all the items to be presented have been set down on paper, the tedious task of classifying and segregating them under logical topics and subtopics is begun. The procedure is much the same as that used in the solution of a complicated mathematical problem. (1) The entire problem (the whole) is studied to determine how the solution can be carried out. (2) The problem is divided into several logical parts. (3) The solution of each part is carried out by dividing it into necessary details, which follow in logical (mathematical) sequence. It is necessary to solve each part in its proper place in the sequence before the next part can be solved. In the mathematical solution the individual is more or less forced to follow a logical plan. It is just as important to do so in the presentation of technical results.

The first step in the procedure of preparing the outline is to divide the report into several main parts or sections such as Summary, Introduction, Experimental Results, Significance of Results, and Conclusions and Recommendations. The sections into which the report is divided, of course, are dependent upon the nature of the subject matter. Even so, the formal report should always have the sections Summary, Introduction, and Conclusions and Recommendations.

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[1] *Ibid.*

After the sections of the report have been decided upon, classify and segregate the topics into their logical section. Then arrange the topics into a logical sequence. Next, the subtopics should be classified and segregated under the proper topic. Then they should be arranged into their logical sequence.

Thus, the plan of presentation is developed by dividing the whole into certain logical sections. Each section is divided into logical parts, and these parts are divided into their logical subdivisions. The related items can be fitted into their logical places in the plan of presentation under the proper topic and subtopic. Such a plan will make for ease of writing. The writer's thoughts will flow easily and freely without confusion. There will be no mental gymnastics or mental precipices left in the finished report to confuse the readers. If the plan of presentation is illogical, writing will be difficult. Time will be saved by correcting any illogical sequences that occur in the outline. The outline should be studied in great detail to make certain that each item blends into a logical plan.

Writing the First Draft.—The third step or phase in the procedure of preparing the technical report is the actual writing of the first draft. Once the writer begins, he should write rapidly and with as few intermissions as possible. It is desirable that one section of the report be written during a given period of writing. This procedure gives better proportion and emphasis than can be secured otherwise.

Subject matter is of greatest importance during writing of the first draft. The writer should not shift his attention from subject matter to manner of expression. This shifting can be avoided if he will refrain from reading what he has written until the first draft is completed. If the first two phases of the procedure of preparing the technical report were well done, it will be a simple matter to correct the manner of expression after the first draft is completed.

Correcting the First Draft.—The fourth phase in the preparation of the technical report is correcting the first draft. Attention in this phase is concentrated on manner of expression and on the readers' requirements. Corrections can be made most effectively if in each reading of the entire rough draft the writer takes up only one type of error at a time. For example, in the first reading he may consider only improvements in grammar, and in the second reading he may consider punctuation.

If during his reading of the first draft of the report the writer has to pause at any point to grasp the sequence of thoughts, he may be sure that the readers will have trouble at that point. Every effort must be made by the writer to eliminate such haziness to obtain high quality in writing. If he insists on high quality, it can be attained although time and patience are required.

The use of transition paragraphs between topics is often helpful to the reader. Such paragraphs occur at the end or at the beginning of the discussion of a topic. A transition paragraph relates what has been discussed to what follows. It serves to connect the topics and show their logical relationship. It gives the reader an insight into the discussion to follow immediately and relates it to what has just been discussed.

Similarly, topic sentences in paragraphs permit the reader to focus his mind at once on the immediate subject. If the first sentence of the paragraph announces in some way the subject of the paragraph, the reader can follow the discourse rapidly.

References to figures and tables should be made just as soon as these will be of help to the reader to grasp the information being presented.

All dogmatic statements should be replaced with less positive statements. In most cases the desired thought can be conveyed by statements that are not so definite and so restricted. Dogmatic statements irritate the average reader, for they give an impression of egotism. In this connection the writer should refrain from the use of the words "I," "we," and "you." He is less likely to create the impression of egotism or familiarity if he writes in the third person than if he writes in the first person.

Although it is the primary purpose of this chapter to discuss the engineering aspects of report writing, it is desirable to point out at this time some of the more common errors and weaknesses in English that should be eliminated from the rough draft during the fourth phase of the preparation of a report.

Each chemical engineer should have available for ready reference the equivalent of "Standard Handbook for Secretaries" by Hutchinson,[1] "A Dictionary of Modern English Usage" by Fowler,[2] and "The King's English" by Fowler.[3] These are invaluable reference books which even if only infrequently used and studied cannot help improving the English usage of most chemical engineers.

In addition to logical and orderly presentation of thoughts, clear writing requires simple words and clear sentence construction. Sentence structure should be consistent and logical. Ambiguity should be eliminated. Singular verbs should be used with singular subjects, and plural verbs with plural subjects. The subject is sometimes separated from the verb by a phrase. It is a good plan to examine the sentence to make certain that the verb and subject agree. Fowler [3] states, "Some writers are as easily drawn off the scent as young hounds. They start with a singular subject;

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[1] HUTCHINSON, LOIS, "Standard Handbook for Secretaries," 3d ed., McGraw-Hill Book Company, Inc., New York, 1941.

[2] FOWLER, H. W., "A Dictionary of Modern English Usage," Oxford University Press, New York, 1944.

[3] FOWLER, H. W., "The King's English," Oxford University Press, New York, 1940.

before they reach the verb, a plural noun attached to an 'of,' or the like, happens to cross, and off they go in the plural, or vice versa."

Another frequent error is the use of the present participle as an unsupported verb, for example, "The data represent over three hundred tests. This being a good representation of the results." The second sentence can be corrected by substitution of "These are" for "This being." The dangling participle or gerund often constitutes a weakness, for example, "The project was abandoned, there being little chance of success." This sentence can be strengthened by changing it to "The project was abandoned because there was little chance of success." The dangling participle gives poor distribution of emphasis and frequently is grammatically incorrect. A participial or gerund phrase at the beginning of a sentence is grammatically correct if its subject is identical with the subject of the main clause. If no action is implied, it is not necessary to have identical subjects. Even so, the use of the present participle in phrases seldom gives the desired effect; hence, each such usage should be challenged.

There is much prejudice against split infinitives, but sometimes it is well to use them when better emphasis can be attained. Fowler[1] states, "The 'split' infinitive has taken such hold upon the consciences of journalists that, instead of warning the novice against splitting his infinitives, we must warn him against a curious superstition that the splitting or not splitting makes the difference between a good and a bad writer."

The misuse of "compare to" for "compare with" is so confusing at times that the reader is at a loss to know just what the writer really means. "Compare to" and "comparable to" should be used only when similarity is being pointed out between things or persons. For instance, "The speed of the rocket is comparable to that of a comet." "Compare with" and "comparable with" should be used when things or persons are being compared as to their dissimilarity. For example, "The yield of gasoline by catalytic cracking is large compared with the yield by thermal cracking."

The word "data" is plural and should have a plural verb. Also, it is "many data" instead of "much data," "few data," instead of "little data," and "large number of data" instead of "large amount of data."

Perhaps the most common examples of the use of superfluous words are "refer *back*," "link *back*" and "consensus *of opinion*." These should be merely "refer," "link," and "consensus."

TYPICAL FORMS OF REPORT

The fundamentals that have been discussed thus far are applicable to the preparation of any written technical report. There are, however, no

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[1] *Ibid.*

such clearly defined fundamentals that apply to the form of the report. In general, this depends upon what the readers prefer. Usually each organization that prepares a number of reports each year has adopted a form that the executives prefer. They are accustomed to their "pet" form, and it will be desirable to use this for that organization.

There are many different forms of reports used in industry. Each of them has its merits. Even so, there are some features of formal and informal reports which are fairly common to the majority of the forms used.

The Formal Report.—In general, the formal report is prepared for two types of reader, *viz.*, those who do not have time to go into the details and those who wish to study the details. One form that has met wide approval by those readers whose time is limited consists of (1) the title sheet, (2) table of contents, (3) summary, (4) introduction, (5) the sections on subject matter, (6) conclusions and recommendations, (7) acknowledgments, (8) references, and (9) appendixes.

The *title sheet* usually presents the title of the report, the identification number of the report, the date, and the names of the authors. Ordinarily, all these items with the exception of the names of the authors will also appear on the front cover. The name of the organization that issues the report should also be given on the front cover. The location of the various items should give evidence of their relative importance and should be consistent with a good proportion and balance on the page.

The *table of contents* should present the section titles, the topics, and the subtopics. These items should be presented so that those of lesser importance are subordinated to those of greater importance. This procedure can be effected by indentation of the topics and subtopics to correspond with their relative importance. It is desirable to limit the length of the table of contents to one or at the very most two pages.

The *summary* is perhaps the most important part of the report, for it is the only part that will be read by many of the readers whose time is limited. Hence, it should be prepared with great care in order to impress even the busiest reader. Usually it is this type of reader to whom the contents of the report must be sold, or the services of the writer of the report will have been nonproductive. Such readers as members of boards of directors, plant managers, and department heads do not ordinarily have the time to read in detail all the reports that come to their desks. Inasmuch as these readers are the ones whom it is usually most desirable to sell, it is essential that the important features of the report be presented in such a way that they will have the time to read them. If they wish to go into more detail on any item covered in the summary, they can read in the report the detailed subject matter that pertains to this item. Thus, too much care and time cannot be devoted to the summary. If the summary is properly written, the interest of many of the busy executives will be so attracted by it that they will read more of the report than they had originally intended.

The summary can probably be written to best advantage after all other sections of the report are completed. It should present as concisely as possible the most important subject matter. It should give a résumé of the important results, conclusions, and recommendations that are presented in more detail in the report. Certainly the summary should not consist merely of a description of the subject matter that is presented in the report. That is one of the functions of the introduction, as will be seen later.

The summary should consist of short, concise, numbered paragraphs each of which possesses a high degree of unity and of coherence. The summary should rarely exceed two and a half pages in length and in most cases should not exceed one and a half pages. The first paragraph should describe the subject matter presented in the report. The second paragraph should state the purpose of the work and of the report. The succeeding paragraphs should state very briefly and concisely the important results and conclusions covered in detail in the report. The final paragraph should present recommendations (if any) and plans for further investigation.

Occasionally, reports will be prepared that do not lend themselves readily to the use of this pattern for the summary. These instances, however, will be relatively few. In general, the pattern can be used effectively.

The *introduction* is possibly second in importance to the summary. It should prepare the reader by clearly describing (1) the subject matter and scope, (2) the purpose, and (3) the plan of presentation. It should advise the reader on what the writer wants to tell him, on why he wants to tell him, and on how he will tell him.

The writer must disclose immediately what he intends to present. The reader will not tolerate a long, rambling discussion before he is told what the subject matter consists of. It is desirable to state what the subject matter is in the first sentence of the introduction or certainly within the first paragraph. The reader is impatient as well as lazy. He wants to know at once what the writer's intentions are. Furthermore, he will not wade through superfluous verbiage before he is advised. It is discourteous to expect him to do so.

The introduction should be as brief and as concise as possible, consistent with adequate fulfillment of its functions. Every effort should be made to focus the attention of the reader on the desired subject matter. The subject matter should be defined quickly with the necessary comment so as to fix it in the mind of the reader.

All relevant information that will orient the reader's mind to and arouse his interest in the detailed subject matter should be presented in the introduction. The historical background of the project is usually very helpful to the reader and suitable material for the introduction.

The *subject matter* should be presented in the simplest and most logical way. Its organization and arrangement may require several important sections. In some cases, the subject matter may consist merely of Results and Discussion or Presentation of Results and Discussion. In contrast with the other sections of the report there is nothing rigid about the method of presentation of the subject matter except that it must be logical, clear, and concise. No mental gaps or mental gymnastics should be left to perplex the reader.

Figures and graphs should be self-sufficient. It is distracting to the reader to have to refer to the text to grasp their significance. The use of good graphs and figures is helpful to the reader in absorbing the subject matter. Sufficient and clear labels should be used.

If feasible, the graphs and figures should be inserted so that they face the discussion pertaining to them. Thus, the reader can look directly at the graph or figure without turning pages in the report to see it as he reads the discussion. This method of presentation frequently entails the use of only a part of the page that faces a graph or figure for a discussion of it. When another graph is presented, the discussion of it should be presented on the page facing it even though the previous page is only partly used. This arrangement makes for more bulk in the report, but it simplifies the reader's task so much that this objection is relatively minor.

The lettering on graphs and figures should be done with instruments (such as LeRoy or Wrico) unless it is done by an expert at freehand lettering. Lettering with instruments, however, usually is superior. Also, in the case of graphs a somewhat more attractive presentation can be obtained if intermediate lines are not reproduced. Every fifth or tenth coordinate line is usually sufficient. This effect can be accomplished easily by using graph paper with light blue lines, as described in Chap. III.

Tables of data also should be self-sufficient. No explanation of the headings should be required in the text. Only the data being discussed should be presented in the sections of the report that deal with subject matter. Tables of detailed data have no place in this part of the report unless all the data are discussed. Large tables of detailed data frighten and confuse the lazy reader. Such tables should be inserted in an appendix at the end of the report. It is sufficient merely to refer to them in the body of the report and to note their location. The reader who is interested in the detailed data can then refer to them at the end of the report, but the uninterested reader will not be forced to wade through them.

The *conclusions* should consist of short, concise, numbered paragraphs. Only essential statements should be included to present the important conclusions and recommendations as set forth in the sections that deal with subject matter. Each conclusion and recommendation as presented should be supported with the essential arguments and fundamentals to drive home the "sale." In this section of the report the writer should tell the reader what he told him in the sections on the subject matter. The conclusions section has several features similar to the summary except that somewhat more supporting argument is presented and no mention is made as to the "what" and "why" of the report.

Acknowledgments should be inserted following conclusions if the writer wishes to express his gratitude for assistance from any person or organization. Such statements should be quite formal, short, and definitely not flowery.

References that have been made throughout the report to the literature, reports, and private communications should be itemized in this section. The usual practice is to list the references alphabetically according to the last name of the authors. In the case of coauthors the last name of the first author is used. The references should be numbered in order. Throughout the report where reference is made it should be identified by the corresponding number in parentheses.

The *appendixes* should be located at the end of the report following references. The chief advantage of appendixes is that they permit inclusion of detailed information that is too bulky and confusing to the average reader to justify presentation with the subject matter. For example, it is desirable to present detailed data in an appendix or appendixes because a few readers will find the data valuable in special cases. But the majority of readers will be confused with a large number of data, and consequently the data should not be presented in detail with the subject matter.

Complicated mathematical derivations fall in the same classification. In general, the writer will have more success in attaining his objective if he presents with the subject matter only the basis of derivation, assumptions made, and the final equation or equations. He can then refer the reader to an appendix for the detailed mathematics. Of course, if the report is being prepared specifically for persons who are active in mathematics, it may be proper to make the detailed mathematics a part of the subject matter. It should be kept in mind, however, that it is not common for an executive to be active in higher mathematics. Thus, a report for this type of person should in general present the detailed mathematics in an appendix.

The Informal Report.—In general, the majority of the reports that the chemical engineer prepares are informal in nature. Two of the more common types of informal report are the memorandum and the letter. The memorandum is impersonal and is not directed to any specific person, whereas the letter is directed to a specific person.

The *memorandum* may be as long as a short formal report, say up to 15 pages. In contrast with the formal report, the memorandum has neither a title sheet nor a table of contents. The title is usually placed at the top of the first page, and the discourse started immediately below. If the memorandum is over 5 pages in length, the subject matter may be divided under topics similar to the formal report. Subtopics should seldom be used.

Since the memorandum is shorter than the average formal report, no words can be wasted in the memorandum before the reader is told what subject matter is presented and why. The subject matter should be defined in the first sentence; and the purpose should be stated within the first paragraph, preferably in the second sentence if possible. Also, if the memorandum is a report on certain work that has been done, the purpose of the work should be given as well as who requested it, and when, if pertinent. It should never be assumed that the reader remembers any of the details surrounding the project. In the case of long memorandums it is frequently desirable to describe very briefly at the end of the first paragraph the plan of presentation.

Thus, the first paragraph of the memorandum serves a similar function to the introduction of a formal report. In the succeeding paragraphs the subject matter should be presented. As in the case of the formal report, it should be treated in a logical, concise, and orderly manner always directed toward the objective. The writer should keep in mind that the readers are interested in the results and not in how the writer spent his time. The work of the writer can be appraised only on the basis of accomplishments, no matter how conscientious he is.

The memorandum is usually signed by the writer and is dated.

It is good practice in transmitting a memorandum of two or more pages to summarize it in a letter of transmittal *of not over one page in length.* The function of the letter of transmittal in this case is the same as for the summary of a formal report, and the same pattern will be found desirable. Of course, the letter of transmittal must be directed to some individual, and that individual is usually the person who requested the work or who is responsible for it.

The *technical letter* ordinarily should not exceed 2 pages in length. Otherwise, it is preferable to prepare a memorandum and to transmit it with a summarizing letter as described above. In general, it is very desirable to limit the length of the letter to 1 page, although in special cases it may be as long as 2½ pages.

The letter must be concise and to the point. As in the case of the memorandum the reader's attention must be focused immediately upon the subject. Economy of words is essential. The writer should be certain, however, to cover all questions raised if the letter is a reply to another. Also, he should be careful that his letter is courteous in every respect.

In some special cases it is satisfactory to write the letter in the first person. However, it is always a good plan to write in the third person, for in the third person form there is no danger of giving the reader an impression of egotism.

The subject should be set forth at the top of the page at some convenient point consistent with a good balance. This position is usually to the right of the name and address of the person to whom the letter is directed. In some industrial organizations, special forms that dispense with the salutation are used for interoffice correspondence. In such forms a place is usually indicated for the subject.

In the case of letters, answers to the questions suggested by the words "who," "when," and "where" are usually more important than in the formal report. Who requested the work, when, and what were the circumstances? Also, where did the problem originate?

QUESTIONS

1. Why does an employer hire chemical engineers?

2. In addition to getting valuable technical results, what must the chemical engineer be able to do?

3. What is the basis of selling technical results?

4. What is the means of selling technical results?

5. What are two essential requirements of expression of thoughts?

6. Name the three types of written technical report.

7. Describe the stereotype report, and cite a typical example of its application.

8. Describe the informal report.

9. What are the essential requirements of the technical report? On what are they based?

10. What six words suggest questions that the report must answer to fulfill the readers' requirements and demands?

11. What are the essential phases or steps in the preparation of the formal report?

12. Describe briefly the first, second, third, and fourth steps or phases in the preparation of the formal report.

13. What are some of the more common errors in English?

14. Give an example of a dangling participle and of the use of a present participle as a verb.

15. Explain distinction between the use of "compare to" and "compare with."

16. Describe very briefly a typical form of formal report.

17. Describe a typical form of informal report.

APPENDIX

Table A.1.—Density and Specific Gravity of Solutions Heavier than Water *

Deg Bé	Sp. gr.	Lb/gal	% by wt.				
			H_2SO_4 at 60°F	HNO_3 at 60°F	HCl at 60°F	NaOH at 15°C	Na_2CO_3 at 15°C
0	1.000	8.328					
1	1.007	8.385	1.02	.....	1.40	0.59	0.74
2	1.014	8.445	2.08	.....	2.82	1.20	1.10
3	1.021	8.504	3.13	.....	4.25	1.85	2.03
4	1.028	8.565	4.21	.....	5.69	2.50	2.72
5	1.036	8.625	5.28	.....	7.15	3.15	3.42
6	1.043	8.688	6.37	.....	8.64	3.79	4.12
7	1.051	8.750	7.45	.....	10.17	4.50	4.81
8	1.058	8.814	8.55	.....	11.71	5.20	5.52
9	1.066	8.879	9.66	.....	13.26	5.86	6.27
10	1.074	8.945	10.77	12.86	14.83	6.58	6.95
11	1.082	9.012	11.89	14.13	16.41	7.30	7.70
12	1.090	9.078	13.01	15.41	18.01	8.07	8.43
13	1.099	9.148	14.13	16.72	19.63	8.78	9.18
14	1.107	9.218	15.25	18.04	21.27	9.50	9.94
15	1.115	9.289	16.38	19.36	22.92	10.30	10.67
16	1.124	9.361	17.53	20.69	24.57	11.06	11.48
17	1.133	9.434	18.71	22.04	26.22	11.90	
18	1.142	9.508	19.89	23.42	27.92	12.69	
19	1.151	9.584	21.07	24.82	29.65	13.50	
20	1.160	9.660	22.25	26.24	31.45	14.35	
21	1.169	9.739	23.43	27.67	33.31	15.15	
22	1.179	9.818	24.61	29.07	35.21	16.00	
23	1.189	9.898	25.81	30.49	37.14	16.91	
24	1.198	9.979	27.03	31.94	39.41	17.81	
25	1.208	10.063	28.28	33.42	41.72	18.71	
26	1.219	10.148	29.53	34.94	.....	19.65	
27	1.229	10.233	30.79	36.48	.....	20.60	
28	1.239	10.321	32.05	38.06	.....	21.55	
29	1.250	10.410	33.33	39.66	.....	22.50	
30	1.261	10.501	34.63	41.30	.....	23.50	
31	1.272	10.592	35.93	43.00	.....	24.48	
32	1.283	10.686	37.26	44.78	.....	25.50	
33	1.295	10.781	38.58	46.58	.....	26.58	
34	1.306	10.879	39.92	48.42	.....	27.65	

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* Badger, W. L., and E. M. Baker, "Inorganic Chemical Technology,' 1st ed., p. 218, McGraw-Hill Book Company, Inc., New York, 1928.

TABLE A.1.—DENSITY AND SPECIFIC GRAVITY OF SOLUTIONS HEAVIER THAN WATER (*Continued*)

Deg Bé	Sp. gr.	Lb/gal	% by wt.				
			H_2SO_4 at 60°F	HNO_3 at 60°F	HCl at 60°F	NaOH at 15°C	Na_2CO_3 at 15°C
35	1.318	10.978	41.27	50.32	.....	28.83	
36	1.330	11.079	42.63	52.30	.....	30.00	
37	1.343	11.181	43.99	54.36	.....	31.20	
38	1.355	11.285	45.35	56.52	.....	32.50	
39	1.368	11.392	46.72	58.82	.....	33.73	
40	1.381	11.501	48.10	61.38	.....	35.00	
41	1.394	11.611	49.47	64.20	.....	36.36	
42	1.408	11.724	50.87	67.18	.....	37.65	
43	1.422	11.839	52.26	70.33	.....	39.06	
44	1.436	11.956	53.66	73.67	.....	40.47	
45	1.450	12.076	55.07	77.17	.....	42.02	
46	1.465	12.197	56.48	81.08	.....	43.58	
47	1.480	12.322	57.90	85.70	.....	45.16	
48	1.495	12.449	59.32	91.35	.....	46.73	
49	1.510	12.579	60.75	.....	.....	48.41	
50	1.526	12.711	62.18	.....	.....	50.10	
51	1.543	12.847	63.66				
52	1.559	12.984	65.13				
53	1.576	13.126	66.63				
54	1.593	13.270	68.13				
55	1.611	13.417	69.65				
56	1.629	13.568	71.17				
57	1.648	13.722	72.75				
58	1.667	13.880	74.36				
59	1.686	14.041	75.99				
60	1.706	14.207	77.67				
61	1.726	14.376	79.43				
62	1.747	14.549	81.30				
63	1.768	14.726	83.34				
64	1.790	14.908	85.66				
65	1.813	15.094	88.65				
66	1.835	15.285	93.19				

TABLE A.2.—CONVERSION TABLE

(Deg API, Specific Gravity, lb/gal)

Deg API	Sp. gr. at 60°/60°F	Lb/gal	Deg API	Sp. gr. at 60°/60°F	Lb/gal	Deg API	Sp. gr. at 60°/60°F	Lb/gal
0	1.0760	8.962	33.5	0.8576	7.141	67.0	0.7128	5.934
0.5	1.0719	8.929	34.0	0.8550	7.119	67.5	0.7111	5.919
1.0	1.0679	8.895	34.5	0.8524	7.098	68.0	0.7093	5.904
1.5	1.0639	8.862	35.0	0.8498	7.076	68.5	0.7075	5.889
2.0	1.0599	8.828	35.5	0.8473	7.055	69.0	0.7057	5.874
2.5	1.0559	8.795	36.0	0.8448	7.034	69.5	0.7040	5.860
3.0	1.0520	8.762	36.5	0.8423	7.013	70.0	0.7022	5.845
3.5	1.0481	8.730	37.0	0.8398	6.993	70.5	0.7005	5.831
4.0	1.0443	8.698	37.5	0.8373	6.972	71.0	0.6988	5.817
4.5	1.0404	8.666	38.0	0.8348	6.951	71.5	0.6970	5.802
5.0	1.0366	8.634	38.5	0.8324	6.930	72.0	0.6953	5.788
5.5	1.0328	8.603	39.0	0.8299	6.910	72.5	0.6936	5.773
6.0	1.0291	8.571	39.5	0.8275	6.890	73.0	0.6919	5.759
6.5	1.0253	8.540	40.0	0.8251	6.870	73.5	0.6902	5.745
7.0	1.0217	8.509	40.5	0.8227	6.850	74.0	0.6886	5.731
7.5	1.0179	8.479	41.0	0.8203	6.830	74.5	0.6869	5.718
8.0	1.0143	8.448	41.5	0.8179	6.810	75.0	0.6852	5.703
8.5	1.0107	8.418	42.0	0.8155	6.790	75.5	0.6836	5.690
9.0	1.0071	8.388	42.5	0.8132	6.771	76.0	0.6819	5.676
9.5	1.0035	8.358	43.0	0.8109	6.752	76.5	0.6803	5.662
10.0	1.0000	8.328	43.5	0.8086	6.732	77.0	0.6787	5.649
10.5	0.9965	8.299	44.0	0.8063	6.713	77.5	0.6770	5.635
11.0	0.9930	8.270	44.5	0.8040	6.694	78.0	0.6754	5.622
11.5	0.9895	8.241	45.0	0.8017	6.675	78.5	0.6738	5.608
12.0	0.9861	8.212	45.5	0.7994	6.656	79.0	0.6722	5.595
12.5	0.9826	8.183	46.0	0.7972	6.637	79.5	0.6706	5.582
13.0	0.9792	8.155	46.5	0.7949	6.618	80.0	0.6690	5.568
13.5	0.9759	8.127	47.0	0.7927	6.600	80.5	0.6675	5.556
14.0	0.9725	8.099	47.5	0.7905	6.582	81.0	0.6659	5.542
14.5	0.9692	8.071	48.0	0.7883	6.563	81.5	0.6643	5.529
15.0	0.9659	8.044	48.5	0.7861	6.545	82.0	0.6628	5.516
15.5	0.9626	8.016	49.0	0.7839	6.526	82.5	0.6612	5.503
16.0	0.9593	7.989	49.5	0.7818	6.509	83.0	0.6597	5.491
16.5	0.9561	7.962	50.0	0.7796	6.490	83.5	0.6581	5.477
17.0	0.9529	7.935	50.5	0.7775	6.473	84.0	0.6566	5.465
17.5	0.9497	7.909	51.0	0.7753	6.455	84.5	0.6551	5.453
18.0	0.9465	7.882	51.5	0.7732	6.437	85.0	0.6536	5.440
18.5	0.9433	7.856	52.0	0.7711	6.420	85.5	0.6521	5.427
19.0	0.9402	7.830	52.5	0.7690	6.402	86.0	0.6506	5.415
19.5	0.9371	7.804	53.0	0.7669	6.385	86.5	0.6491	5.402
20.0	0.9340	7.778	53.5	0.7649	6.368	87.0	0.6476	5.390
20.5	0.9309	7.752	54.0	0.7628	6.350	87.5	0.6461	5.377
21.0	0.9279	7.727	54.5	0.7608	6.334	88.0	0.6446	5.365
21.5	0.9248	7.701	55.0	0.7587	6.316	88.5	0.6432	5.353
22.0	0.9218	7.676	55.5	0.7567	6.300	89.0	0.6417	5.341
22.5	0.9188	7.651	56.0	0.7547	6.283	89.5	0.6403	5.329
23.0	0.9159	7.627	56.5	0.7527	6.266	90.0	0.6388	5.316
23.5	0.9129	7.602	57.0	0.7507	6.249	90.5	0.6374	5.305
24.0	0.9100	7.578	57.5	0.7487	6.233	91.0	0.6360	5.293
24.5	0.9071	7.554	58.0	0.7467	6.216	91.5	0.6345	5.281
25.0	0.9042	7.529	58.5	0.7447	6.199	92.0	0.6331	5.269
25.5	0.9013	7.505	59.0	0.7428	6.184	92.5	0.6317	5.257
26.0	0.8984	7.481	59.5	0.7408	6.167	93.0	0.6303	5.246
26.5	0.8956	7.458	60.0	0.7389	6.151	93.5	0.6289	5.234
27.0	0.8927	7.434	60.5	0.7370	6.135	94.0	0.6275	5.222
27.5	0.8899	7.410	61.0	0.7351	6.119	94.5	0.6261	5.210
28.0	0.8871	7.387	61.5	0.7332	6.103	95.0	0.6247	5.199
28.5	0.8844	7.364	62.0	0.7313	6.087	95.5	0.6233	5.187
29.0	0.8816	7.341	62.5	0.7294	6.072	96.0	0.6220	5.176
29.5	0.8789	7.318	63.0	0.7275	6.056	96.5	0.6206	5.164
30.0	0.8762	7.296	63.5	0.7256	6.040	97.0	0.6193	5.154
30.5	0.8735	7.273	64.0	0.7238	6.025	97.5	0.6179	5.142
31.0	0.8708	7.251	64.5	0.7219	6.010	98.0	0.6166	5.131
31.5	0.8681	7.228	65.0	0.7201	5.994	98.5	0.6152	5.120
32.0	0.8654	7.206	65.5	0.7183	5.979	99.0	0.6139	5.109
32.5	0.8628	7.184	66.0	0.7165	5.964	99.5	0.6126	5.098
33.0	0.8602	7.163	66.5	0.7146	5.949	100.0	0.6112	5.086

Table A.3.—Mean Molal Heat Capacities of Gases between 60°F and Temperature Given at Atmospheric Pressure

(Btu/lb-mole/deg F)

Deg F	H_2	N_2	O_2	Air	CO	CO_2	H_2O	SO_2	CH_4	C_2H_2	C_2H_4	C_3H_8
0	6.84	6.95	6.98	6.93	6.95	8.45	7.97	9.19	8.11	9.86	9.65	15.40
60	6.86	6.96	7.00	6.94	6.97	8.70	7.99	9.38	8.30	10.25	10.20	16.25
500	6.96	7.02	7.23	7.04	7.04	9.98	8.19	10.38	9.91	12.13	13.29	21.90
1000	7.00	7.17	7.55	7.24	7.23	10.92	8.54	11.27	11.76	13.35	16.01	27.85
1500	7.07	7.37	7.80	7.44	7.45	11.60	8.93	11.82	—	—	—	—
2000	7.16	7.57	8.00	7.63	7.65	12.10	9.33	12.19	—	—	—	—
2500	7.28	7.72	8.16	7.77	7.80	12.46	9.70	12.44	—	—	—	—
3000	7.39	7.85	8.26	7.91	7.93	12.76	10.04	12.62	—	—	—	—
3500	7.51	7.96	8.40	8.01	8.04	12.98	10.35	12.76	—	—	—	—
4000	7.63	8.06	8.49	8.09	8.13	13.17	10.64	12.88	—	—	—	—
4500	7.75	8.15	8.60	8.19	8.22	13.33	10.89	12.98	—	—	—	—
5000	7.85	8.22	8.68	8.25	8.27	13.45	11.11	13.05	—	—	—	—
5500	7.97	8.30	8.83	8.33	8.36	13.61	11.42	13.16	—	—	—	—

General equation for sensible heat above T_1:

$$\Delta H_{T_1} = \alpha(T_2 - T_1) + \beta\left[\left(\frac{T_2}{100}\right)^2 - \left(\frac{T_1}{100}\right)^2\right] + \gamma\left[\left(\frac{T_2}{100}\right)^3 - \left(\frac{T_1}{100}\right)^3\right]$$

Values of α, β, and γ for several compounds are given as follows:

	α	β	γ	Reference
CO_2	6.85	23.7	−0.254	*
H_2O	6.89	18.25	−0.106	†
N_2	6.30	5.05	−0.0355	†
O_2	6.13	8.30	−0.0829	*
Air	6.27	5.80	−0.0472	*
H_2	6.88	0.183	+0.0287	†
CO	6.25	5.80	−0.0472	†
SO_2	8.12	18.95	−0.2165	†

* Justi, E., and H. Lüder, *Forsch. Gebiete Ingenieurw.*, **6**, 211 (1935).
† Bryant, W. M. D., *Ind. Eng. Chem.*, **25**, 820 (1933).

TABLE A.4.—INTEGRAL HEATS OF SOLUTION *

Moles of H_2O/ mole of solute	1000 Btu/lb-Mole of Solute										
	HBr(*g*)	HI(*g*)	HCl(*g*)	H_2SO_4	HNO_3	KOH	NaOH	NH_3(*g*)	$CaCl_2$	NaCl	NH_4Cl
0	0	0	0	0	0	0	0	0	0	0	0
1	−19.1	−16.2	−10.8	−12.6	−6.1	−5.8	−3.6	−12.6	—	—	—
2	−25.0	−22.7	−20.7	−18.0	−8.7	−11.7	−8.3	−14.0	—	—	—
3	−28.1	−26.8	−24.1	−21.1	−10.3	−17.3	−12.6	−14.4	—	—	—
4	−30.4	−29.1	−25.7	−23.0	−11.2	−19.8	−15.1	−14.6	—	—	—
5	−31.5	−31.0	−27.0	−24.3	−11.9	−20.9	−16.7	−14.75	−21.6	+0.9	+5.4
6	−32.6	−32.2	−27.7	−25.4	−12.6	−21.4	−17.8	−14.9	—	—	—
7	−33.3	−32.5	−28.4	−26.1	−12.7	−21.8	−18.2	−15.0	—	—	—
8	−34.0	−33.1	−28.8	−27.0	−12.8	−22.1	−18.4	−15.1	—	—	—
9	−34.1	−33.4	−29.0	−27.4	−12.9	−22.3	−18.55	−15.1	—	—	—
10	−34.2	−33.6	−29.2	−27.7	−13.0	−22.5	−18.7	−15.1	−27.1	+1.35	+6.3
12	−34.4	−33.8	−29.3	−28.4	−13.1	−22.7	−18.9	−15.1	—	—	—
15	−34.5	−34.2	−29.9	−29.2	−13.2	−22.9	−18.9	−15.1	—	—	—
20	−35.1	−34.4	−30.2	−30.8	−13.5	−22.9	−18.5	−15.1	−27.7	+1.8	+7.2

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* HOUGEN, O. A., and K. M. WATSON, "Chemical Process Principles," Part One, pp. 275, 276, John Wiley & Sons, Inc., New York, 1943.

TABLE A.5.—HEATS OF COMBUSTION OF SPECIFIC COMPOUNDS*

	Formula	Mol. wt.	State	1000 Btu/lb-mole liberated = $-\Delta H_c$†	
				Gross	Net
Paraffins:					
Methane	CH_4	16	*g*	383.0	344.9
Ethane	C_2H_6	30	*g*	671.0	613.8
Propane	C_3H_8	44	*g*	955.0	878.7
Isobutane	C_4H_{10}	58	*g*	1230.0	1134.7
n-Butane	C_4H_{10}	58	*g*	1238.3	1143.0
Isopentane	C_5H_{12}	72	*g*	1518	1403.6
n-Pentane	C_5H_{12}	72	*g*	1521	1406.6
n-Hexane	C_6H_{14}	86	*l*	1804	1670.5
n-Heptane	C_7H_{16}	100	*l*	2087	1934.4
n-Octane	C_8H_{18}	114	*l*	2370	2198
Iso-Octane	C_8H_{18}	114	*l*	2345	2173
Naphthenes:					
Cyclopropane	C_3H_6	42	*g*	894	837
Cyclobutane	C_4H_8	56	*l*	1143	1067
Cyclopentane	C_5H_{10}	70	*l*	1415	1320
Cyclohexane	C_6H_{12}	84	*l*	1692	1577
Methylcyclohexane	C_7H_{14}	98	*l*	1965	1831
Olefins:					
Ethylene	C_2H_4	28	*g*	607	569
Propylene	C_3H_6	42	*g*	885	828
Isobutylene	C_4H_8	56	*g*	1163	1087
Butene-2	C_4H_8	56	*g*	1159	1083
Butene-1	C_4H_8	56	*g*	1169	1093
Aromatics:					
Benzene	C_6H_6	78	*l*	1408	1351
Toluene	C_7H_8	92	*l*	1681	1605
O-Xylene	C_8H_{10}	106	*l*	1963	1868
m-Xylene	C_8H_{10}	106	*l*	1963	1868
p-Xylene	C_8H_{10}	106	*l*	1958	1863
Naphthalene	$C_{10}H_8$	128	*s*	2226	2150
Alcohols:					
Methanol	CH_3OH	32	*l*	307	269
Ethanol	C_2H_5OH	46	*l*	590	533
Isopropanol	C_3H_7OH	60	*l*	855	779
Aldehydes and ketones:					
Formaldehyde	CH_2O	30	*g*	241	222
Acetaldehyde	C_2H_4O	44	*g*	504	466
Acetone	C_3H_6O	58	*l*	768	711
Miscellaneous:					
Hydrogen	H_2	2	*g*	122.9	103.8
Carbon (graphite)	C	12	*s*	169.0	169.0
Carbon monoxide	CO	28	*g*	121.2	121.2
Sulfur [to $SO_2(g)$]	S	32	*s*	127.5	127.5
Sulfur [to $SO_3(g)$]	S	32	*s*	169	169

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* PERRY, J. H., "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941; DOSS, M. P., "Physical Constants of Principal Hydrocarbons," 4th ed., The Texas Company, New York, 1943; "International Critical Tables," Vol. V, p. 162, McGraw-Hill Book Company, Inc., New York, 1929.

† Net heat of combustion is equal to gross heat minus 19.07 times moles of water formed.

TABLE A.6.—HEAT OF COMBUSTION OF PETROLEUM OILS *

Deg API	Net heating value,† 1000 Btu/gal liberated	Weight ratio H/C
0	170.1	0.092
2	150.6	0.096
4	149.3	0.102
6	147.9	0.106
8	146.6	0.110
10	145.3	0.114
12	144.0	0.118
14	142.8	0.121
16	141.5	0.125
18	140.3	0.128
20	139.0	0.130
22	137.8	0.132
24	136.6	0.134
26	135.5	0.136
28	134.4	0.1375
30	133.2	0.139
32	132.1	0.140
34	130.9	0.1405
36	129.8	0.141
38	128.6	0.1415
40	127.5	0.142
42	126.3	0.1425

* Courtesy of Standard Oil Company (Indiana) Research Department.

† Basis: 60°F. (liquid).

TABLE A.7.—HEAT OF COMBUSTION OF HYDROCARBON GASES

Av. mol. wt.	Sp. gr. relative to air	Net value, Btu/cu ft *	Wt. ratio H/C
10	0.345	595	0.446
12	0.414	715	0.378
14	0.483	810	0.358
16	0.552	910	0.333
18	0.620	1020	0.308
20	0.690	1120	0.292
22	0.768	1210	0.274
24	0.827	1315	0.264
26	0.896	1415	0.252
28	0.965	1520	0.245
30	1.035	1615	0.237
35	1.207	1865	0.222
40	1.380	2120	0.210
45	1.550	2360	0.202
50	1.723	2610	0.194
55	1.895	2860	0.190
60	2.067	3100	0.185

* Basis: 60°F and atmospheric pressure.

TABLE A.8.—CRITICAL CONSTANTS *

Substance	Critical properties		
	Deg R	Atm	Cu ft/lb-mole
Acetylene	556	62.0	1.80
Air	238	37.2	1.32
Ammonia	730	111.5	1.16
Benzene	1010	47.7	4.11
n-Butane	766	36.0	4.12 ‡
Carbon dioxide	547	73.0	1.53
Carbon monoxide	241	35.0	1.44
Chlorine	750	76.1	1.99
Cyclohexane	996	40.4	4.97
Ethane	549	48.8	2.28
Ethanol	929	63.1	2.67
Ethylene	509	50.9	2.04
Helium	9.4	2.3	0.93
n-Heptane	971	26.8	6.84
n-Hexane	914	29.5	5.88
Hydrogen	59.7	12.8	1.03
Hydrogen chloride	585	81.6	1.39
Hydrogen sulfide	672	88.9	—
Isobutane	733	37.0	3.96 ‡
Isopentane	830	32.8	4.92
Methane	343	45.8	1.58
Methanol	923	78.7	1.88
Methyl chloride	750	65.8	2.19
Nitrogen	227	33.5	1.44
n-Octane	1024	24.6	7.80
Oxygen	278	49.7	1.19
n-Pentane	845	33.0	4.97
Propane	665	42.0	3.12 †
Propylene	656	45.0	2.88 ‡
Sulfur dioxide	774	77.7	1.97
Sulfur trioxide	884	83.8	2.02
Water	1165 †	218.0 †	0.91 †

* PERRY, J. H., "Chemical Engineers' Handbook," 2d ed., p. 476, McGraw-Hill Book Company, Inc., New York, 1941.

† KEENAN, J. H., and F. G. KEYES, "Steam Tables," John Wiley & Sons, Inc., New York, 1936.

‡ DOSS, M. P., "Physical Constants of Principal Hydrocarbons," 4th ed., The Texas Company, New York, 1943.

Table A.9.—Effective Liquid Density and Vapor Pressure

	Liquid density at 60°F ‡		Vapor pressure at 100°F,* lb/sq in. abs
	Lb/gal	Deg API	
Paraffins:			
Methane	2.5	.....	5480 §
Ethane	3.3	.....	786 §
Propane	4.239	146.5	195
Isobutane	4.697	119.4	74
n-Butane	4.863	110.8	52
Isopentane	5.201	94.8	21.0
n-Pentane	5.251	92.8	15.5
n-Hexane	5.526	81.6	5.0
n-Heptane	5.727	74.2	1.6
Iso-octane	5.793	71.8	1.5
n-Octane	5.885	68.6	0.6
Olefins:			
Ethylene	3.3	...	1290 §
Propylene	4.2	....	229
Isobutylene	5.018	103.2	61
Butene-2	5.118	98.6	53
Butene-1	5.001	104.3	49
Naphthenes:			
Cyclopentane	6.320 *	54.0 *	9.4
Cyclohexane	6.520	49.2	3.0
Methylcyclohexane	6.435 *	51.6 *	1.5
Aromatics:			
Benzene	7.346 *	28.9 *	3.1
Toluene	7.259 *	30.8 *	1.1
o-Xylene	7.353	28.8	0.3
m-Xylene	7.219	31.7	0.4
p-Xylene	7.194	32.3	0.4
Miscellaneous:†			
Water	8.328	10.0	1.0
Ammonia	5.136	97.8	212
Hydrogen sulfide	6.580	47.6	385

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* Doss, M. P., "Physical Constants of Principal Hydrocarbons," 4th ed., The Texas Company, New York, 1943.

† PERRY, J. H., "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

‡ California Natural Gasoline Association.

§ Extrapolated vapor-pressure curve on a Cox chart.

TABLE A.10.—THERMAL CONDUCTIVITIES OF MATERIALS *

	Btu/(hr)(sq ft)(deg F)(1/ft)					
	32°F	100°F	200°F	600°F	1000°F	1500°F
Nonmetallic (solid):						
Asbestos	0.087	0.097	0.110	0.125		
Coke (petroleum)	0.27	0.27	0.27	0.27	0.27	
Coke (powdered)	0.11	0.11	0.11			
Cotton	0.032	0.035	0.039			
Cork board	....	0.025				
Cork, ground	....	0.025				
Diatomaceous earth brick						
For temp. up to 1600°F	....	0.054	0.056	0.065	0.073	
For temp. up to 2000°F	....	0.127	0.130	0.143	0.158	0.176
For temp. up to 2500°F	....	0.128	0.131	0.148	0.163	0.183
Glass						
Borosilicate	....	0.63				
Soda	....	0.37				
Window	....	0.45				
Graphite (dense)	86.7					
Graphite (powdered)	....	0.104				
Gypsum, molded and dry	....	0.25				
Hair felt	....	0.021				
Ice	1.3					
Kapok	....	0.020				
Magnesia, 85%	....	0.039	0.041			
Paper	....	0.075				
Paraffin wax	0.14					
Rock wool	....	0.030	0.034	0.057		
Sand, dry	....	0.19				
Sawdust	....	0.03				
Wood						
Oak	....	0.12				
Pine, white	....	0.087				
Wool	0.022	0.027	0.033			
Wool felt	....	0.03				
Metals:						
Aluminum	117	118	119	134		
Brass (70 Cu, 30 Zn)	56	58	60	66		
Cast iron	32	31	30	26		
Copper, pure	224	221	218	212		
Lead	20	....	19	18		
Nickel	36	35	34	32		
Silver	242	240	238			
Steel, mild	....	....	26	25		
Tin	36	35	34			
Zinc	65	....	64	59		
Liquids:						
Ammonia	0.29					
Benzene	....	0.092				
Ethyl alcohol, 100%	0.105					
Hexane	....	0.080				
Methyl alcohol	0.124					
Octane	....	0.083				
Petroleum and products †						
Toluene	....	0.086				
Water	0.330	0.363	0.410			
Xylene	0.090					
Gases:						
Air	0.014	0.016	0.018	0.027		
Ammonia	0.013	0.016	0.018			
Carbon dioxide	0.0085	....	0.0133	0.0228		
Carbon monoxide	0.0135					
Ethane	0.0106	....	0.0175			
Hydrogen	0.100	....	0.128	0.179		
Methane	0.0175	0.0210				
Steam	....	....	0.0135	0.025		

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* McADAMS, W. H., "Heat Transmission," 2d ed., McGraw-Hill Book Company, Inc., New York, 1942.

† $k = \frac{0.068}{S}[1 - 0.0003(t - 32)]$

where S = sp. gr., 60°/60°
t = deg F
k = Btu/(hr)(sq ft)(deg F)(1/ft)

TABLE A.11.—HEATS OF FUSION AND VAPORIZATION OF A FEW COMPOUNDS *

Compound	Latent heat at 1.0 atm			
	Fusion		Vaporization	
	Btu/lb-mole	Deg F	Btu/lb-mole	Deg F
Water	2,580	32	17,500	212
Methane	403	−296	3,670	−258
Carbon tetrachloride	1,157	− 11	13,100	170
Carbon dioxide	3,420	− 72	10,850	− 82
Hydrogen bromide	1,035	−124	7,580	− 88
Hydrogen fluoride	1,970	−117	13,400	28
Hydrogen chloride	857	−174	6,950	−121
Nitrogen	310	−346	2,400	−320
Oxygen	192	−182	2,930	−297
Sulfur dioxide	3,180	−104	10,730	23

* PERRY, J. H., "Chemical Engineers' Handbook," 2d ed., pp. 496–514, McGraw-Hill Book Company, Inc., New York, 1941.

TABLE A.12.—DIMENSIONS OF WELDED AND SEAMLESS PIPE *

In.		Nominal i.d., in. for Schedule No.									
Nominal pipe size	O.d.	10	20	30	40	60	80	100	120	140	160
⅛	0.405	—	—	—	0.269	—	0.215	—	—	—	—
¼	0.540	—	—	—	0.364	—	0.302	—	—	—	—
⅜	0.675	—	—	—	0.493	—	0.423	—	—	—	—
½	0.840	—	—	—	0.622	—	0.546	—	—	—	0.466
¾	1.050	—	—	—	0.824	—	0.742	—	—	—	0.614
	1.315	—	—	—	1.049	—	0.957	—	—	—	0.815
1¼	1.660	—	—	—	1.380	—	1.278	—	—	—	1.160
1½	1.900	—	—	—	1.610	—	1.500	—	—	—	1.338
2	2.375	—	—	—	2.067	—	1.939	—	—	—	1.689
2½	2.875	—	—	—	2.469	—	2.323	—	—	—	2.125
3	3.500	—	—	—	3.068	—	2.900	—	—	—	2.626
3½	4.000	—	—	—	3.548	—	3.364	—	—	—	—
4	4.500	—	—	—	4.026	—	3.826	—	3.626	—	3.438
5	5.563	—	—	—	5.047	—	4.813	—	4.563	—	4.313
6	6.625	—	—	—	6.065	—	5.761	—	5.501	—	5.189
8	8.625	—	8.125	8.071	7.981	7.813	7.625	7.439	7.189	7.001	6.813
10	10.750	—	10.250	10.136	10.020	9.750	9.564	9.314	9.064	8.750	8.250
12	12.750	—	12.250	12.090	11.938	11.626	11.376	11.064	10.750	10.500	10.126
14 o.d.	14.000	13.5	13.376	13.250	13.126	12.814	12.500	12.126	11.876	11.500	11.188
16 o.d.	16.000	15.5	15.376	15.250	15.000	14.688	14.314	13.938	13.564	13.126	12.876
18 o.d.	18.000	17.5	17.376	17.126	16.876	16.564	16.126	15.688	15.314	14.876	14.500
20 o.d.	20.000	19.5	19.250	19.000	18.814	18.376	17.938	17.500	17.000	16.500	16.126
24 o.d.	24.000	23.5	23.250	22.876	22.626	22.126	21.564	21.000	20.500	19.876	19.376
30 o.d.	30.000	29.376	29.000	28.750	—	—	—	—	—	—	—

* The American Standards Association approved Standard ASA-B36.1C in 1939, which made the former terms "standard," "extra strong," etc., obsolete. The schedule numbers are an approximate index of the allowable pressure for the pipe as given by the formula:

$$P = \frac{(\text{schedule number})(S)}{1000}$$

where P is the allowable pressure in pounds per square inch and S is the allowable tensile strength in pounds per square inch. The former "standard pipe" corresponds to Schedule 40 for 10-in. pipe and smaller. The former "extra-strong" pipe corresponds to Schedule 80 for 8-in. pipe and smaller.

TABLE A.13.—MISCELLANEOUS CONVERSION FACTORS

Length

1 mile	5280 feet
1 rod	16.5 feet
1 yard	3 feet
1 foot	12 inches
1 inch	2.54 centimeters
1 kilometer	1000 meters
1 meter	100 centimeters
1 micron	10^{-6} meter
1 angstrom unit	10^{-10} meter

Mass

1 ton (short)	2000 pounds
1 hundredweight	100 pounds
1 pound	16 ounces
1 pound	7000 grains
1 pound	453.6 grams
1 kilogram	1000 grams
1 pound-mole	pounds equal to molecular weight
1 gram-mole	grams equal to molecular weight

Volume

1 barrel	42 gallons
1 gallon	4 quarts
1 gallon	231 cubic inches
1 gallon	128 fluid ounces
1 British gallon	1.2 U.S. gallons
1 quart	2 pints
1 pint	4 gills
1 liter	1000 cubic centimeters
1 stere	1000 liters
1 pound-mole (gas)	359 cubic feet at 32 degrees Fahrenheit and 1 atmosphere
1 pound-mole (gas)	379 cubic feet at 60 degrees Fahrenheit and 1 atmosphere
1 pound-mole (gas)	453.6 gram-moles
1 gram-mole (gas)	22.4 liters at 0 degrees centigrade and 1 atmosphere

Force

1 pound	32.2 poundal
1 pound	444.8 dynes
1 poundal	1 lb ft/(sec)(sec)
1 dyne	1 g cm/(sec)(sec)

Pressure

1 atmosphere	14.7 pounds per square inch
1 atmosphere	760 millimeters of mercury
1 atmosphere	29.9 inches of mercury
1 pound per square inch	2.31 feet of water

TABLE A.13.—MISCELLANEOUS CONVERSION FACTORS (*Continued*)

Temperature	
Degrees Fahrenheit	1.8 (degrees centigrade) + 32
Degrees Kelvin	degrees centigrade + 273
Degrees Rankine	degrees Fahrenheit + 460
Degrees Rankine	1.8 (degrees Kelvin)
Energy	
1 British thermal unit (Btu)	778 foot-pounds
1 British thermal unit	1054 joules
1 British thermal unit	252 gram-calories
1 foot-pound	32.2 foot-poundals
Power	
1 horsepower	33,000 foot-pounds per minute
1 horsepower	746 watts
1 horsepower	42.4 Btu per minute
1 kilowatt	1000 watts
1 ton of refrigeration	200 Btu per minute
1 boiler horsepower	33,475 Btu per hour
1 boiler horsepower	34.5 pounds of water evaporated per hour from and at 212 degrees Fahrenheit

TABLE A.14.—SATURATED STEAM: TEMPERATURE TABLE *

Temp., deg F	Absolute pressure		Specific volume, cu ft/lb		Enthalpy, Btu/lb		
	lb/sq in.	In. Hg 32°F	Sat. liquid	Sat. vapor	Sat. liquid	Latent heat	Sat. vapor
32	0.0886	0.1806	0.01602	3305.7	0	1075.1	1075.1
34	0.0961	0.1957	0.01602	3060.4	2.01	1074.0	1076.0
36	0.1041	0.2120	0.01602	2836.6	4.03	1072.9	1076.9
38	0.1126	0.2292	0.01602	2632.2	6.04	1071.7	1077.7
40	0.1217	0.2478	0.01602	2445.1	8.05	1070.5	1078.6
42	0.1315	0.2677	0.01602	2271.8	10.06	1069.3	1079.4
44	0.1420	0.2891	0.01602	2112.2	12.06	1068.2	1080.3
46	0.1532	0.3119	0.01602	1965.5	14.07	1067.1	1081.2
48	0.1652	0.3364	0.01602	1829.9	16.07	1065.9	1082.0
50	0.1780	0.3624	0.01602	1704.9	18.07	1064.8	1082.9
52	0.1918	0.3905	0.01603	1588.4	20.07	1063.6	1083.7
54	0.2063	0.4200	0.01603	1482.4	22.07	1062.5	1084.6
56	0.2219	0.4518	0.01603	1383.5	24.07	1061.4	1085.5
58	0.2384	0.4854	0.01603	1292.7	26.07	1060.2	1086.3
60	0.2561	0.5214	0.01603	1208.1	28.07	1059.1	1087.2
62	0.2749	0.5597	0.01604	1129.7	30.06	1057.9	1088.0
64	0.2949	0.6004	0.01604	1057.1	32.06	1056.8	1088.9
66	0.3162	0.6438	0.01604	989.6	34.06	1055.7	1089.8
68	0.3388	0.6898	0.01605	927.0	36.05	1054.5	1090.6
70	0.3628	0.7387	0.01605	868.9	38.05	1053.4	1091.5
72	0.3883	0.7906	0.01606	814.9	40.04	1052.3	1092.3
74	0.4153	0.8456	0.01606	764.7	42.04	1051.2	1093.2
76	0.4440	0.9040	0.01607	718.0	44.03	1050.1	1094.1
78	0.4744	0.9659	0.01607	674.4	46.03	1048.9	1094.9
80	0.5067	1.032	0.01607	633.7	48.02	1047.8	1095.8
82	0.5409	1.101	0.01608	595.8	50.02	1046.6	1096.6
84	0.5772	1.175	0.01608	560.4	52.01	1045.5	1097.5
86	0.6153	1.253	0.01609	527.6	54.01	1044.4	1098.4
88	0.6555	1.335	0.01609	497.0	56.00	1043.2	1099.2
90	0.6980	1.421	0.01610	468.4	58.00	1042.1	1100.1
92	0.7429	1.513	0.01611	441.7	59.99	1040.9	1100.9
94	0.7902	1.609	0.01611	416.7	61.98	1039.8	1101.8
96	0.8403	1.711	0.01612	393.2	63.98	1038.7	1102.7
98	0.8930	1.818	0.01613	371.3	65.98	1037.5	1103.5
100	0.9487	1.932	0.01613	350.8	67.97	1036.4	1104.4
102	1.0072	2.051	0.01614	331.5	69.96	1035.2	1105.2
104	1.0689	2.176	0.01614	313.5	71.96	1034.1	1106.1
106	1.1338	2.308	0.01615	296.5	73.95	1033.0	1107.0
108	1.2020	2.447	0.01616	280.7	75.94	1032.0	1107.9
110	1.274	2.594	0.01617	265.7	77.94	1030.9	1108.8
112	1.350	2.749	0.01617	251.6	79.93	1029.7	1109.6
114	1.429	2.909	0.01618	238.5	81.93	1028.6	1110.5
116	1.512	3.078	0.01619	226.2	83.92	1027.5	1111.4
118	1.600	3.258	0.01620	214.5	85.92	1026.4	1112.3

* Abridged version of steam tables as published by Combustion Engineering Co.

TABLE A.14.—SATURATED STEAM: TEMPERATURE TABLE * (*Continued*)

Temp., deg F	Absolute pressure		Specific volume, cu ft/lb		Enthalpy, Btu/lb		
	lb/sq in.	In. Hg 32°F	Sat. liquid	Sat. vapor	Sat. liquid	Latent heat	Sat. vapor
120	1.692	3.445	0.01620	203.47	87.91	1025.3	1113.2
122	1.788	3.640	0.01621	193.18	89.91	1024.1	1114.0
124	1.889	3.846	0.01622	183.46	91.90	1023.0	1114.9
126	1.995	4.062	0.01623	174.28	93.90	1021.8	1115.7
128	2.105	4.286	0.01624	165.72	95.90	1020.7	1116.6
130	2.221	4.522	0.01625	157.57	98.89	1019.5	1117.4
132	2.343	4.770	0.01626	149.85	99.89	1018.3	1118.2
134	2.470	5.029	0.01626	142.61	101.89	1017.2	1119.1
136	2.603	5.300	0.01627	135.75	103.88	1016.0	1119.9
138	2.742	5.583	0.01628	129.28	105.88	1014.9	1120.8
140	2.887	5.878	0.01629	123.18	107.88	1013.7	1121.6
142	3.039	6.187	0.01630	117.39	109.88	1012.5	1122.4
144	3.198	6.511	0.01631	111.90	111.88	1011.3	1123.2
146	3.363	6.847	0.01632	106.74	113.88	1010.2	1124.1
148	3.536	7.199	0.01633	101.84	115.87	1009.0	1124.9
150	3.716	7.566	0.01634	97.20	117.87	1007.8	1125.7
152	3.904	7.948	0.01635	92.81	119.87	1006.7	1126.6
154	4.100	8.348	0.01636	88.64	121.87	1005.5	1127.4
156	4.305	8.765	0.01637	84.68	123.87	1004.4	1128.3
158	4.518	9.199	0.01638	79.92	125.87	1003.2	1129.1
160	4.739	9.649	0.01639	77.39	127.87	1002.0	1129.9
162	4.970	10.12	0.01640	74.02	129.88	1000.8	1130.7
164	5.210	10.61	0.01642	70.81	131.88	999.7	1131.6
166	5.460	11.12	0.01643	67.78	133.88	998.5	1132.4
168	5.720	11.65	0.01644	64.89	135.88	997.3	1133.2
170	5.990	12.20	0.01645	62.14	137.89	996.1	1134.0
172	6.272	12.77	0.01646	59.52	139.89	995.0	1134.9
174	6.565	13.37	0.01647	57.03	141.89	993.8	1135.7
176	6.869	13.99	0.01648	54.66	143.90	992.6	1136.5
178	7.184	14.63	0.01650	52.41	145.90	991.4	1137.3
180	7.510	15.29	0.01651	50.28	147.91	990.2	1138.1
182	7.849	15.98	0.01652	48.24	149.92	989.0	1138.9
184	8.201	16.70	0.01653	46.30	151.92	987.8	1139.7
186	8.566	17.44	0.01654	44.45	153.93	986.6	1140.5
188	8.944	18.21	0.01656	42.69	155.94	985.3	1141.3
190	9.336	19.01	0.01657	41.01	157.95	984.1	1142.1
192	9.744	19.84	0.01658	39.40	159.95	982.8	1142.8
194	10.168	20.70	0.01659	37.86	161.96	981.5	1143.5
196	10.605	21.59	0.01661	36.40	163.97	980.3	1144.3
198	11.057	22.51	0.01662	35.00	165.98	979.0	1145.0
200	11.525	23.46	0.01663	33.67	167.99	977.8	1145.8
202	12.010	24.45	0.01665	32.39	170.01	976.8	1146.6
204	12.512	25.47	0.01666	31.17	172.02	975.3	1147.3

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* Abridged version of steam tables as published by Combustion Engineering Co.

TABLE A.14.—SATURATED STEAM: TEMPERATURE TABLE * (*Continued*)

Temp., deg F	Absolute pressure		Specific volume, cu ft/lb		Enthalpy, Btu/lb		
	lb/sq in.	In. Hg 32°F	Sat. liquid	Sat. vapor	Sat. liquid	Latent heat	Sat. vapor
206	13.031	26.53	0.01667	30.01	174.03	974.1	1148.1
208	13.568	27.62	0.01669	28.90	176.04	972.8	1148.8
210	14.123	28.75	0.01670	27.83	178.06	971.5	1149.6
212	14.696	29.92	0.01672	26.83	180.07	970.3	1150.4
215	15.591		0.01674	25.37	183.10	968.3	1151.4
220	17.188		0.01677	23.16	188.14	965.2	1153.3
225	18.915		0.01681	21.17	193.18	961.9	1155.1
230	20.78		0.01684	19.388	198.22	958.7	1156.9
235	22.80		0.01688	17.778	203.28	955.3	1158.6
240	24.97		0.01692	16.324	208.34	952.1	1160.4
245	27.31		0.01696	15.027	213.41	948.7	1162.1
250	29.82		0.01700	13.841	218.48	945.3	1163.8
260	35.43		0.01708	11.771	228.65	938.6	1167.3
270	41.85		0.01717	10.070	238.84	931.8	1170.6
280	49.20		0.01726	8.651	249.06	924.6	1173.7
290	57.55		0.01735	7.465	259.31	917.4	1176.7
300	67.01		0.01745	6.471	269.60	910.1	1179.7
310	77.68		0.01755	5.628	279.92	902.6	1182.5
320	89.65		0.01765	4.915	290.29	895.0	1185.3
330	103.03		0.01776	4.310	300.69	887.1	1187.8
340	117.99		0.01788	3.789	311.14	879.2	1190.3
350	134.62		0.01799	3.342	321.64	871.0	1192.6
360	153.01		0.01811	2.958	332.19	862.5	1194.7
370	173.33		0.01823	2.625	342.79	853.8	1196.6
380	195.70		0.01836	2.336	253.45	844.9	1198.4
390	220.29		0.01850	2.083	364.17	835.7	1199.9
400	247.25		0.01864	1.8632	374.97	826.2	1201.2
420	308.82		0.01894	1.4995	396.78	806.7	1203.5
440	381.59		0.01926	1.2166	418.91	785.9	1204.8
460	466.97		0.0196	0.9941	441.42	763.6	1205.0
480	566.12		0.0200	0.8172	464.37	739.8	1204.2
500	680.80		0.0204	0.6748	487.80	714.2	1202.0
525	848.37		0.0210	0.5338	518.0	679.2	1197.2
550	1045.6		0.0218	0.4239	594.3	640.9	1190.2
575	1275.7		0.0226	0.3369	582.1	597.4	1179.5
600	1543.2		0.0236	0.2668	616.8	548.4	1165.2
650	2208.8		0.0268	0.1616	696.0	422.7	1118.7
700	3094.1		0.0369	0.0758	823.9	171.7	995.6
705.34 **	3206.2		0.0541	0.0541	910.3	0	910.3

* Abridged version of steam tables as published by Combustion Engineering Co.

** Critical temperature.

TABLE A.15.—SUPERHEATED STEAM *

Abs. press., lb/sq in. (sat. temp.)		Sat. water	Sat. steam	Temperature, deg. Fahrenheit								
				200	250	300	350	400	450	500	600	700
	Sh†			98.24	148.24	198.24	248.24	298.24	348.24	398.24	498.24	598.24
1	v‡	0.0161	333.79	392.5	422.5	452.1	482.1	511.7	541.8	571.3	630.9	690.6
(101.76)	h§	69.72	1105.2	1149.2	1171.9	1194.4	1217.3	1240.2	1263.5	1286.7	1333.9	1382.1
	Sh			37.75	87.75	137.75	187.75	237.75	287.75	337.75	437.75	537.75
5	v	0.0164	73.600	78.17	84.24	90.21	96.26	102.19	108.23	114.16	126.11	138.05
(162.25)	h	130.13	1130.8	1148.3	1171.1	1193.6	1216.6	1239.8	1263.0	1286.1	1333.5	1381.8
	Sh			6.79	56.79	106.79	156.79	206.79	256.79	306.79	406.79	506.79
10	v	0.0166	38.462	38.88	41.96	44.98	48.02	51.01	54.04	57.02	63.01	68.99
(193.21)	h	161.17	1143.3	1146.7	1170.2	1192.8	1216.0	1239.3	1262.5	1285.8	1333.3	1381.6
	Sh				38.00	88.00	138.00	188.00	238.00	288.00	388.00	488.00
14.696	v	0.0167	26.828		28.44	30.52	32.61	34.65	36.73	38.75	42.83	46.91
(212.00)	h	180.07	1150.4		1169.2	1192.0	1215.4	1238.9	1262.1	1285.4	1333.0	1381.4
	Sh				36.97	86.97	136.97	186.97	236.97	286.97	386.97	486.97
15	v	0.0167	26.320		27.86	29.90	31.94	33.95	35.98	37.97	41.98	45.97
(213.03)	h	181.11	1150.7		1169.2	1192.0	1215.4	1238.9	1262.1	1285.4	1333.0	1381.4
	Sh				22.04	72.04	122.04	172.04	222.04	272.04	372.04	472.04
20	v	0.0168	20.110		20.81	22.36	23.91	25.43	26.95	28.45	31.46	34.46
(227.96)	h	196.16	1156.1		1168.0	1191.1	1214.8	1238.4	1261.6	1285.0	1332.7	1381.2
	Sh				9.93	59.93	109.93	159.93	209.93	259.93	359.93	549.93
25	v	0.0169	16.321		16.58	17.84	19.08	20.30	21.53	22.73	25.15	27.55
(240.07)	h	208.41	1160.4		1166.3	1190.2	1214.1	1237.9	1261.1	1284.6	1332.4	1381.0
	Sh					49.66	99.66	149.66	199.66	249.66	349.66	449.66
30	v	0.0170	13.763			14.82	15.87	16.89	17.91	18.92	20.94	22.94
(250.34)	h	218.83	1164.0			1189.2	1213.4	1237.4	1260.6	1284.2	1332.1	1380.8
	Sh					40.72	90.72	140.72	190.72	240.72	340.72	440.72
35	v	0.0171	11.907			12.66	13.57	14.45	15.33	16.20	17.94	19.66
(259.28)	h	227.92	1167.0			1188.2	1212.7	1236.9	1260.1	1283.8	1331.9	1380.6
	Sh					32.76	82.76	132.76	182.76	232.76	332.76	432.76
40	v	0.0172	10.506			11.04	11.84	12.62	13.40	14.16	15.68	17.19
(267.24)	h	236.02	1169.7			1187.1	1211.9	1236.4	1259.6	1283.4	1331.6	1380.4
	Sh					25.55	75.55	125.55	175.55	225.55	325.55	425.55
45	v	0.0172	9.408			9.785	10.50	11.20	11.89	12.57	13.93	15.27
(274.45)	h	243.38	1172.0			1185.9	1211.1	1235.8	1259.1	1283.0	1331.3	1380.1
	Sh					18.99	68.99	118.99	168.99	218.99	318.99	418.99
50	v	0.0173	8.522			8.777	9.430	10.06	10.69	11.30	12.53	13.74
(281.01)	h	250.09	1174.0			1184.6	1210.3	1235.2	1258.6	1282.6	1331.0	1379.9
	Sh					12.93	62.93	112.93	162.93	212.93	312.93	412.93
55	v	0.0173	7.792			7.950	8.553	9.130	9.703	10.26	11.38	12.48
(287.07)	h	256.30	1175.8			1183.2	1209.4	1234.6	1258.2	1282.2	1330.7	1379.7
	Sh					7.29	57.29	107.29	157.29	207.29	307.29	407.29
60	v	0.0174	7.179			7.260	7.821	8.353	8.882	9.398	10.42	11.44
(292.71)	h	262.10	1177.5			1181.8	1208.5	1234.0	1257.7	1281.8	1330.4	1379.5
	Sh					2.03	52.03	102.03	152.03	202.03	302.02	402.03
65	v	0.0174	6.654			6.674	7.202	7.696	8.187	8.665	9.614	10.55
(297.97)	h	267.51	1179.1			1180.4	1207.6	1233.4	1257.2	1281.4	1330.1	1379.3
	Sh						47.08	97.08	147.08	197.08	297.08	397.08
70	v	0.0175	6.210				6.671	7.132	7.592	8.036	8.920	9.791
(302.92)	h	272.61	1180.5				1206.7	1232.8	1256.7	1281.0	1329.9	1379.0
	Sh						42.40	92.40	142.40	192.40	292.40	392.40
75	v	0.0175	5.820				6.210	6.644	7.076	7.492	8.319	9.133
(307.60)	h	277.44	1181.9				1205.8	1232.2	1256.2	1280.6	1329.6	1378.8

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* Abridged version of steam tables as published by Combustion Engineering Co.

† Superheat, deg F.

‡ Specific volume, cu ft/lb.

§ Enthalpy, Btu/lb.

TABLE A.15.—SUPERHEATED STEAM (*Continued*)

Abs. press., lb/sq in. (sat. temp.)		Sat. water	Sat. Steam	Temperature, deg. Fahrenheit								
				340	360	380	400	420	450	500	600	700
	Sh			27.97	47.97	67.97	87.97	107.97	137.97	187.97	287.97	387.97
80	v	0.0176	5.476	5.720	5.889	6.055	6.217	6.384	6.623	7.015	7.793	8.558
(312.03)	h	282.02	1183.1	1200.0	1211.0	1221.2	1231.5	1240.3	1255.7	1280.2	1329.3	1378.5
	Sh			23.75	43.75	63.75	83.75	103.75	133.75	183.75	283.75	383.75
85	v	0.0176	5.169	5.368	5.528	5.685	5.839	5.995	6.226	6.594	7.329	8.050
(316.25)	h	286.40	1184.3	1198.5	1210.0	1220.5	1230.7	1239.7	1255.1	1279.7	1329.0	1378.3
	Sh			19.73	39.73	59.73	79.73	99.73	129.73	179.73	279.73	379.73
90	v	0.0177	4.898	5.055	5.208	5.357	5.504	5.653	5.869	6.220	6.916	7.599
(320.27)	h	290.57	1185.4	1197.3	1209.0	1219.8	1230.0	1239.1	1254.5	1279.3	1328.7	1378.1
	Sh			15.87	35.87	55.87	75.87	95.87	125.87	175.87	275.87	375.87
95	v	0.0177	4.653	4.773	4.921	5.063	5.205	5.346	5.552	5.886	6.547	7.195
(324.13)	h	294.58	1186.4	1196.0	1208.0	1219.0	1229.3	1238.6	1254.0	1278.9	1328.4	1377.8
	Sh			12.17	32.17	52.17	72.17	92.17	122.17	172.17	272.17	372.17
100	v	0.0177	4.433	4.520	4.663	4.801	4.936	5.070	5.266	5.589	6.217	6.836
(327.83)	h	298.43	1187.3	1194.9	1207.0	1218.3	1228.4	1238.6	1253.7	1278.6	1327.9	1377.5
	Sh			5.21	25.21	45.21	65.21	85.21	115.21	165.21	265.21	365.21
110	v	0.0178	4.050	4.084	4.217	4.345	4.469	4.592	4.773	5.069	5.643	6.208
(334.79)	h	305.69	1189.0	1192.2	1204.9	1216.4	1226.9	1236.9	1252.4	1277.5	1327.4	1377.1
	Sh				18.74	38.74	58.74	78.74	108.74	158.74	258.74	358.74
120	v	0.0179	3.728		3.845	3.963	4.079	4.194	4.361	4.635	5.165	5.685
(341.26)	h	312.46	1190.6		1202.7	1214.7	1225.4	1235.7	1251.4	1276.7	1326.8	1376.7
	Sh				12.69	32.69	52.69	72.69	102.69	152.69	252.69	352.69
130	v	0.0180	3.455		3.528	3.641	3.750	3.857	4.013	4.268	4.760	5.242
(347.31)	h	318.81	1192.0		1200.4	1212.7	1223.6	1234.3	1250.3	1275.8	1326.1	1376.1
	Sh				6.97	26.97	46.97	66.97	96.97	146.97	246.97	346.97
140	v	0.0180	3.220		3.258	3.364	3.467	3.567	3.715	3.954	4.413	4.862
(353.02)	h	324.83	1193.3		1198.0	1210.6	1221.8	1232.9	1249.1	1275.0	1325.5	1375.7
	Sh					21.57	41.57	61.57	91.57	141.57	241.57	341.57
150	v	0.0181	3.016			3.124	3.221	3.317	3.456	3.681	4.112	4.533
(358.43)	h	330.53	1194.4			1208.4	1220.0	1231.4	1248.0	1274.1	1324.9	1375.1
	Sh					16.45	36.45	56.45	86.45	136.45	236.45	336.45
160	v	0.0182	2.834			2.913	3.006	3.097	3.230	3.443	3.849	4.245
(363.55)	h	335.95	1195.5			1206.0	1218.3	1230.0	1246.9	1273.2	1324.1	1374.7

Abs. press., lb/sq in. (sat. temp.)		Sat. water	Sat. steam	Temperature, deg. Fahrenheit								
				400	420	440	460	480	500	550	600	700
	Sh			31.58	51.58	71.58	91.58	111.58	131.58	181.58	231.58	331.58
170	v	0.0182	2.674	2.816	2.903	2.988	3.071	3.151	3.232	3.426	3.617	3.991
(368.42)	h	341.11	1196.3	1216.5	1228.4	1240.5	1251.3	1261.8	1272.3	1298.2	1323.5	1374.2
	Sh			26.92	46.92	66.92	86.92	106.92	126.92	176.92	226.92	326.92
180	v	0.0183	2.532	2.648	2.731	2.812	2.892	2.968	3.045	3.229	3.410	3.765
(373.08)	h	346.07	1197.2	1214.6	1226.8	1239.2	1250.2	1260.8	1271.5	1297.4	1322.8	1373.7
	Sh			22.45	42.45	62.45	82.45	102.45	122.45	172.45	222.45	322.45
190	v	0.0183	2.404	2.496	2.576	2.654	2.731	2.804	2.877	3.053	3.225	3.563
(377.55)	h	350.83	1198.0	1212.7	1225.1	1237.7	1249.0	1259.8	1270.5	1296.6	1322.1	1373.1
	Sh			18.18	38.18	58.18	78.18	98.18	118.18	168.18	218.18	318.18
200	v	0.0184	2.288	2.360	2.437	2.512	2.585	2.656	2.726	2.895	3.059	3.381
(381.82)	h	355.40	1198.7	1210.8	1223.7	1236.3	1247.9	1258.7	1269.4	1295.6	1321.4	1372.5
	Sh			14.07	34.07	54.07	74.07	94.07	114.07	164.07	214.07	314.07
210	v	0.0184	2.183	2.237	2.311	2.384	2.454	2.522	2.589	2.751	2.909	3.216
(385.93)	h	359.80	1199.4	1208.8	1221.8	1234.7	1246.5	1257.7	1268.5	1295.0	1320.7	1372.1

TABLE A.15.—SUPERHEATED STEAM (*Continued*)

Abs. press., lb/sq in. (sat. temp.)		Sat. water	Sat. steam	Temperature, deg. Fahrenheit								
				400	420	440	460	480	500	550	600	700
220 (389.89)	Sh			10.11	30.11	50.11	70.11	90.11	110.11	160.11	210.11	310.11
	v	0.0185	2.086	2.124	2.196	2.267	2.335	2.400	2.465	2.621	2.772	3.067
	h	364.05	1199.9	1206.8	1220.1	1233.2	1245.2	1256.7	1267.5	1294.1	1320.0	1371.6
230 (393.70)	Sh			6.30	26.30	46.30	66.30	86.30	106.30	156.30	206.30	306.30
	v	0.0186	1.9989	2.021	2.091	2.160	2.226	2.289	2.352	2.502	2.647	2.930
	h	368.16	1200.4	1204.9	1218.3	1231.6	1243.8	1255.6	1266.7	1293.3	1319.3	1371.1
240 (397.40)	Sh				22.60	42.60	62.60	82.60	102.60	152.60	202.60	302.60
	v	0.0186	1.9176		1.995	2.062	2.126	2.187	2.247	2.392	2.532	2.805
	h	372.16	1200.9		1216.6	1230.0	1242.5	1254.4	1265.7	1292.5	1318.6	1370.5

Abs. press., lb/sq in. (sat. temp.)		Sat. water	Sat. Steam	Temperature, deg. Fahrenheit								
				420	440	460	480	500	520	550	600	700
250 (400.97)	Sh			19.03	39.03	59.03	79.03	99.03	119.03	149.03	199.03	299.03
	v	0.0187	1.8431	1.9065	1.9711	2.0334	2.0932	2.1515	2.2085	2.2920	2.4272	2.6897
	h	376.04	1201.4	1214.6	1228.3	1241.0	1253.2	1264.7	1274.5	1291.6	1317.9	1370.0
260 (404.43)	Sh			15.57	35.57	55.57	75.57	95.57	115.57	145.57	195.57	295.57
	v	0.0187	1.7742	1.8246	1.8876	1.9482	2.0063	2.0631	2.1185	2.1991	2.3299	2.5833
	h	379.78	1201.8	1212.8	1226.6	1239.5	1252.0	1263.6	1273.8	1290.8	1317.1	1369.5
270 (407.79)	Sh			12.21	32.21	52.21	72.21	92.21	112.21	142.41	192.21	292.21
	v	0.0188	1.7101	1.7486	1.8101	1.8692	1.9259	1.9810	2.0350	2.1131	2.2399	2.4847
	h	383.43	1202.2	1211.0	1224.9	1238.0	1250.6	1262.5	1273.0	1290.0	1316.4	1369.0
280 (411.06)	Sh			8.94	28.94	48.94	68.94	88.94	108.94	138.94	188.94	288.94
	v	0.0188	1.6504	1.6780	1.7381	1.7957	1.8512	1.9048	1.9575	2.0334	2.1562	2.3932
	h	386.99	1202.5	1209.0	1223.2	1236.5	1249.4	1261.5	1272.6	1289.1	1315.7	1368.5
300 (417.33)	Sh			2.67	22.67	42.67	62.67	82.67	102.67	132.67	182.67	282.67
	v	0.0189	1.5426	1.5506	1.6082	1.6634	1.7164	1.7677	1.8172	1.8896	2.0056	2.2286
	h	393.85	1203.2	1205.2	1219.5	1233.4	1246.6	1259.2	1270.5	1287.4	1314.4	1367.4
350 (431.71)	Sh				8.29	28.29	48.29	68.29	88.29	118.29	168.29	268.29
	v	0.0191	1.3255		1.3472	1.3976	1.4460	1.4923	1.5377	1.6016	1.7041	1.8991
	h	409.70	1204.4		1210.3	1224.8	1239.5	1252.9	1265.5	1282.9	1310.6	1364.7

Abs. Press., lb/sq in. (sat. temp.)		Sat. water	Sat. steam	Temperature, deg. Fahrenheit								
				460	480	500	520	540	560	580	600	700
440 (444.58)	Sh			15.42	35.42	55.42	75.42	95.42	115.42	135.42	155.42	255.42
	v	0.0193	1.1609	1.1972	1.2422	1.2849	1.3269	1.3660	1.4042	1.4413	1.4777	1.6522
	h	424.02	1204.9	1216.5	1231.6	1245.9	1259.9	1272.4	1284.3	1295.8	1307.0	1362.1
450 (456.27)	Sh			3.73	23.73	43.73	63.73	83.73	103.73	123.73	143.73	243.73
	v	0.0195	1.0318	1.0401	1.0824	1.1230	1.1617	1.1982	1.2337	1.2681	1.3013	1.4593
	h	437.18	1205.0	1207.9	1223.7	1238.7	1253.8	1266.9	1280.0	1291.8	1303.1	1359.1
500 (467.00)	Sh				13.00	33.00	53.00	73.00	93.00	113.00	133.00	233.00
	v	0.0197	0.9274		0.9538	0.9926	1.0290	1.0636	1.0969	1.1292	1.1600	1.3051
	h	449.40	1204.9		1215.3	1213.4	1246.6	1261.1	1275.0	1287.3	1299.3	1356.3

TABLE A.15.—SUPERHEATED STEAM (*Continued*)

Abs. press., lb/sq in. (sat. temp.)		Sat. water	Sat. steam	Temperature, deg. Fahrenheit							
				500	520	540	560	580	600	650	700
	Sh			23.06	43.06	63.06	83.06	103.06	123.06	173.06	223.06
550	v	0.0199	0.8416	0.8851	0.9198	0.9530	0.9846	1.0151	1.0441	1.1132	1.1791
(476.94)	h	460.83	1204.4	1223.4	1240.0	1254.8	1269.6	1282.9	1295.2	1324.9	1353.5
	Sh			13.79	33.79	53.79	73.79	93.79	113.79	163.79	213.79
600	v	0.0201	0.7695	0.7945	0.8284	0.8605	0.8907	0.9194	0.9471	1.0123	1.0738
(486.21)	h	471.59	1203.6	1215.6	1232.5	1248.3	1263.7	1278.1	1290.9	1321.4	1350.5
	Sh				16.91	36.91	56.91	76.91	96.91	146.91	196.91
700	v	0.0205	0.6552		0.6830	0.7133	0.7419	0.7687	0.7941	0.8534	0.9084
(503.09)	h	494.49	1201.6		1217.1	1234.7	1251.3	1266.8	1281.9	1314.3	1344.6

Abs. press., lb/sq in. (sat. temp.)		Sat. water	Sat. steam	Temperature, deg. Fahrenheit							
				520	540	560	580	600	620	650	700
	Sh			1.80	21.80	41.80	61.80	81.80	101.80	131.80	181.80
800	v	0.0209	0.5685	0.5714	0.6013	0.6288	0.6545	0.6785	0.7013	0.7336	0.7838
(518.20)	h	509.7	1198.8	1200.3	1220.0	1238.2	1255.3	1271.4	1286.5	1306.8	1338.4
	Sh				8.06	28.06	48.06	68.06	88.06	118.06	168.06
900	v	0.0212	0.5006		0.5123	0.5394	0.5644	0.5876	0.6094	0.6399	0.6866
(531.94)	h	526.6	1195.6		1204.0	1224.2	1242.6	1260.0	1276.5	1298.6	1331.8

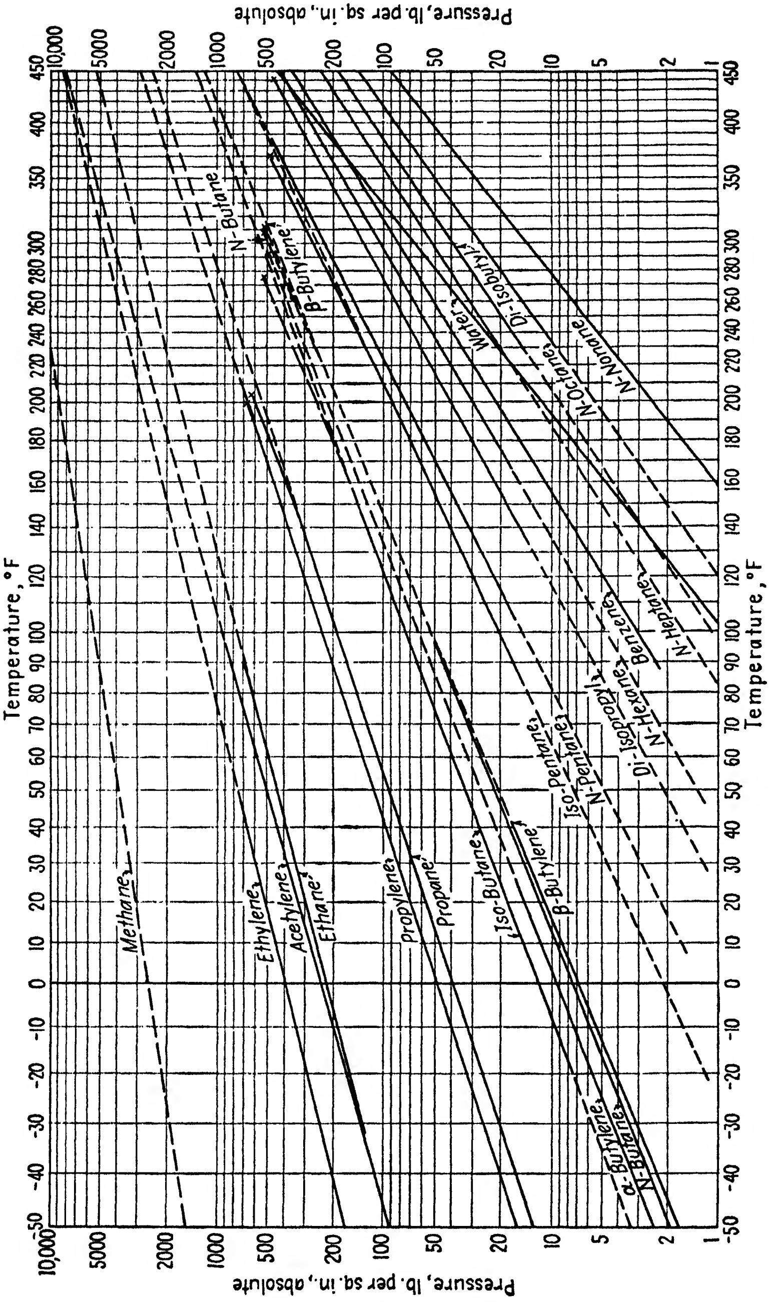


FIG. A.1.—Vapor-pressure curves of hydrocarbons. (*Perry, J. H., "Chemical Engineers' Handbook."*)

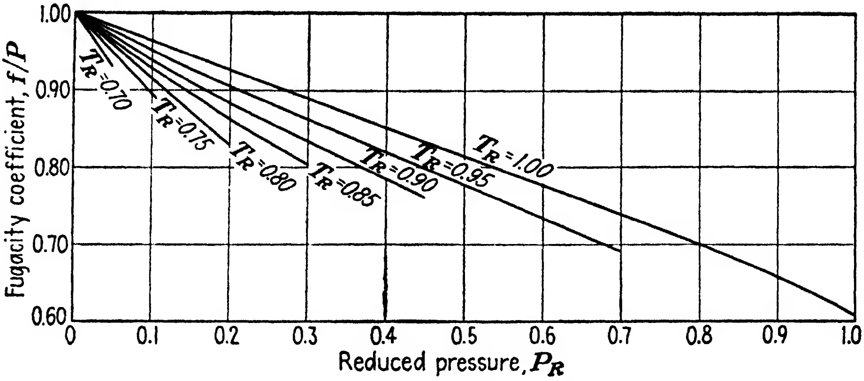


Fig. A.2.—Fugacity coefficient at low reduced temperatures and pressures. [*Newton, H. R., Ind. Eng. Chem.*, **27**, 302 (1935).]

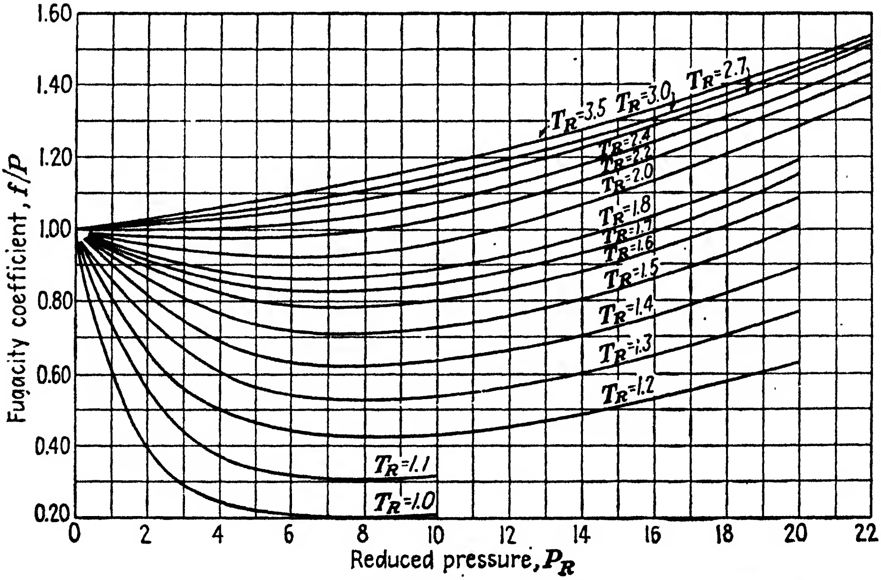


Fig. A.3.—Fugacity coefficients at intermediate reduced temperatures and pressures. [*Newton, H. R., Ind. Eng. Chem.*, **27**, 302 (1935).]

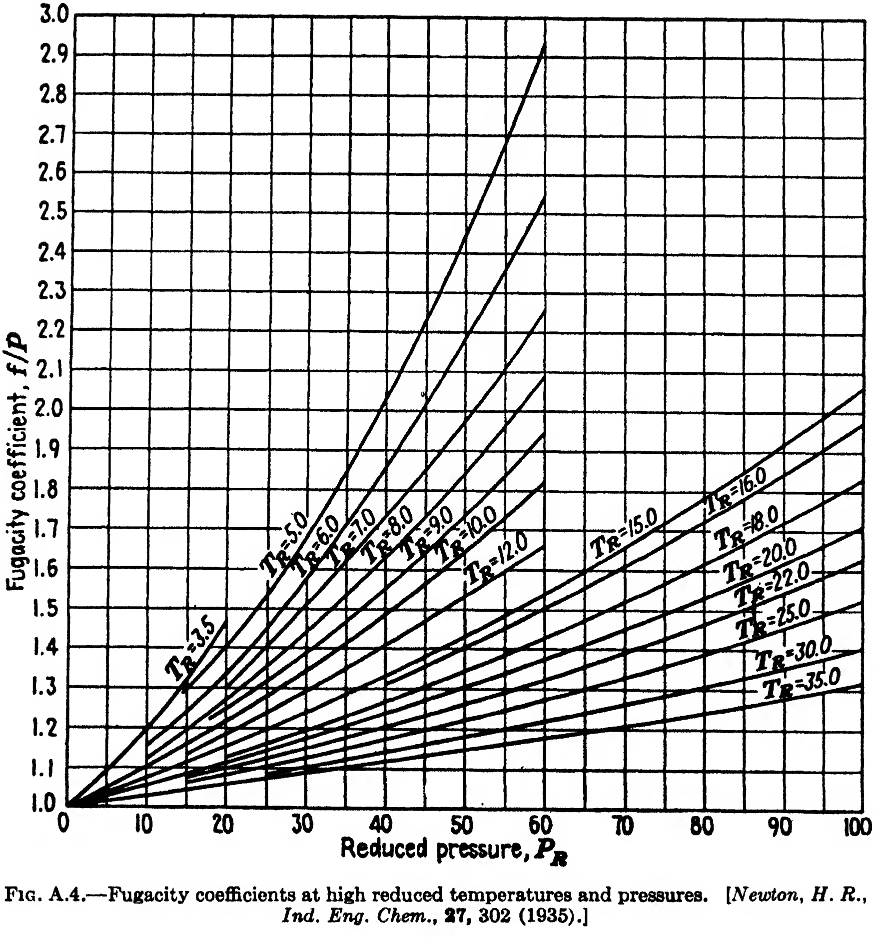
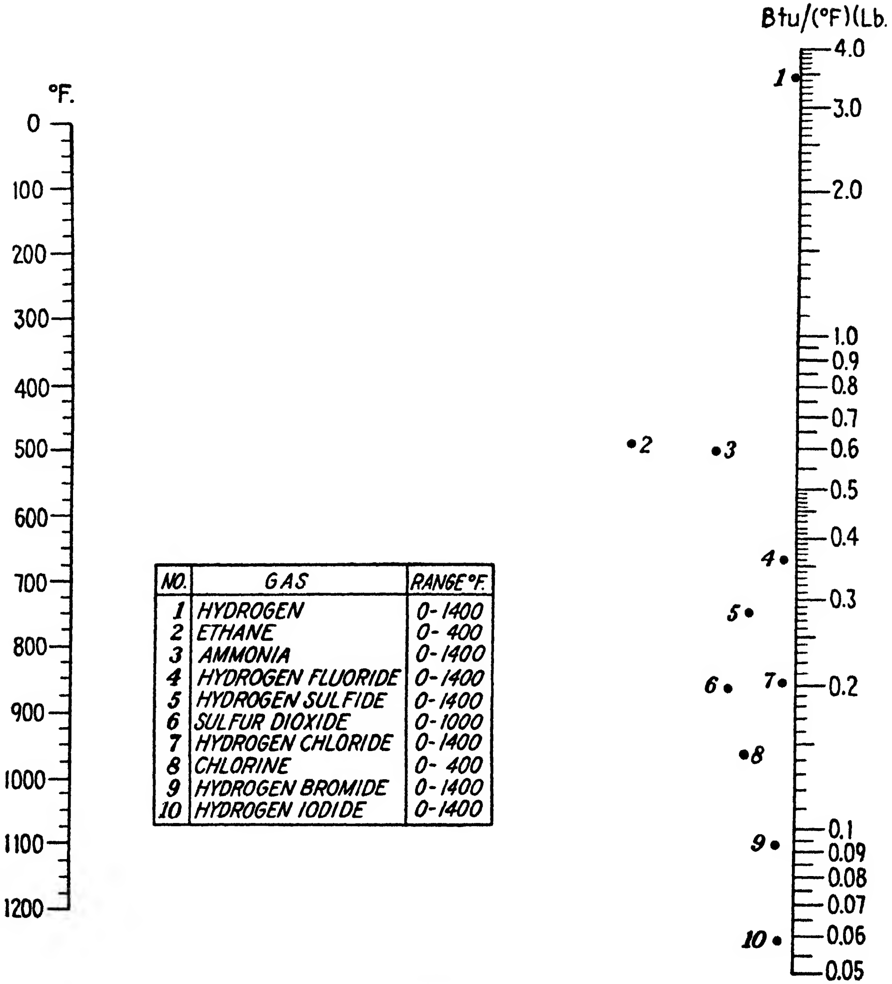
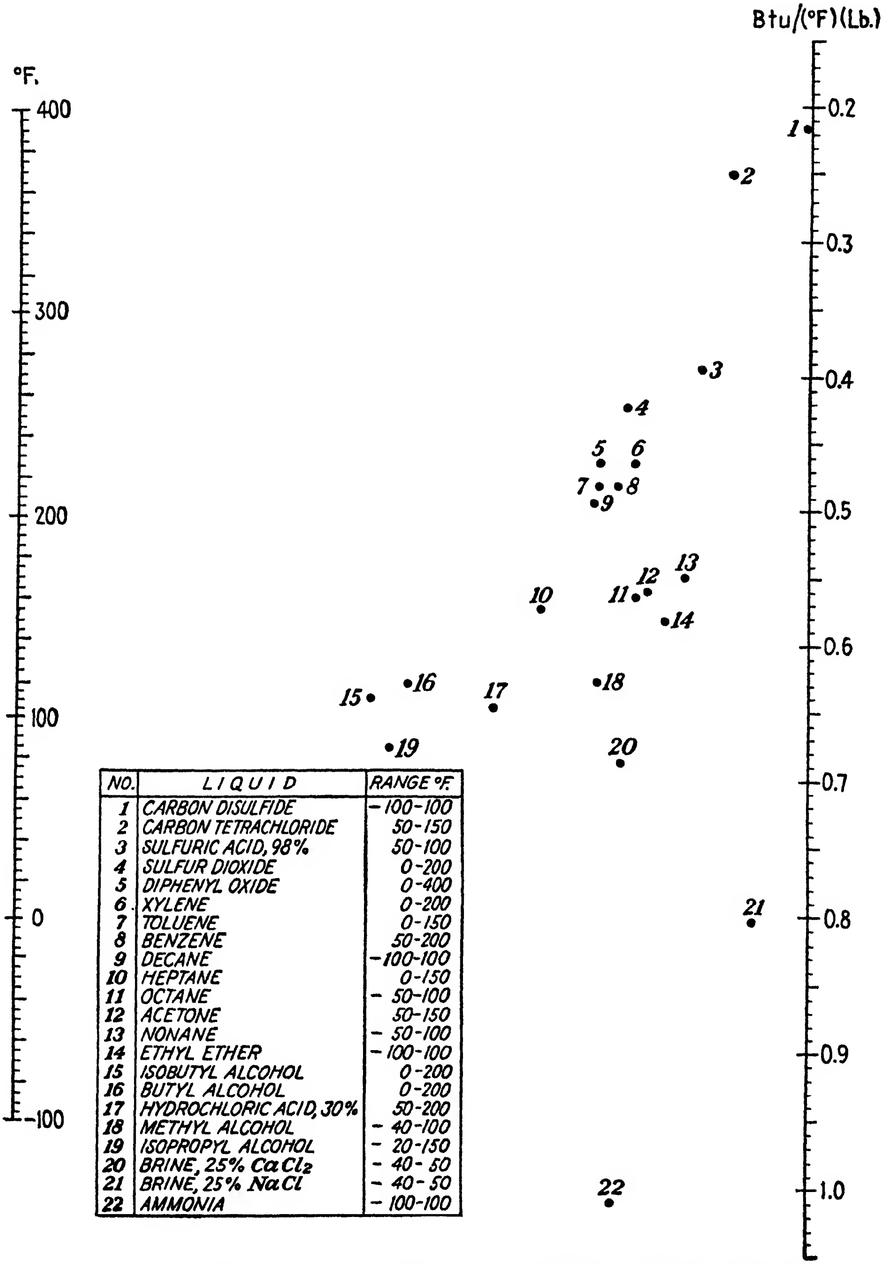


FIG. A.4.—Fugacity coefficients at high reduced temperatures and pressures. [*Newton, H. R., Ind. Eng. Chem.*, **27**, 302 (1935).]



NO.	GAS	RANGE °F.
1	HYDROGEN	0-1400
2	ETHANE	0- 400
3	AMMONIA	0-1400
4	HYDROGEN FLUORIDE	0-1400
5	HYDROGEN SULFIDE	0-1400
6	SULFUR DIOXIDE	0-1000
7	HYDROGEN CHLORIDE	0-1400
8	CHLORINE	0- 400
9	HYDROGEN BROMIDE	0-1400
10	HYDROGEN IODIDE	0-1400

FIG. A.5.—Heat capacity of gases. (*Perry, J. H., "Chemical Engineers' Handbook."*)



NO.	LIQUID	RANGE °F.
1	CARBON DISULFIDE	-100-100
2	CARBON TETRACHLORIDE	50-150
3	SULFURIC ACID, 98%	50-100
4	SULFUR DIOXIDE	0-200
5	DIPHENYL OXIDE	0-400
6	XYLENE	0-200
7	TOLUENE	0-150
8	BENZENE	50-200
9	DECANE	-100-100
10	HEPTANE	0-150
11	OCTANE	- 50-100
12	ACETONE	50-150
13	NONANE	- 50-100
14	ETHYL ETHER	- 100-100
15	ISOBUTYL ALCOHOL	0-200
16	BUTYL ALCOHOL	0-200
17	HYDROCHLORIC ACID, 30%	50-200
18	METHYL ALCOHOL	- 40-100
19	ISOPROPYL ALCOHOL	- 20-150
20	BRINE, 25% $CaCl_2$	- 40- 50
21	BRINE, 25% NaCl	- 40- 50
22	AMMONIA	- 100-100

FIG. A.6.—Heat capacity of liquids. (*Perry, J. H., "Chemical Engineers' Handbook."*)

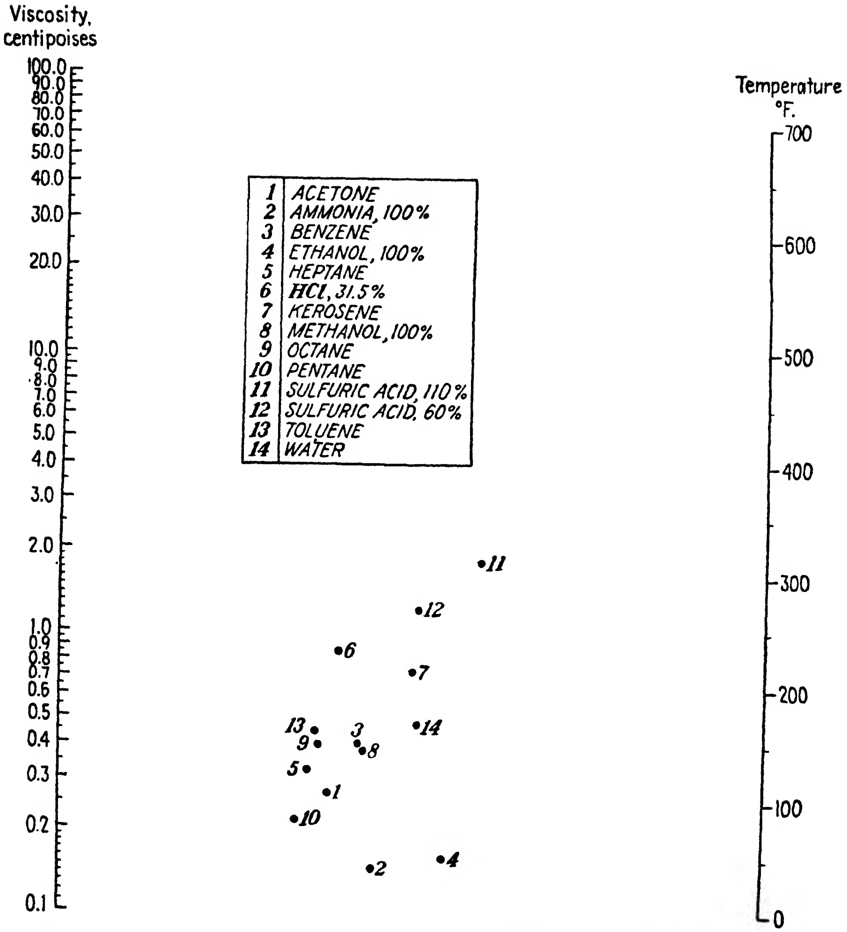
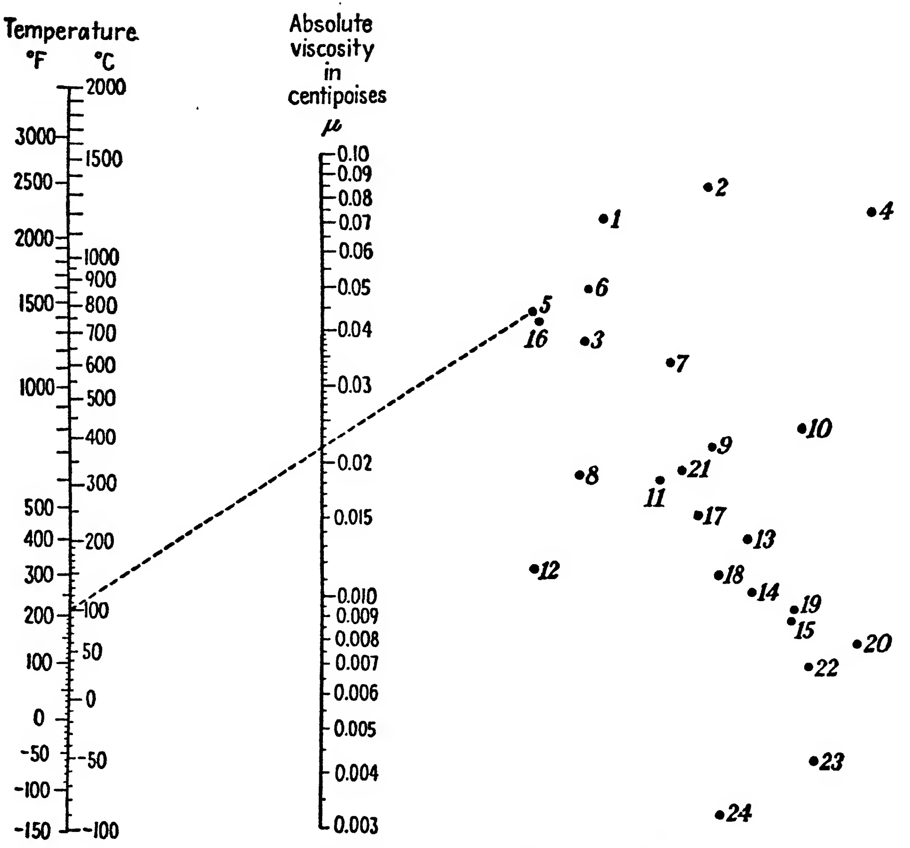


FIG. A.7.—Viscosity of liquids. (*Perry, J. H., "Chemical Engineers' Handbook."*)



No.	Gas or vapor
1	O_2
2	NO
3	CO_2
4	HCL
5	AIR
6	N_2
7	SO_2
8	CH_4
9	H_2O
10	NH_3
11	C_2H_4
12	H_2
13	C_3H_6
14	αC_4H_8
15	Iso-C_5H_{10}
16	CO
17	C_2H_6
18	C_3H_8
19	N-C_4H_{10}
20	Iso-C_5H_{12}
21	C_2H_2
22	N-C_5H_{12}
23	N-C_7H_{16}
24	N-C_9H_{20}

FIG. A.8.—Viscosity of gases. (*Perry, J. H., "Chemical Engineers' Handbook."*)

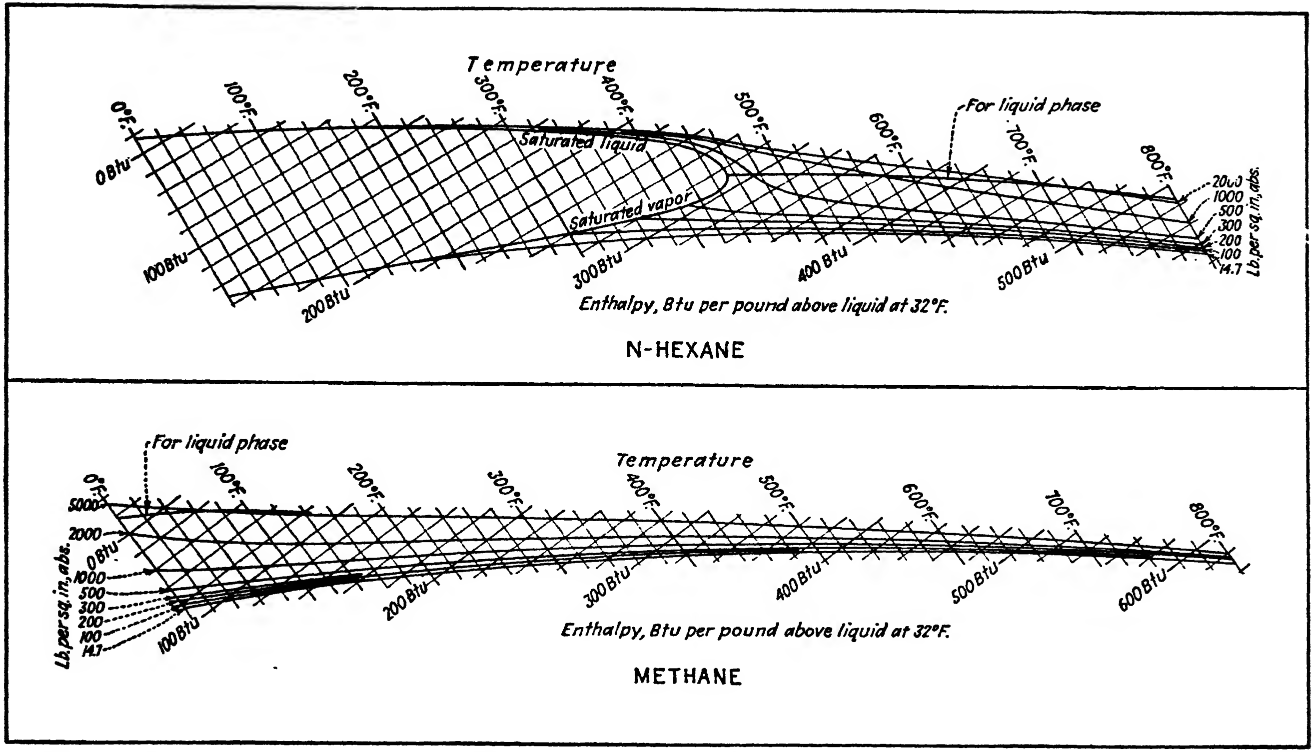


FIG. A.9.—Enthalpy charts for methane and n-hexane. [*Courtesy of Standard Oil Co. (Ind.). Chart prepared in 1937 by W. C. Edmister and D. H. Pollack.*]

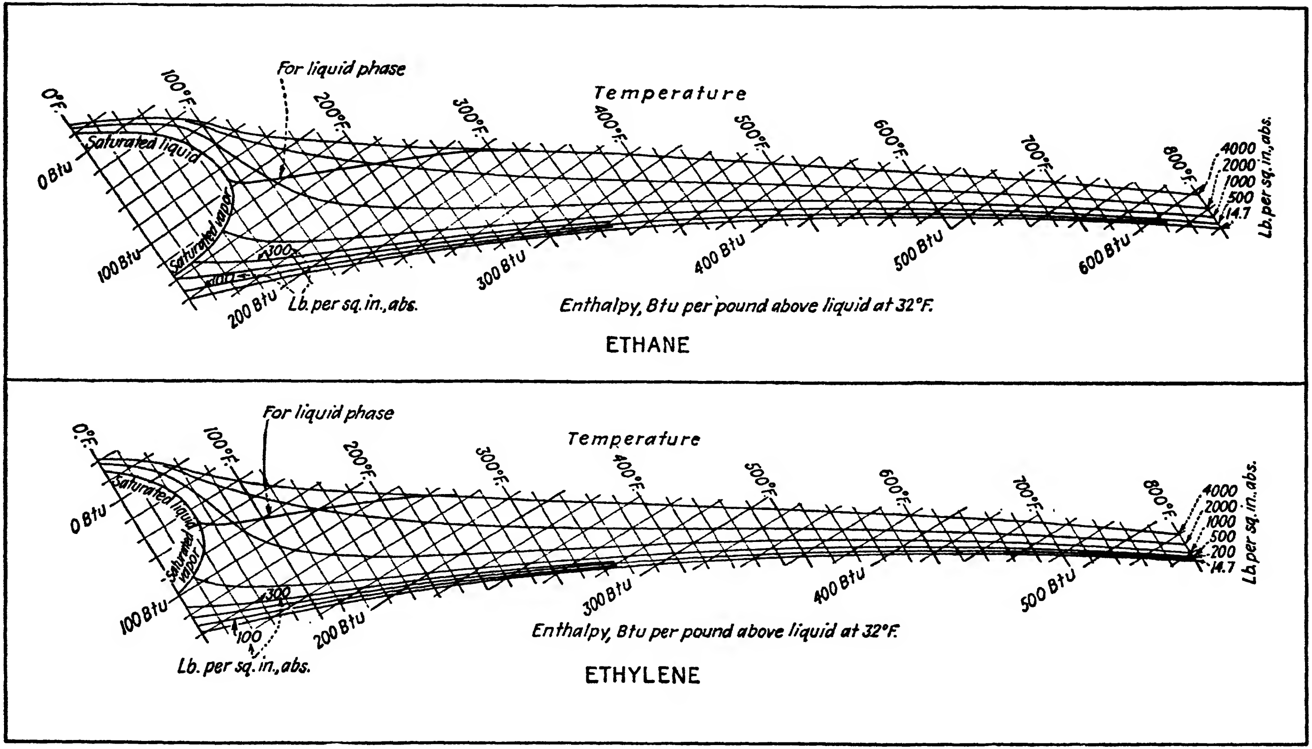


FIG. A.10.—Enthalpy charts for ethylene and ethane. [*Courtesy of Standard Oil Co. (Ind.). Chart prepared in* 1937 *by W. C. Edmister and D. H. Pollack.*]

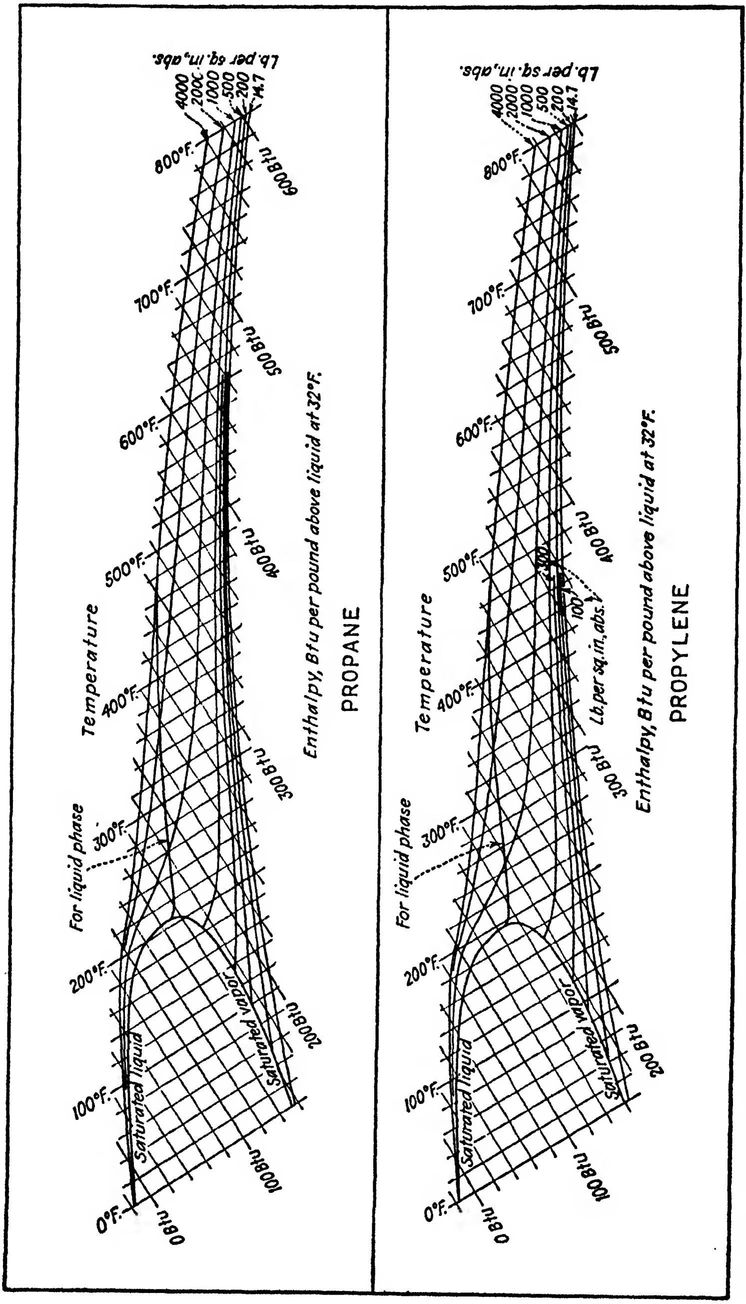
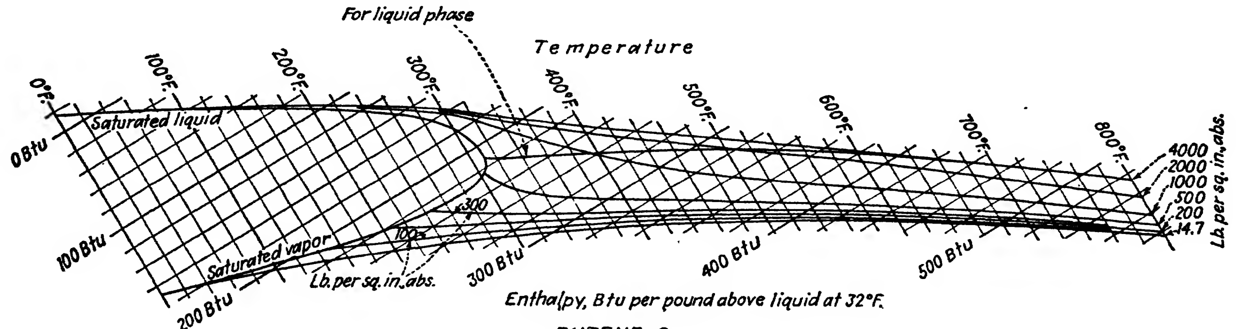
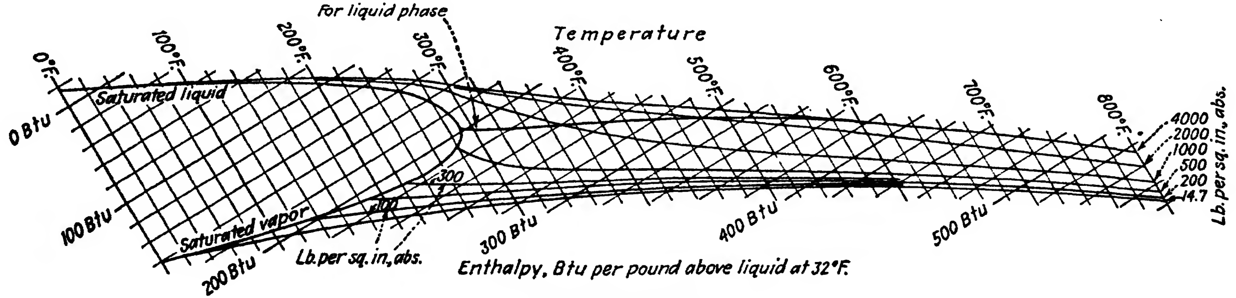


FIG. A.11.—Enthalpy charts for propylene and propane. [*Courtesy of Standard Oil Co. (Ind.). Chart prepared in 1937 by W. C. Edmister and D. H. Pollack.*]



BUTENE-2



ISO-BUTYLENE
(USE ALSO FOR BUTENE-1)

FIG. A.12.—Enthalpy charts for butenes. [*Courtesy of Standard Oil Co. (Ind.). Chart prepared in* 1937 *by W. C. Edmister and D. H. Pollack.*]

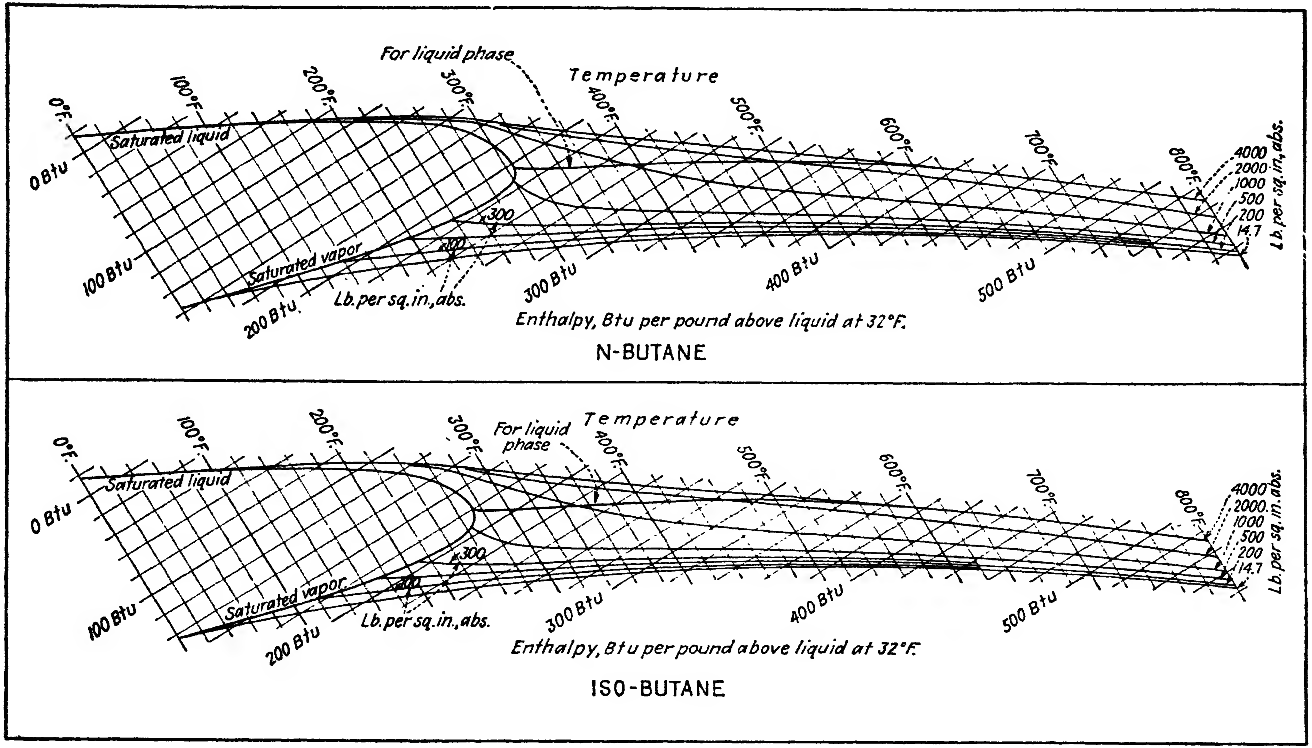


FIG. A.13.—Enthalpy charts for isobutane and *n*-butane. [*Courtesy of Standard Oil Co. (Ind.). Chart prepared in* 1937 *by W. C. Edmister and D. H. Pollack.*]

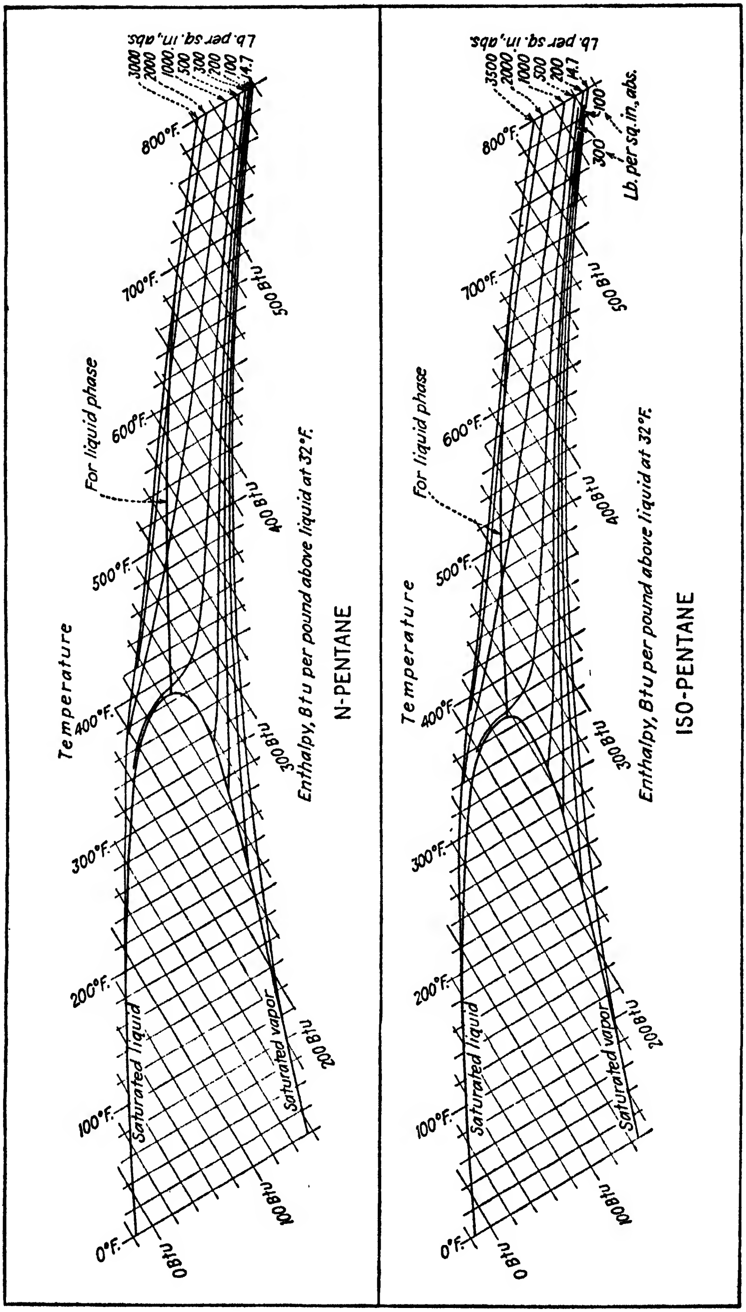


FIG. A.14.—Enthalpy charts for isopentane and *n*-pentane. [*Courtesy of Standard Oil Co. (Ind.). Chart prepared in 1937 by W. C. Edmister and D. H. Pollack.*]

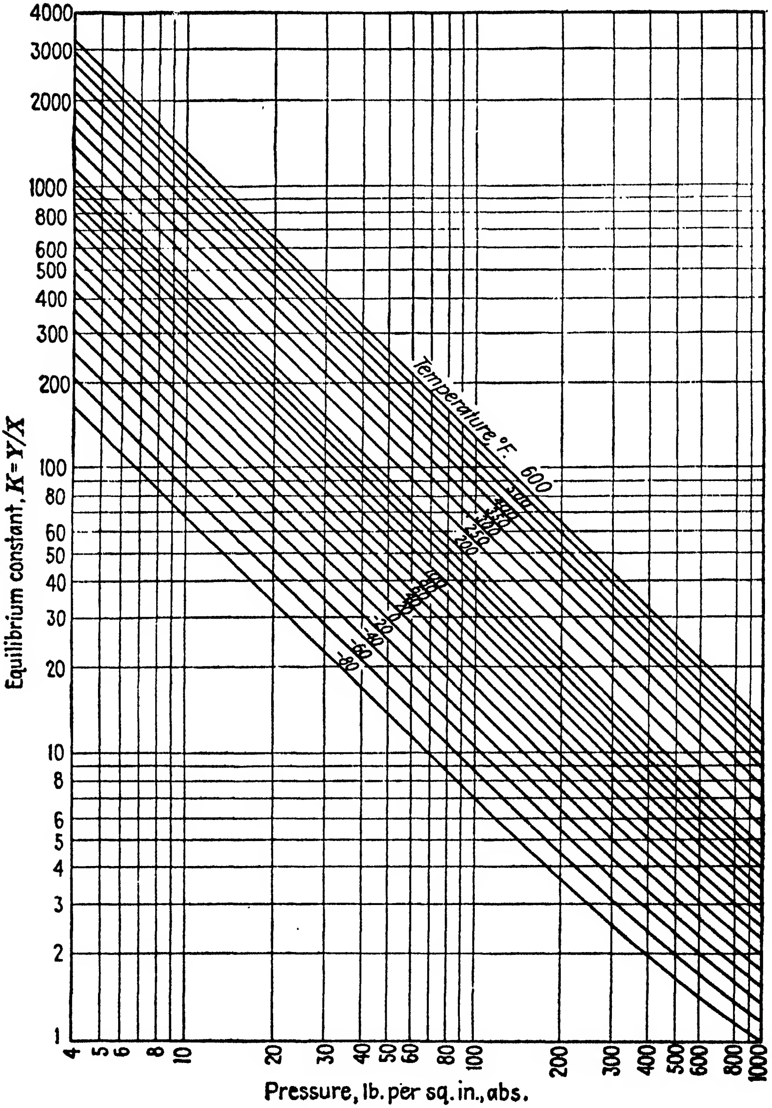


Fig. A.15.—Phase equilibrium constants for methane.

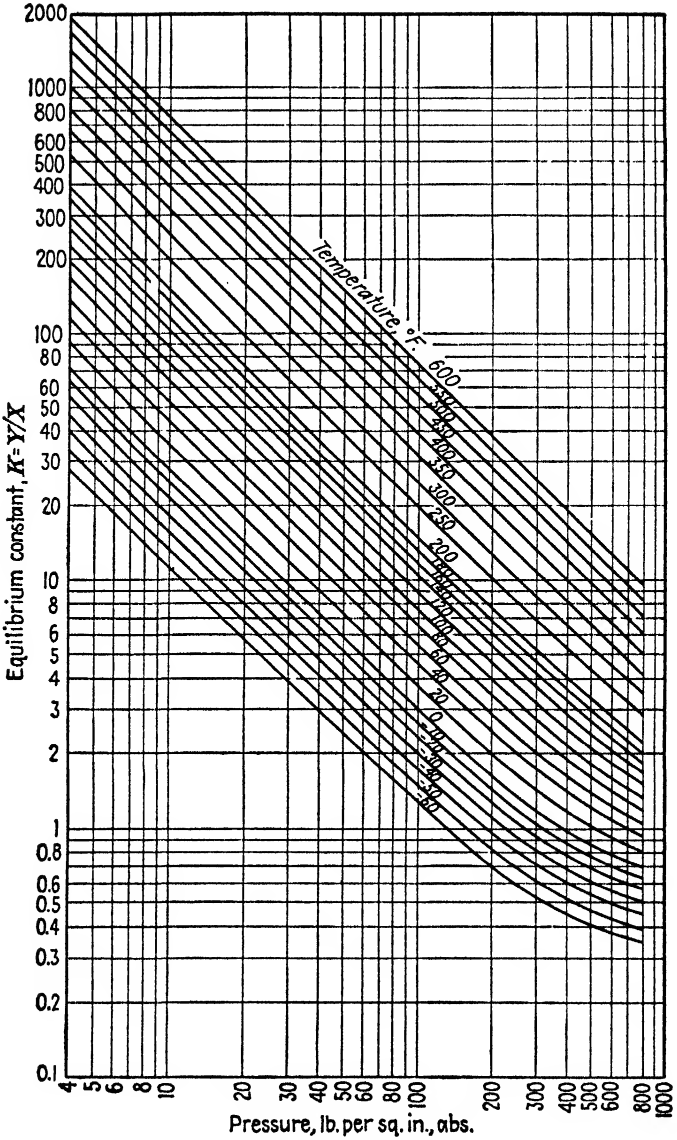


FIG. A.16.—Phase equilibrium constants for ethylene.

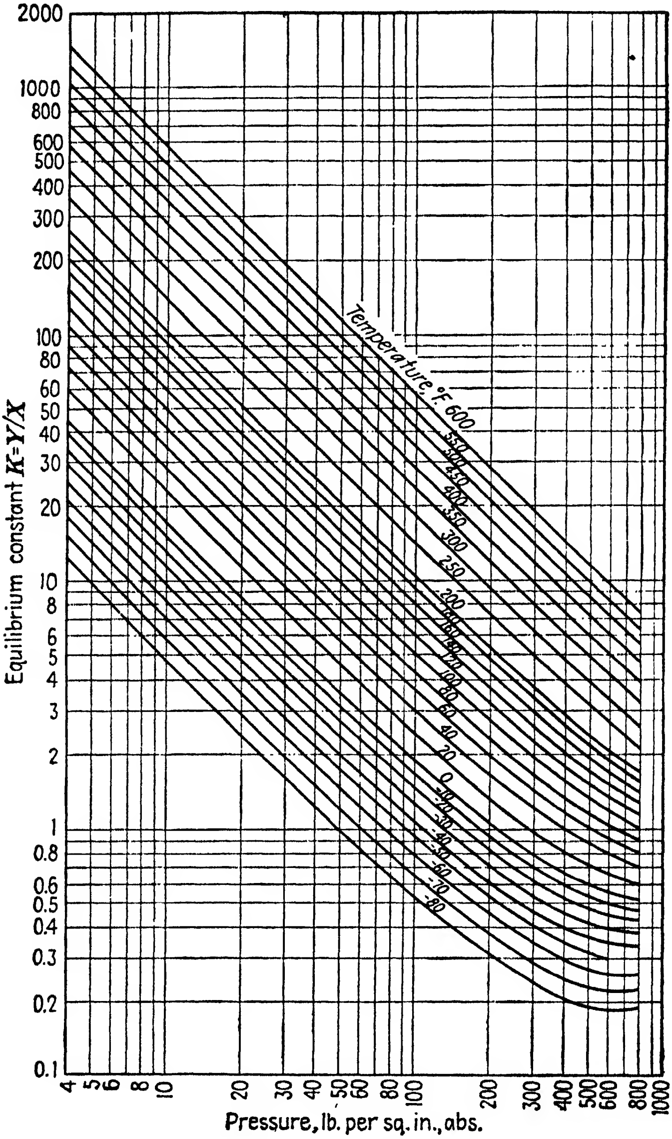


Fig. A.17.—Phase equilibrium constants for ethane.

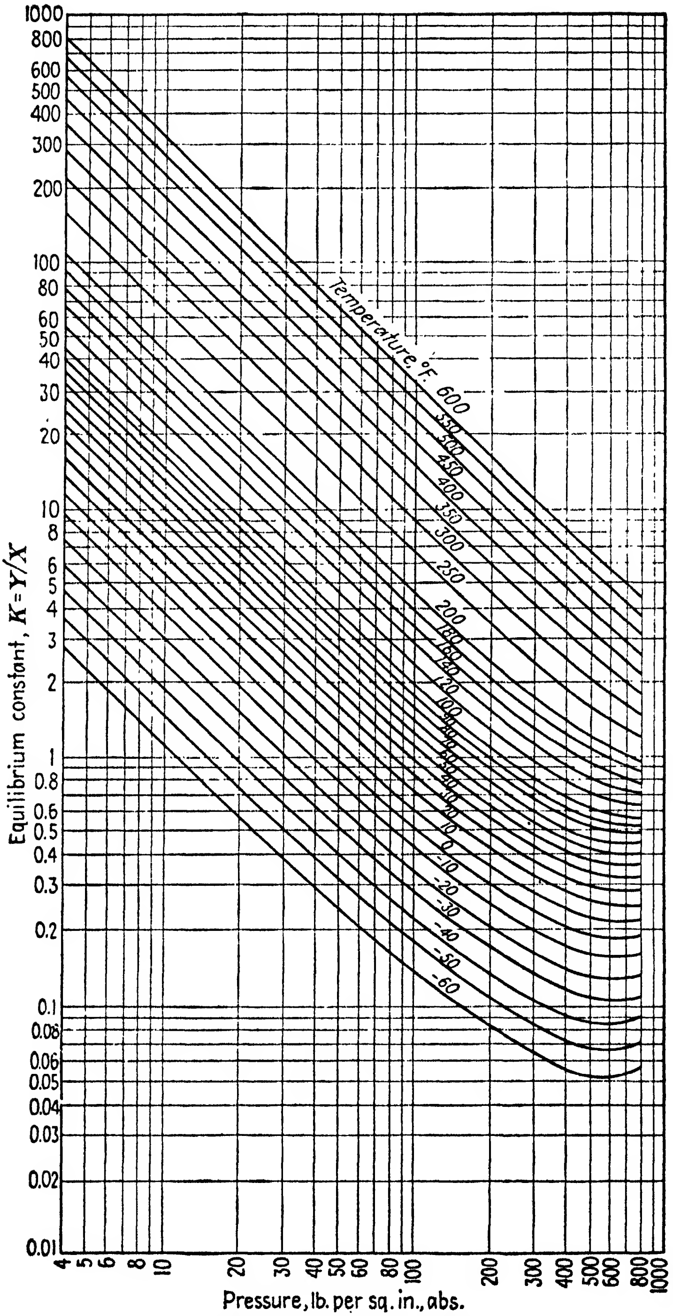


Fig. A.18.—Phase equilibrium constants for propylene.

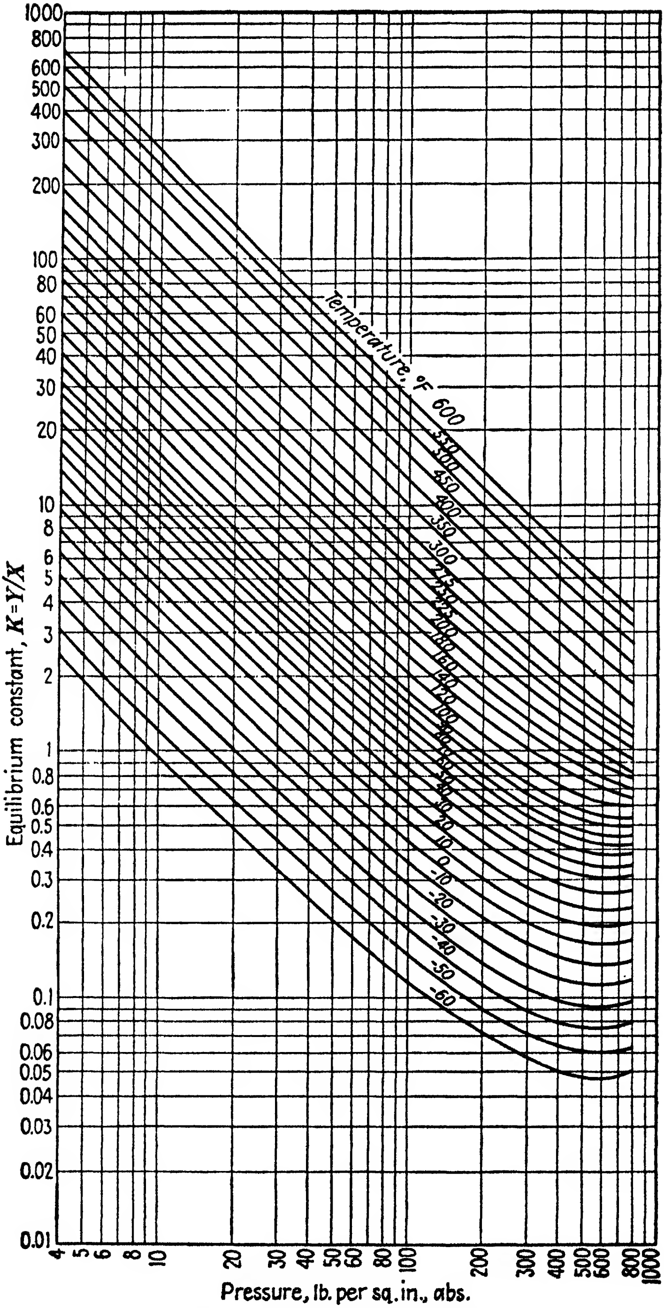


FIG. A.19.—Phase equilibrium constants for propane.

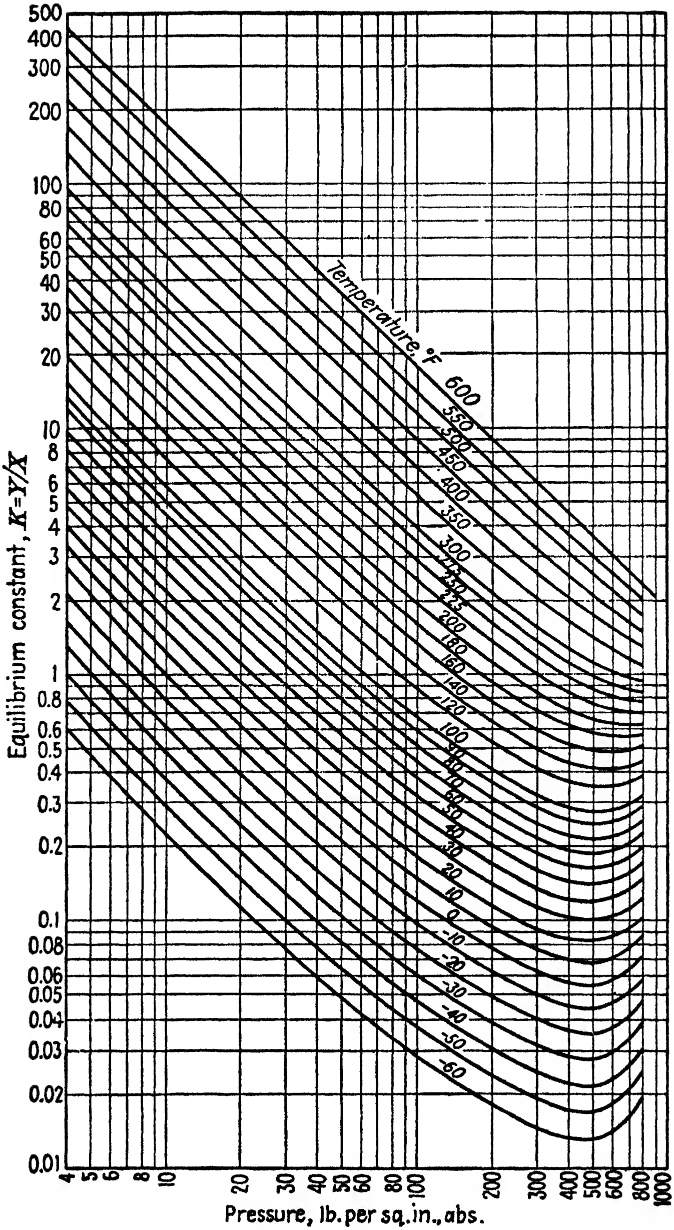


FIG. A,20.—Phase equilibrium constants for isobutylene.

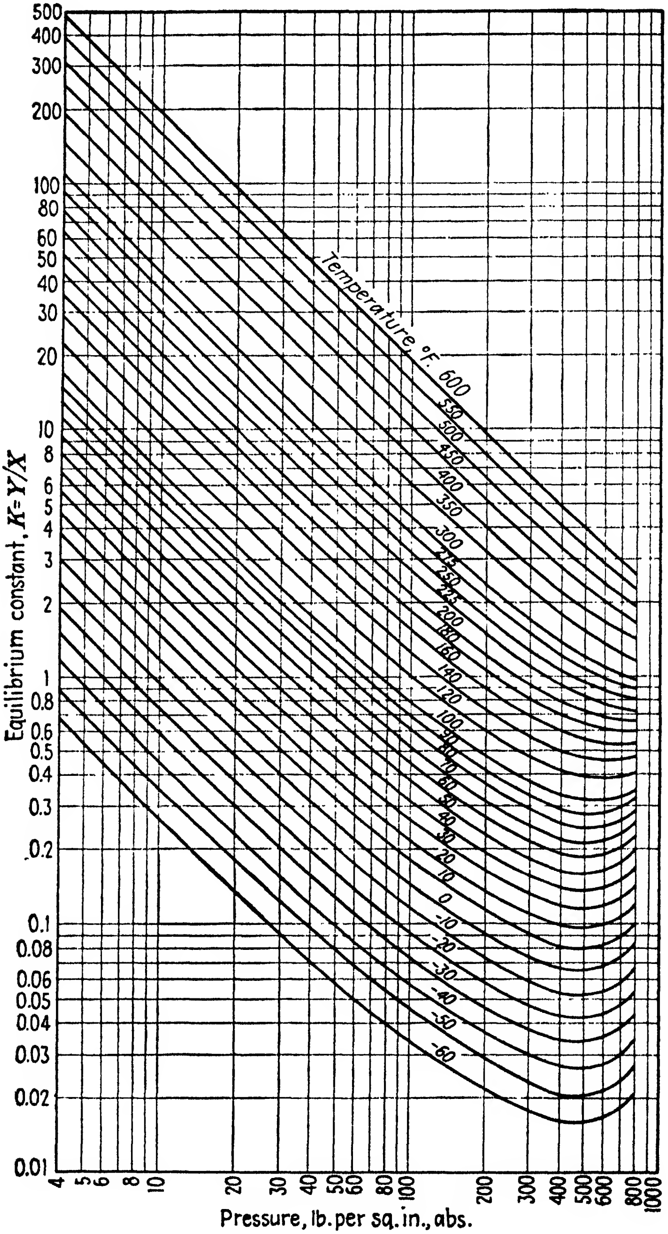


FIG. A.21.—Phase equilibrium constants for isobutane.

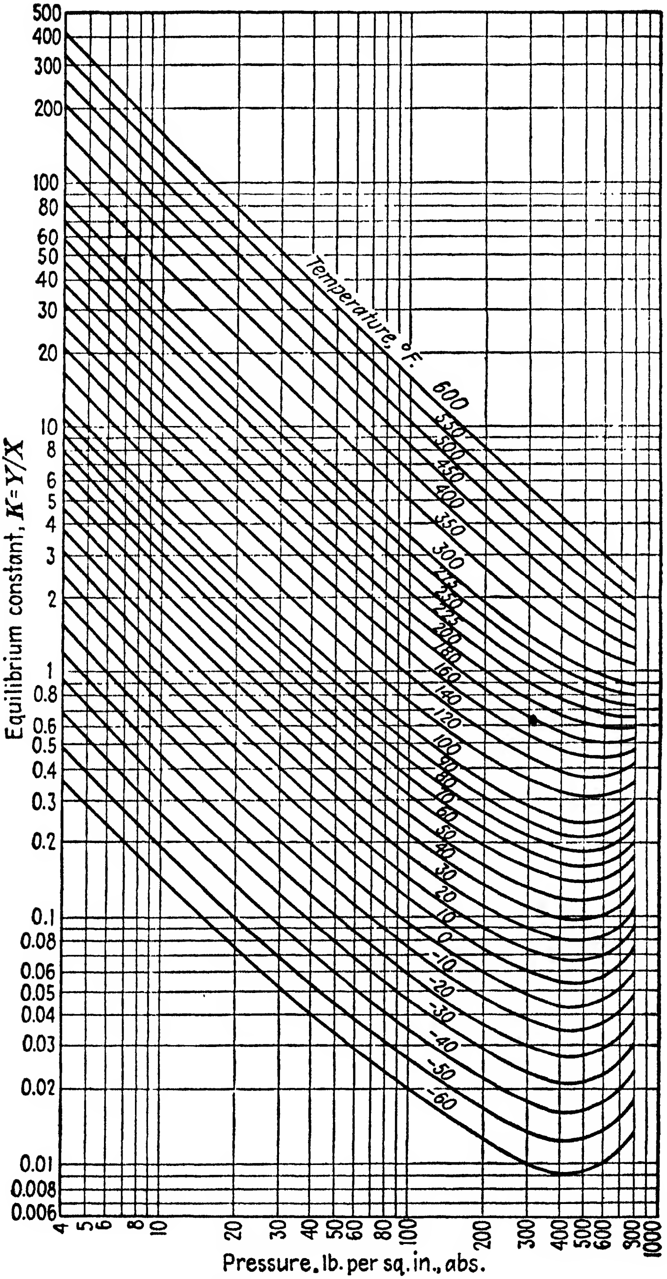


FIG. A.22.—Phase equilibrium constants for *n*-butane.

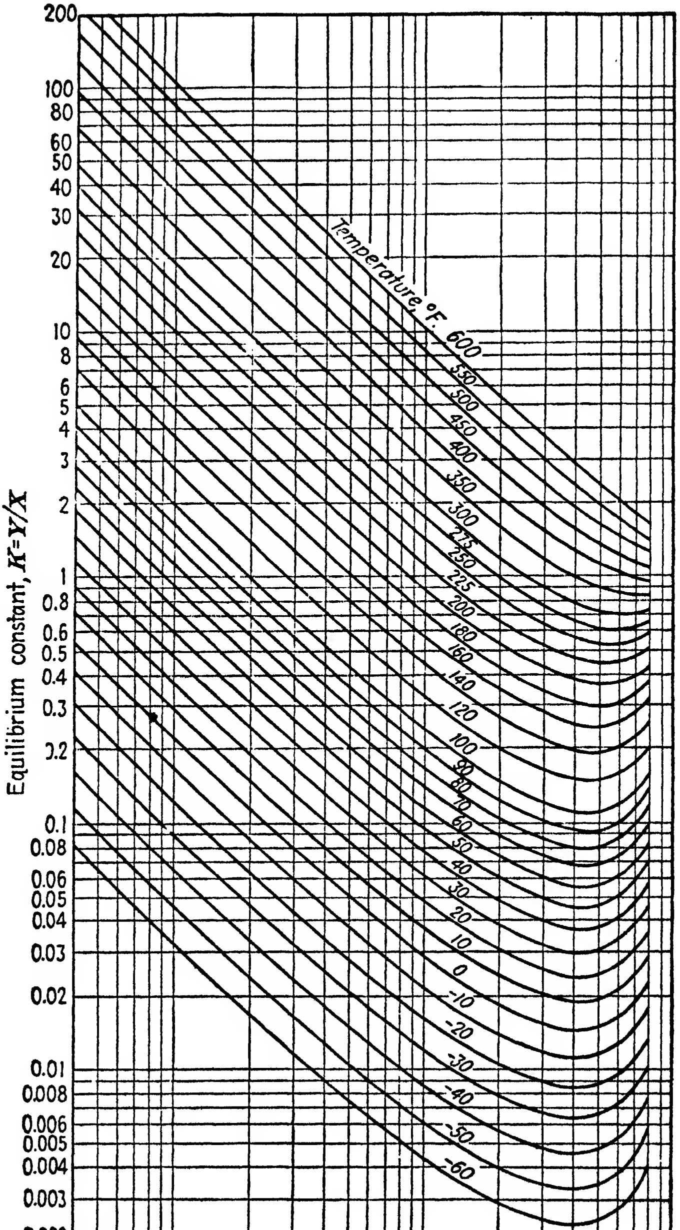


FIG. A.23.—Phase equilibrium constants for isopentane.

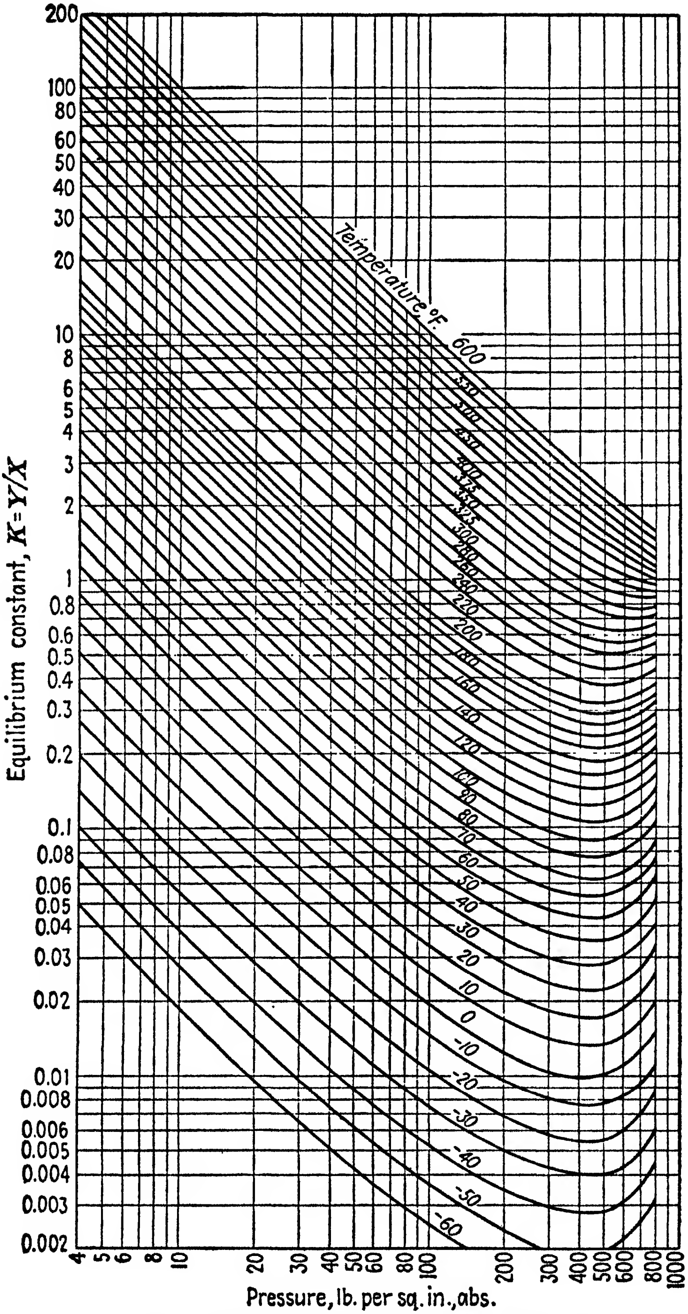


FIG. A.24.—Phase equilibrium constants for *n*-pentane.

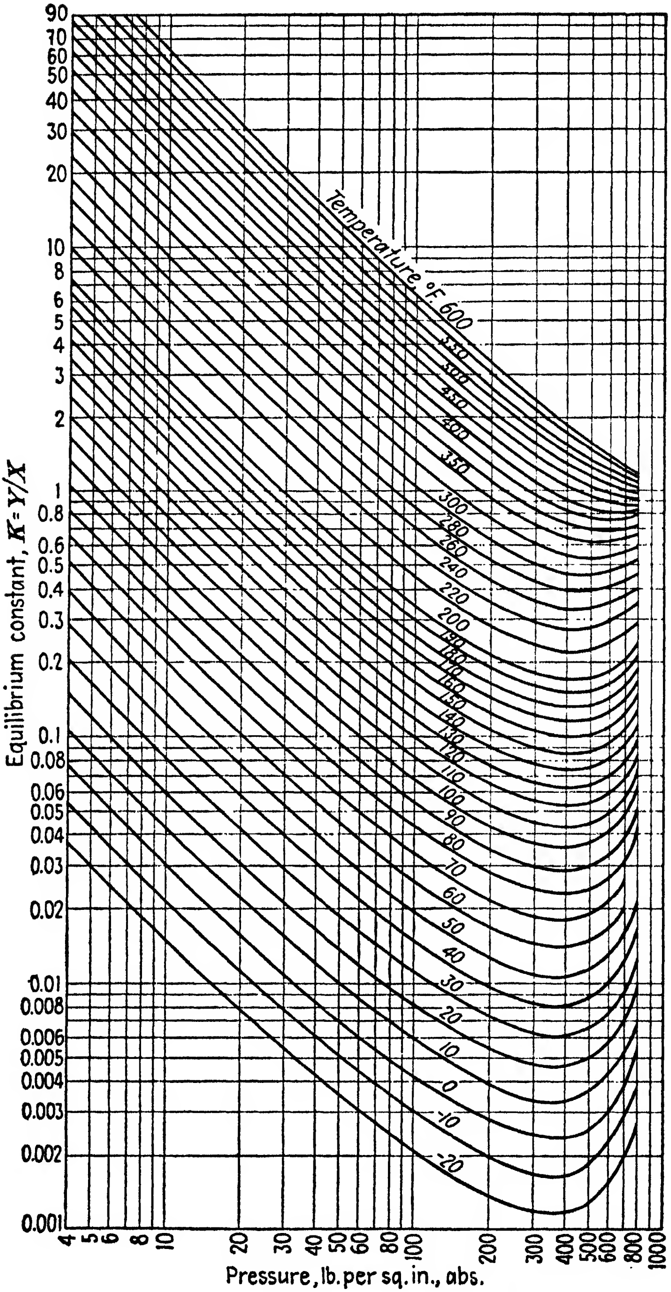


FIG. A.25.—Phase equilibrium constants for n-hexane.

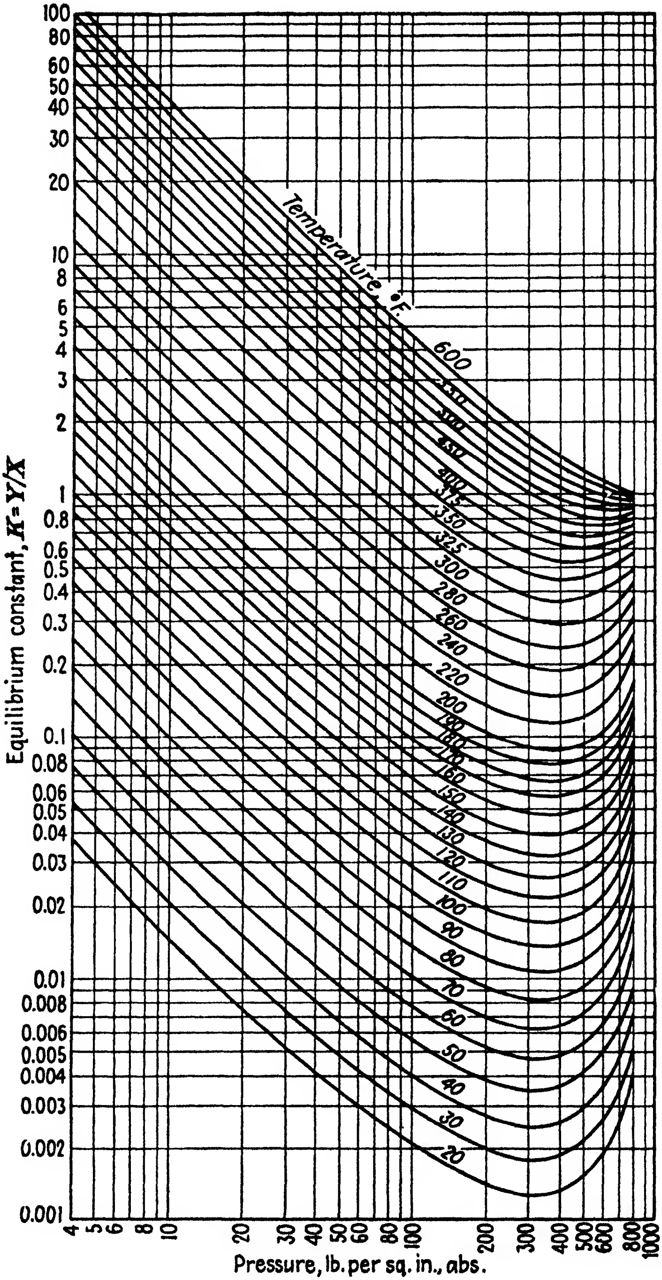


FIG. A.26.—Phase equilibrium constants for *n*-heptane.

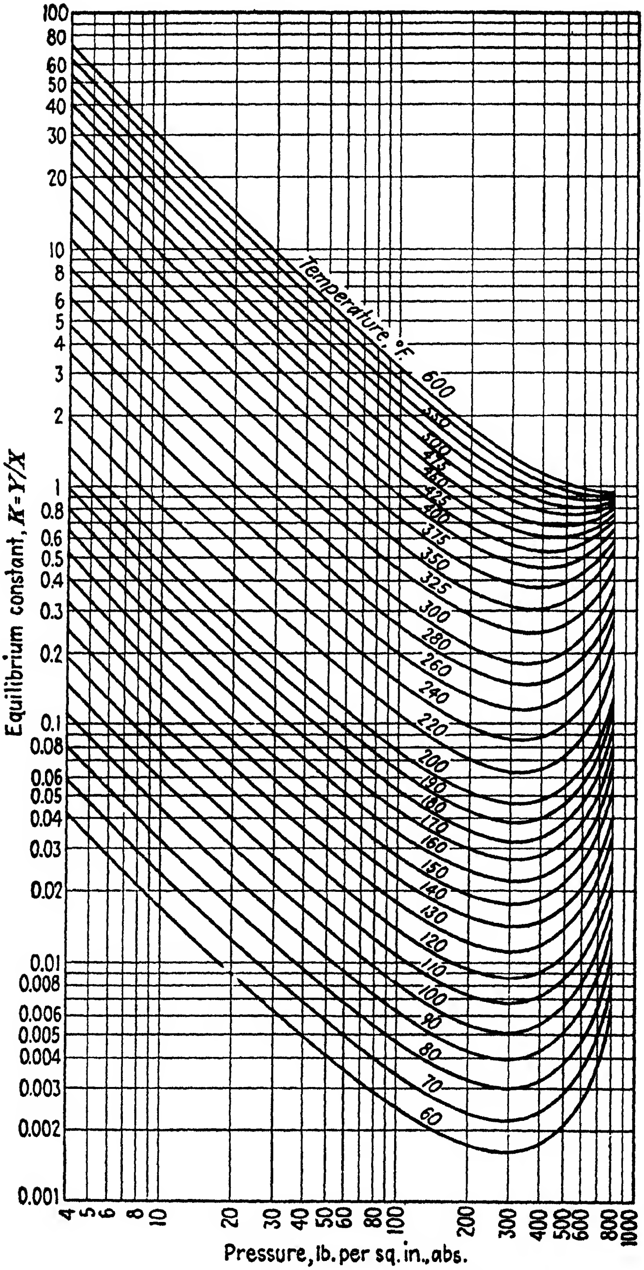


FIG. A.27.—Phase equilibrium constants for *n*-octane.

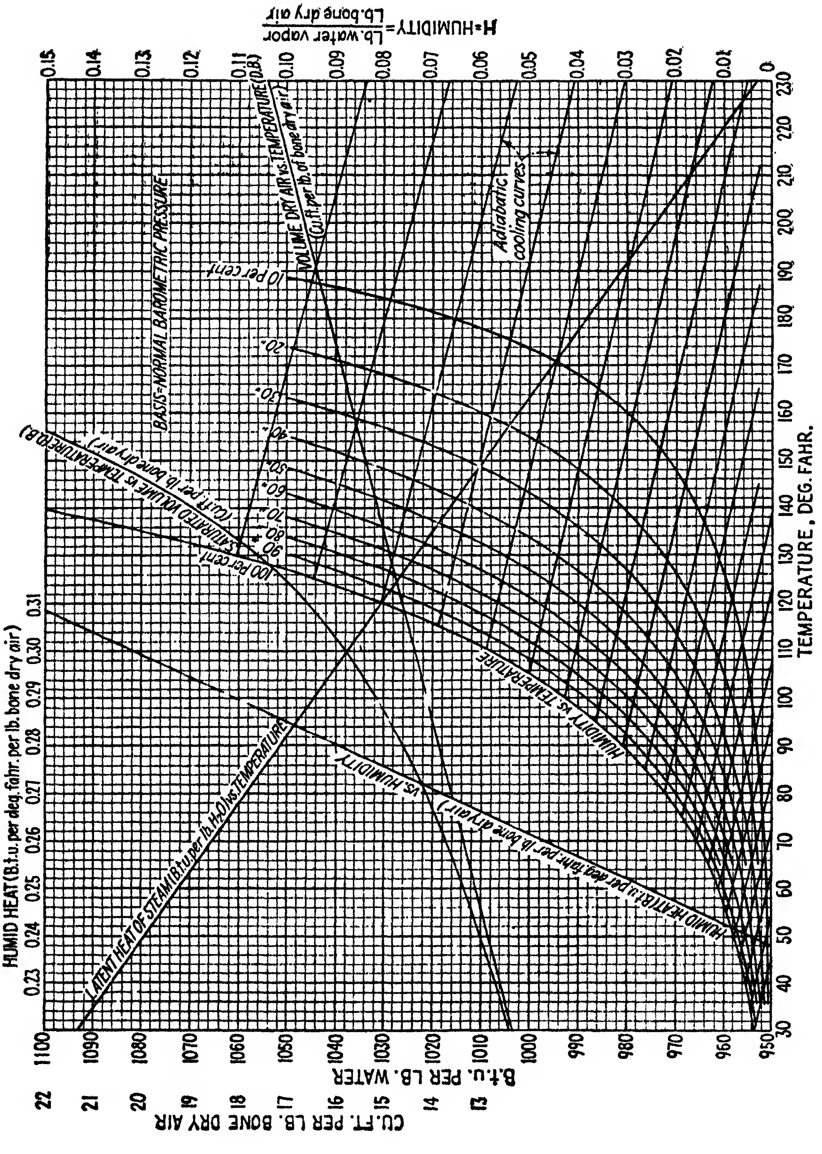


FIG. A.28.—Psychrometric chart.

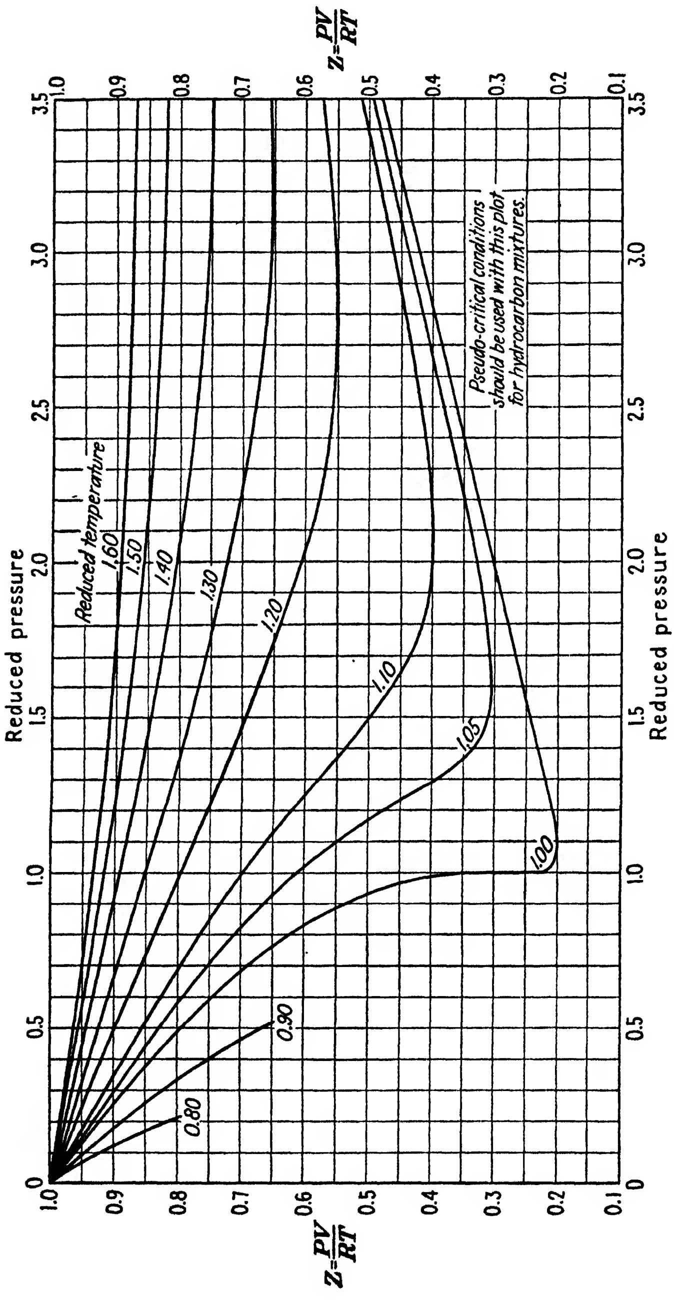


FIG. A.29.—Reduced equation of state for hydrocarbons.

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