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ELECTROCAPILLARITY

ELECTROCAPILLARITY

THE CHEMISTRY AND PHYSICS OF ELECTRODES AND OTHER CHARGED SURFACES

by

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With 56 diagrams and 1 plate

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PREFACE

It has not been easy to find a concise title which would clearly indicate the scope and contents of this book. Rather than use a cumbrous descriptive title I have fallen back on the word Electrocapillarity which is exact, although it may not convey the full scope of the contents to every one. The book deals with potential differences at electrified interfaces, the origin and nature of the effects that arise therefrom, and with electrode equilibria and kinetics. It is not at all concerned with the extensive uses which have been found for reversible electrodes for determining the thermodynamic properties of electrolytes, of which there are a number of excellent accounts in text-books of electrochemistry and thermodynamical chemistry.

It will be seen that the subject-matter forms quite an extensive field, and touches upon many branches of scientific activity, from the behaviour of proteins to the passivity of metals. Electrocapillarity is no new science. Its foundations were laid in the nineteenth century by Quincke, Lippmann, Helmholtz and Nernst among others. In the earlier years of the present century, the foundations so laid were brilliantly extended by Gouy, v.Smoluchowski, Freundlich, Hardy and many others. In more recent times the field has attracted an ever-increasing body of workers and has widened considerably. It now has important contacts with industry and biology which are likely to be extended in the future.

Apart from some historical sketches, I have not dealt much with the older work, and most of the book is devoted to the work of the last fifteen years. I have generally given most attention to topics which have not been adequately treated in other works, and some subjects for which adequate reviews exist elsewhere, e.g. polarographic studies, phase boundary potentials between two liquids, corrosion of metals, I have barely mentioned.

A more complete account of electrokinetic phenomena and their applications, such as is fortunately available in Dr. H. A. Abramson's *Electrokinetic Phenomena* (Chemical Catalog Co., 1934), would itself require a larger book than this. Here I have only attempted a fairly concise survey of the present position of the subject, with an account of some recent important applications.

My chief motive in writing this book has been to give a connected account of the work with which I have been associated and to present the subject as it appears to me as a result of these studies. But I trust that it will not be thought that I have dealt unduly with my own work, or have neglected the contributions of others. In some cases I have given interpretations of my own which go beyond or differ from those previously published. I do not think the reader will have any difficulty in distinguishing my own views from the reported views of others, of which the source is almost always given.

I am much indebted to my colleague, Dr. T. R. Bolam, for contributing a section on the electrokinetic behaviour of heteropolar surfaces, and to Dr. D. A. MacInnes and Dr. H. A. Abramson for permission to reproduce illustrations. I would also like to express my sincere gratitude to my former students and colleagues, C. Ockrent, G. Armstrong, A. Wightman, F. R. Himsworth, W. M. Leslie, G. Drever, J. D. Pearson and I. M. Barclay for their efforts, to which such progress as we have been able to make in the study of electrode processes is mainly due, and to Dr. I. M. Barclay for his help with the proof-reading.

The Discussion on Electrical Double Layers which is being arranged by the Faraday Society for September, 1939, comes too late for me to make use of the contributed papers, and I suggest that the report of this discussion (published January, 1940) should be used to supplement Chapters IV and V.

EDINBURGH, *June*, 1939

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The illustration facing p. 98 is reproduced by courtesy of the Faraday Society, London.

ELECTROCAPILLARITY

CHAPTER I

THE SEAT OF THE ELECTROMOTIVE FORCE IN THE GALVANIC CELL

GALVANIC electricity was discovered by Luigi Galvani in 1780 in the course of experiments on the effect of electric discharges, derived from statical machines, on frog's nerves. He noticed that when frogs were hung up by brass wires driven through the spine, muscular contractions of the legs, similar to those produced by electric discharges, occurred when the feet touched an iron plate. No effect was produced by contact with electrical insulators, and it was necessary for the brass wires to be in electrical contact with the iron. Galvani considered that the wire and plate merely provided a conducting path for the discharge of the electricity of the nerves; but later Volta showed that contact of two dissimilar metals was essential to produce the effect. About 1800 he made the most important observation that when discs of two metals were put in contact, insulated and then separated, they are found to have acquired electric charges of opposite sign. To account for this he made the hypothesis that different metals have different powers of attraction for electricity, so that when two metals are put in contact, electricity passes from that which has the less to that which has the greater attraction. He experimented with different metals and found that they could be arranged in a series such that every metal was positive with respect to those succeeding it, and gave the following estimates of the "contact force" between them :—

$$\mathrm{Zn}\underbrace{\quad}_{5}\mathrm{Pb}\underbrace{\quad}_{1}\mathrm{Sn}\underbrace{\quad}_{1}\mathrm{Fe}\underbrace{\quad}_{2}\mathrm{Cu}\underbrace{\quad}_{3}\mathrm{Ag}$$

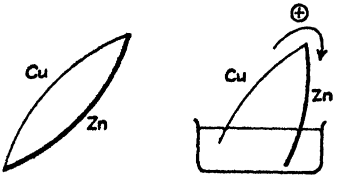
He also constructed the first galvanic cell, a pile of alternate discs of copper and zinc, each pair being separated from the next by moistened paper. This pile was capable of producing electric sparks, and Pfaff, in 1801, proved the identity of its electricity with that of the frictional machine by showing it to be capable of charging a Leyden jar.

It was soon found that the voltaic pile was capable of producing chemical actions. Nicholson and Carlisle found that if two wires from the pile were placed in water, decomposition occurred; hydrogen being liberated at the wire connected with the zinc and oxygen at that connected with the copper pole. Cruickshank found that metallic salts were also decomposed; for example, with a solution of copper sulphate, copper is deposited at one wire and oxygen and sulphuric acid is formed at the other. Davy showed that in the production of electricity by the pile, chemical action on the zinc takes place.

The galvanic cell in its simplest form consists of two metals separated by a suitable solution or solutions. Thus, if we place plates of copper and zinc in a solution of sulphuric acid, and connect them by a wire, a positive current through the wire flows from the copper to the zinc. The copper plate is therefore called the positive and the zinc the negative pole. In the production of the current zinc dissolves into the solution, and hydrogen is formed at the surface of the copper. This hydrogen is troublesome because it increases the resistance of the cell, and therefore steps were taken to prevent its formation. If the solution round the copper contains copper sulphate, as in the Daniell cell, instead of the liberation of hydrogen we get the deposition of copper. In other batteries the hydrogen was removed by chemical oxidation, by means of nitric acid, or potassium dichromate, which involves the use as the positive pole of an unattackable conductor, such as platinum or graphite.

Volta supposed that the current was set up by the unequal attractions of the two metals for electricity at their junction. When copper and zinc are put in contact and separated, the zinc becomes positively and the copper negatively charged, i.e. there is a tendency for *positive* electricity to pass from the copper to the zinc. If two strips of the metals are placed in contact at each end, Fig. 1 (*a*), there is no current because the effects at the two junctions oppose and balance each other. But if they are placed in contact at one end, as in Fig. 1 (*b*), with the other ends dipping into an aqueous solution, the tendency of positive electricity to pass from copper to zinc at their junction is unbalanced and there is a current from the copper to the zinc through the metallic contact, returning from zinc to copper through the solution.

Fabroni objected to Volta's explanation, and considered that the electricity was developed by chemical actions at the contact of the metals with the solution. Thus a controversy began, which went on, without any clear decision being reached, during the whole of the nineteenth century. Those who adopted Volta's view could not deny the occurrence of chemical actions in the cell accompanying the production of the current, but they regarded these as secondary results of the passage of the current through the solution and not the primary cause of it. But the chemical view became increasingly difficult to set aside as new evidence of the intimate connection between the chemical action and the production of the current became available. Faraday discovered the laws of electrolysis, viz. the passage of equal amounts of electricity through various solutions produces chemically equivalent quantities of chemical action, and conversely, in galvanic cells, in the absence of secondary reactions, equivalent quantities of chemical action are required to produce equal amounts of current. The experiments of Joule on the equivalence of different forms of energy led Kelvin and Helmholtz to the enunciation of the principle of the conservation of energy, and its application to the galvanic cell. Kelvin argued that the electrical energy produced in the working of the cell must be equal to the energy of the chemical reaction taking place. When the reaction occurs without producing electrical energy, this energy is given out as heat; when it occurs in the cell an equivalent amount of electrical energy, which can itself be converted into heat, appears. He was able to support this by the reasonable agreement of the thermochemical heats of reaction with the electrical energy of a number of cells. This agreement is now known to be to some extent fortuitous. Kelvin overlooked the fact that some heat may



(a) (b)

I. 1.

be evolved (or absorbed) in the working of the cell. The correct application of the conservation of energy to the galvanic cell is

$$\begin{array}{c}\text{Energy of chemical}\\ \text{reaction}\end{array} = \begin{array}{c}\text{Electrical energy}\\ \text{produced}\end{array} + \begin{array}{c}\text{Heat given out in}\\ \text{working of cell.}\end{array}$$

Kelvin assumed the last term to be zero, which is by no means always the case.

The thermodynamics of the galvanic cell was completed later by Gibbs and Helmholtz, who showed that the electrical energy produced in a reversible cell is equal not to the total energy, but to the *free energy* of the chemical reaction, i.e. to the maximum amount of work the reaction is capable of performing. The difference between the free energy and the total energy of the reaction, which may be positive or negative, appears in the cell as heat absorbed or evolved.

The electrical energy produced by the galvanic cell was thus completely accounted for as the free energy of the chemical reaction, but the question of the mechanism of its action, whereby chemical energy is converted into electrical energy, remained unsolved. Volta's observation of the electrification of two metals by contact was never disproved. In fact, means were found of measuring the difference of potential of two metals which had been in contact. Kelvin used the quadrant electrometer ; Kohlrausch a compensation method in which the two metals were brought to different potentials by means of an outside battery until no charge would pass from the one metal to the other on contact. The difference of potential required to balance the Volta effect in this way was assumed to be equal to the contact difference of potential of the two metals. Although it was found difficult to obtain entirely reproducible measurements in this way, the values obtained being dependent on the state and previous treatment of the metals, the contact potential difference of two metals was invariably found to be a comparatively large quantity, of the same order of magnitude as the electromotive force of the galvanic cell. The values of Pellat[1] and Ayrton and Perry,[2] together with the electromotive forces of

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[1] *J. de physique*, **16**, 68, 1880.

[2] *Proc. Roy. Soc.*, No. 186, 1878 ; *Phil. Trans.*, **171**, 15, 1880.

cells made up of the two metals on normal solutions of their salts, are quoted in the following table :—

TABLE I

Metal Pair.	Pellat.		Ayrton and Perry.		Electromotive Force of Cell.
	Clean.	Scratched.	Commercial Zinc.	Amalgamated Zinc.	
Zinc—					
Tin .	·25	·35	·28	·46	0·62
Lead .	·15	·31	·20	·35	0·64
Iron .	·56	·70	·60	·74	0·32
Nickel .	·47	·63	—	—	0·51
Copper	·71	·86	·75	·89	1·1
Silver .	·91	1·12	—	—	1·56
Platinum	—	—	·98	1·13	—

In 1886 a discussion took place at the Institution of Electrical Engineers,[3] at which the various theories as to the origin of the electromotive force were cogently argued by their protagonists. Sir Oliver Lodge opened the discussion with a statement of the "chemical" theory [4] Since the electrical energy of the cell is derived from the energy of the chemical reaction, which obviously takes place at the contacts of the metals with the solution, the seat of the electromotive force must be located there. No obvious change occurs at the metal junction which could provide energy and so make it an important contributor to the electromotive force. The Volta potential difference does not therefore represent the true contact potential difference of two metals, but is a spurious effect due to the action of the atmosphere on the metals at the moment of separation.

It had been observed that the order of metals in the Volta contact series was very much the same as the order of their heats of oxidation. Lodge therefore attempted to explain the Volta effect by supposing that metals had a sort of differential attraction

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[3] *J. Inst. Elect. Engineers*, **14**, 1886.

[4] For a lengthy summary of the controversy and statement of his views, see *Phil. Mag.*, **19**, 153, 254, 340, 1885 ; see also *Proc. Physical Soc.* (London), **17**, 369, 1900.

for the oxygen of the atmosphere. He says: "Let us regard the air as a dielectric bath of oxygen, in which the metals are immersed, and picture a piece of zinc surrounded by oxygen molecules which are straining at it, and endeavouring to combine with it. They may indeed partially succeed; but suppose they do not, we have here a strong potential chemical action or chemical strain, which must probably be accompanied by some physical phenomenon. Now remember that oxygen is an electronegative element; and without endeavouring to examine too precisely what signification is involved in that statement, it will not be out of accord with orthodox views if we assume that it means that at least any dissociated oxygen atoms are negatively charged. . . . Granting something equivalent to this . . . we perceive that the strain of the oxygen towards the zinc will result in what I metaphorically call a slackening up, or attempted compression, of the negative electricity in it, i.e. to a rise of negative potential. We may therefore say that zinc is at a lower potential than the air surrounding it, and that the step of potential in crossing the boundary from zinc to air is closely connected with the chemical affinity between zinc and oxygen. Observe that this step of potential does not obviously nor probably depend on the amount of oxygen present. It is possible that a few million molecules may be as effective as a large number. Note also that the step of potential is by no means caused by actual oxidation: in so far as the zinc surface is tarnished by oxidation the strain will be diminished and the step of potential become less."

According to this ingenious theory each metal thus acquires in the presence of oxygen a characteristic potential, which is determined by its affinity for oxygen. When two metals are put in contact, "a rush of electricity must take place" from the one at the higher to the one at the lower potential, until their potentials are equalised. Thus when they are separated, as in Volta's experiment, the two metals will be found to be oppositely charged. If this is correct, the Volta effect should disappear in a non-oxidising atmosphere or in a vacuum. The advocates of the "contact" theory, notably Ayrton and Perry,[5] made experiments to test this point. It was found that replacing the air by other gases or by a moderate vacuum

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[5] See *Phil. Mag.*, **21**, 51, 1886.

certainly has some effect on the Volta potential, but it does not cause a very great change. This, however, did not satisfy the other side, who could always say that the few million molecules of oxygen required could easily be present even in the most carefully conducted experiments. No experimental decision between these conflicting views was at that time possible.

The crux of the problem was this: if the metal junction is a large contributor to the total electromotive force, where does the energy which it gives to the current come from? At the junctions of the metals with the solution, chemical reactions are taking place, which can provide the necessary energy, but at the metal junction there is no obvious change which can supply energy to the current. Clerk Maxwell had laid it down that if there is a change of potential at a point where no other effect which can provide energy occurs, the energy gained must come from the absorption of heat.* Now an absorption of heat in the passage of a current from one metal to another had been observed in the Peltier effect. It was therefore argued that the true contact potential difference is that equivalent to the Peltier heat, which is at most a millivolt or two and in many cases not more than a few microvolts.

The fallacy of this argument was stated by Perry in the discussion referred to above in the following words: "We ask . . . why we must assume that, when electricity rises in potential suddenly at a place in the circuit, energy must come in from outside. . . . Suppose we grant that electricity gains in potential-energy in flowing from copper to zinc, do we know so much of an electric current as to assert that when the electricity gains potential-energy it does not lose an equivalent quantity of some other kind of energy? Why may we not assume, for example, that electricity loses *tension-energy* in passing from copper to zinc, so that if it gets potential-energy it loses tension-energy." Thus, no difficulty arises from the

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* "If we cause an electric current to pass from copper to zinc, the heat generated in the conductor per unit of electricity is a measure of the work done by the current, for no chemical or other change is effected. Part of this heat arises from the work done in overcoming ordinary resistance within the copper and the zinc. This part may be diminished indefinitely by letting the electricity pass very slowly. The remainder of the heat arises from the work done in overcoming the e.m.f. from the Zn to the Cu, and the amount of this heat per unit of electricity is a measure of the e.m.f."

point of view of the energy contributed by the metal contact if it be supposed that electricity has a different tension-energy, or what nowadays might be called intrinsic-energy, in each metal.* This is the same as Volta's original hypothesis of each metal having a specific "attraction" for electricity.

Nothing material was contributed to the solution of the problem during the rest of the nineteenth century, except Nernst's theory of the origin of the potential difference at the junction of metals and their salt solutions, which, though it did not touch the question of the metal contact, served to focus attention more closely on the electrodes as the more important parts of the galvanic cell. Then came the discovery of the electron and the new interpretations of electrical phenomena which it gave rise to. The conclusive proof of the existence of large metal contact potential differences came finally from the study of the emission of electrons from metals by heating (thermionics) and when exposed to light (photoelectricity).

Our knowledge of the emission of electrons by incandescent metals is largely due, at least in its earlier stages, to the investigations of Richardson.[6] His work, which was confirmed and extended by Langmuir, demonstrated that the electron emission of perfectly pure metals in a very good vacuum is a definite quantity, an intrinsic property of the metal. The dependence of the rate of emission of electrons on the temperature can be represented by expressions of the form

$$n = A\sqrt{T}e^{-\phi/kT}$$

where A is a constant characteristic of the metal, k the universal gas constant, and ϕ a quantity called the *thermionic work function*

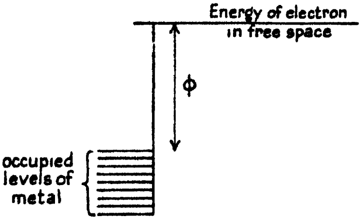
---

* Pellat used a similar argument (which is really derived from Helmholtz). Discussing Pellat's views Lodge says: "He makes use of an unpleasantly plausible reasoning, which . . . when unexpectedly suggested, is so painfully benumbing that it is worth while to quote it. . . . Two metals, A and B, put into contact are at different potentials, the difference A/B being due to and equal to the e.m.f. of contact. There is, then, at the junction not only the contact-force E, but also the equal opposite force $-dV$, due to the difference of potential established. Either of these forces alone would resist or aid the passage of electricity across the junction . . . but both together will do nothing of the sort; and so if there be any Peltier effect, it must be due to some small residual phenomenon," etc.

[6] E.g. *Phil. Mag.*, **24**, 592, 1912.

of the metal, which represents the loss of energy suffered by an electron in escaping from the metal.*

In the more recently developed formulation in terms of quantum mechanics, there are in a piece of metal a large number of *energy-levels* each of which can accommodate two electrons. The electrons of the metal which give rise to its metallic conduction are distributed among these levels in such a way that the lowest levels are filled first. Taking the energy of an electron in free space as zero, ϕ is the energy in the negative direction of the highest occupied level of the metal and is therefore the amount of energy which must be provided to liberate an electron.



I. 2.

Similarly in the study of the photoelectric effect, it was found that there is a limiting or threshold frequency of light, which is characteristic of each metal, below which no electrons are emitted. Above the threshold frequency electrons having a range of velocities are emitted, but the *maximum* kinetic energy of the emitted electrons increases with the frequency of the light according to Einstein's equation

$$\tfrac{1}{2}mv^2 = h\nu - \phi.$$

Here $h\nu$ is the quantum of energy provided by the incident light; in escaping from the metal an electron loses at least the energy ϕ, and emerges with kinetic energy $\tfrac{1}{2}mv^2$. At the threshold frequency $\tfrac{1}{2}mv^2 = 0$ and therefore $\phi = h\nu_0$.

The thermionic work function can be determined in either of these ways. Suppose we have two metals, in contact with each other, having thermionic work functions ϕ_1 and ϕ_2. If the metals are at the same electrical potential, the energy required for the transfer of an electron from the first to the second will be $\phi_1 - \phi_2$. If there is a difference of electrical potential V_{12} between the metals, the energy required is reduced to $\phi_1 - \phi_2 - V_{12}$. So when electricity flows from one metal to another, the difference of potential being

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* ϕ is usually stated in *electron-volts*, i.e. the change of energy of an electron in passing through a potential difference of 1 volt.

the contact potential difference V_{12}, the energy required per electron transferred, which will be absorbed as heat, is

$$q = \phi_1 - \phi_2 - V_{12} \quad . \quad . \quad . \quad . \quad (1)$$

q is the *Peltier heat* effect, which is known from thermoelectric theory, as well as direct measurement, to be very small. No appreciable error is made if it is assumed to be negligible, and then the contact difference of potential is

$$V_{12} = \phi_1 - \phi_2 \quad . \quad . \quad . \quad . \quad (2)$$

This conclusion was verified by Millikan and his co-workers [7] by means of the arrangement shown in Fig. 3. Two plates of different metals, A, B, are arranged so that the under one can be illuminated by the light source L. A variable potential difference P is applied to the plates by means of the battery and rheostat R.

The electrometer E measures the rate of flow of electrons between the plates A and B. When the under plate A is illuminated by light of frequency ν, the maximum energy of the emitted electrons is given by

$$\tfrac{1}{2}mv^2 = h\nu - \phi_A.$$

Now suppose that the plates are at electrical potentials V_A and V_B. The work done by an electron in passing from one plate to the other is $-(V_B - V_A)$. It therefore follows that unless $\frac{1}{2}mv^2$ (the maximum energy of the electrons) is greater than $(V_B - V_A)$, no electrons emitted at A will succeed in reaching the plate B. The difference of potential between the two plates is made up of that applied by the battery P, together with the contact potential difference V_{AB} of the two metals, i.e.

$$V_B - V_A = P + V_{AB}.$$

Therefore no electrons will reach the plate B, unless

$$\tfrac{1}{2}mv^2 = h\nu - \phi_A > (P + V_{AB}).$$

If P_M is the applied potential difference which just prevents the emitted electrons from reaching B, we thus have

$$h\nu - \phi_A = (P_M - V_{AB}).$$

---

[7] *Physical Rev.*, **7**, 18, 1916; **18**, 236, 1921; Hennings and Kadesch, *ibid.*, **8**, 217, 1916.

When ϕ_A is known (it is determined by the threshold frequency as $h\nu_0$), it is therefore possible to determine V_{AB}. The existence of a contact potential difference between two metals, the magnitude of which is given by (2), was conclusively proved by these experiments.

TABLE II. CONTACT P.DS. AND ELECTROMOTIVE FORCES IN GALVANIC CELLS

	ϕ	$V_{M/Zn} = \phi_M - \phi_{Zn}$	$E_M - E_{Zn}$
K	2·12	− 1·45	− 2·16
Na	2·29	− 1·28	− 1·95
Li	2·28	− 1·29	− 2·20
Ca	3·20	− 0·37	− 2·11
Mg	3·68	+ 0·11	− 0·7
Zn	3·57	0·0	0·0
Cd	3·68	+ 0·11	+ 0·36
Fe	4·72	+ 1·15	+ 0·32
Sn	4·38	+ 0·81	+ 0·62
Pb	3·95	+ 0·38	+ 0·63
Cu	4·16	+ 0·59	+ 1·10
Ag	4·68	+ 1·11	+ 1·56

In 1916 Langmuir [8] pointed out that these discoveries proved conclusively the existence of large potential differences at the metal junctions of a galvanic cell, which, in fact, are of the same order of magnitude as the electromotive force of the whole cell. Table II shows (*a*) values of the thermionic work functions of a number of metals; * (*b*) the differences between these values and that of zinc, i.e. by (2) the contact differences of potential between zinc and the other metals; (*c*) approximate values of the electromotive forces of galvanic cells, made up of zinc on the one hand and the other metal on the other, dipping into normal solutions of their salts. It can be seen that in most cases the metal contact potential difference is a large part of the electromotive force of the cell.

This being so, how is the dependence of the electromotive force on the energy of the whole cell reaction to be explained? The answer, as pointed out by the writer in 1924,[9] is that the energy of transfer of electrons from one metal to another is itself an important part of the cell reaction.

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[8] *Trans. Amer. Electrochem. Soc.*, **29**, 125, 1916.

* The most modern values of ϕ are given in this table, not those available in 1916.

[9] *Phil. Mag.*, **48**, 927, 1924.

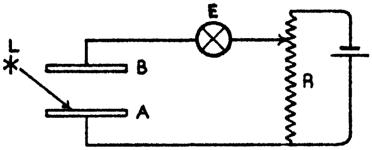
Consider the Daniell cell in its simplest form (Fig. 3). When the cell yields current, zinc dissolves from the negative pole and copper is deposited at the positive pole and the whole cell reaction is

$$Zn + Cu^{++}_{(aq)} = Cu + Zn^{++}_{(aq)}$$

Different component parts of this reaction occur at different parts of the cell. At the zinc electrode zinc ions pass into the solution, leaving their complement of electrons in the metal, i.e. representing an electron in metallic zinc as $\epsilon(Zn)$, the reaction here is

$$Zn = Zn^{++}_{(aq)} + 2\epsilon(Zn).$$

The electrons pass round the external circuit from the zinc to the copper, passing over the junction Zn/Cu on the way. At the copper electrode copper ions are deposited from the solution, and together with the electrons which have passed through the outside circuit form metallic copper, viz.



I. 3.

$$Cu^{++}_{(aq)} + 2\epsilon(Cu) = Cu.$$

At each junction a potential difference arises, which is equivalent to the energy of the process which occurs there, less the comparatively small Peltier heat which may be dissipated at each junction in the passage of current. The energy changes in the solution of metal ions at the electrodes are of a similar order of magnitude, leaving the transfer of electrons at the junction as the major component of the energy of the whole reaction, so that the electromotive forces generally show a fairly close parallelism with the contact potentials.

A current is obtained from a galvanic cell because, in order to complete the reaction, electrons must pass from one metal to the other, and this can only occur if the metals are in contact, or, when separated, if joined by a conducting wire.

CHAPTER II

THE THERMODYNAMICS OF ELECTRODE POTENTIALS

It will be convenient to give at this stage, for readers who are not acquainted with the subject, a short summary of the application of thermodynamics to electrode potentials. For a more complete account reference should be made to works on chemical thermodynamics.*

The electromotive force (E) of a galvanic cell is the potential difference between the poles when no current is passing. This is a measure of the maximum electrical work which is obtained when unit quantity of electricity passes from one pole to the other. The maximum amount of electrical energy obtained when a Faraday (**F**) of electricity is taken from a cell is thus E**F**.

A galvanic cell functions in the thermodynamic sense as a reversible engine when its electromotive force is balanced by an equal and opposite potential difference derived from an outside source. For if the opposing potential difference is slightly decreased, the cell reaction will take place and the maximum amount of electrical work will be done in the passage of the current against the applied potential difference. If the opposing potential difference is made slightly greater than the electromotive force of the cell, a current will pass through the cell in the reverse direction and the cell reaction will be made, with an expenditure of energy only slightly greater than in the previous case, to proceed in the reverse direction.

When so balanced by an opposing potential difference, the cell reaction takes place under the conditions of thermodynamic reversibility, and it therefore yields as electrical energy the maximum work of which it is capable. This is equal, under the usual conditions of constant temperature and pressure, to the decrease of

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* E.g. the author's *Fundamentals of Chemical Thermodynamics* (Macmillan & Co.).

free energy in the cell reaction ($-\Delta F$). Thus for z equivalents of chemical action, which in a cell produce $z\mathbf{F}$ coulombs of electricity, we have

$$z\mathbf{F}E = -\Delta F.$$

The free energy change is related to the heat of the reaction at constant pressure, or heat content change (ΔH), by

$$\Delta F = \Delta H - T\Delta S,$$

where ΔS is the entropy change in the reaction, which is also given by

$$\Delta S = -d(\Delta F)/dT = z\mathbf{F}(dE/dT).$$

Thus we have

$$\underset{\substack{\text{Electrical energy}\\ \text{obtained.}}}{zE\mathbf{F}} = \underset{\substack{\text{Heat evolved}\\ \text{in reaction.}}}{-\Delta H} + \underset{\substack{\text{Heat absorbed in}\\ \text{working of the cell.}}}{zT\mathbf{F}(dE/dT)}.$$

The usual convention is that ΔH is taken as positive for an absorption of heat; hence $-\Delta H$ is the heat evolved when the reaction is carried out in a calorimeter, no electrical energy being obtained. In the cell we obtain the electrical energy $zE\mathbf{F}$; if this is greater than the whole heat of the reaction $-\Delta H$, the quantity of heat represented by the last term must be absorbed in the working of the cell to satisfy the conservation of energy, while if $zE\mathbf{F} < -\Delta H$ heat is evolved in the working of the cell.

In the Daniell cell the reaction which takes place when the cell yields current is

$$\mathrm{Zn} + \mathrm{Cu}^{++}(aq) = \mathrm{Cu} + \mathrm{Zn}^{++}(aq).$$

Two Faradays are obtained when the amount of chemical action represented by this equation takes place, and the maximum electrical energy yielded is thus $zE\mathbf{F}$, which is equal to the free energy decrease in the reaction, i.e.

$$zE\mathbf{F} = -\Delta F.$$

The free energy change in the reaction (ΔF) is equal to the free energy of the products minus the free energy of the reactants, or

$$\Delta F = F_{Cu} + F_{Zn^{++}(aq)} - F_{Zn} - F_{Cu^{++}(aq)},$$

where the F's represent the free energies of the quantities of these substances which are represented by the chemical symbols. The free energies of metallic zinc and copper are constants at a given temperature, but the free energies of the ions Cu^{++}, Zn^{++} are functions of their concentrations in the solution. In modern thermodynamical theory they are represented by

$$F_{Zn^{++}} = F^o{}_{Zn^{++}} + RT \log_e \alpha_{Zn^{++}},$$
$$F_{Cu^{++}} = F^o{}_{Cu^{++}} + RT \log_e \alpha_{Cu^{++}},$$

where $F^o{}_{Zn^{++}}$ and $F^o{}_{Cu^{++}}$ are constants and $\alpha_{Zn^{++}}$, $\alpha_{Cu^{++}}$ the activities of zinc and copper ions in the solutions, which become equal to their concentrations when the latter are very small. Introducing these values we have

$$2E\mathbf{F} = -(F_{Cu} - F_{Zn} + F^o{}_{Zn^{++}} - F^o{}_{Cu^{++}}) \\ - RT \log_e \alpha_{Zn^{++}} + RT \log_e \alpha_{Cu^{++}},$$

or $$E = E^o + \frac{RT}{2\mathbf{F}} \log_e \alpha_{Cu^{++}} - \frac{RT}{2\mathbf{F}} \log_e \alpha_{Zn^{++}},$$

where E^o is written in place of

$$-(F_{Cu} - F_{Zn} + F^o{}_{Zn^{++}} - F^o{}_{Cu^{++}}).$$

If the zinc half of the cell is kept the same, the variation of the electromotive force with the copper ion concentration will be given by

$$E = \text{const.} + \frac{RT}{2\mathbf{F}} \log_e \alpha_{Cu^{++}},$$

or $$E = \text{const.} + \frac{RT}{2\mathbf{F}} \cdot 2{\cdot}303 \cdot \log_{10} \alpha_{Cu^{++}}.$$

The factor $(RT/\mathbf{F})\ 2{\cdot}303$ has the value 0·058 at 18° C., and 0·0591 at 25° C.

These expressions can be generalised so as to cover galvanic cells of all types. Suppose that the reaction which occurs when the cell yields current is

$$A + B + C + \text{etc.} = K + L + M + \text{etc.},$$

where A and K are solids, B, C, L, M, etc., dissolved substances.

Let z Faradays of electricity be produced in the reaction represented by this equation. Then if α_B, α_C, . . . α_L, α_M . . . are the activities of the various dissolved substances, the free energy in the reaction can be expressed as

$$\Delta F = \Delta F^o + RT \log_e \frac{\alpha_L \cdot \alpha_M \ldots}{\alpha_B \cdot \alpha_C \ldots},$$

where ΔF^o is the free energy change when all the dissolved substances are at unit activity. Since $zE\mathbf{F} = -\Delta F$, we thus have

$$E = -\frac{\Delta F^o}{z\mathbf{F}} + \frac{RT}{z\mathbf{F}} \log_e \frac{\alpha_B \cdot \alpha_C \ldots}{\alpha_L \cdot \alpha_M \ldots} \qquad . \qquad . \quad (1)$$

where $-\Delta F^o/z\mathbf{F}$ is a constant for the given reaction at a given temperature which may be written as E^o. If one of the substances taking part in the reaction is a gas, the activity may be replaced by the pressure.

Standard Electrode Potentials. The reversible hydrogen electrode, which is set up by bubbling hydrogen over a platinised platinum electrode in a solution containing hydrogen ions, has been universally adopted as the standard with reference to which the potentials of other electrodes are stated. Consider, for example, the cell formed by combining such a hydrogen electrode with a copper electrode in a solution of copper ions :

$$H_2 \mid H^+ \quad Cu^{++} \mid Cu.$$

When a positive current passes from left to right, the cell reaction is

$$H_2 + Cu^{++} = Cu + 2H^+,$$

and the electromotive force, taking the sign as that of the right-hand side, is therefore

$$E = E^o + \frac{RT}{2\mathbf{F}} \log \frac{\alpha_{Cu^{++}} \cdot p_{H_2}}{\alpha^2_{H^+}}.$$

E^o, the standard electromotive force, is that obtained with unit activities of the ions and unit pressure (1 atmosphere) of hydrogen gas. It is evidently the difference between potential of the copper electrode and that of the hydrogen electrode, each under the standard conditions, i.e.

$$E^o = E^o(Cu) - E^o(H_2).$$

In the standard hydrogen scale $E^o(H_2)$ is taken arbitrarily as zero, and on this scale the standard potential of the copper electrode, which may be written E^o_H, is thus the standard electromotive force of the above cell.

The corresponding free energy change in the reaction $H_2 + Cu^{++} = Cu + 2H^+$ is $\Delta F = -2E^o\mathbf{F}$. It is, however, more convenient to represent the free energy change as that of the reverse reaction

$Cu + 2H^+ = Cu^{++} + H_2$, i.e. that of the solution of the metal with the liberation of hydrogen, for which $\Delta F = 2E\mathbf{F}$. In general, if ΔF is the free energy change of the reaction

$$M + zH^+ = M^{+z} + z/2\, H_2,$$

the standard electrode potential of the metal as defined above is given by $\Delta F = zE\mathbf{F}$. Table I gives values for some of the commoner metals, together with the corresponding free energy and heat content changes in kcals. The latter is the heat absorbed when a gram-atom of the metal is dissolved in an aqueous acid solution at infinite dilution. In thermochemical tables the heat contents of the elements at a given temperature (25°) are all taken as zero, and the heat of formation of any compound or derivative from its element or elements is taken as its heat content. On this basis

TABLE I. STANDARD ELECTRODE POTENTIALS AND HEATS OF SOLUTION OF METALS

	E^0_H	ΔF° *	ΔH° †	$T\Delta S^{\circ}$
Li, Li^+	− 2·957	− 68·25 ‡	− 66·63	1·62
Na, Na^+	− 2·712	− 62·59	− 57·48	5·11
K, K^+	− 2·922	− 67·43	− 60·27	7·16
Rb, Rb^+	− 2·924	− 67·47 ‡	− 61·04	6·43
Tl, Tl^+	− 0·3363	− 7·76	+ 0·8	8·6
Ag, Ag^+	+ 0·7995	+ 18·44	+ 25·2	6·8
Cd, Cd^{++}	− 0·4020	− 18·55	− 17·6	0·7
Zn, Zn^{++}	− 0·7620	− 35·17	− 36·3	− 1·1
Fe, Fe^{++}	− 0·440	− 20·31	− 20·6	− 0·3
Sn, Sn^{++}	− 0·136	− 6·28	− 2·39*	3·89
Pb, Pb^{++}	− 0·126	− 5·81	− 0·2	5·6
Cu, Cu^{++}	+ 0·3348	+ 15·91	+ 15·1	− 0·8
Hg, Hg^{++}	+ 0·854	+ 39·68	+ 41·6	1·9
2Hg, Hg_2^{++}	+ 0·7986	+ 36·85	+ 40·16*	3·31

$$\Delta H = H_{M^{+z}} - zH_{H^+},$$

i.e. the heat absorbed in the reaction is the difference between the heat contents in the solution of the metal ions and that of the equivalent of hydrogen ions. Since we cannot at present determine

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* Latimer, Hicks and Schutz, *J. Chem. Physics*, **2**, 82, 1934; Latimer, *Chem. Reviews*, **18**, 319, 1936; *Oxidation States of the Elements*, 1938.

† Bichowski and Rossini, *Thermochemistry of Chemical Substances*, 1936.

‡ Latimer, using ionic entropies, calculates for Li/Li^+, $\Delta F^{\circ} = -70{,}700$, for Rb/Rb^+, $\Delta F^{\circ} = -68{,}800$.

these quantities separately, we can arbitrarily take H_{H^+}, the heat of formation of hydrogen ions, as zero and then ΔH can be described as the heat of formation of the metal ions. This convention gives rise to no difficulties in practice since all operations which can be carried out, or which occur in a cell, either give the sum of the heats of formation of two ions of opposite charge or the difference of the heats of formation of two ions of like charge, and the heat of any ionic reaction can be obtained by subtracting the heat contents of the reacting ions from those of the products.

In exactly the same way, if the free energy of formation of hydrogen ions is taken as zero, ΔF^o represents the free energy of formation of the given ion from its element, and can be briefly described, on this convention, as the standard free energy of the ion. The free energy change in an ionic reaction is also simply obtained by subtracting the free energies of the reacting ions from those of the products.

Table I also gives $\Delta H^o - \Delta F^o = T\Delta S^o$, where ΔS^o is the entropy change in the cell reaction under the standard conditions. This is equal to

$$\Delta S^o = S^o{}_{M^{+z}} + z/2S_{H_2} - S_M - zS^o{}_{H^+},$$

where S_{H_2}, S_M are the molar entropy of hydrogen and the atomic entropy of the metal at the given temperature (25°). These quantities can be evaluated by heat capacity measurements from near absolute zero upwards, so that from ΔS^o we can determine $S^o_{M^{+z}} - zS^o_{H^+}$, i.e. the difference between the standard entropy of the metal ions and that of an equivalent quantity of hydrogen ions. For convenience in tabulation we can also arbitrarily take $S^o_{H^+}$ as zero, and refer to $S^o_{M^{+z}} - zS^o_{H^+}$ as the standard entropy of the given ion. The entropies of the common ions as obtained in this way, and also by other methods, such as from the entropy and entropy of solution of solid salts, are given in Table II.*

Many attempts have been made to calculate the standard electrode potentials of the metals from their more fundamental properties. In some cases these calculations were misdirected, for the

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* The values given here may differ in some cases from those derived from Table I, because other data have been taken into account in assessing the best established values.

problem belongs to general thermodynamics and does not at all depend on the mechanism of the cell or the location of potential differences inside it. If the heat of the cell reaction is known (the more fundamental problem of what determines the heat of solution of metals is considered later) it is only necessary to find the *entropy change*, when the free energy change and thus the electromotive force can be calculated. Many of the entropy values in Table II have been obtained from measurements not involving the galvanic cells and may be legitimately used to calculate electromotive forces. For example, the standard entropy of Al^{+++} is derived from the entropy of the cæsium alum $CsAl(SO_4)_2\ 12H_2O$, its heat of solution and solubility.[1] The heat of solution of aluminium in a dilute acid solution is $\Delta H^o = -127{,}000$ cals. The entropy change in the reaction

TABLE II. ENTROPIES OF METALS AND AQUEOUS IONS AT 25° C.[*]

H_2	31·23	H^+	0·0	Cu	7·97	Cu^{++}	− 26·5
Li	6·7	Li^+	4·7	Zn	9·95	Zn^{++}	− 25·7
Na	12·2	Na^+	14·0	Cd	12·3	Cd^{++}	− 16·4
K	15·2	K^+	24·2	Sn	12 3	Sn^{++}	− 4·9
Rb	18·1	Rb^+	28·7	Hg	18·5	Hg_2^{++}	17·7
Tl	15·5	Tl^+	30·5	Pb	15·6	Pb^{++}	3·9
Ag	10·2	Ag^+	17·5	Fe	6·5	Fe^{++}	− 25·9
Mg	7·76	Mg^{++}	− 31·6			Fe^{+++}	− 61
Cu	9·9	Cu^{++}	− 11·4	Al	6·73	Al^{+++}	− 76
Sr	—	Sr^{++}	− 7·3	Cl_2	53·31	Cl^-	13·5
Ba	—	Ba^{++}	2·3	$Br_2(l)$	36·8	Br^-	19·7
				$I_2(s)$	27·9	I^-	25·3

$$\begin{array}{cccc} Al + & 3H^+ = & Al^{+++} + & 3/2H_2 \\ 6{\cdot}73 & 0 & -76 & 46{\cdot}85 \end{array}$$

is − 36 units, hence

$$\Delta F^o = \Delta H^o + 298 \times 36 = -115{,}500 \text{ cals.}$$

and

$$E^o = \Delta F^o/3\mathrm{F} = -1{\cdot}67 \text{ volts.}$$

The electrode potential of aluminium is difficult to measure for the surface is usually covered by an oxide film, which interferes with the electrode equilibrium. This figure differs considerably from

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[*] Latimer, Schutz and Hicks, *J. Chem. Physics*, **2**, 82, 1934; Latimer, Pitzer and Smith, *J. Amer. Chem. Soc.*, **60**, 1829, 1938; Kelley, *U.S. Bur. of Mines, Bull.* No. 394, 1935; Latimer, *Oxidation States of the Elements* (Prentice-Hall, N.Y., 1938).

[1] *J. Amer. Chem. Soc.*, **50**, 2202, 1928.

that obtained in attempts to measure it directly. Similarly, calculations have been made of the electrode potentials of other metals which cannot easily be measured, and the results are given in Table III.[2]

TABLE III. SOME CALCULATED ELECTRODE POTENTIALS OF METALS AT 15° C.

Reaction	ΔH°	ΔS°	ΔF°	E°
$Be + 2H^+ = Be^{++} + H_2$	− 85·0	− 21	− 78·7	− 1·70
$Mg + 2H^+ = Mg^{++} + H_2$	− 110·23	+ 8·2	− 107·78	− 2·34
$Ca + 2H^+ = Ca^{++} + H_2$	− 129·74	+ 9·9	− 132·70	− 2·87
$Sr + 2H^+ = Sr^{++} + H_2$	− 130·04	+ 10·6	− 133·20	− 2·89
$Ba + 2H^+ = Ba^{++} + H_2$	− 128·36	+ 18·4	− 133·85	− 2·90
$Al + 3H^+ = Al^{+++} + 3/2H_2$	− 126·3	− 36·0	− 115·50	− 1·67

Not much progress has been made in accounting theoretically for the entropies of ions in solution. Latimer and Buffington[3] found that for ions of a given charge the *entropy of solution*, i.e. the difference between the entropy of the gaseous ions and that in solution, varied approximately in inverse proportion to the radius of the ion.* It is thus possible to estimate from its crystallographic radius the entropy in solution of an ion for which other data is lacking, and knowing the heat of solution of the metal the standard potential can thus be calculated. The values given in Table III for beryllium and strontium were arrived at in this way. Since the entropy term is small compared with the heat of solution, the uncertainty of such values is probably not very great.

Electrode Potentials in Non-Aqueous Solvents. The accurate determination of standard electrode potentials in non-aqueous solvents presents great difficulties and few reliable values are available. In the first place it is necessary to find the activity coefficients of the salts in the solutions employed, so that the measured values can be extrapolated to a state corresponding to complete ionisation at infinite dilution. In non-aqueous solvents salts behave with much less regularity than in water and extensive

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[2] *J. Physical Chem.*, **31**, 1267, 1927; *Chem. Reviews*, **18**, 347, 1936; revised in Latimer's *Oxidation States of the Elements*.

[3] *J. Amer. Chem. Soc.*, **48**, 2297, 1926.

* A more elaborate theory has been given by Eley and Evans (*Trans. Faraday Soc.*, **34**, 1093, 1938) which accounts for the values very well, but there is a considerable number of adjustable factors.

investigations are necessary to give the required data. The behaviour of simple salts in methyl and ethyl alcohols comes nearest to water in this respect, and a series of determinations has been made by A. MacFarlane and Sir H. Hartley in these solvents, which are given in Table IV. It can be seen that the values in these solvents are somewhat more negative, but do not differ greatly from those in water.

TABLE IV. STANDARD ELECTRODE POTENTIALS IN NON-AQUEOUS SOLVENTS

	H_2O	CH_3OH *	C_2H_5OH *	NH_3 †
Li, Li^+	− 2·958	− 3·095	− 3·042	—
Na, Na^+	− 2·712	− 2·728	− 2·657	− 1·84
K, K^+	− 2·922	—	—	− 1·98
Tl, Tl^+	− 0·336	− 0·379	− 0·343	—
Ag, Ag^+	+ 0·799	+ 0·764	+ 0·749	+ 0·83
Zn, Zn^{++}	− 0·758	—	—	− 0·52
Cd, Cd^{++}	− 0·397	—	—	− 0·18
Pb, Pb^{++}	− 0·127	—	—	+ 0·33
Cu, Cu^{++}	+ 0·345	—	—	+ 0·43
Cl_2, Cl^-	+ 1·359	+ 1·116	+ 1·048	+ 1·28
Br_2, Br^-	+ 1·065	+ 0·837	+ 0·777	+ 1·08
I_2, I^-	+ 0·536	+ 0·357	+ 0·305	+ 0·70

Ammonia is a solvent of great interest, and the more active metals at least give well-defined electrode potentials in it. Some recent values of W. A. Pleskow and collaborators are given in Table IV.

Electrodes of the Second Kind. Another common type of electrode consists of a metal in contact with a saturated solution of one of its (slightly soluble) salts containing also a soluble salt having the same anion. Electrodes of this type are commonly employed as standard electrodes on account of their stability and ease of preparation, and since they are reversible to the anion they are sometimes called "electrodes of the second kind." For example, a silver-silver chloride electrode is made by covering silver with a coating of silver chloride and immersing it in a solution of a soluble chloride. When a positive current is passed from the electrode to the solution silver ions pass into solution, but since the solution is

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* A. MacFarlane and Sir H. Hartley, *Phil. Mag.*, **13**, 425, 1932; **20**, 611, 1935.

† W. A. Pleskow and collaborators, *Acta Physicochimica, U.R.S.S.*, **1**, 713, 871, 1935; **2**, 615, 621, 679, 1935.

already saturated with respect to silver chloride, the result is the deposition of silver chloride, i.e. the reaction is

$$Ag + Cl^- + \oplus \rightarrow AgCl(s),$$

and the reverse reaction occurs when the current is passed in the opposite direction. Since the chloride ion is the only dissolved substance which takes part in the reaction, the electrode potential is determined by the chloride-ion concentration.

If this electrode is coupled up with a hydrogen electrode, we get the cell

$$H_2 \mid H^+ \;\; Cl^-, AgCl(s) \mid Ag.$$

When a positive current passes from left to right, the cell reaction is *

$$\tfrac{1}{2}H_2 + AgCl(s) = Ag + H^+ + Cl^-$$

for the passage of a Faraday of current. By (1) the electromotive force is

$$E = E^o + \frac{RT}{\mathbf{F}} \log \frac{p^{\frac{1}{2}}_{H_2}}{\alpha_{H^+} \,.\, \alpha_{Cl^-}},$$

or, for unit pressure of hydrogen and unit activity of hydrogen,

$$E = E^o - \frac{RT}{\mathbf{F}} \,.\, \log \alpha_{Cl^-}.$$

E^o is the standard electrode potential and $E^o\mathbf{F} = -\Delta F^o$ is the free energy change in the cell reaction as written above, under the standard conditions. The following table gives some values of E^o :—

TABLE V. STANDARD ELECTRODE POTENTIALS OF ELECTRODES OF THE SECOND KIND

Electrode	*Reaction*	E^o
$Ag, AgCl(s), Cl^-$	$H_2 + AgCl(s) = Ag + H^+ + Cl^-$	+ 0·2221
$Ag, AgBr(s), Br^-$	$\tfrac{1}{2}H_2 + AgBr(s) = Ag + H^+ + Br^-$	+ 0·0712
$Ag, AgI(s), I^-$	$\tfrac{1}{2}H_2 + AgI(s) = Ag + H^+ + I^-$	− 0·1522
$Hg, Hg_2Cl_2(s), Cl^-$	$\tfrac{1}{2}H_2 + \tfrac{1}{2}Hg_2Cl_2(s) = Hg + H^+ + Cl^-$	− 0·2676
$Hg, Hg_2Br_2(s), Br^-$	$\tfrac{1}{2}H_2 + \tfrac{1}{2}Hg_2Br_2(s) = Hg + H^+ + Br^-$	− 0·138
$Hg, Hg_2SO_4(s), SO_4^-$	$\tfrac{1}{2}H_2 + \tfrac{1}{2}Hg_2SO_4(s) = Hg + H^+ + \tfrac{1}{2}SO_4^-$	− 0·6141
$Hg, HgO(s, red), OH^-$	$H_2 + HgO(s) + H_2O = Hg + 2H^+ + 2OH^-$	− 0·097
$Pb, PbO\ (s, red), OH^-$	$H_2 + PbO\ (s) + H_2O = Pb + 2H^+ + 2OH^-$	− 0·579

Oxidation Potentials. Fundamentally many oxidation-reduction processes consist in the loss of electrons by the oxidant and

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* There is no necessity for a liquid junction in this cell, for the same solution of hydrochloric acid may be used at both electrodes.

their gain by the reductant. Bancroft[4] was the first to attempt to measure the oxidising or reducing power of solutions, by placing in them chemically inert electrodes and measuring the potentials set up thereat. Later it was realised that in order to realise a stable reversible potential it is necessary that both the oxidised and reduced forms of the substance shall be present in the solution. A typical electrode of this kind is an inert metal, such as platinum, dipping into a solution containing ferrous and ferric ions. Here the electrode process is the oxidation of ferrous to ferric ions, or *vice versa*, which consists in the loss or gain of one electron per ion, viz.

$$Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon.$$

If a positive current is taken from the electrode, i.e. if electrons pass into the electrode from the outside circuit, ferric ions are reduced, while when a current passes in the reverse direction ferrous ions lose electrons to the electrode and become ferric ions. If this electrode is coupled with a hydrogen electrode, forming the cell

$$H_2 \mid H^+ \;\; Fe^{++}, Fe^{+++} \mid Pt,$$

the cell reaction is

$$\tfrac{1}{2}H_2 + Fe^{+++} = H^+ + Fe^{++},$$

and it is easily shown by (1) that for constant hydrogen pressure and hydrogen-ion concentration, the electromotive force is given by

$$E = E^o + \frac{RT}{\mathbf{F}} \log \left(\frac{\alpha_{Fe^{+++}}}{\alpha_{Fe^{++}}}\right),$$

where $\alpha_{Fe^{+++}}$ $\alpha_{Fe^{++}}$ are the activities of ferric and ferrous ions in the solution, which may be replaced by the concentrations if the solution is reasonably dilute. This relation was first confirmed experimentally by Peters.[5] The general relation is

$$E = E^o + \frac{RT}{z\mathbf{F}} \log \frac{\alpha_O}{\alpha_R},$$

where α_O, α_R are the activities of the oxidising and reducing ions respectively and z is the change of valency. E^o, which is called the

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[4] *Z. physikal. Chem.*, **10**, 394, 1892; earlier experiments were made by Becquerel, *Ann. Chim. Phys.*, **23**, 244, 1823; cf. Neumann, *Z. physikal. Chem.*, **14**, 193, 1894.

[5] *Z. physikal. Chem.*, **26**, 193, 1898.

normal or standard electrode potential, measures the oxidising or reducing power of the system. Some of the values obtained with simple ionic systems, stated with reference to the standard hydrogen potential, are given in Table VI. A positive value means that a solution containing the ions at equal concentrations is capable of oxidising H_2 to H^+ under the standard conditions; while a negative value means that the solution can reduce H^+ to H_2.

TABLE VI. STANDARD OXIDATION POTENTIALS OF IONIC SYSTEMS (VOLTS)

Co^{++}, Co^{+++}	+ 1·82	$MnO_4^{=}$, MnO_4^-	+ 0·662
Ce^{+++}, Ce^{++++}	+ 1·61	$W(CN)_8^{-3}$, $W(CN)_8^{-4}$	+ 0·485
Mn^{++}, Mn^{+++}	+ 1·51	$Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$	+ 0·466
Tl^+, Tl^{+++}	+ 1·21	Cu^+, Cu^{++}	+ 0·167
$IrCl_6^{-3}$, $IrCl_6^{-2}$	+ 1·021	Sn^{++}, Sn^{++++}	+ 0·154
$Mo(CN)_8^{-3}$, $Mo(CN)_8^{-4}$	+ 0·82	Ti^{+++}, Ti^{++++}	− 0·37
Hg_2^{++}, Hg^{++}	+ 0·88	Cr^{++}, Cr^{+++}	− 0·40
Fe^{++}, Fe^{+++}	+ 0·772		

There are also many oxidation-reduction processes, which give rise to reversible potentials at inert electrodes, in which the reaction involves hydrogen ions and the electrode potential is therefore a function of the p_H (acidity) of the solution. These are of two classes: (1) reactions involving oxyacid ions, (2) reactions in which either the oxidised or reduced form is an acid or base.

A typical example of the former is the bromine-bromate potential, obtained with an inert electrode in a solution containing bromine and bromate ions. The electrode reaction may be represented as

$$BrO_3^- + 6H^+ + 5\epsilon = \tfrac{1}{2}Br_2 + 3H_2O,$$

and the electrode potential is

$$E = E^o + \frac{RT}{5\mathbf{F}} \log \frac{\alpha_{BrO_3^-} \cdot \alpha^6_{H^+}}{\alpha^{\frac{1}{2}}_{Br_2}}.$$

The most widely investigated example of the second class is the quinone-hydroquinone electrode. Here hydrogen ions are involved because quinone is non-acidic, while hydroquinone is a weak acid. The electrode reaction is

$$C_6H_4O_2 + 2H^+ + 2\epsilon = C_6H_4(OH)_2,$$

and the electrode potential is therefore expressed by

$$E = E^o + \frac{RT}{2\mathbf{F}} \log \frac{\alpha_Q \cdot \alpha^2_{H^+}}{\alpha_{Hy}}$$

or $$E = E^{o} + \frac{RT}{2\mathrm{F}} \log \frac{\alpha_{Q}}{\alpha_{Hy}} + \frac{RT}{\mathrm{F}} \log \alpha_{H^+}.$$

(Q = Quinone, Hy = Hydroquinone)

The standard electrode potential is usually stated for a saturated solution of quinhydrone, which is the molecular compound $C_6H_4O_2 \cdot C_6H_4(OH)_2$.

TABLE VII. OXIDATION POTENTIALS INVOLVING HYDROGEN IONS

Electrode	*Reaction*	*E°*
$PbO_2(s)$, $PbSO_4(s)$, H_2SO_4	$PbO_2+4H^{+}+SO_4^{-}+2\epsilon=PbSO_4(s)+2H_2O$	+ 1·6797
MnO_4^{-}, MnO_2, H^{+}	$MnO_4^{-} + 4H^{+} + 3\epsilon = MnO_2(s) + 2H_2O$	+ 1·586
BrO_3^{-}, Br_2, H^{+}	$BrO_3^{-} + 6H^{+} + 3\epsilon = \frac{1}{2}Br_2(l) + 3H_2O$	+ 1·491
$MnO_2(s)$, Mn^{++}, H^{+}	$MnO_2 + 4H^{+} + 2\epsilon = Mn^{++} + 2H_2O$	+ 1·332
VO_2^{+}, VO^{++}, H^{+}	$VO_2^{+} + 2H^{+} + 2 = VO^{++} + H_2O$	+ 1·000
H_3AsO_4, H_3AsO_3, H^{+}	$H_3AsO_4 + 2H^{+} + 2\epsilon = H_3AsO_3 + H_2O$	+ 0·57
UO_2SO_4, $U(SO_4)_2$, H^{+}	$UO_2SO_4+4H^{+}+SO_4^{-}+2\epsilon=U(SO_4)_2+2H_2O$	+ 0·36
$VOSO_4$, $(VO)_2SO_4$, SO_4^{-}	$VOSO_4 + \epsilon = (VO_2)SO_4 + \frac{1}{2}SO_4^{-}$	+ 0·3
$(VO_2)SO_4$, VSO_4, H^{+}	$\frac{1}{2}(VO_2)SO_4+2H^{+}+\frac{1}{2}SO_4^{-}+\epsilon=VSO_4+H_2O$	− 0·21
IO_4^{-}, $I_2(s)$, OH^{-}	$IO_4^{-} + 8H_2O + 14\epsilon = I_2 + 16OH^{-}$	− 0·33
IO_4^{-}, IO_3^{-}, OH^{-}	$IO_4^{-} + H_2O + 2\epsilon = IO_3^{-} + 2OH^{-}$	− 0·68
Quinhydrone	$C_6H_4O_2 + 2H^{+} + 2\epsilon = C_6H_4(OH)_2$	+ 0·6997
Methylene blue	[Methylene blue] + $2H^{+} + 2\epsilon =$ [Methylene white]	+ 0·53

Potential Differences between Two Phases. The potential difference between two phases which have common ions can also be formulated in another way. Gibbs showed that the condition of equilibrium between two phases, in contact with each other, is that the " chemical potential " of each neutral component which is common to both phases must be the same in both. The " chemical potential " of Gibbs (Gibbs's μ) is now often known as the partial free energy and is defined by equations such as

$$\bar{F}_1 \text{ (or } \mu_1) = \left(\frac{dF}{dn_1}\right)_{T,\, P,\, n_2\ n_3,\, \text{etc.}},$$

$$\bar{F}_2 \text{ (or } \mu_2) = \left(\frac{dF}{dn_2}\right)_{T,\, P,\, n_1,\, n_3,\, \text{etc.}},$$

where F is the free energy of a given phase, which contains n_1 mols of component 1, n_2 mols of component 2, etc. The partial free energy of the first component in a given phase is thus the rate of increase of the free energy of this phase with the amount of this component, when the temperature, pressure and quantities of the other components remain unchanged. Now, if $\bar{F}_1'$ is the partial free energy of component 1 in a first phase and $\bar{F}_1''$ that in another phase which is in contact with it, a condition of equilibrium between the two phases is that

$$\bar{F}_1' = \bar{F}_1'' \quad . \quad . \quad . \quad . \quad (1)$$

and the same applies to each component which is present in both of the phases.

For components which are electrically charged (i.e. ions) it is also necessary to take account of the difference of electrical potential between the two phases, since electrical work will be performed when a charged body is moved from one phase and another. It can be shown that the condition then becomes [6]

$$\bar{F}_1' + eV' = \bar{F}_1'' + eV'' \quad . \quad . \quad . \quad (2)$$

where V′, V″ are the electrical potentials of the two phases and e is the charge carried by a mol of the substance. Guggenheim [7] called the quantity $(\bar{F}_1 + eV)$ the electrochemical potential and suggested that since it is impossible to determine single potential differences, it is not possible to determine how much of this quantity is to be regarded as $\bar{F}_1$ and how much eV. The question of the meaning of single potential differences is discussed in Chapter IV. Meanwhile this formulation may be regarded as a very convenient way of expressing the potential difference at certain phase boundaries, particularly when neither phase is a metal.

For example, consider a salt such as silver chloride in contact with a saturated aqueous solution. We can consider that the ions Ag^+ and Cl^- are common to both phases. Hence, for equilibrium, it is required that

$$\left.\begin{aligned} \bar{F}'_{Ag^+} + \mathbf{F}V' &= \bar{F}''_{Ag^+} + \mathbf{F}V'', \\ \bar{F}'_{Cl^-} - \mathbf{F}V' &= \bar{F}''_{Cl^-} - \mathbf{F}V'', \end{aligned}\right\} \quad . \quad . \quad (3)$$

where the single dash refers to the solid and the double dash to the solution. The charge (e) on a mol of silver ions in $+\ \mathbf{F}$ and that on a mol of chloride ions $-\ \mathbf{F}$.

We may observe in passing that the V's may be eliminated by adding these equations, viz.

$$\bar{F}'_{Ag^+} + \bar{F}'_{Cl^-} = \bar{F}''_{Ag^+} + \bar{F}''_{Cl^-},$$

or

$$\bar{F}'_{AgCl} = \bar{F}''_{AgCl};$$

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[6] Butler, *Proc. Roy. Soc.*, **112A**, 129, 1926.

[7] *J. Physical Chem.*, **33**, 842, 1929; **34**, 1540, 1930; cf. Brönsted, *Z. physikal. Chem.*, **143**, 301, 1929.

where $\bar{F}'_{Ag^+} + \bar{F}'_{Cl^-} = F'_{AgCl}$ is the free energy of a mol of solid AgCl and $\bar{F}''_{Ag^+} + \bar{F}''_{Cl^-} = \bar{F}''_{AgCl}$ is the partial molar free energy of silver chloride in the solution. Writing

$$\left.\begin{aligned}\bar{F}''_{Ag^+} &= \bar{F}^o{}_{Ag^+} + RT \log \alpha_{Ag^+},\\ \bar{F}''_{Cl^-} &= \bar{F}^o{}_{Cl^-} + RT \log \alpha_{Cl^-},\end{aligned}\right\} \quad . \quad . \quad (4)$$

where $\bar{F}^o{}_{g^+}$, $\bar{F}^o{}_{Cl^-}$ are constants, we have

$$RT \log \alpha_{Ag^+} + RT \log \alpha_{Cl^-} = \text{const.}$$

or

$$\alpha_{Ag^+} \times \alpha_{Cl^-} = \text{const.}$$

which is the familiar law of solubility product.

The potential difference between the solid silver chloride and the solution by (3) is

$$V' - V'' = (\bar{F}''_{Ag^+} - \bar{F}'_{Ag^+})/\mathbf{F} = (\bar{F}'_{Cl^-} - \bar{F}''_{Cl^-})/\mathbf{F}$$

or, using (4),

$$V' - V'' = \text{const.} + \frac{RT}{\mathbf{F}} \log \alpha_{Ag^+}$$

or, alternatively,

$$V' - V'' = \text{const.} - \frac{RT}{\mathbf{F}} \log \alpha_{Cl^-}.$$

We thus see that the potential difference between silver chloride and its saturated solutions varies with the silver ion concentration in the same way as that of a metallic silver electrode.

A form of this expression was first used by Haber,[8] who made some exploratory measurements. Kolthoff and Sanders[9] have confirmed it by measuring the potential difference across membranes of silver halides, the two sides of which were in different concentrations of silver nitrate.

Numerous measurements have been made with cells containing interfaces between aqueous and non-aqueous liquids, particularly by Beutner, Loeb and Baur. The situation is rather confused, and the reader is referred to summaries by Dole (*Theoretical Electrochemistry*, p. 380), and by N. K. Adam (*Physics and Chemistry of Surfaces*, 2nd edition, 1938, p. 359).

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[8] *Ann. Physik*, **26**, 927, 1908.

[9] *J. Amer. Chem. Soc.*, **59**, 416, 1936. Tendeloo (*Rec. trav. chim.*, **55**, 227, 1936; *J. Biol. Chem.*, **113**, 333, 1936) found similar relations with the calcium-ion concentration at fluorite membranes, but this has been denied by Anderson (*ibid.*, **115**, 333, 1936) and Kolthoff (*loc. cit.*).

CHAPTER III

THE MECHANISM AND ENERGETICS OF REVERSIBLE ELECTRODE POTENTIALS

The Electrode Potentials of Metals. We now turn to the consideration of the mechanisms whereby potential differences arise at the various junctions. In 1889 Nernst[1] put forward his theory of the origin of the potential difference between a metal and a solution containing its ions. He considered it to arise from phenomena similar to those which give rise to the solubility of neutral substances. A substance like sugar has a certain tendency to dissolve in a solvent such as water which is measured by its "solution pressure." When placed in contact with water, solution occurs until, when equilibrium is attained, the solution pressure is balanced by the osmotic pressure of the sugar in the solution. Similarly, a metal has a "solution pressure," but only positive ions and *not neutral metal atoms* can dissolve, leaving their complement of electrons in the metal. Suppose that the metal is placed in a solution in which the osmotic pressure of the ions is less than the solution pressure of the metal. Metal ions will dissolve, but they cannot continue to do so indefinitely because the metal is thereby left with a negative charge and the solution acquires a positive charge. The positive charges of the ions which have passed into the solution and the negative charges on the metal form an "electrical double layer," Fig. 1 (*a*), which ions must now cross in their passage into the solution. This double layer tends to prevent the solution of ions, for ions which are crossing the double layer are repelled by the positive charges on the solution side and attracted by the negative charges of the metal. The solution of ions will thus come to an end when the forces of the electrical double layer are sufficiently powerful

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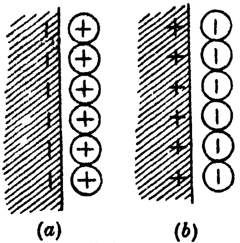
[1] *Z. physikal. Chem.*, 4, 129, 1899.

to prevent the solution of any more ions ; i.e. when the electrical work done by an ion in crossing the double layer is sufficient to balance the tendency to dissolve, because the solution pressure of the metal is greater than the osmotic pressure of its ions in the solution.

When the osmotic pressure of the ions in solution is greater than the solution pressure of the metal, metal ions will deposit on the surface of the metal and a double layer will be set up in the reverse direction, consisting of the deposited metal ions on the metal, and the equivalent of negative ions which have been left in the solution on the other side (Fig. 1 (*b*)).



III. 1.

In order to calculate the potential difference on this conception Nernst supposed that equilibrium was established when the work obtainable by the solution of the ions is equal (and opposite) to the electrical work done by them in crossing the double layer. The former he evaluated by a purely formal analogy with a thermodynamical dilution process as $RT \log P/p$, for a gram molecule of ions. P is the solution pressure of the metal and p the osmotic pressure of the ions in the solution. If the valency of the ions is z, the electrical work obtained when they cross the potential difference V of the double layer is $zV\mathbf{F}$,[*] so that the condition of equilibrium is

$$RT \log P/p + zVF = 0\,;$$

$$V = \frac{RT}{z\mathbf{F}} \log p/P.$$

Since the osmotic pressure p is proportional to the concentration of the ions, this can be written as

$$V = V^o + \frac{RT}{z\mathbf{F}} \log c,$$

which is the observed relation, at any rate in very dilute solutions.[†]

Although it can be made in this way to give rise to the correct thermodynamical relationship between the potential difference and

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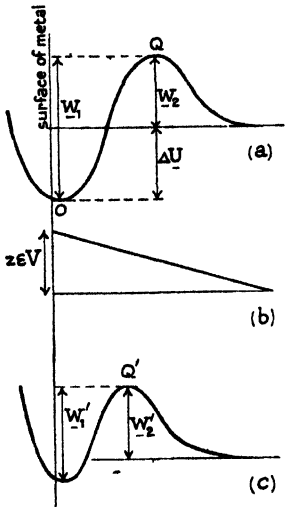
[*] We take the sign of V as that of the metal with respect to the solution.

[†] See the thermodynamical derivation, p. 15.

the concentration (the argument is not strictly legitimate, for the dilution formula *RT* log *P*/*p* cannot be properly applied to a change of phase), doubts have often been expressed as to whether Nernst's conception has any real physical basis. For example, Lehfeldt [2] pointed out that the values of *P* calculated from the observed electrode potentials vary from the extremely great (e.g. $9{\cdot}9 \times 10^{18}$ atmospheres for zinc) to the almost infinitely small ($1{\cdot}5 \times 10^{-36}$ atmospheres for palladium); quantities to which it is difficult to give a real physical significance.*



III. 2.

A more definite physical picture of the process was given in 1924 [3] by J. A. V. Butler. According to the electronic theory of metals, the atoms of a metal are supposed to be largely dissociated into metal ions and free electrons. A metal ion at the surface of a metal is held by the lattice forces, and work must be done in order to move it from its position of equilibrium in the surface layer, i.e. it is in a position of low potential energy. On the other hand, an ion is held in the solution by the forces of hydration, and work must be done to remove it from its solvation sheath to a sufficient extent to permit it to take its place in the surface of the crystal. The variation of these forces with distance from the metal surface was therefore supposed to give rise to a potential diagram like Fig. 2 (*a*).† The equilibrium position of an ion in the crystal surface is at the position of minimum potential O. Between O and Q the attractive

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[2] *Phil. Mag.*, **48**, 430, 1899.

* A good deal of this variation arises from the inclusion of the metal contact potential difference in the value of the "electrode potential." If this were subtracted the range of values would probably be physically possible.

[3] *Trans. Faraday Soc.*, **19**, 729, 1924.

† The *potential* here is a physical potential due to forces other than coulomb forces between electric charges.

In the original paper the diagram given was for the variation of the force with distance. It is here converted into the corresponding potential diagram.

forces of the metal predominate; between Q and the interior of the solution the predominant attraction is towards the solution. In order to pass into the solution a surface ion must acquire sufficient energy to pass over the potential barrier at Q. If N_1 is the number of ions in unit surface of the metal, the rate at which this happens is given as $\theta_1 = N_1\sqrt{T}A'e^{-W_1/kT}$; where W_1 is the difference of potential at O and Q. Similarly, before an ion can deposit from the interior of the solution it must have enough energy to reach Q, and if W_2 is the height of Q above the potential in the solution, and c the concentration in the solution, the rate of deposition will be $\theta_2 = c\sqrt{T}Ae^{-W_2/kT}$. Thus if $\theta_2 > \theta_1$ ions will be deposited at a greater rate than they pass into solution, and an electrical double layer, similar to that described by Nernst, will be set up. Equilibrium will be reached when the electrical forces so arising bring about the equality of θ_1 and θ_2.

Now suppose that in the equilibrium state there is a fall of the electrical potential across the double layer similar to that shown in Fig. 2 (*b*). This will be superimposed on the potential due to the other forces, and the variation of the combined potentials with distance from the surface will be as shown in Fig. 2 (*c*). Q′ is the new maximum of the potential curve, and the height of the barrier from O to Q′ is now $W_1 - z\epsilon V_1$ and from the interior of the solution to Q′, $W_2 + z\epsilon V_2$, where $V_1 + V_2 = V$ is the whole potential difference between the solution and the metal. z is the valency of the ion and e the unit electronic charge, so that $z\epsilon V$ is the electrical work done by an ion in crossing the double layer. Then the rates at which the ions pass Q′ in both directions are

$$\theta_1 = N_1\sqrt{T}A'\,e^{-(W_1 - z\epsilon V_1)/kT}\,; \quad \theta_2 = cA\sqrt{T}\,e^{-(W_2 + z\epsilon V_2)/kT}.$$

For equilibrium $\theta_1 = \theta_2$ and therefore

$$\frac{(V_1 + V_2)z\epsilon}{kT} = \frac{W_1 - W_2}{kT} + \log\left(\frac{cA}{N_1A'}\right),$$

or, since $V_1 + V_2 = V$ (the total electrical potential difference) and $W_1 - W_2 = \Delta U$, the difference between the energy of an ion in the solution and in the metal, we have

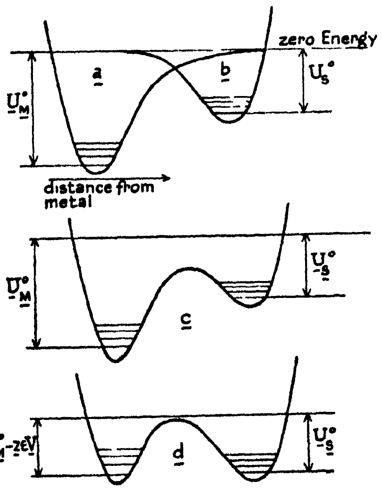
$$V = \frac{\Delta U}{z\epsilon} + \frac{kT}{z\epsilon}\log c + \frac{kT}{z\epsilon}\log\left(\frac{A}{N_1A'}\right).$$

Writing the more familiar $RT/z\mathrm{F}$ instead of $kT/z\epsilon$, we obtain the Nernst expression

$$V = V^o + RT/z\mathrm{F} \log c,$$

where V^o is given as $\Delta U/z\epsilon + kT/z\epsilon \log (A/N_1A')$. The normal potential difference V^o is thus determined mainly by the energy change in the transfer of ions from the metal to the solution, together with certain statistical constants which were not precisely evaluated.

In 1931 Gurney and Fowler[4] worked out a very similar conception, using the methods of quantum mechanics. The variation of the energy of a metal ion near the surface of the metal is represented by Fig. 3 (*a*). The horizontal line represents the energy of the isolated ion *in vacuo*, and U_M^o is the energy lost when it is bound to the surface of the metal in an equilibrium position. The energy of an ion, in quantum mechanics, is not now variable by infinitesimal amounts, but there are a number of discrete energy levels in the "dip" of the curve representing possible states of oscillation of the ion. The lowest of these levels, in which the ion has its minimum energy, is called the "ground level." The probability of an ion being in one of the higher levels depends on the temperature, the higher the temperature the greater the probability of the ion being in one of the higher levels.



III. 3.

A similar idealised picture may be made of the energy of an ion in the vicinity of a water molecule, or group of water molecules (Fig. 3 (*b*)). Here U_S^o is the hydration energy of the ion. Combining these two curves we obtain Fig. 3 (*c*), for representing the

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[4] Gurney and Fowler, *Proc. Roy. Soc.*, 136A, 378, 1932.

variation of the energy of the ion in the region between the metal and the neighbouring water molecule or molecules. When the energy levels of the ion in the solution are higher than those of the (uncharged) metal, as in Fig. 3 (*c*), there will be a greater tendency for ions to pass from the solution to the metal than *vice versa*. In such a case ions will be deposited on the metal, and an electrical double layer will be established as in Nernst's theory, giving the metal a positive electrical potential with respect to the solution. Let the electrical potential difference between metal and solution be V. If we suppose that the electrical potential of the solution remains zero, all the energy levels of the metal will be raised by the amount $z\epsilon V$, where $z\epsilon$ is the charge on the ion, as in Fig. 3 (*d*). The energy of lowest metal level is now $U^o_M - z\epsilon V$.

According to quantum statistics the probability of an ion at the surface of the metal being in an energy level between U and $U + dU$ is given by the expression

$$F(U)dU = 1/kT\{e^{-(U^o_M - z\epsilon V - U)/kT} \,.\, dU\},$$

where $U^o_M - z\epsilon V$ is the energy of the ground level. To obtain the probability of transfer of ions having energies between these limits to unoccupied levels on the solution side, we must multiply this by (1) the number of such unoccupied levels, which for a dilute solution Gurney and Fowler regard as proportional to the number of water molecules N_W adjacent to the metal, (2) a probability factor. Similarly, the probability of an ion in the solution having energies between U and $U + dU$ is $1/kT(e^{-(U^o_S - U)/kT})$, where U^o_S is the ground level for an ion in the solution. The probability of the transfer of ions having energies between these limits to a position on the surface of the metal is proportional to this quantity and to the number of ions (N_S) in the vicinity of the metal.

For equilibrium the probabilities of transfer, for levels between the given energy limits, must be equal; so that the condition of equilibrium is

$$N_W e^{-(U^o - z\epsilon V - U)/kT} = \beta N_S e^{-(U^o_S - U)/kT},$$

where β is a probability factor containing various effects which are not more precisely evaluated. Therefore

$$V = \frac{U^o_M - U^o_S}{z\epsilon} + \frac{kT}{z\epsilon} \log\left(\frac{\beta N_S}{N_W}\right),$$

or, since N_S is proportional to the concentration of the ions in the solution, and $U_M^0 - U_S^0$ is the difference of energy of an ion in the two ground levels,

$$V = \frac{\Delta U}{z\epsilon} + \frac{kT}{z\epsilon} \log c + \text{const.}$$

Factors Determining the Electrode Potentials. In Chapter II we saw that the standard electrode potential of a metal is related to its heat of solution by $zEF = \Delta H^o - T\Delta S^o$. The more fundamental problem of accounting for these quantities in terms of the primary properties of atoms and ions remains. It can be seen from Table III, Chapter II, that the entropy term, although not by any means constant, is comparatively small. The order of the heats of solution is the same as that of the electrode potentials, and in attempting to distinguish the factors which determine the position of a metal in the electrochemical series it is sufficient to consider the former only.

For this purpose the heat of solution of a metal must be analysed into its constituent parts, i.e. into parts most easily related to fundamental properties of the metal and the ion.

For this purpose the reaction

$$M + H^+ \rightarrow \tfrac{1}{2}H_2 + M^+$$

may be effected by the following series of operations :—

$$\begin{tikzcd}
M \arrow[r, "\mathfrak{I}_+"] & M^+ \arrow[d, "-W^+"] & + & \left.\begin{matrix}\epsilon \\ H^+\end{matrix}\right\} \arrow[r, "\mathfrak{I}_{H^+}"] & H \arrow[r, "\frac{1}{2}D"] & \frac{1}{2}H_2. \\
{[M]} \arrow[u, "\chi"] & (M^+) & & (H^+) \arrow[u, "W_{H^+}"'] & &
\end{tikzcd}$$

(1) The atom is vaporised. (Sublimation energy χ.)

(2) The vapour atoms are ionised into metal ions and electrons. The energy required is measured by the ionisation potential of the metal atom $\mathfrak{I}^+$; or in the case of a polyvalent ion by the sum of the ionisation potentials $\mathfrak{I}^+$, $\mathfrak{I}^{++}$, etc., for the removal of successive electrons.

(3) The isolated metal ions are dissolved in water. (Heat evolved = hydration energy W^+.)

(4) The equivalent of hydrogen ions is removed from water. (Heat absorbed = hydration energy of H$^+$, W_{H^+}.)

(5) They are combined with the electrons formed in stage (2). (Heat evolved = $\mathfrak{T}_{H^+}$, the ionisation energy of the hydrogen atom.)

(6) The resulting hydrogen atoms combine to form molecular hydrogen. (Heat evolved = $\frac{1}{2}D_{H_2}$ per equivalent, where D_{H_2} = dissociation energy of the hydrogen molecule.)

Thus we obtain for a univalent ion,

$$\Delta H_{\infty} = \chi + \mathfrak{T}^+ - W^+ - (\tfrac{1}{2}D_{H_2} + \mathfrak{T}_{H^+} - W_{H^+}) \quad . \quad (3)$$

or for a z-valent ion,

$$\Delta H_{\infty} = \chi + \mathfrak{T}^+ + \mathfrak{T}^{++}, \text{ etc.}, - W^+ - z(\tfrac{1}{2}D_{H_2} + \mathfrak{T}_{H^+} - W_{H^+}) \quad (3a)$$

The position of a metal in the series is thus determined by $\chi + \mathfrak{T}^+ - W^+$. The heats of vaporisation of metals can be determined from their vapour pressure curves; the ionisation potentials can be found by spectroscopic measurements and also by determining the minimum kinetic energy of electrons which can produce ionisation in the metal vapour. The evaluation of the hydration energies is a more difficult matter.

The Hydration of Ions. If χ and the quantities $\mathfrak{T}^+$, $\mathfrak{T}_{H^+}$, D_{H_2} are known, it is evidently possible to find $W^+ - W_{H^+}$ by (3) from ΔH_{∞}. A similar quantity for the negative halide ions, viz. $W^- + W_{H^+}$, is obtained from the heat of the reaction

$$\tfrac{1}{2}X_2 + \tfrac{1}{2}H_2 = (X^- + H^+)aq, \quad \Delta H_{\overline{\infty}}$$

This reaction can be effected by the following series of processes:

$$\begin{tikzcd}
X & & H \arrow[r, "\mathfrak{T}_{H^+} - \mathfrak{T}_{X^-}"] & X^- \arrow[d, "-W_{X^-}"] & & H^+ \arrow[d, "-W_{H^+}."] \\
X_2 \arrow[u, "\tfrac{1}{2}\chi_{X_2} + \tfrac{1}{2}D_{X_2}"] & + & H_2 \arrow[u, "\tfrac{1}{2}D_{H_2}"] \arrow[r, "\Delta H_{\infty}"] & (X^-) & + & (H^+)
\end{tikzcd}$$

(1) The molecules X$_2$, H$_2$ are vaporised (if necessary) and then dissociated into gaseous atoms. The energy required per atom is $\frac{1}{2}\chi_{X_2} + \frac{1}{2}D_{X_2}$, $\frac{1}{2}D_{H_2}$, where χ_{X_2} is the heat of vaporisation and D_{X_2} the heat of dissociation of the molecular halogen.

(2) An electron is transferred from a hydrogen atom to a halogen

atom. Energy required is $\mathfrak{T}_{H^+} - \mathfrak{T}_{X^-}$, where $\mathfrak{T}_{X^-}$ is the ionisation energy of the isolated halide ion or the *electron affinity* of the halogen atom.

(3) The two gaseous ions are dissolved in water. The energy gained is $W_{X^-} + W_{H^+}$.

Summing these terms, we see that

$$\Delta H_{\infty} = \tfrac{1}{2}\chi_{X_2} + \tfrac{1}{2}D_{X_2} - \mathfrak{T}_{X^-} - W_{X^-} + (\tfrac{1}{2}D_{H_2} + \mathfrak{T}_{H^+} - W_{H^+}). \qquad (4)$$

Therefore from (3) and (4) we have

$$\begin{aligned} W^+ &= H_g^+ - \Delta H_{\infty}^+ - (\tfrac{1}{2}D_{H_2} + \mathfrak{T}_{H^+} - W_{H^+}), \\ W^- &= H_g^- - \Delta H_{\infty}^- + (\tfrac{1}{2}D_{H_2} + \mathfrak{T}_{H^+} - W_{H^+}), \end{aligned} \qquad . \quad (5)$$

where $H_g^+ = \chi_M + \mathfrak{T}^+$ and $H_g^- = \tfrac{1}{2}\chi_{X_2} + \tfrac{1}{2}D_{X_2} - \mathfrak{T}_{X^-}$ are the energies of formation from the elements of the positive and negative gaseous ions in their usual form. The sum of the hydration energies of equivalent positive and negative ions can thus be easily obtained if H_g^+, H_g^- and the heats of formation of the ions in solution ΔH_{∞}^+, ΔH_{∞}^- are known. All these quantities are given in a convenient tabular form in Bichowski and Rossini's compilation of thermochemical data,[5] and the values given below are derived from these.

Unfortunately, although the ionisation energies of the metal atoms can be determined with great accuracy by spectroscopic methods, it has proved difficult to get measurements of the electron affinities of the halogens. Sherman [6] reversed the calculation and used the lattice energies of all the alkali halides, *calculated* from their lattice constants, to determine the electron affinities of the halogens. More recently a number of experimental determinations have been made by various methods which agree on the whole, and after comparing the various figures Bichowski and Rossini adopted the values given in Table I.

Table II shows some of the sums $W^+ + W^-$ obtained in this way. These values are necessarily additive for the different ions, and if the value of the hydration energy of a single ion were known, it would be possible to determine that of the others. There is,

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[5] *The Thermochemistry of Chemical Substances* (Reinhold Pub. Corp., New York, 1936).

[6] *Chemical Reviews*, **11**, 93, 1932.

however, no way of measuring the hydration energy of one kind of ion, since all operations which are practicable with solutions involve ions of two kinds, and the theoretical calculation of absolute hydration energies has not yet given values on which any great reliance can be placed. By comparing salts of a series of cations with a constant anion, it can be seen that the hydration energy decreases with the size of the latter and it is in fact approximately inversely proportional to the ionic radius, as measured in crystals. The most reasonable way at present available of splitting these sums into their separate parts is to assume that positive and negative ions of the same size and charge have equal hydration energies. The potassium and fluoride ions are crystallographically of the same size, so that the hydration energy of KF (193·1 kcals.) might be supposed to be divided equally between them. Bernal and Fowler have, however, suggested [7] that owing to the different orientation of water molecules round similar positive and negative ions, the hydration energy of a negative ion is about 2 per cent. greater than that of a similar positive ion. On this basis one would assign (in round numbers) 98 kcals. to F^- and 95 kcals. to K^+. The values

TABLE I. CALCULATION OF H_g^+, H_g^- FOR SOME UNIVALENT IONS

	$\frac{1}{2}\chi + \frac{1}{2}D$	$\mathfrak{T}^-$	H_g^-	H_∞^-
$\frac{1}{2}F_2 \rightarrow F^-$	31·75	98	− 66·3	− 78·2
$\frac{1}{2}Cl_2 \rightarrow Cl^-$	28·90	90	− 61	− 39·69
$\frac{1}{2}Br_2 \rightarrow Br^-$	26·88	88·5	− 61·6	− 28·67
$\frac{1}{2}I_2 \rightarrow I^-$	25·59	78·6	− 53·0	− 13·37
	χ	$\mathfrak{T}^+$	H_g^+	H_∞^+
$Li \rightarrow Li^+$	39·0	124·25	163·25	− 66·63
$Na \rightarrow Na^+$	25·9	119·45	145·35	− 57·48
$K \rightarrow K^+$	19·8	101·1	120·90	− 60·27
$Rb \rightarrow Rb^+$	18·9	97·35	116·25	− 61·04
$\frac{1}{2}H_2 \rightarrow H^+$	51·9*	313·7	365·6	0·00

TABLE II. $W^+ + W^-$ FOR IONS OF SOME SALTS

LiF	241·8	LiCl	208·6	LiBr	197·6	LiI	190·3
NaF	214·7	NaCl	181·5	AgBr	175·3	ZnI_2	615·6
KF	193·1	KCl	159·9	TlBr	148·0	NiI_2	617·6
RbF	189·2	RbCl	156·0	HBr	332·7	CoI_2	603·3
CsF	183·6	CsCl	150·4	$CaBr_2$	527·6	CdI_2	562·8

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* $\frac{1}{2}D_{H_2}$.

[7] *J. Chem. Physics*, 1, 515, 1933.

of the individual hydration energies so obtained are given in Table III.*

TABLE III. HYDRATION ENERGIES OF IONS

H^+	280	Be^{++}	713	Zn^{++}	523	Al^{+++}	1151
Li^+	144	Mg^{++}	498	Fe^{++}	507	Ga^{+++}	1139
Na^+	117	Ca^{++}	421	Cd^{++}	470	In^{+++}	1035
K^+	95	Sr^{++}	383	Co^{++}	510	Tl^{+++}	1052
Rb^+	91	Ba^{++}	347	Ni^{++}	525	Cr^{+++}	1062
Cs^+	86	F^-	98	Sn^{++}	424	Cr^{++}	500
Tl^+	95	Cl^-	65	Pb^{++}	394	Hg^{++}	474
Ag^+	132	Br^-	53	Cu^{++}	542		
NH_4^+	97	I^-	46	Mn^{++}	484		

It will be realised that this method of division is somewhat arbitrary. However, the order and differences between the values of either positive or negative ions would be unchanged by any other basis of division. These values all refer to 25° C.

The Electrochemical Series. We have seen that the electrode potential of a metal is determined mainly by $\chi + \Sigma\mathfrak{T}^+ - W^+$. $\chi + \Sigma\mathfrak{T}^+$ is the energy required to dissociate the metal into gaseous ions and free electrons and W^+ the energy of hydration of the ions. Since these are both quantities which vary through the periodic table in a complex manner, and it is also impossible to compare all the ions in the same state of valency, it is evident that no simple explanation can be given of the order of the metals in the electrochemical series. But there are some significant regularities which can be made out and accounted for, which are illustrated by the data given in Table IV, where the above quantities are given uniformly in electron-volts (1 electron-volt = 23·066 kcals.).

In the first place the metals may be divided into those of the main groups (Na, Mg, Al, etc.) and those of the sub-groups (Cu, Zn, Ga, etc.). The former follow the inert gases in the periodic table and their stable ions have the inert gas structure. It will be noticed that in these cases the hydration energy is nearly equal to the ionisa-

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* When a value for W_{H^+} has been obtained ($\frac{1}{2}D_{H_2} + \mathfrak{T}_{H^+} - W_{H^+}$) in (5) can be evaluated. Taking W_{H^+} as 280, this term is 85·6; and the hydration energies of the ions can then be evaluated directly as

$$W_+ = H_g^+ - H_\infty^+ - 85{\cdot}6z$$
$$W_- = H_g^- - H_\infty^- + 85{\cdot}6z.$$

tion energy $\Sigma\mathfrak{T}^+$. Bernal and Fowler have pointed out [8] that this means that the process of hydration is equivalent to restoring the

TABLE IV. FACTORS DETERMINING THE ELECTRODE POTENTIALS OF METALS [*]

	3 Li$^+$	4 Be^{++}
E^0	−2·96	−1·7
χ	1·69	3·25
$\Sigma\mathfrak{T}^+$	5·36	27·40
W^+	6·24	30·9

	11 Na$^+$	12 Mg^{++}	13 Al^{+++}
E^0	−2·71	−2·31	−1·70
χ	1·12	1·57	2·39
$\Sigma\mathfrak{T}^+$	5·12	22·57	53·01
W^+	5·07	21·62	49·9

	19 K$^+$	20 Ca^{++}	21 Sc^{+++}	22-28	29 Cu$^+$	30 Zn^{++}	31 Ga^{+++}
E^0	−2·92	−2·86			0·43	−0·76	− 0·52
χ	0·86	2·52			3·52	1·19	2·25
$\Sigma\mathfrak{T}^+$	4·32	17·91			7·68	27·25	57
W^+	4·13	18·28			—	22·68	49·3

	37 Rb$^+$	38 Sr^{++}	47 Ag$^+$	48 Cd^{++}	49 In^{+++}
E^0	−2·92	−2·90	0·80	−0·40	(0·35)
χ	0·82	2·04	2·95	1·16	2·25
$\Sigma\mathfrak{T}^+$	4·16	16·65	7·54	25·80	52·4
W^+	3·96	16·6	5·73	20·39	45

	55 Cs$^+$	56 Ba^{++}	79 Au$^+$	80 Hg^{++}	81 Tl^{+++}
E^0	—	−2·91	(1·5)	0·80	0·69
χ	0·81	2·12	4·0	0·63	1·74
$\Sigma\mathfrak{T}^+$	3·87	15·14	9·18	29·03	56·09
W^+	3·73	15·1	—	20·57	45·7

	22 Ti^{++}	23 V^{++}	24 Cr^{++}	25 Mn^{++}	26 Fe^{++}	27 Co^{++}	28 Ni^{++}	29 Cu^{++}	30 Zn^{++}
E^0	—	—	−0·56	(−1·1)	−0·44	−0·27	−0·23	+0·344	−0·76
χ	4·3	3·7	3·8	3·2	4·1	3·7	3·7	3·5	1·19
$\Sigma\mathfrak{T}^+$	20·4	20·8	23·3	23·11	23·99	25·1	25·8	27·9	27·25
W^+	—	—	21·7	21·0	22·0	22·1	22·8	23·5	23·1

electrons which have been removed from the metal atom in forming the ion. All these metals have high negative potentials, but when

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[8] *Loc. cit.*

[*] $\Sigma\mathfrak{T}^+$ here is the spectroscopic value which corresponds to the ionisation energy at absolute zero, while the other values refer to 25° C.

we look at the corresponding metals and ions of the sub-groups (Cu, Zn, etc.), which have much more positive electrode potentials, we see that the difference is largely due to the relatively greater values of $\Sigma\mathfrak{T}^+$.

Between the main and sub-groups of the long periods come the transitional elements, e.g. in the first long period we have the following series :—

	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3d Electrons in M-shell	—	—	—	1	2	3	5	5	6	7	8	10	10
4s Electrons in N-shell	0	1	2	2	2	2	1	2	2	2	2	1	2

The transition series from Sc to Cu marks the building up of an inner group of 10 (*3d*) electrons, which is completed at Cu. The ionisation energies for the corresponding divalent ions are given in Table IV. With the exception of chromium, which has only one electron in the outer group, $\Sigma\mathfrak{T}^+$ increases steadily from Sc to Cu, and zinc, which has a complete (*3d*) group and the two valency electrons outside, shows a definite fall. This is paralleled by the electrode potential which becomes increasingly positive * throughout the series as far as Cu, and with zinc show a marked decrease. This is not, however, the whole story for the other factors are significant, indeed the changes of W^+ are parallel, though not so great as those of $\Sigma\mathfrak{T}^+$, and the small sublimation energy of zinc must be an important factor in determining its more negative potential.

The electrode potential measures in fact the difference between the energy of interaction of metal ions with electrons in the metal and with water in solution.

The Metal-Solution Interface Potential Difference. Having considered what determines the energy change of the whole cell reaction, we can now return to the galvanic cell itself and see whether it is possible to determine how the electromotive force is distributed among the various junctions. Consider the cell

$$\begin{array}{ccccccccc} \mathrm{M} & | & \mathrm{M}^+ & | & \mathrm{H}^+, \mathrm{H}_2 & | & \mathrm{Pt} & | & \mathrm{M} \\ \mathrm{II} & & \mathrm{I} & & \mathrm{IV} & & \mathrm{III} & & \mathrm{II} \end{array}$$

The electromotive force E_H is the sum of the potential differences of the various junctions, viz.

$$E_H = {}_{\mathrm{I}}V_{\mathrm{II}} + {}_{\mathrm{II}}V_{\mathrm{III}} + {}_{\mathrm{III}}V_{\mathrm{IV}}.$$

---

* **Except Mn, the value for which is uncertain.**

The potential difference ${}_{\mathrm{I}}V_{\mathrm{IV}}$ between the two solutions usually amounts to only a few millivolts and can be neglected. The Volta p.d., ${}_{\mathrm{II}}V_{\mathrm{III}}$, between the two metals is practically equal to the difference between their work functions $\phi_M - \phi_{Pt}$, so that if we substract this quantity from E_H, we get

$$E_H - (\phi_M - \phi_{Pt}) = {}_{\mathrm{I}}V_{\mathrm{II}} + {}_{\mathrm{III}}V_{\mathrm{IV}},$$

i.e. a quantity which differs from the single potential difference between the metal and the solution by a constant, which is the single p.d. of the hydrogen (platinum) electrode.

TABLE V. CALCULATION OF RELATIVE METAL-SOLUTION INTERFACE POTENTIAL DIFFERENCES

	E°_H	ϕ_M	${}_M V_{Pt}$	$E^\circ_H - {}_M V_{Pt}$
$H_2(Pt) \rightarrow H^+$	0·0	6·45	—	0·0
$Li \rightarrow Li^+$	− 2·96	2·28	4·17	+1·21
$Na \rightarrow Na^+$	− 2·71	2·29	4·16	1·45
$K \rightarrow K^+$	− 2·92	2·12	4·33	1·41
$Rb \rightarrow Rb^+$	− 2·92	2·16	4·29	1·37
$Tl \rightarrow Tl^+$	− 0·34	3·68	2·77	2·43
$Ag \rightarrow Ag^+$	+ 0·80	4·68	1·77	2·57
$Mg \rightarrow Mg^{++}$	− 2·34	3·68	2·77	0·43
$Ca \rightarrow Ca^{++}$	− 2·87	3·20	3·25	0·38
$Zn \rightarrow Zn^{++}$	− 0·76	3·57	2·78	2·02
$Fe \rightarrow Fe^{++}$	− 0·44	4·72	1·73	1·29
$Cd \rightarrow Cd^{++}$	− 0·40	3·68	2·77	2·37
$Ni \rightarrow Ni^{++}$	− 0·25	5·01	1·44	1·19
$Sn \rightarrow Sn^{++}$	− 0·14	4·38	2·07	1·83
$Pb \rightarrow Pb^{++}$	− 0·13	3·95	2·5	2·37
$Cu \rightarrow Cu^{++}$	+ 0·33	4·16	2·29	2·62
$Hg \rightarrow Hg^{++}$	+ 0·85	4·52	1·93	2·78

Until recently sufficiently reliable values of the thermionic or photoelectric work functions of metals were not available; but in the last few years, owing principally to Fowler's elucidation of the theory of the photoelectric effect, reasonably reliable values for many of the metals have been obtained. Those used below are taken mainly from a collection by Klein and Lange [9] of all the data then available. In Table V we give (1) the standard electrode potentials of the metals (i.e. the electromotive force of cell (A) for

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[9] *Z. Elektrochem.*, **43**, 570, 1937. These figures usually agree within ± 0·1 volt with those quoted in *Tables Annuelles*, § 41, 1 (1937).

unit activities of the ions), (2) the work function ϕ_M, (3) the Volta potential difference ${}_M V_{Pt}$ between the metals and platinum, (4) the difference $E^0_H - {}_M V_{Pt}$, which is equal to the sum of the two metal-solution interface p.ds.

The latter differs from the single p.d. between the metal and the solution by a constant, viz. the single p.d. of the hydrogen electrode. If this, or the absolute value of any single p.d. were known, all the others could be determined. It can be seen that the order of the single p.ds. differs considerably from the order of the metals in the electrochemical series.

We shall return in the next chapter to the question of the experimental determination of single potential differences, but we may notice here that the metal-solution p.d. could be calculated if the energy and entropy change of the electrode process, viz. the transfer of metal ions from the metal to the solution, are known. The former might be evaluated by the following operations :—

$$\begin{tikzcd}
M \arrow[r, "\mathfrak{T}^+"] & \epsilon + M^+ \arrow[d, "W"] \arrow[dl, "\phi"'] \\
{[M]} \arrow[u, "\chi"] \arrow[r, "\Delta U"'] & (M^+aq)
\end{tikzcd}$$

The metal is vaporised (χ), and the vapour atoms ionised into metal ions and electrons ($\mathfrak{T}^+$), and the latter are returned to the metal ($-\phi$) while the former are hydrated ($-W$). The total change of energy is *

$$\Delta U = \chi + \mathfrak{T}^+ - \phi - W.$$

ΔU can thus be determined if the hydration energies of individual ions are known. We have already pointed out that this involves some method of division of the sum of the hydration energies of the ions of a salt into the constituent parts, and the value of ΔU will be determined by the principle adopted in making the division. The same applies to the individual entropies of hydration.

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* For a z-valent ion, for ϕ write $z\phi$, etc.

We have already mentioned one method of dividing up the hydration energies of the ions of a salt, viz. that suggested by Bernal and Fowler (p. 37). Latimer, Pitzer and Slansky [10] have suggested another method, which makes use of the free energy of hydration, which is obtained for the ions of a salt in the usual way from the energies and entropies of hydration. According to Born's simple theory, the free energy of hydration of an ion should be related to the ionic radius by

$$-\Delta F = \frac{N\epsilon^2}{2r}[1 - 1/D].$$

They find good linear relations between ΔF and $1/r$, if instead of the crystal radii, effective radii r_e of the ions are employed, which are obtained by adding to the former 0·1 Å. for negative and 0·85 Å. for positive ions. The division of the values between positive and negative ions are then adjusted so that both lie on the same curve. The individual entropies of hydration are obtained in the same way. In this way they obtain the individual free energies, entropies and heats of hydration given in Table VI. They differ considerably from those given in Table III.

TABLE VI. FREE ENERGIES AND HEATS OF HYDRATION OF INDIVIDUAL IONS (LATIMER)

	r_e	$-\Delta F^\circ$ Hydr.	$-\Delta S^\circ$ Hydr.	ΔH° Hydr.
Li^+	1·45	114·6	22	121·2
Na^+	1·80	89·7	17	94·6
K^+	2·18	73·5	8	75·8
Rb^+	2·33	67·5	6	69·2
F^-	1·46	113·9	29	122·6
Cl^-	1·91	84·2	15	88·7
Br^-	2·05	78·0	12	81·4
I^-	2·26	70·0	7	72·1

On this basis the free energy change in the transfer of sodium from the metal to the solution can be calculated as follows:—

$$\left.\begin{array}{lll} Na(s) & \to Na(g), & \Delta F = 18{\cdot}7 \\ Na(g) & \to Na^+ + \epsilon(g), & \Delta F = 118{\cdot}1 \\ Na^+(g) & \to Na^+(aq), & \Delta F = -89{\cdot}7 \\ \epsilon(g) & \to \epsilon(Na), & \Delta F = -52{\cdot}8 \end{array}\right\} \begin{array}{l} Na \to Na^+(aq), \\ \Delta F = -5{\cdot}7, \\ V = -0{\cdot}25 \text{ volts.} \end{array}$$

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[10] *J. Chem. Physics*, **7**, 108, 1939; cf. *Chem. Revs.*, **18**, 349, 1936. This has been criticised by Frumkin (*J. Chem. Physics*, **7**, 552, 1939).

In the cell

$$\overset{2\cdot98\longrightarrow}{\overline{\mathrm{Hg}\ \overset{\xrightarrow{2\cdot23}}{|}\ \mathrm{Na}\ \overset{\xrightarrow{0\cdot25}}{|}\ \mathrm{Na^+}\,(aq),\quad \mathrm{Cl^-},\quad \mathrm{HgCl}\ |\ \mathrm{Hg}}};\quad E = 2\cdot98 \text{ volts},$$

we have

$$_{Hg}V_{Na} = -\,2\cdot23 \text{ (Table V)},\ V_{Na\rightarrow Na^+} = -\,0\cdot25,$$

hence the absolute p.d. of the calomel electrode is $2\cdot98 - 2\cdot23 - 0\cdot25 = 0\cdot5$ volts, which is in fair agreement with the electrocapillary value (see Chap. IV).

Mechanism of Oxidation-Reduction Electrodes. Nernst and others[11] regarded these electrodes as gas electrodes, the oxidation-reduction process being supposed to give rise to an equilibrium concentration of hydrogen or oxygen on the electrode surface, which gives rise to the potential difference. In many cases the equilibrium concentrations required are such that it is difficult to regard them as having any real physical meaning. In 1924 Butler[12] showed that the potential difference could arise from the transfer of electrons between the electrode and the ions in solution. If the thermionic work function of the metal is ϕ_M, the rate at which electrons escape at the temperature T was represented as $Ae^{-\phi_M/kT}$. If there is also an electrical potential difference V between the metal and the solution, the work done by an electron in escaping from the metal is $\phi_M + eV$ and the rate of escape becomes $Ae^{-(\phi_M+\epsilon V)/kT}$. The rate of transfer of electrons from the metal to (say) ferric ions in the solution would thus be proportional to this quantity and to the concentration x of ferric ions near the electrode, i.e.

$$\theta_1 = A'xe^{-(\phi_M + \epsilon V)/kT}.$$

Similarly, if J is the work required to remove an electron from a ferrous ion in the solution (its ionisation potential), the rate of transfer of electrons from ferrous ions to the metal may be supposed to be proportional to $e^{-J/kT}$ and to their concentration y near the electrode, i.e.

$$\theta_2 = A''ye^{-J/kT}.$$

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[11] Nernst and Lessing, *C. Zent.*, **2**, 241, 1902; Friedenhagen, *Z. anorg. Chem.*, **29**, 396, 1902.

[12] *Trans. Faraday Soc.*, **19**, 734, 1924.

The equilibrium potential difference is that at which the rates of transfer of electrons to and from the metal are the same, i.e. $\theta_1 = \theta_2$, or

$$A'x\, e^{-(\phi_M + \epsilon V)/kT} = A''y\, e^{-J/kT},$$

so that

$$V = \frac{J - \phi_M}{\epsilon} + kT \log \frac{x}{y} + \text{const.}$$

Assuming that the concentrations of the ions near the electrode are the same as in the bulk of the solution,* i.e. $x/y = c_{Fe^{+++}}/c_{Fe^{++}}$, this equation is in agreement with the thermodynamical relation, and it identifies the important factors determining the potential difference as J and ϕ_M. In a complete cell, however, ϕ_M appears again in the metal junction potential difference between the electrode metal and the metal of the other electrode, so that the significant quantity is J, the ionisation potential of the ions of lower valency in the solution.

This quantity is not the same as the ionisation potential of the ferrous ion, i.e. the energy required to remove an electron from Fe^{++}, *in vacuo*. When a ferrous ion becomes a ferric ion in solution the hydration energy changes and the difference of hydration energy must be included in J. If W_2, W_3 are the hydration energies of ferrous and ferric ions, it can be seen from the accompanying scheme that the ionisation energy in solution is

$${}_2J_3 = {}_2\mathfrak{T}_3 - (W_3 - W_2) = {}_2\mathfrak{T}_3 - \Delta W,^{13}$$

where ${}_2\mathfrak{T}_3$ is the ionisation energy of the third electron of the iron atom *in vacuo*, and ΔW the difference of hydration energies of Fe^{+++} and Fe^{++}.

$$\begin{tikzcd}
Fe^{++} \arrow[r, "{}_2\mathfrak{T}_3"] & Fe^{+++} & \text{(gas)} \\
(Fe^{++}) \arrow[u, "W_2"'] \arrow[r, "{}_2J_3"'] & (Fe^{+++}) \arrow[u, "W_3"'] & \text{(solution)}
\end{tikzcd}$$

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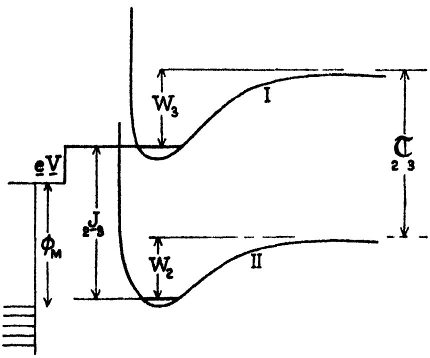
* A more elaborate hypothesis, involving the *adsorption* of the ions on the electrode, was made in the original paper.

[13] R. W. Gurney, *Ions in Solution* (Camb. Univ. Press, 1936).

A better picture of this process is given by means of the more recently developed potential diagrams. In Fig. 4, curve I represents the interaction of a Fe^{+++} ion with a water molecule (actually several water molecules take part in the hydration process, but the diagram would then be impossibly complicated). The hydration energy of the ferric ion at its lowest level is represented by the distance W_3. Curve II is a similar representation of the hydration of the Fe^{++} ion, with hydration energy W_2. The whole curve is displaced downwards a distance ${}_2\mathfrak{T}_3$, to represent the difference of energy of Fe^{++} and Fe^{+++} *in vacuo*. The ionisation energy in any hydrated state is represented by the vertical distance between the two curves, and therefore if the hydrated ferrous ion in its lowest hydration level loses an electron, the ionisation energy ${}_2J_3$ is required.



III. 4.

The highest occupied electron level of the metal has an energy ϕ_M lower than that of an electron in space. If the electrical potential of the metal with respect to the solution is V, the energy required to remove electrons from the metal will be $\phi_M + \epsilon V$, so that the highest occupied electron levels are shown displaced downwards a distance $\phi_M + \epsilon V$ relative to the hydrated Fe^{++} ion. An electron transfer from the ions to the metal can occur if ${}_2J_3 < \phi_M + \epsilon V$, and in the reverse direction if ${}_2J_3 > \phi_M + \epsilon V$. The condition of equilibrium, when electron transfers occur at equal rates in both directions, is thus approximately *

$${}_2J_3 = \phi_M + \epsilon V \quad \text{or} \quad V = ({}_2J_3 - \phi_M)/\epsilon.$$

Ionisation Potentials in Solution. We will consider a little further the nature of the quantity J. It can, of course, be cal-

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* Actually at temperatures above absolute zero the occupation of electron levels does not finish sharply at ϕ_M, some occupied levels will occur at energies $< \phi_M$ and some unoccupied levels and energies $> \phi_M$; and all the ions will not be in their lowest hydration levels.

culated from $\mathfrak{T}$ and the W's, when these are known, but it happens that the higher ionisation potentials of many of the elements which give accessible oxidation potentials have not been determined. However $\mathfrak{T} - \Delta W$ can be obtained directly from the heat of the cell reaction. Consider the reaction *

$$\mathrm{Fe}^{++}(aq) + H^{+}(aq) = \mathrm{Fe}^{+++}(aq) + \tfrac{1}{2}\mathrm{H}_2 \quad . \quad . \quad (\alpha)$$

The heat of this reaction is easily found, for it is merely the difference between the heats of the two reactions

$$\begin{aligned} \mathrm{Fe} + 2\mathrm{H}^{+}\,(aq) &= \mathrm{Fe}^{++}\,(aq) + \mathrm{H}_2, \\ \mathrm{Fe} + 3\mathrm{H}^{+}\,(aq) &= \mathrm{Fe}^{+++}\,(aq) + 3/2\,\mathrm{H}_2, \end{aligned}$$

i.e. the difference between the heats of formation of ferrous and ferric ions in aqueous solution. The reaction may also be regarded as the sum of the processes

$$\mathrm{Fe}^{++}\,(aq) = \mathrm{Fe}^{+++}\,(aq) + \epsilon, \quad . \quad . \quad . \quad (\beta)$$

$$\mathrm{H}^{+}\,(aq) + \epsilon = \tfrac{1}{2}H_2 \quad . \quad . \quad . \quad . \quad . \quad (\gamma)$$

The energy change in β is ${}_2J_r$ and that in γ has already been found to be $-(\tfrac{1}{2}D_2 + \mathfrak{T}_{H^+} - W_{H^+}) = -86$ kcals. per equivalent. Hence ${}_2J_3 = \Delta H_\alpha + 86$. The following table gives values of J in cases for which the data exist:—

TABLE VII. CALCULATION OF J FROM HEATS OF OXIDATION REACTIONS

	ΔH_α	J (kcals.)	J (e-volts)	$E^0_{H_2}$	$T\Delta S$ (e-volts)
$\mathrm{Cr}^{++} \rightarrow \mathrm{Cr}^{+++}$	−21·8	65	2·82	−0·40	−0·6
$\mathrm{Fe}^{++} \rightarrow \mathrm{Fe}^{+++}$	+11·3	97	4·2	+0·77	−0·28
$\mathrm{Mn}^{++} \rightarrow \mathrm{Mn}^{+++}$	24·2	110	4·77	+1·58	−0·53
$\mathrm{Tl}^{+} \rightarrow \mathrm{Tl}^{+++}$	27·2	2 × 100	2 × 4·31	+1·21	−0·63
$\tfrac{1}{2}\mathrm{Hg}_2^{++} \rightarrow \mathrm{Hg}^{++}$	21·6	108	4·65	+0·88	+0·05
$\mathrm{Fe(CN)}_6^{-4} \rightarrow \mathrm{Fe(CN)}_6^{-3}$	25·1	111	4·79	+0·47	+0·62
$\mathrm{IrCl}_6^{-3} \rightarrow \mathrm{IrCl}_6^{-2}$	34·3	120	5·20	+1·02	+0·46

There is a close parallelism between J and E only in the cases in which the valency change is the same. The reason for the absence of correlation in other cases is of course the variation of the entropy change in the reaction. This quantity, which is given as $T\Delta S$ in the last column, is comparatively large, and since it depends on the

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* The oxidation potential of $\mathrm{Fe}^{++} \rightarrow \mathrm{Fe}^{+++}$, on the standard hydrogen scale, measures the free energy change in this reaction.

charges on the ions it varies considerably with the type of valency change. It is evident that even if the values of J were independently available, they could only be used for predicting the oxidation potentials if due attention were paid to the entropy changes.

Stability of Ionic Species in Solution. The ions which can exist in solution are limited by (*a*) conditions imposed by the solvent; (*b*) conditions imposed by possible interactions among themselves.

Conditions imposed by the solvent. If the oxidation potential is more negative than the reversible hydrogen potential of the solution, i.e. $E_{M^{I}/M^{II}} < E_{H_2}$, the reaction $M^{I} + zH^{+} \rightarrow M^{II} + (z/2)H_2$ can occur, and therefore hydrogen may be liberated from the solvent. The possible oxidation potentials do not, however, end sharply at any value, for the oxidation potential depends on the relative concentrations of the ions, and the hydrogen electrode potential depends on the acidity of the solution and becomes more negative with decreasing acidity. The standard value of the Cr^{++}/Cr^{+++} potential in aqueous solution is given as $-$ 0·4 volts, which means that when the concentrations of the ions are the same, the chromous ion is unstable in a normal acid solution. The rate of liberation of hydrogen may, however, be small.

On the other hand, if the oxidation potential is more positive than the reversible oxygen potential of the solution, oxygen may be liberated. The value of this has been calculated as + 1·23 volts in a solution of normal acidity and decreasing the acidity makes the potential more negative. When the oxidation potential is appreciably greater than this, the ion in the higher state of oxidation will be unstable. A well-known example of this is the cobaltic ion, which slowly liberates oxygen in aqueous solutions. The standard oxidation potential of Co^{++}/Co^{+++} is about 1·82 volts, i.e. appreciably greater than the potential of the oxygen electrode.

The realisable oxidation potentials in aqueous solution therefore extend over a range of only about 2 volts, from about $-$ 0·4 to + 1·8 volts. In systems having lower values the ion in the lower state and, for higher values, the ion in the higher state of oxidation will be unstable.* But it is possible that solvents might

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* The limitations imposed by the solvent are discussed by Gurney, *loc. cit.*, ref. 13.

be found in which a greater range of oxidation potentials would be accessible.

Conditions imposed by interactions between the ions. Consider the cell Pt | M^+, M^{++} | M^+ | M. When a positive current passes from left to right the reaction at the left-hand electrode is $M^+ \rightarrow M^{++} + \epsilon$ and that at the right-hand electrode $M^+ + \epsilon \rightarrow M$. The cell reaction is therefore $2M^+ = M + M^{++}$, and this yields work if $E = E_{M/M^+} - E_{M^+, M^{++}} > 0$. Therefore if $E_{M/M^+} > E_{M^+, M^{++}}$, the reaction $2M^+ = M + M^{++}$ can occur spontaneously and the ion M^+ will be unstable. For the stability of the ion M^+ it is thus necessary that $E_{M/M^+} < E_{M^+, M^{++}}$; and similarly, it can be shown that for the stability of all the ions it is necessary that

$$E_{M/M^+} < E_{M^+, M^{++}} < E_{M^{++}, M^{+++}}, \text{ etc.}$$

If the sign of any one of these inequalities is reversed, then the ion which appears on each side of the inequality is unstable.

Inferences from the Ionisation Potentials of Elements. We have seen that the electrode potential can only be determined precisely from J when the corresponding entropy change is taken into account. Nevertheless, in considering the stability of ions a considerable latitude is permissible, and it is possible to draw useful conclusions from this quantity even if the entropy change is neglected. The rules for the stability of ions can then be expressed as follows :—

(1) It can be seen from Table VII that the possible values of J in aqueous solution extend from about 2·8 to 6. If $J < 2{\cdot}8$, the ion in the lower state of oxidation is unstable, while if $J > 6$, the higher ion is unstable.

(2) If

$$\begin{aligned} {}_0J_1 &= {}_0\mathfrak{T}_1 - (W_1 - \chi), & M &\rightarrow M^+ \\ {}_1J_2 &= {}_1\mathfrak{T}_2 - (W_2 - W_1), & M^+ &\rightarrow M^{++} \\ {}_2J_3 &= {}_2\mathfrak{T}_3 - (W_3 - W_2), & M^{++} &\rightarrow M^{+++} \\ &\text{etc.} \end{aligned}$$

The condition given above can be stated approximately by

$${}_0J_1 < {}_1J_2 < {}_2J_3 < \text{etc.}$$

If, for example, ${}_2J_3 < {}_1J_2$, then the ion M^{++} is unstable.

In that case we may further inquire what is the position with regard to M^+. Consider the reaction

$$3M^+ = M^{+++} + 2M.$$

The energy required to form $3M^+$ is $3\,{}_0J_1$ and that required for M^{+++} is

$$\chi + {}_0\mathfrak{T}_1 + {}_1\mathfrak{T}_2 + {}_2\mathfrak{T}_3 - W_3 = {}_0J_1 + {}_1J_2 + {}_2J_3.$$

If M^+ is stable,

$$ {}_0J_1 + {}_1J_2 + {}_2J_3 - 3\,{}_0J_1 > 0, $$

or

$$ 2\,{}_0J_1 < {}_1J_2 + {}_2J_3 $$

Similarly, for the stability of M^{++}, the condition

$$ 2\,{}_1J_2 < {}_2J_3 + {}_3J_4 $$

must be satisfied; and for stability of the ion M^{+++} the reaction

$$3M^{+++} = M^+ + 2M^{++++}$$

gives the condition

$$ {}_1J_2 + {}_2J_3 < 2\,{}_3J_4. $$

The successive ionisation potentials of the elements *in vacuo*, determined spectroscopically, are given in Table VIII. Since these invariably increase progressively as electrons are removed, all the ions are stable *in vacuo*. Thus the metal vapour at a sufficiently high temperature to cause partial ionisation will contain a certain amount of M^+, a smaller amount of M^{++}, and a still smaller amount of M^{+++} according to the energies required to remove successive electrons. But in aqueous solution the order of the J's may be quite different.

The hydration energies depend chiefly on the charge of the ion, and to get a general idea of the magnitude of the J's, we may use the following average values :—

	M^o	M^+	M^{++}	M^{+++}	
W or χ	2	5	20	48	*e*-volts
ΔW		3	15	28	*e*-volts

Using these figures we get the following values of the J's. These will be incorrect in so far as the hydration energies differ from the average values used and a latitude of ± 2*e*-volts must be allowed in individual cases, but nevertheless it is sufficient to indicate in most cases the stable ions (Table IX).

TABLE VIII. SUCCESSIVE IONISATION POTENTIALS OF THE ELEMENTS

	${}_0\mathfrak{T}_1$	${}_1\mathfrak{T}_2$	${}_2\mathfrak{T}_3$	${}_3\mathfrak{T}_4$
3 Li	5·36	75·26	121·8	—
4 Be	9·28	11·12	153·1	216·6
5 B	8·26	25·00	37·75	258·1
6 C	11·22	24·27	47·65	64·2
11 Na	5·12	47·06	70·72	—
12 Mg	7·61	14·96	79·72	108·9
13 Al	5·96	18·74	28·31	119·4
14 Si	8·12	16·27	33·35	44·9
19 K	4·32	31·66	46·5	—
20 Ca	6·09	11·82	50·96	69·7
21 Sc	~6·7	~12·8	24·61	~73·9
22 Ti	6·81	~13·6	~27·6	43·0
23 V	6·71	14·1	~26·4	~48
24 Cr	6·74	~16·6	—	—
25 Mn	7·41	15·7	—	—
26 Fe	7·83	16·16	—	—
27 Co	7·81	17·3	—	—
28 Ni	7·61	18·2	—	—
29 Cu	7·68	20·2	—	—
30 Zn	9·36	17·9	40	—
31 Ga	5·97	20·4	~30·6	63·8
32 Ge	8·09	15·9	34·1	45·5
37 Rb	4·16	27·4	~47	~80
38 Sr	5·67	11·0	—	—
39 Y	~6·5	12·3	20·4	—
40 Zr	6·9	14·0	24·0	33·8
47 Ag	7·54	21·4	35·9	—
48 Cd	8·96	16·8	38·0	—
49 In	5·76	18·8	27·9	57·8
50 Sn	7·30	~14·5	30·5	39·4
55 Cs	3·87	23·4	~35	~51
56 Ba	5·19	9·9	—	—
57 La	5·6	11·4	~20·4	—
58 Ce	6·54	14·8	—	~36·5
79 Au	9·18	19·9	—	—
80 Hg	10·38	18·6	34·3	—
81 Tl	6·07	20·3	29·7	50·5
82 Pb	7·38	15·0	~31·9	42·1
83 Bi	—	16·6	25·4	45·1

TABLE IX. APPROXIMATE VALUES OF J

	${}_0J_1$	${}_1J_2$	${}_2J_3$	${}_3J_4$		${}_0J_1$	${}_1J_2$	${}_2J_3$	${}_3J_4$
Li	2	60	—	—	Co	5	2	—	—
Be	6	3	125	—	Ni	5	3	—	—
B	5	10	10	—	Cu	5	5	—	—
C	8	9	20	—	Zn	9	3	12	—
Na	2	32	—	—	Rb	1	12	19	—
Mg	5	0	51	—	Sr	3	− 4	15	—
Al	3	4	0	>60	Y	4	− 3	− 8	—
Si	5	1	5	—	Ag	5	6	9	—
K	1	17	—	—	Cd	6	2	10	—
Ca	3	− 3	33	—	In	3	4	0	*ca.* 10
Sc	4	− 2	0	—	Sn	4	0	2	*ca.* 0
Ti	4	− 1	− 1	—	Ce	3	0	?	*ca.* 0
V	4	− 1	− 2	—	Au	6	5	—	—
Cr	4	2	*ca.* 0	—	Hg	7	3	6	*ca.* 20
Mn	4	1	*ca.* 0	—	Tl	3	5	2	*ca.* 10
Fe	5	1	—	—	Pb	4	0	4	*ca.* 0

For example, if we take the alkali metals, we see that the ions Li^{++}, Na^{++}, etc., are obviously unstable because the high values of ${}_1J_2$ would give rise to very high oxidation potentials in aqueous solution. For the same reason the ions Mg^{+++}, Ca^{+++}, Al^{++++}, etc., cannot exist. Mg^+ does not occur because ${}_0J_1 > {}_1J_2$, and Al^{++} because ${}_1J_2 > {}_2J_3$, while Al^+ is also unstable because

$$2\,{}_0J_1 > {}_1J_2 + {}_2J_3.$$

The ionisation potentials of the transitional elements are rather incomplete, but we see that the singly charged ions of Ti, V, Cr, Mn, Fe, Co, Ni are unstable because ${}_0J_1 < {}_1J_2$. With copper the approximate equality of ${}_0J_1$ and ${}_1J_2$ indicates the possibility of both Cu^+ and Cu^{++}. With zinc and cadmium the stable ion is clearly that with a double charge. With silver, Ag^+ is the most stable ion, but Ag^{++} is almost within the limit of stability. With thallium, Tl^{++} is clearly unstable, but Tl^+ and Tl^{+++} can exist since

$$2\,{}_0J_1 < {}_1J_2 + {}_2J_3.$$

On the other hand, with Sn and Pb, Sn^+ and Pb^+ cannot exist since $2\,{}_0J_1 > {}_1J_2 + {}_2J_3$, while the relations ${}_1J_2 < {}_2J_3$ and (probably) $2\,{}_1J_2 < {}_2J_3 + {}_3J_4$ give rise to the stability of Sn^{++} and Pb^{++}.

Complex Ions. When potassium cyanide is added to a solution of a silver salt, the silver cyanide first formed redissolves owing to the formation of the complex ions $Ag(CN)_2^-$. The potential of a silver electrode in such a solution is much more negative than that in the original solution, which may be interpreted as due to the depression of the concentration of simple silver ions through the formation of the complex ions. In this way it was calculated that in a 0·05 *m* solution of $K_2Ag(CN)_3$, containing an excess of 0·95*m* KCN, the silver ion concentration was 8×10^{-24} gm.-ions per litre, or about 5 ions per litre. Nevertheless, such solutions readily give rise to stable potentials at silver electrodes, and some of the characteristic reactions of silver ions, e.g. the precipitation of silver sulphide, occur rapidly. At one time there was a considerable amount of discussion about the meaning and reality of such small concentrations.[14] It was recognised that such a figure was merely a statistical average, representing the fraction of the time during which the silver ion was free, and that the formation and decomposition of the complex might occur quite rapidly. Yet if it is assumed that the decomposition reaction $Ag(CN)_3^{-} \rightarrow Ag^{+} + 3CN^{-}$ is sufficiently rapid to account for the rapidity of reactions, then it must be supposed that on account of the law equilibrium concentration of Ag^{+} the reverse reaction must be enormously faster, and Haber calculated that to produce this result the ions would have to move together with a velocity greater than that of light. The conclusion, therefore, was that the decomposition of the complex ions was not a necessary preliminary to their taking part in the establishment of electrode potentials or in reactions.

It is difficult now to understand the unwillingness of scientists at this period to believe that a silver electrode potential could be established except by the participation of " free " silver ions. But the behaviour of such an electrode can easily be understood in terms of the more recent concepts developed above. The hydrated silver ion in water is itself really a " complex " ion. When some or all of the water molecules in contact with the ion are replaced by other molecules, the potential energy of the silver ion in the solution is changed. Thus the silver ion in $Ag(CN)_3^{-}$ is in a state of lower potential energy than that in the hydrated ion $Ag^{+}(H_2O)_x$.* The

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[14] Cf. a controversy by Haber, Danneel, Bodländer and Abegg, in *Z. f. Elektrochem.*, 1904.

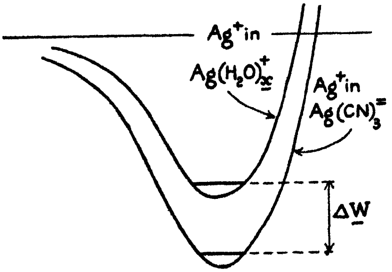
* The ion is necessarily in a state of lower energy in a stable complex than when hydrated with water; otherwise the latter state would be more stable.

magnitude of these energy differences can be found in some cases from the available thermochemical data. The following table gives the heats of formation of various complex ions of silver and mercury in aqueous solution from the metal and the dissolved anion.* From them we can find the energy change W, analogous to the hydration energy, which occurs when a gaseous metal ion is brought into a solution containing the anions and the complex ions are formed.

TABLE X. HEATS OF FORMATION OF COMPLEX IONS IN AQUEOUS SOLUTION

	$Ag^+(H_2O)_x$	$Ag(CN)_2^-$	$Ag(CN)_3^=$	AgI_2^-	
ΔH	25·2	− 8·05	− 5·7	− 13·7	
W	132	164	162	171	
	$Hg^{++}(H_2O)_x$	$HgCl_4^=$	$AgBr_4^=$	$HgI_4^=$	$Hg(CN)_4^=$
ΔH	+ 41·6	− 27·9	− 15·5	+ 1·9	− 14·9
W	474	543	531	514	530
	$Fe^{++}(H_2O)_x$	$Fe(CN)_6^{\equiv}$	$Fe^{+++}(H_2O)_x$	$Fe(CN)_6^{\equiv}$	
ΔH	− 20·6	− 87·8	− 9·3	− 62·7	
W	507	574	—	—	

The energy of Ag^+ in the complex ion is now represented, as in Fig. 5, by a curve which is deeper than the water curve by the amount $\Delta W = W_{\text{complex}} - W_{H_2O}$. Neglecting the entropy differences, the corresponding displacement of the electrode potential is $\Delta E = \Delta W/z\epsilon$.



III. 5.

When complex ions of two different valencies can exist, there are oxidation reactions of the type

$$Fe(CN)_6^{\equiv} \rightarrow Fe(CN)_6^{=} + \epsilon,$$

some of which have already been mentioned, which give rise to oxidation potentials. The displacement of the electrode potential when the simple hydrated ions become complex ions follows no general rule, as can be seen from the examples in Table XI.

When comparing the simple hydrated ions with the complex ions, it is necessary to remember that when the complex ions contain

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* I.e. ΔH for the reaction $Ag + 3CN^- + H^+ = Ag(CN)_3^= + \frac{1}{2}H_2$.

TABLE XI. INFLUENCE OF COMPLEX FORMATION ON OXIDATION POTENTIALS

	$E°$ (volts)		$E°$
Co^{++}, Co^{+++}	*ca.* + 1·84	$Fe(phth)_3^{++}$, $Fe(phth)_3^{+++}$ *	+ 1·14
$Co(CN)_6^{-4}$, $Co(CN)_6^{-3}$	− 0·8	$Fe(dipy)_3^{++}$, $Fe(dipy)_3^{+++}$, *ca.* *	+ 1·1
$Co(NH_3)_6^{++}$, $Co(NH_3)_6^{+++}$	+ 0·1	$Fe(nitrophth)_3^{++}$, $Fe(nitrophth)_3^{+++}$	+ 1·25
Fe^{++}, Fe^{+++}	+ 0·77		
$Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$	+ 0·47	$Fe(CN)_5H_2O^{-3}$, $Fe(CN)_5H_2O^{-2}$	+ 0·49
$Fe(CN)_5(NH_3)^{-3}$, $Fe(CN)_5(NH_3)^{-2}$	+ 0·37	$Fe(CN)_5(NO_2)^{-3}$, $Fe(CN)_5(NO_2)^{-2}$	+ 0·52

anions there is a change in the total charge of the ions and consequently in the ionic type of the reaction, e.g. the change of charge of + 2 to + 3 in the oxidation of ferrous to ferric becomes − 4 to − 3 in the change ferro- to ferricyanide. The entropies of the ions depend very largely on the magnitudes of the ionic charges and consequently the entropy changes in the two reactions will be very different. This is confirmed by the data in Table VII, from which the following figures are extracted :—

	ΔH†	$T\Delta S$†	E
Fe^{++}, Fe^{+++}	0·49	− 0·28	+ 0·77
$Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$	1·09	+ 0·62	+ 0·47

In general we may expect that when the oxidation process gives rise to a decrease of negative charge in the complex ions, instead of the increase of positive charge in the simple hydrated ions, the oxidation potential will be considerably reduced on this account, i.e. the oxidised ion will be appreciably more stable as the complex ion. Thus the simple cobaltic ion is barely stable in aqueous solution, but the cobalticyanide ion is readily formed by the oxidation of cobaltocyanide solutions with oxygen.

When the complex ions have the same charges as the original hydrated ions, the difference of entropy may be expected to be much smaller, and probably the most important factor will be the effect of complex formation on the ionisation energy. Writing the ionisation energy as $J = \mathfrak{I} - \Delta W$, where $\mathfrak{I}$ is the ionisation potential of the isolated metal ions and ΔW the difference of solvation energy of the two ions, we see that the effect of complex formation depends on the changes of ΔW. If the ion of higher charge is more firmly bound in the complex than the lower ion relatively to water, i.e. $\Delta W_{complex} > \Delta W_{water}$, the oxidation potential will be decreased. But sufficient data for a further analysis is not available.

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* phth = *o*-phenanthroline. dipy = dipyridyl. † In electron-volts.

CHAPTER IV

ELECTRICAL DOUBLE LAYERS

Single Potential Differences and Null Electrodes. It is impossible to make a direct measurement of the potential difference between a metal and a solution, but many attempts have been made to estimate its magnitude indirectly from effects associated with the double layer, such as the electrocapillary curve and various electrokinetic phenomena. It cannot be said that any conclusive information about the magnitude of the potential difference has been obtained in this way, but in the course of experiments which had as their main object either the determination of a single potential difference or the preparation of a *null electrode*, much information about the properties of double layers has been obtained, which is the basis of the present state of knowledge. It is therefore appropriate to begin the discussion of the nature and properties of double layers by a short account of this work.

It has been suggested[1] that the single potential difference between two phases has no physical meaning, since it cannot be measured, and in any case it is probably impossible to distinguish the electrical potential difference and the difference of the Gibbs "chemical potential." It is true that no direct measurement is conceivable, but we shall see that it is possible to learn much about the distribution of electric charges about an interface, and it seems to the writer that there is no obstacle in theory, although at present experiment may be some distance from this achievement, to obtaining a fairly complete knowledge of the charge distribution at an interface, not only of that of ions but also that produced by the orientation of polar molecules, and from this the potential difference could be determined.

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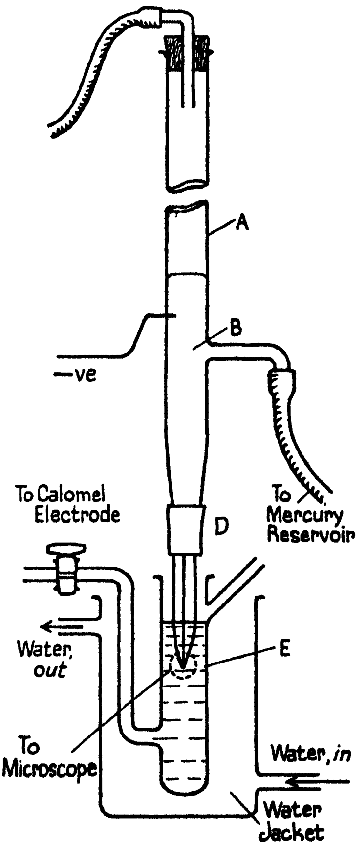
[1] E. A. Guggenheim, *J. Physical Chem.*, 33, 842, 1929.

It might be said that such a potential difference would depend on theory and be open to revision. The same is true of many physical quantities. It is the idea of a directly measurable potential difference between two phases which has no meaning, not the idea of the potential difference itself.

The Electrocapillary Curve. When a mercury electrode is polarised its surface tension changes. Lippmann[2] was the first to examine this effect quantitatively, and he made use of it in the electrometer which bears his name. It is usually studied in an arrangement similar to that shown in Fig. 1. A column of mercury ends in a fine tapering capillary tube, which dips into the solution. In contact with the solution there is also an unpolarisable electrode or simply a large pool of mercury. When a battery is connected to the large electrode and the capillary electrode, the potential of the former charges very little, and practically the whole of the applied potential difference is employed in polarising the capillary electrode, i.e. its potential difference changes until it differs from the large electrode by an amount equal to the applied potential difference. The surface tension of the mercury-solution interface is measured by the height of the mercury column required to bring the meniscus to a fixed point in the capillary tube.



IV. 1.—Apparatus for determining electrocapillary curves.

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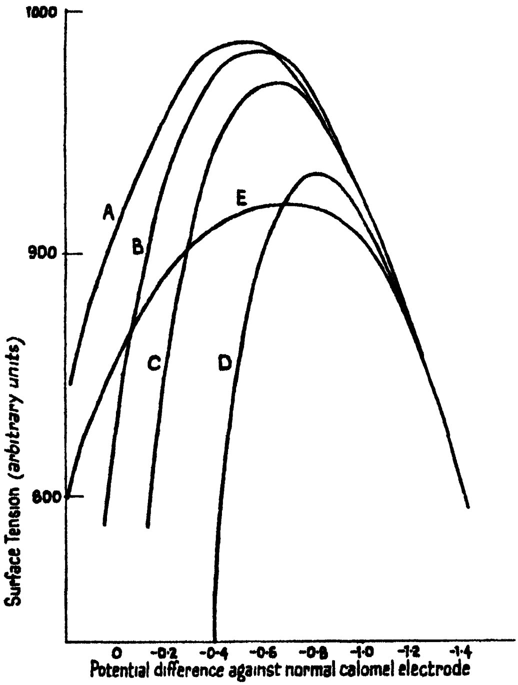
[2] *Pogg. Ann.*, **149**, 547, 1873; *Ann. d. Chim. et d. Phys.*, **5**, 494, 1875; **12**, 265, 1877.

The surface tension of mercury, polarised to various potentials, can also be determined by the drop weight method.[3] This is particularly suitable for non-aqueous liquids, since if the liquid does not wet the glass perfectly the accuracy of the capillary method is greatly diminished.

As the mercury electrode is made more negative, the surface tension first increases to a maximum and then decreases (Fig. 2). The theory of this effect was investigated by Lippmann and J. W. Gibbs (see p. 89), who both obtained the expression

$$\frac{d\sigma}{dV} = -\frac{dq}{ds} = -[e],$$

where σ is the surface tension, V the potential difference, q is the charge associated with area s of surface and therefore $[e]$ is the charge on unit area of surface. $[e]$ was identified by Helmholtz with the charge on each side of the double layer. At the maximum of the curve, where $d\sigma/dV = 0$, $[e] = 0$ and the potential difference arising from the double layer is therefore zero.



IV. 2.—Electrocapillary curves of (A) N/10 NH_4NO_3, (B) N/1 KCl, (C) N/1 KBr, (D) N/1 KI, (E) N/1 KCl + N/10 phenol. (Wightman.)

This simple theory is not sufficient to account for all the facts, for the curves obtained depend on the nature of the solution. Dis-

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[3] Kučera, *Ann. Physik*, **11**, 529, 698, 1903; Craxford and McKay, *J. Physical Chem.*, **39**, 545, 1935.

solved substances may be divided into two classes, according to whether their capillary activity, i.e. their effect on the shape of the curve, is great or small. The extensive work of Gouy [4] showed that active anions depress the positive (left) branch of the curve, while active cations depress the negative branch. This is due to the adsorption of the ions at the mercury surface, and the amount adsorbed, and therefore also the lowering of the surface tension caused thereby, varies with the potential difference. Anions are increasingly adsorbed as the mercury becomes more positive and cations as the mercury becomes more negative. Many organic substances cause a truncation of the curve, caused by their adsorption in the region of the maximum, which is diminished by both positive and negative polarisation.

If the double layer is regarded as a condenser with capacity K, the relation between the charge of the double layer and the potential difference it produces is $[e] = KV$, and when this is introduced into (1), we obtain by integrating

$$\sigma = \sigma_0 - \tfrac{1}{2}KV^2,$$

i.e. for a constant capacity we should get a simple parabolic curve. In inactive solutions, such as those of alkali nitrates, a close approximation to a parabolic curve is in fact obtained and the simple theory may then be regarded as reasonably adequate. At the maximum of the curve the potential difference can be taken as zero. This occurs at a potential of − 0·56 volts with reference to the normal calomel electrode, and the absolute potential difference of the latter is therefore + 0·56 volts.

Dropping Electrodes. If a mercury electrode is rapidly expanded the potential difference falls because the establishment of the double layer is comparatively slow, and if the increase of surface is great enough the charge density of the double layer may be reduced almost to zero. Helmholtz [5] realised this in the *dropping electrode* in which a very fine jet of mercury is projected into the solution in such a way that it breaks into drops just as it comes in contact with the surface of the solution. Paschen [6] found that it

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[4] *Ann. Chim. Phys.* (7), **29**, 145, 1903 ; (8), **8**, 291, 1906 ; (8), **9**, 75, 1906 ; *Ann. phys.* (9), **7**, 129, 1917.

[5] *Wiss. Abhand.*, I, 936.

[6] *Wied. Ann.*, **41**, 801, 1890 ; other papers, *ibid.*, **39**, **40**, **41**, **43**.

was not so much a question of stretching the surface, so that the existing charge was reduced to zero, as of allowing the mercury to remain in contact with the surface for so short a time that the double layer has no time to be formed. Once the mercury has broken into droplets it is not in electrical contact with the unbroken jet of mercury, and it is the potential of the end of this jet, at the point where it breaks into droplets, which is measured. It was found that under these conditions, and in a non-oxidising atmosphere, the potential of the dropping electrode is always the same as the maximum of the electrocapillary curve, and this holds good whether the solution contains capillary active substances or not.[7]

A mercury electrode in a solution of potassium chloride or some similar inactive salt is on the positive side of the electrocapillary maximum, i.e. the latter is reached when the electrode is negatively polarised. The potential of mercury may, however, also be made more negative by adding certain salts to the solution, e.g. sulphides, cyanides, which form complex ions with mercury. By this means it is possible to prepare an electrode which naturally exhibits the potential of the electrocapillary maximum, and therefore the dropping electrode has the same potential as a stationary one.[8] Such electrodes were called *null electrodes.* According to the simple theory the double layer potential difference at such an electrode should be zero. Unfortunately, however, the substances which change the potential at the electrode are themselves capillary-active ions which displace the maximum of the electrocapillary curve. The potentials exhibited by mercury in various null solutions do not agree with each other,[9] and therefore the potential difference between the mercury and the null solution cannot be invariably zero.

Electrocapillary Phenomena with Amalgams and Other Metals. It would be interesting to obtain electrocapillary curves with other metals, but the surface tension of solid metals cannot easily be measured.* Experiments of this kind have, however, been made

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[7] Cf. Paschen (*loc. cit.*); Smith and Moss, ref. 9; Frumkin, *Z. f. physikal. Chem.*, **103**, 55, 1923.

[8] Palmer, *Z. f. physikal. Chem.*, **59**, 129, 1907.

[9] S. W. J. Smith, *Z. f. physikal. Chem.*, **32**, 433, 1900; S. W. J. Smith and Moss, *Phil. Mag.*, **15**, 478, 1908.

* See p. 61.

with metallic amalgams and gallium, which melts at 30° C. Early experiments with amalgams [10] gave curves similar to those obtained with pure mercury, but more recent work by Frumkin and collaborators [11] has shown that in some cases the potential of the electrocapillary maximum is considerably displaced by comparatively small concentrations of other metals. The results obtained with thallium amalgams are given in Table I.

TABLE I. ELECTROCAPILLARY DATA FOR THALLIUM AMALGAMS IN Na_2SO_4

°/₀ Tl	$V_{max.}$	Dropping Electrode
0·0	− 0·48	—
1·0	− 0·67	− 0·668
3·55	− 0·73	—
10·35	− 0·80	− 0·792
33·9	− 0·92	− 0·898
41·5	− 0·93	—

It can be seen that $V_{max.}$, which is the potential of the electrocapillary maximum, referred to the normal calomel electrode, still agrees with the potential of a dropping electrode of the same amalgam. It was also found to be possible to prepare null solutions by adding suitable amounts of thallous salts to the solution, so that the electrode potential became the same as that of the electrocapillary maximum, and in such solutions a still electrode and a dropping electrode had the same potential.

The electrocapillary curve of metallic gallium was studied at 36° C. in normal potassium chloride [12] and its maximum was at — 0·9 volts with respect to the normal calomel electrode.

An interesting method of measuring the surface tension between a solid metal and a solution, first used by Möller,[13] has recently been developed by Frumkin to determine the capillary curves of solid metals.[14] It is based on the variation of the angle of contact

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[10] Rothmund, *Z. physikal. Chem.*, **15**, 1, 1894; Gouy, *Ann. Physique* (9), **6**, 5, 1916; Christiansen, *Drudes Ann.*, **16**, 382, 1905.

[11] Frumkin and Gorodetzkaya, *Z. physikal. Chem.*, **136**, 451, 1928; Frumkin and Cirves, *J. Physical Chem.*, **34**, 74, 1930; Frumkin, *Colloid Symp.*, VII, p. 99, 1930.

[12] Frumkin and Gorodetzkaya, *Z. physikal. Chem.*, **136**, 215, 1928; Muratazejew and Gorodetzkaya, *Acta Physicochimica, U.R.S.S.*, **4**, 75, 1936.

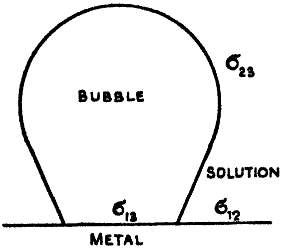
[13] G. Möller, *Ann. Physik* (4), **27**, 665, 1908; *Z. physikal. Chem.*, **65**, 226, 1908.

[14] See A. Frumkin, "Couche Double," *Act. Scient.*, No. 373, Paris, 1936.

of a gas bubble with the surface on which it rests with the polarisation of the latter. The magnitude of this angle is given (Fig. 3) by

$$\cos \theta = \frac{\sigma_{1,3} - \sigma_{1,2}}{\sigma_{2,3}},$$

where $\sigma_{1,2}$ is the surface tension between the metal and the solution. The surface tension $\sigma_{2,3}$ between the bubble and the solution is unaffected by polarisation and that between the metal and the bubble ($\sigma_{1,3}$) only slightly, owing to the film of moisture between them. Curves similar to the electrocapillary curve are thus obtained by plotting the contact angle against the potential of the metal. With mercury the maximum of the curve is in the same region as that previously found; with platinum at about 0·0 volts with respect to the normal calomel electrode.[15] Similar curves are obtained when a droplet of paraffin oil or toluene is used in place of a gas bubble.[16]



IV. 3.

The maximum size which bubbles or droplets can reach before becoming detached from the surface is a function of the angle of contact, and the size of the bubbles of gas liberated at an electrode varies with the polarisation of the electrode. If the bubble size is plotted against the electrode potential, a curve similar to the electrocapillary curve is obtained.[17] The mechanism of the adhesion of bubbles to a mercury surface has also been studied.[18]

Electrokinetic Methods. There is a large group of phenomena which occurs on the displacement of a liquid along the boundary surface of a charged solid, i.e. when there is a potential difference between the solid and the liquid. At the moment we need only consider these phenomena in so far as they can be used as indicators of the sign and magnitude of this potential difference. These phenomena may be grouped into two classes:—

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[15] A. Frumkin, A. Gorodetzkaja, B. Kabanow and N. Nekrassow, *Phys. Z. der Sowjetunion*, **1**, 255, 1932; **5**, 418, 1934.

[16] Cf. B. Kabanow, *Kolloid Z.*, **65**, 101, 1933.

[17] B. Kabanow and A. Frumkin, *Z. physikal. Chem.*, **165**, 433, 1933; **166**, 316, 1933.

[18] Frumkin and Gorodetzkaja, *Acta Physicochimica*, **9**, 313, 1938.

(A) Effects produced by an applied electromotive force.
  (1) Movement of charged particles (cataphoresis).
  (2) Movement of liquid when charged surface is fixed (electroendosmose).

(B) Effects produced by the relative motion of the solid and liquid.
  (1) Streaming potentials produced when the liquid moves relatively to a solid surface.
  (2) Potential differences arising from the movement of charged particles in liquid.[19]

Cataphoretic effects are the most important. A colloidal particle of a metal, with the double layer which surrounds it in solution, is rather like the central ion in the Debye-Hückel theory of strong electrolytes, which is supposed to be surrounded by an ionic atmosphere which is predominantly of the opposite charge. Recent investigations have shown that there is no essential difference between the two cases,[20] which may be treated on similar lines. Thus a positively charged particle will move in an electric field towards the cathode, and the direction of movement may be used to determine the sign of the charge carried by the particle.

Billiter used this phenomenon to investigate the sign of the charge of colloidal metals in appropriate solutions.[21] Null solutions can be prepared in which no motion takes place and the potential of a massive piece of the metal in such a solution can be determined. Assuming that the potential of the particles is the same as that of the massive metal, the null potential of the latter is found. For example, with silver the null potential was found to be about + 0·2 volts with reference to the normal calomel electrode.

However, the nature of the surface of colloidal particles is very imperfectly known, and it is doubtful if it is at all comparable with the surface of the massive metal. It is frequently found that the charges of the particles are greatly influenced by the adsorption of hydrogen or hydroxyl ions. To overcome this difficulty attempts

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[19] See J. Billiter, *Drudes Ann.*, **11**, 902, 1903; *Z. Elektrochem.*, **8**, 638, 1902.

[20] McBain and Laing, *J. Physical Chem.*, **33**, 673, 706, 1929.

[21] For summary see J. Billiter, *Monatshefte*, **53-54**, 813, 1929.

have been made to find the motion of massive pieces of metal. Billiter himself experimented with small particles of the metal suspended by fine quartz fibres. A. Garrison [22] used a silver needle suspended over a quandrant arranged that the electric field on each half caused a turning movement in the same direction and varied the silver ion concentration until no movement occurred when the electric field was applied. The results agreed with Billiter's experiments giving a " null " potential at + 0·1 to + 0·2 with respect to the normal calomel electrode. Christiansen allowed mercury droplets to fall vertically through a solution and applied an electric field at right angles to the direction of motion.[23] The drops are deflected according to the sign of their charge. A similar method was used by Frumkin,[24] who prepared a null solution in which no deflection occurred. The potential of mercury in the null solution was — 0·53 volts with respect to the N-calomel electrode, in substantial agreement with the electrocapillary maximum. Balaschora and Frumkin [25] have also examined the deflection of fine platinum wires in an electric field.

Bennewitz and Schulz [26] connected two similar silver electrodes in a solution of a silver salt, through a galvanometer. When one of the electrodes is rubbed, the double layer is disturbed and a current flows through the galvanometer to restore equilibrium. If, however, ammonia is added to the solution, a point is reached at which rubbing causes no current. It is inferred that there is then no double layer at the electrode, which is a null electrode. The potential at which this occurred was + 0·19 volts with respect to the N-calomel electrode.

Other Methods. (1) *Adsorption methods.* M. Proskurnin and A. Frumkin [27] found that when a large piece of silver foil is brought into contact with a dilute silver nitrate solution, measurable changes of the silver ion concentration occur owing to adsorption and the magnitude of the effect depends on the electrode potential of the

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[22] *J. Amer. Chem. Soc.*, **45**, 37, 1923.

[23] *Ann. Physik*, **12**, 1072, 1903.

[24] *J. Russ. Phys. Chem. Soc.*, **49**, 207, 1917.

[25] *Compt. rend. Acad. Sci., U.R.S.S.*, **20**, 449, 1938.

[26] *Z. physikal. Chem.*, **124**, 115, 1926 ; see also *ibid.*, **125**, 144, 1927 ; **153**, 443, 1931 ; **154**, 113, 1931.

[27] *Ibid.*, **155**, 29, 1931.

silver, the adsorption being positive in the stronger solutions and negative in the weaker ones. At a concentration of about 2×10^{-5} N, the adsorption was zero, and the authors regarded this as a null solution. The potential of the electrode in this solution is $E_h = 0{\cdot}51$ volt, which agrees with the value of Billiter and Bennewitz.

(2) *The ionisation method.* In any electromotive force measurement two electrodes are necessary. The air above a solution can be made conducting by the use of radioactive radiations, and it is then possible to measure the p.d. between two electrodes, one in the solution and the other in the air above it. Measurements of this kind were first made by M. Andauer.[28] Unfortunately this introduces two new boundaries at which potential differences may arise: (1) the surface of the solution, (2) the surface of the test electrode in the gas; and the total difference of potential measured is

$$\Delta V_1 = \Delta V \text{ (M/solution)} + \Delta V \text{ (solution/gas)} + \Delta V \text{ (gas/test)}.$$

Klein and Lange[29] attempted to eliminate the latter by making similar observations in the absence of the solution. The measured value is then

$$\Delta V_2 = \Delta V \text{ (M/gas)} + \Delta V \text{ (gas/test)}$$

and

$$\Delta V_1 - \Delta V_2 = \Delta V \text{ (M/solution)} + \Delta V \text{ (solution/gas)} - \Delta V \text{ (M/gas)}.$$

It was found that when suitable precautions were taken the measured value of ΔV_1 varied with the ion concentration of the solution by $\Delta V_1 = \text{const.} + 0{\cdot}058 \log c$ (for univalent ions) over a wide range of concentration. From this it is concluded that the potential difference between the solution and the air is not affected by the concentration of the ions, and when the latter is reasonably small is equal to that of pure water. It is supposed that this "intrinsic" potential difference of water exists at the boundary of the water with the metal as well as at the air surface, so that ΔV (M/solution) can be regarded as the sum of the intrinsic potential differences of

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[28] *Z. physikal. Chem.*, **125**, 135, 1927; **138**, 357, 1928; Andauer and Lange, **166**, 219, 1933.

[29] *Z. Elektrochemie*, **43**, 570, 1937; **44**, 542, 562, 1938; cf. Fink and Dehmel, *Trans. Amer. Elect. Soc.*, **70**, 281, 1936.

the metal and the water and the p.d. due to the double layer, i.e.

$$\Delta V\,(\text{M/solution}) = \Delta \text{V}\,(\text{M/gas}) - \Delta V\,(\text{solution/gas}) + \Delta V\,(\text{double layer}).$$

Hence, $\Delta V_1 - \Delta V_2 = \Delta V$ (double layer).

The value of the double layer potential difference of mercury in a mercurous salt solution of unit activity was found in this way to be + 0·69 volts. This does not agree with the value derived from electrocapillary measurements. If a mercury null solution is taken as having a potential of − 0·56 volts with respect to the normal calomel electrode, the absolute potential of the latter will be + 0·56 volts. The measured difference of potential between the normal calomel electrode and a mercury electrode in a solution of mercurous ions of unit activity is, however, 0·51.

Summary. The following table summarises the "null electrode" potentials of different metals, as determined by various methods. The determinations by electrocapillary and electrokinetic methods for each metal are fairly consistent.

TABLE II. POTENTIALS OF "NULL ELECTRODES"

Metal	Method	Potential of Null Electrode with Reference to *n*-calomel
Hg	Electrocapillary curves. Dropping electrodes in inactive solutions.	− 0·56 volts.
Ga	Electrocapillary curves.	− 0·9
Pt	Contact angle.	0·0
Ag	Cataphoresis of suspended particles.	+ 0·2
	Motion of massive metal.	+ 0·1 to 0·2
	Adsorption of ions.	+ 0·23
	Disturbance of potential by rubbing.	+ 0·19

If a cell were made of two "null electrodes" of different metals, it is evident that on the assumption that the potential difference between each metal and the solution is zero, the electromotive force of the cell is equal to the metal junction p.d. between the metals. Thus if the "null electrode" potential of mercury is $-0{\cdot}56$ and that of silver about $+0{\cdot}2$ volts, with respect to the *n*-calomel electrode, the electromotive force of the cell composed of the two null electrodes is 0·8 volts; and this should be equal to the metal junction p.d. between mercury and silver. This, however, appears to be small according to the best thermoelectric measurements, so that it appears that a null electrode does not necessarily have zero p.d., and it must be concluded that either the methods fail to measure the whole of the potential difference of the double layer, or the ionic double layer is only responsible for part of the total potential difference between the metal and the solution.

THE PROPERTIES OF THE DOUBLE LAYER

Capacity of the Double Layer. Helmholtz [30] regarded the double layer as a condenser of constant capacity, i.e. with equal charges on the metal and in the solution facing each other at a constant distance δ. The potential difference between the plates of such a condenser is

$$V = 4\pi e\delta/D,$$

where e is the charge per unit surface on each side of the double layer, and D the dielectric constant of the medium. The capacity is thus

$$\frac{de}{dV} = \frac{e}{V} = \frac{D}{4\pi\delta}.$$

Three methods of determining the double layer capacity have been used.

Capacity from electrocapillary curves. From Lippmann's equation, we have

$$e = -\,d\sigma/dV$$

and

$$\frac{de}{dV} = -\,d^2\sigma/dV^2.$$

It is evident that if the capacity were constant, the electrocapillary curves would be exact parabolas. This is, however, only

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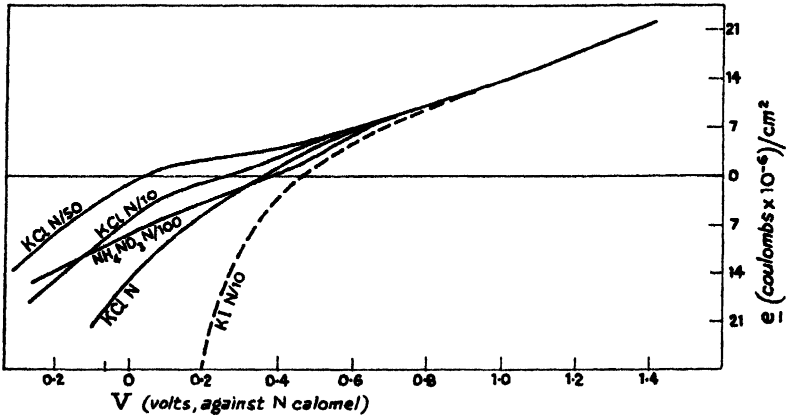
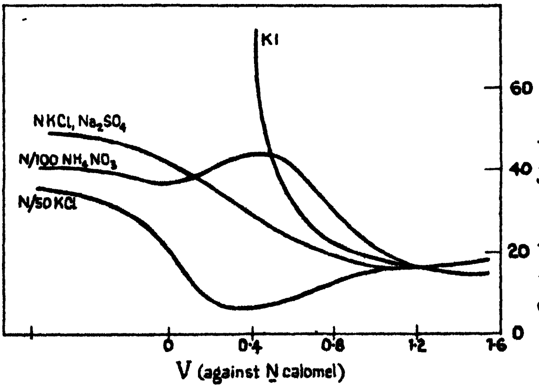
[30] *Monats. Preuss. Akad. Sci.*, Nov. 1881; *Wied. Ann.*, 7, 337, 1879.

the case in rare instances, such as potassium nitrate solutions[31] which are stated to give an approximately constant capacity of 13 microfarads/cm.^{2} Fig. 4 (*a*) shows some curves of $-e$ or $d\sigma/dV$,



IV. 4 (*a*).—$e = d\sigma/dV$ from electrocapillary curves. The curves have been displaced horizontally a little, so that the negative branches, which are identical in shape, coincide with that of NKCl.



IV. 4 (*b*).—Types of capacity curves.

and the shapes of the corresponding capacity curves are indicated in Fig. 4 (*b*).[32] Since the left-hand branch of the electrocapillary curve is usually steeper than the right-hand branch, the capacity

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[31] Krüger and Kromreich, *Z. Elektrochem.*, **19**, 620, 1913.
[32] Data from Butler and Wightman, *J. Physical Chem.*, **35**, 3293, 1931.

increases as the potential becomes more positive, and the rise is particularly marked when capillary-active ions, such as iodide ions, are present. The capacity of the right-hand branch determined by Gouy is usually 17-18 microfarads/cm.^{2} [33]

Units.—V is usually expressed in volts and e in coulombs/cm.^{2} The capacity e/V is then in farads/cm.^{2} To convert to electrostatic units, we have the following factors :—

$$1 \text{ coulomb} = 300 \times 10^7 \text{ e.s. units},$$
$$1 \text{ volt} = \tfrac{1}{300} \text{ e.s. units},$$
$$1 \text{ farad} = 9 \times 10'' \text{ e.s. units}.$$

Thus, a capacity of 18×10^{-6} farads/cm.^{2} $= 162 \times 10^5$ e.s. units. Then, in this case, we have

$$D/4\pi\delta = 162 \times 10^5 \text{ e.s. units},$$

and

$$\delta = D/4\pi \times 162 \times 10^5 = 0{\cdot}5 \times 10^{-8}\, D \text{ e.s. units}.$$

If D is taken as unity, the thickness of the double layer is thus 0·5 Å.

When e is determined from the electrocapillary curve by

$$e = -\,d\sigma/dV,$$

σ is usually expressed in ergs/cm.^{2} and V in volts. Then

$-\,300(d\sigma/dV)$ is the charge e in e.s. units,

and $10^{-7}(d\sigma/dV)$ is the charge e in coulombs.

$10^{-7}\,(d^2\sigma/dV^2)$ is the capacity in coulombs per cm.^{2} per volt.

Frumkin (*Phil. Mag.*, **40**, 375, 1920) gives for mercury in $2n$ H_2SO_4, saturated with Hg_2SO_4,

$$(d\sigma/dV)_{v=0} = -\,390 \text{ ergs/cm.}^2 \times \text{volts}.$$

The charge e is therefore 39×10^{-6} coulombs/cm.^{2}

Dropping electrode method. This was initiated by Varley,[34] who showed that when mercury flows from a reservoir into a solution, forming drops which recoalesce in a pool at the bottom of the vessel, a current may flow along a wire joining the two masses of mercury (see Fig. 5). However, if the dropping electrode is polarised by an auxiliary circuit to the potential of the electrocapillary maximum, or if the solution is a " null solution," no current flows. The formation of drops is equivalent to an expansion of the upper mercury

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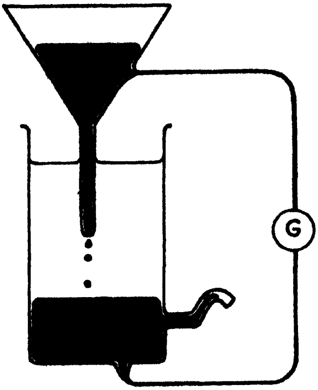
[33] *Ann. Chim. Phys.* (7), **29**, 159, 1903.
[34] *Phil. Trans.*, **101**, 129, 1871.

surface, and if it were insulated the potential would change until it reached that of the electrocapillary maximum. It is, however, connected by a wire with the much larger mercury electrode below, and its potential will therefore remain constant and equal to that of the larger electrode, and to provide the necessary charge a current will flow through the connecting wire. If the area of the droplets formed is known, it is possible to determine the charge per unit area. This method was developed by Lippmann[35] and more recently measurements have been made by Frumkin[36] and by L. St. J. Philpot.[37] The former compared the value of e determined in this way, with that given by $-d\sigma/dV$, and in general found good agreement. The latter determined the charge on the surface when polarised to various potentials by an auxiliary circuit. The results are shown in Fig. 6. The curves of charge against potential obtained in hydrochloric have two nearly linear parts (corresponding in each case to a constant capacity), joined by a non-linear portion. The capacities of the linear parts on each side of the point of zero charge were



IV. 5.—Dropping electrode.

	Positive Side	*Negative Side*
HCl	53·7	23·3 microfarads.
NaCl	57·3	23·6 ,,

Direct measurement of the capacity. If a current i is passed into an electrode for a time dt, and conditions are such that no charged ions or electrons can cross the double layer, then the charge on the double layer is increased by $de = idt$. If the consequent increase of the potential difference is dV, the capacity of the electrode is

$$B = \frac{de}{dV} = \frac{i\,dt}{dV}.$$

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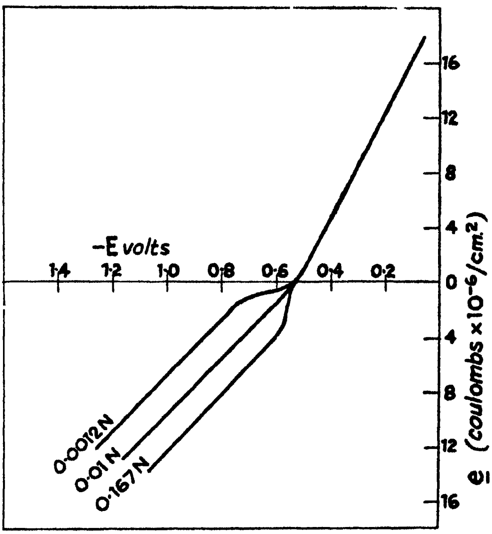
[35] *Loc. cit.*

[36] *Z. physikal. Chem.*, **103**, 55, 1923.

[37] *Phil. Mag.*, **13**, 775, 1932.

The rate of charge of the potential difference of electrodes, after starting the current, and also after stopping a steady current, was first investigated by Oberbeck,[38] Pring,[39] and Le Blanc.[40] The work of the first two showed that a deposited layer of metal only a few atoms thick has the electromotive properties of the massive metal. No very clear conclusions seem to emerge from the experiments of the latter. Knobe[41] made similar experiments with electrodes at which hydrogen was liberated, and Newbery[42] also examined with an oscillograph the changes of potential which occur on stopping and starting the current.



IV. 6.—Capacity of mercury surface in hydrochloric acid (Philpot).

The subject was clarified in 1928 by the careful experiments of Bowden and Rideal,[43] who followed the rapid changes at the beginning of the electrolysis by photographing on a rapidly moving film the movements of the fibre of an Einthoven string galvanometer, which registered the potential of the electrode. In this way they determined the quantity of electricity passed in reaching the potentials at which hydrogen is liberated at cathodes of various metals in sulphuric acid solutions which had been carefully freed from oxygen and saturated with hydrogen. When oxygen is present the changes are much slower. Fig. 7 shows a typical result obtained with a mercury electrode using a current density of

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[38] *Wied. Ann.*, **31**, 337, 1887.

[39] *Z. Elektrochem.*, **19**, 255, 1913.

[40] Abh. Bunsen-Ges., No. 3.

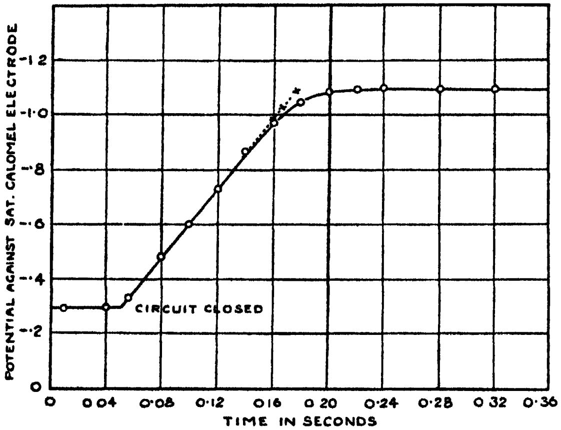
[41] *J. Amer. Chem. Soc.*, **46**, 2613, 1924.

[42] *Proc. Roy. Soc.*, **107A**, 486, 1925; **111A**, 182, 1926; **114A**, 103, 1927; **119A**, 680, 686, 1928.

[43] *Ibid.*, **120A**, 59, 80, 1928; Bowden and O'Connor, *ibid.*, **128A**, 317, 1930.

5×10^{-7} amps./cm.^{2} When the circuit is closed, the potential rises linearly with time, from — 0·3 volts to — 0·9 volts (measured with reference to the saturated calomel electrode). Here the rate of change begins to decrease and the electrode potential finally remains constant at — 1·1 volts, at which steady electrolysis with the liberation of hydrogen takes place.

In this final state electrons are evidently being transferred from the metal to hydrogen ions in the solution at a rate equal to the current. But as we shall see when we come to consider the hydrogen overvoltage, the rate of this process diminishes very rapidly as the electrode potential becomes more positive, and is negligible below — 0·8 volts. We can thus conclude that when the current is started electrons move along the wire and positive ions migrate through the solution towards the electrode, but practically no electrons (or ions) succeed in crossing the double layer. The result of the flow of current is thus an increase in the charge on each side of the double layer and therefore an increase of the potential difference. The slope of the initial linear part of the curve (*idt*/*dV*) is the capacity of the double layer.



IV. 7.—Change of potential of mercury electrode on starting cathodic current. (Bowden and Rideal, *Proc. Roy. Soc.*, vol. 120, 1928.)

In this way Bowden and Rideal found that mercury electrodes had a capacity of 6 microfarads/cm.^{2}, and figures of the same order of magnitude were obtained by other investigators.[44] The real areas of solid metal electrodes cannot be easily determined, but assuming that equal areas of different metals have equal capacities, the measurement of the capacity gives a measure of the area. Taking the area of the mercury electrode as that measured it was found that the real area of bright platinum was 2 to 4 times its apparent area. The effect of different kinds of treatment on the double layer capacity of nickel and the relative areas are given below.

TABLE III. CAPACITY AND RELATIVE AREA OF NICKEL SURFACES

	Polished	*Activated*	*Annealed*	*Electroplated*	*Rolled*
B	75	276	65	72	35×10^{-6}
$\frac{\text{Real Area}}{\text{Apparent Area}}$	13	46	11	12	6

It is also possible to determine the capacity by using alternating current and balancing the electrode capacity against a known capacity in a capacity bridge. This method was first used by Krüger,[45] who obtained values between 7 and 10 microfarads/cm.^{2} M. Proskurnin and A. Frumkin,[46] using this method recently, with stringently purified solutions, have obtained considerably higher values at negatively polarised mercury (18-20 microfarads/cm.^{2}) and suggest that the lower values obtained by Bowden, Rideal and others were due to the partial covering of the electrode surface by adsorbed paraffins and other impurities. The capacity was not appreciably changed by freezing the mercury.[47] Fig. 8 (*a*) shows that the results of these measurements are in good agreement with those calculated from the electrocapillary curve. The addition of adsorbable organic substances, such as oleic acid, cetyl alcohol, etc., greatly reduces the capacity in the middle part of the curve.[48] It is only in this region that adsorption occurs.

[44] E. Baars, *Ber. Ges. Förd. Naturwiss.*, Marburg, **63**, 213, 1928; Brandes, *Z. physikal. Chem.*, **142**A, 97, 1929; T. Erdey-Grúz and M. Volmer, *ibid.*, **150**A, 203, 1930; T. Erdey-Grúz and G. G. Kromrey, *ibid.*, **157**A, 213, 1931.

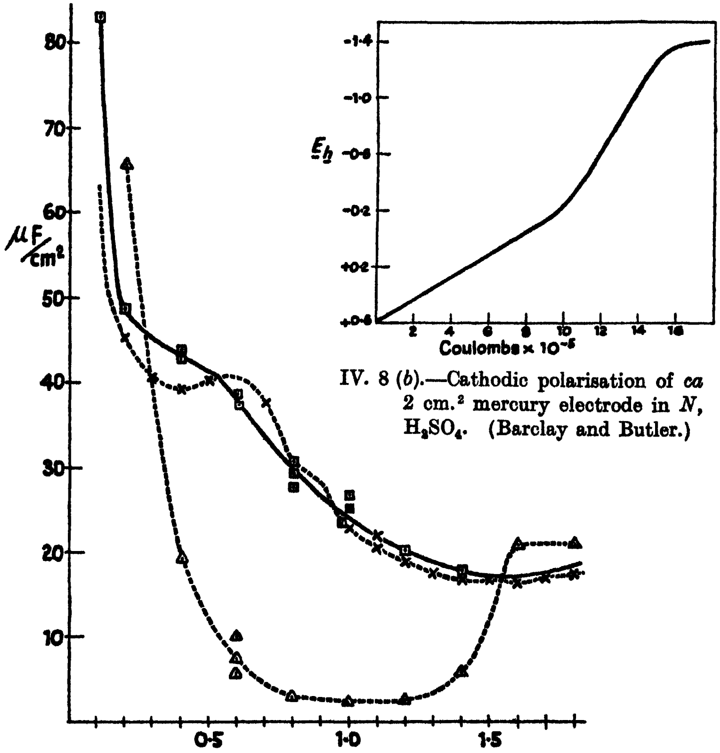
[45] *Z. physikal. Chem.*, **45**, 1, 1903; *Ann. d. Phys.* [4], **21**, 701, 1906; *Z. f. Elektrochem.*, **19**, 620, 1913.

[46] *Trans. Faraday Soc.*, **31**, 110, 1935; T. Borissowa and M. Proskurnin, *Acta Physicochim., U.R.S.S.*, **4**, 819, 1936.

[47] Gorodezkaya and Frumkin, *Acta Physicochim.*, **9**, 45, 1938.

[48] Cf. A. Gorodezkaya and A. Frumkin, *C. rend. Acad. Sci., U.R.S.S.*, **18**, 639, 1938; Ksenofontov, Proskurnin and Gorodezkaya, *Acta Physicochim.*, **9**, 39, 1938.

Barclay and Butler[49] have recently studied the cathodic polarisation of freshly made mercury surfaces, recording the change of potential with time for constant currents by means of a cathode ray oscillograph. Under these circumstances comparatively large currents can be used and the whole record is obtained in times of the order of 0·01 sec., when the effects of traces of oxygen, etc., are comparatively unimportant. Fig. 8 (*b*) shows a typical result in *N*, H_2SO_4. The initial potential is about $E_h = +0{\cdot}6$ and the curve of potential against charge shows two distinct stages. In the first (α) the capacity is about 60×10^{-6} coulombs/volt/cm.^{2},



IV. 8 (*b*).—Cathodic polarisation of *ca* 2 cm.^{2} mercury electrode in *N*, H_2SO_4. (Barclay and Butler.)

IV. 8 (*a*).—Capacities of a mercury surface in *N*, Na_2SO_4. ——— from electrocapillary curve; — —×— — observed at clean surface; ——△—— after contamination with picein.

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[49] *Trans. Faraday Soc.*, Jan. 1940.

and at about $E_h = 0{\cdot}3$ where the second stage (β) begins, it falls to about 20×10^{-6}. This behaviour is obviously very similar to that found by Philpot (Fig. 6). Organic substances greatly reduce the capacity in the region (β), e.g. a concentration of *n*-amyl alcohol of 0·1 *N* reduces the capacity to 40 per cent. of its original value and further increase of the concentration causes little change. On the other hand, the addition of pyridine has very little effect. This is in accordance with the electrocapillary curves (p. 81), which indicate that little adsorption takes place at the initial potential.

A mercury surface cannot be anodically polarised, since mercury ions then pass into solution, but experiments have been made on the capacity of platinum anodes in the neighbourhood of the potentials at which oxygen is liberated. Bowden found that the capacity of a platinum electrode in this region was 380 microfarads per cm.^{2} of apparent area, or taking the real area of 3·3 times the apparent area the capacity is 110 microfarads/cm.[50] Armstrong, Himsworth and Butler obtained values about a third as great, viz. about 100 microfarads/cm.^{2} of apparent area.[51]

Theories of the Structure of the Double Layer. Helmholtz's conception of the double layer as two surface charges separated by a constant distance, requires a constant capacity and is obviously inadequate. Gouy [52] pointed out that the ions of the double layer could not be concentrated at a definite distance from the surface, because there must be an equilibrium between the electrical forces which are responsible for the existence of the double layer and the osmotic forces which tend to maintain homogeneity. On this account there will be no sudden change in the concentration of any kind of ions in the vicinity of the double layer, but merely a gradual increase of concentration of ions of one sign and a rarefaction of ions of the other sign. Only slight changes of concentration are required.

D. L. Chapman [53] developed this conception by introducing Poisson's equation to find the equilibrium distribution of ions in such a diffuse layer. His calculation was in fact very similar to

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[50] *Proc. Roy. Soc.*, **125**A, 446, 1929.

[51] *Ibid.*, **143**A, 89, 1933.

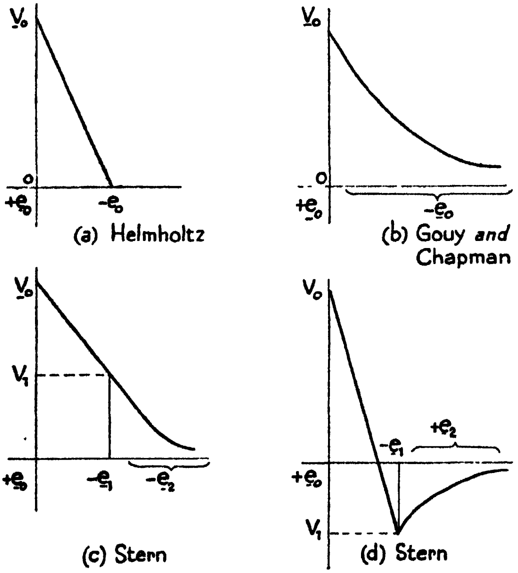
[52] *J. de physique* (4), **9**, 457, 1910; *Annales de phys.*, **7**, 129, 1917; cf. Bikerman, *Z. physikal. Chem.*, **163**, 378, 1933.

[53] *Phil. Mag.*, **25**, 475, 1913; cf. Herzfeld, *Phys. Z.*, **21**, 28, 1920.

that used later by Debye and Hückel to determine the distribution of ions in the ionic atmosphere round a given ion (see p. 108). The result was

$$e = \sqrt{\frac{DRT\,c}{2\pi}}\left(e^{\frac{\varepsilon V}{2RT}} - e^{-\frac{\varepsilon V}{2RT}}\right)$$

where D is the dielectric constant of the medium and c the concentration of the salt. For small potential differences this gives capacities of about 240 microfarads/cm.^{2}, which are much too great.



IV. 9.—Types of double layer, showing variation of potential with distance from surface and location of charges.

In 1924 Stern[54] suggested a type of double layer which is a combination of the simple Helmholtz fixed layer with the Gouy-Chapman diffuse layer. If there is a total charge e_0 on the electrode, it is supposed that the corresponding charge $-e_0$ in the solution is made up of (1) adsorbed ions having the charge $-e_1$ and (2) a diffuse Gouy layer of charge $-e_2$. e_1 and e_2 may be of the same or opposite signs, but it is of course always necessary that $e_0 = e_1 + e_2$. The variations of the potential difference with distance from the electrode in the two cases are shown in Fig. 9, (*c*) and (*d*).

The charge on the diffuse layer is given, as in Chapman's calculation, by

$$e_2 = \sqrt{\frac{DRT\,c}{2\pi}}\,(e^{FV_1/2RT} - e^{-FV_1/2RT}).$$

[54] *Z. Elektrochem.*, **30**, 508, 1924.

If ϕ_+ and ϕ_- are the adsorption energies of the positive and negative ions respectively, it is shown that the charge of the adsorbed layer is

$$e_1 = \mathbf{F}N\left(\frac{1}{2 + \frac{1}{c}e^{\frac{\phi_- - \mathbf{F}V_1}{RT}}} - \frac{1}{2 + \frac{1}{c}e^{\frac{\phi_+ + \mathbf{F}V_1}{RT}}}\right)$$

and the total charge on the metal is

$$e_0 = e_1 + e_2 = K_0(V_0 - V_1),$$

where $K_0 = d/4\pi\delta$ is the capacity of the adsorbed layer by virtue of its being separated from the electrode by a space of thickness δ and dielectric constant d (which need not be the same as that of the medium D).*

From these equations it is deduced [55] that when e_0 is large

$$\frac{de_0}{dV_0} = K_0,$$

i.e. the observed capacity approaches the capacity of the adsorbed layer, and for a constant and numerically large value of e_0,

$$V_0 = \text{const.} \pm \frac{RT}{\mathbf{F}} \log c,$$

the sign of $RT/\mathbf{F} \log c$ being opposite to that of e_0. Thus, the theoretical curve representing e_0 in terms of ψ_0 has two nearly linear portions of slope approximately equal to K_0, which move apart along the axis of e_0 with increasing dilution, at a rate of

$$(2RT/\mathbf{F}) \log c.$$

They are gained by a non-linear portion. This form of curve is peculiar to Stern's theory. By suitable adjustment of constants the linear or non-linear portions can be made to predominate, giving in the two limiting cases the wholly linear curve of the Helmholtz theory, and the wholly non-linear curve of the Chapman-Gouy theory.[56]

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* This is Stern's expression. It would seem to be more natural to write

$$e_1 = e_0 - e_2 = K_0(V_0 - V_1).$$

[55] Cf. Philpot, *loc. cit.*, ref. 37.

[56] For a discussion of Stern's theory, see Urban and White, *J. Physical Chem.*, **36**, 3157, 1932.

Philpot found that Stern's equation was the only one which represented his curves (Fig. 6); but it was necessary to use different values of K_0 on the positive and negative branches, i.e. K_0 depends on the nature of the adsorbed ion.

Electrocapillary Curves and Adsorption at Charged Interfaces. Two interpretations have been given of the electrocapillary curve, (1) the electrostatic theory of Helmholtz, (2) the adsorption theory of Gibbs. The general adsorption equation of Gibbs, connecting the surface tension and adsorption at an interface with the concentration of the substances, may be written in the form

$$d\sigma + \Gamma_1 d\bar{F}_1 + \Gamma_2 d\bar{F}_2 \ldots = 0,$$

where σ is the surface tension, Γ_1, Γ_2, etc., the amounts of the various substances adsorbed, and $\bar{F}_1$, $\bar{F}_2$ their partial free energies (given by Gibbs as the chemical potentials μ_1, μ_2, etc.). The way in which the amounts adsorbed are arrived at must be clearly defined. A surface is drawn close to, but not necessarily coincident with the actual interface, and then Γ_1 is defined as the difference between the amount of the substance actually present near the interface and that which would be present in the same volume if the phases were completely homogeneous up to the hypothetical dividing surface. This dividing surface may then be so placed that the adsorption of one component, e.g. the solvent, is zero. Thus, if Γ_1 is taken as zero, we have

$$d\sigma + \Gamma_2 d\bar{F}_2 + \Gamma_3 d\bar{F}_3 \ldots = 0,$$

where Γ_2, Γ_3, etc., are the amounts of the different solutes adsorbed; or for one solute, expressing the free energy in terms of the activity by means of the equation

$$\bar{F}_2 = \text{const.} + RT \log \alpha_2,$$

we have

$$-\frac{d\sigma}{d\bar{F}_2} = -\frac{d\sigma}{RTd \log \alpha_2} = \Gamma_2.$$

Gibbs [57] applied this equation to the interpretation of the electrocapillary curve. Suppose that we have a mercury electrode in a solution containing mercurous ions, which we will represent for

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[57] *Scientific Papers*, I, 219.

simplicity as Hg^+. When the electrode is polarised by the application of an external electromotive force,* the concentration of mercurous ions near the electrode, which is required for equilibrium, will be changed. The relation between the electrode potential and the activity of mercurous ions, assuming equilibrium, is

$$V = V^o + \frac{RT}{\mathbf{F}} \log \alpha_{Hg^+}.$$

In accordance with Gibbs's equation, the variation of the surface tension with the mercurous ion activity will be given by

$$-\frac{d\sigma}{RT \log \alpha_{Hg^+}} = -\frac{d\sigma}{\mathbf{F} \, . \, dV} = \Gamma_{Hg^+}.$$

This indicates that on the left-hand (ascending) branch of the electrocapillary curve, where the surface tension increases as V becomes more negative, Γ_{Hg^+} is positive; while on the descending branch Γ_{Hg^+} is negative. Warbourg [58] identified $\mathbf{F}\Gamma_{Hg^+}$ with the charge on the Helmholtz double layer, and this equation is then identical with that derived by Helmholtz.

Attempts have been made to check this relation experimentally by a direct measurement of the adsorption of mercury ions by mercury in mercurous sulphate solutions. Lewis [59] and Patrick [60] measured the amount of mercurous sulphate carried down when mercury droplets are streamed through a solution. Schofield [61] compared the directly measured adsorption with that determined from the electrocapillary curve, and found good agreement in the solutions which were richer in mercurous sulphate.

Modified forms of this equation have been deduced by numerous authors.[62] The derivation is unsatisfactory, however, because it assumes that the electrode is always in equilibrium with the solution

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* The mercury electrode can only be polarised if the concentration of mercurous ions is very small. Concentration changes can then be brought about by polarisation, since the rate of diffusion of mercury ions from the solution to near the electrode will be small.

[58] *Wied. Ann.*, [9], **41**, 1, 1890.

[59] *Z. physikal. Chem.*, **77**, 129, 1910.

[60] *Ibid.*, **86**, 545, 1914; Patrick and Bachman, *J. Physical. Chem.*, **30**, 134, 1926.

[61] *Phil. Mag.*, **1**, 641, 1926.

[62] Krüger and Kromreich, *Z. Elektrochem.*, **19**, 617, 1913; W. C. McC. Lewis, *Z. physikal. Chem.*, **73**, 129, 1910; van Laar, *ibid.*, **41**, 385, 1902; Frumkin, *Phil. Mag.*, **40**, 363, 375, 1920; *Z. physikal. Chem.*, **103**, 55, 1923; *Z. f. physik*, **35**, 792, 1926.

It is supposed that the sole effect of polarisation is to change the concentration of the ions which determine the potential difference. It is obvious that equilibrium is not maintained when a mercury electrode is polarised under the conditions which exist in the capillary electrometer. In the unpolarised state the concentration of mercurous ions is small, and the equilibrium concentrations at negative polarisations are so small as to have no physical meaning, and it is impossible to regard the surface tension as determined by them. A thermodynamical treatment of the electrocapillary curve therefore gives rise to considerable difficulty. This is discussed further in the Appendix (p. 89). Here we shall regard the surface tension between mercury and the solution as produced by two effects: (1) the electrostatic effect of the charge of the double layer, (2) the effect of the various adsorbed ions and neutral molecules. The former is given by the Helmholtz equation

$$d\sigma = e\,dV,$$

and the latter by the Gibbs equation

$$d\sigma = -\Gamma_2 d\bar{F}_2 - \Gamma_3 d\bar{F}_3 -, \text{ etc.}$$

Combining these, we have

$$d\sigma = e\,dV - \sum \Gamma_2\, d\bar{F}_2,$$

and by integration this gives

$$\sigma = \sigma_0 + \int e\,dV - \sum \int \Gamma_2 d\bar{F}_2 \qquad . \quad . \quad (1)$$

where σ_0 is the surface tension of an uncharged mercury surface in pure water. $\int \Gamma_2 d\bar{F}_2$ is the lowering of the surface tension produced by component 2, etc. Differentiating with respect to V, we obtain

$$\frac{d\sigma}{dV} = e - \frac{d\int \Gamma_2\, d\bar{F}_2}{dV} - \frac{d\int \Gamma_3\, d\bar{F}_3}{dV}, \text{ etc.}$$

These expressions can only be evaluated if Γ_2, etc., are known as a function of V as well as of $\bar{F}_2$.

Adsorption of simple ions. We have seen (Fig. 2) that capillary active ions, such as bromide and iodide, cause a considerable lowering of the electrocapillary curve on the left-hand side. This may be regarded as due to the adsorption of bromide or iodide ions, which is negligible on the extreme right (negative branch) of the curve but begins to be apparent on the right-hand side of the maximum and increases rapidly towards the left. The lowering of the surface tension produced by the adsorption of ions of one species may be given as

$$\Delta\sigma = \int \Gamma \,.\, d\bar{F} \quad . \quad . \quad . \quad . \quad (2)$$

where Γ is a function, both of the potential difference and of the concentration. If the potential difference between the solution and the electrode is V, the work done by an ion of charge ϵ when it becomes adsorbed may be expressed as $w = \alpha\epsilon V$, i.e. it may be supposed that in becoming adsorbed it passes through a fraction α of the whole potential difference. If Γ_0 is the amount adsorbed from a given solution when $V = 0$, the amount adsorbed for the potential difference V is therefore

$$\Gamma = \Gamma_0 \, e^{-\alpha\epsilon V/kT} \quad . \quad . \quad . \quad . \quad (3)$$

and introducing this into (2), we have

$$\Delta\sigma = e^{-\alpha\epsilon V/kT} \int \Gamma_0 \, dF,$$

or

$$\Delta\sigma = \Delta\sigma_0 \, e^{-\alpha\epsilon V/kT},$$

i.e.

$$\log (\Delta\sigma) = \text{const.} - \alpha\epsilon V/kT.$$

Butler [63] found that this equation holds quite well for the lowering of surface tension produced by iodides.* The value of α was about 0·12, so that only a comparatively small fraction of the whole potential difference is effective.

Adsorption of neutral molecules. Most soluble organic substances produce a truncation of the electrocapillary curve (Fig. 2), i.e. there is a lowering of the surface tension in the region of the maximum which decreases on either side, and often ultimately disappears. Many curves of this kind were obtained by Gouy. He usually added the organic substance to a M/2 solution of sodium sulphate (the primitive solution). The surface tension lowering produced by the organic substance is determined by subtracting the values for its solution from that of the primitive solution. Some examples

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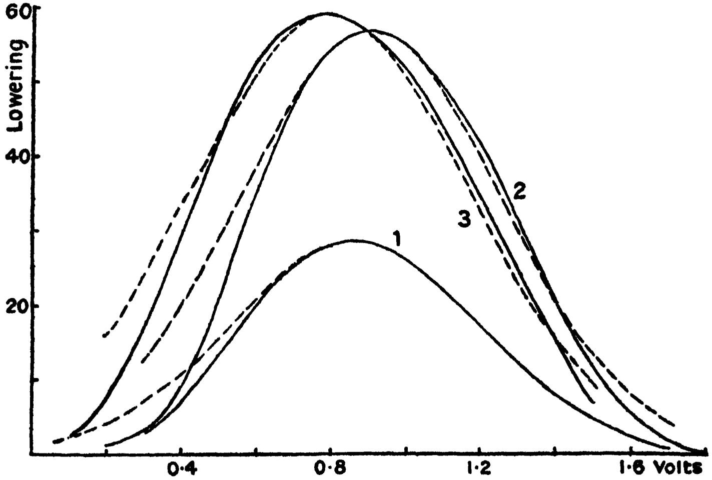
[63] *Proc. Roy. Soc.*, **113A**, 594, 1927.

* $\Delta\sigma$ was taken as the difference between σ for KCl and σ for KI for a given value of V. This is not quite accurate, because the chloride also produces a small lowering of surface tension, as compared with the symmetrical nitrate solutions.

of the curves obtained, which may be called "adsorption curves," are given in Figs. 10 and 11.*

The first theoretical explanation of this phenomenon was given by Frumkin.[64] He expressed the work done in adsorption, on account of electric forces at the interface as the sum of two terms, (1) a general term, due to the smaller dielectric constant and greater length of the organic molecule than water, which he evaluated as $\frac{1}{2}(c - c')\psi^2$, where c is the capacity of the double layer per unit surface in the pure solvent, c' that when the surface is saturated with the adsorbed substance, and ψ the potential difference ; (2) a term dependent on the dipole moment of the adsorbed molecules, and given as $c'\psi_N\psi$, where ψ_N is the potential difference due to a complete layer of dipoles. Writing the total work done by the electric forces (the sum of these two) as ϕs, the effect of the potential difference is equivalent to a concentration change of $e^{\phi s/RT}$. This was introduced into rather complicated adsorption equations and accounted for the curves of amyl alcohol solutions.



IV. 10.—Adsorption curves of (1) acetic acid (M/1), (2) propionic acid (M/1), (3) monochloracetic acid (M/1). (*Proc. Roy. Soc.*)

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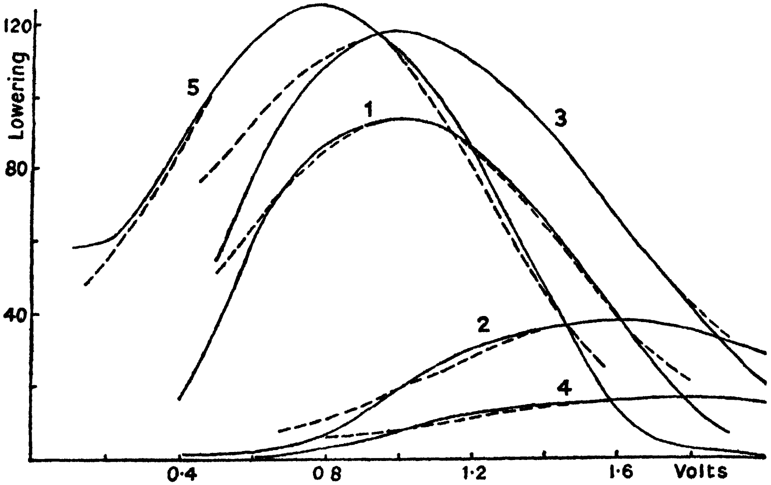
* Kabanow has studied the effect of surface active substances on the contact angle between mercury and hydrogen bubbles, and compared it with the electrocapillary curves (*Acta Physicochim.*, **6**, 701, 1937).

[64] *Z. physik.*, **35**, 792, 1926.

A somewhat different theory was given by Butler.[65] In electrostatic theory the work done when an element of dielectric of volume δv is moved from a place where the electric field is E to a place where it is zero, is

$$w = \delta v \, . \, \tfrac{1}{2}\alpha E^2,$$

where $\alpha =$ polarisability. Now, consider a solution containing molecules A and B. Suppose that a molecule B of volume δv_B is moved from a place where the field strength is zero to a place where the field strength is E. An equal volume of molecules A must move in the opposite direction and the work done against the electric forces in the transfer is



IV. 11.—Adsorption curves of (1) triethylamine (M/10), (2) triethylamine sulphate (M/10), (3) isobutylamine (M/1), (4) isobutylamine sulphate (M/1), (5) pyrrhol (sat.). (*Proc. Roy. Soc.*)

$$w = \tfrac{1}{2}(\alpha_A - \alpha_B)\, E^2 \, . \, \delta v_B \qquad . \quad . \quad . \quad (4)$$

where α_A, α_B are the polarisabilities of the two substances. From this it follows that if Γ is the amount of the substance B adsorbed at a surface where the electric field strength is E, and Γ_0 the adsorption for $E = 0$,

$$\Gamma = \Gamma_0 \, e^{-\frac{1}{2}(\alpha_A - \alpha_B)E^2 . \delta v_B},$$

or by (2),

$$\Delta\sigma = \Delta\sigma_0 \, . \, e^{-\frac{1}{2}(\alpha_A - \alpha_B)E^2 . \delta v_B}.$$

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[65] *Proc. Roy. Soc.*, 122A, 399, 1929.

On the assumption that E is proportional to the potential difference V, this can be written as

$$\Delta\sigma = \Delta\sigma_0 \,.\, e^{-aV_2}.$$

This indicates that $\Delta\sigma$ is a maximum at $V = 0$, i.e. the maxima of the adsorption curves should all occur at the same value of V. The shape of the curves is generally in good agreement with this equation, but the position of the maximum varies. This can be accounted for if the permanent dipoles of the molecules are taken into account. Thus, in the absence of the electric field, let the adsorbed molecules have a polarisation p per unit volume. The work done in bringing a molecule B into a field of intensity E is then $(\frac{1}{2}\alpha_B E^2 + p_B E)\delta v_B$. If the permanent polarisation of the solvent (A) is similarly p_A, the work of adsorption at an interface when the electric field is E is

$$w = \tfrac{1}{2}\{(\alpha_A - \alpha_B)E^2 + (p_A - p_B)E\}\delta v_B,$$

and putting $\Gamma = \Gamma_0 e^{-w/kT}$, this gives an equation of the form

$$\Gamma = \Gamma_0 \,.\, e^{-(aV^2+bV)},$$

and therefore, for a given solution,

$$\Delta\sigma = \Delta\sigma_0 \,.\, e^{-(aV^2+bV)}.$$

This can easily be transformed * to

$$\Delta\sigma = \Delta\sigma_m \, e^{\;(aV-\;Vm)^2},$$

where $\Delta\sigma m$ is the maximum lowering of the surface tension and Vm the potential at which it occurs. The meaning of this equation in ordinary language is as follows: a is positive if the solvent is more polarisable than an equal volume of the solute. Then the solvent molecules are attracted to the surface relatively more strongly than the solute as the field strength increases and the adsorption of the solute is therefore decreased.

The agreement of this equation with the observed is usually better on the right-hand side than the left, where the observed lowerings fall off more rapidly. This is probably due to the adsorption of the inorganic anions of the primitive solution in this

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* $aV^2 + bV = a(V + b/2a)^2 - b^2/4a^2 = a(V - V_m)^2 - b^2/4a^2$, if $V_m = -\,b/2a \,.\, \Delta\sigma_m = \Delta\sigma_0 \,.\, eb^2/4a^2$.

region, which reduces the adsorption of the other solute. Table IV gives the characteristics of the curves of some solutes.

TABLE IV. CHARACTERISTICS OF ADSORPTION CURVES

Substance	*Concentration*	*a*	V_m*	$\Delta\sigma_m$
CH_3OH	M	2·7	−0·90	7·4
C_2H_5OH	M	4·1	0·96	27·2
$C_3H_7OH(n)$	M	3·3	0·95	79·8
$C_4H_9OH(n)$	M/10	5·0	0·92	49·1
C_6H_5OH	M/10	3·2	0·78	91·3
$C_6H_4 . CH_3 . OH$ (*o*)	*sat.*	1·9	0·78	139·0
$C_6H_4(OH)_2$ (*o*)	M/10	2·4	0·64	82·6
$C_6H_4(OH)_2$ (*p*)	M/10	2·6	0·60	82·4
$N(CH_3)_4OH$	M/10	1·7	1·85	33·7
$N(C_2H_5)_4OH$	M/10	1·7	1·65	63·0
$S(C_2H_5)_3OH$	M/10	1·2	1·74	61·8
$N(C_2H_5)(CH_3)_3OH$	M/10	1·6	1·80	36·5

The values of *a* are of the same order of magnitude as those calculated by the use of (4). For molecules of a similar nature, they should increase with the size of the molecule. This is sometimes the case, but it must be remembered that the field strength at the surface is not constant over any great distance, and a considerable part of large solute molecules may be right outside the double layer.

Adsorption of organic ions. If the organic molecule carries a charge ϵ, the work of adsorption is increased by ϵV. The result is therefore of the same form as the effect of permanent dipoles, viz. a displacement of the adsorption curve along the V axis. In accordance with this it is found from Gouy's data that positive organic ions, such as substituted ammonium derivatives, have a maximum adsorption on the extreme negative side of the curve. On the other hand, it was found that the displacement of the maximum of adsorption of negative ions, e.g. salicylate, benzoate, etc., towards the positive side was comparatively small.[66] The reason for this [67] was found to be the adsorption of the anion of the primitive solution on the positive side of the electrocapillary curve, which interfered with the adsorption of the organic anion. When the concentration

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* Measured against the electrode Hg, Hg_2, SO_4, Na_2SO_4 (M/2). The potential of this electrode is $E_h = +0{\cdot}66$.

[66] Butler and Ockrent, *J. Physical Chem.*, **34**, 2286, 1930.

[67] Butler and Wightman, *ibid.*, **35**, 3293, 1931.

of the inorganic salt is considerably reduced, the maximum adsorption of organic anions is found at the positive end of the electrocapillary curve as expected.

Organic inhibitors of corrosion. It has been known for some time that some organic substances reduce the rate of solution of metals in acids and also inhibit the corrosion of iron, etc. It has been found that organic bases are particularly effective,[68] especially those of high molecular weight. For example, Rhodes and Kuhn [69] give the following figures, among others, for the inhibiting power (as per cent.) of solutions containing 10 millimols per litre of the base on the solution of iron in acid.

Toluidine	7·3	Acridine	82·4
Aniline	14·5	β naphthoquinoline	91·2
Quinoline	49·4	Phenylacridine	95·4

Mann, Lauer and Hultin [70] studied the effect of concentration and obtained curves very similar to the adsorption isotherms and also observed that aliphatic amines have a considerable inhibiting power, especially tri-butyl and tri-amyl amines.

It is evident that these substances reduce the rate of solution by forming an adsorbed film on the metal. To be effective for this purpose it is necessary that the compound should be adsorbed at the fairly negative potential at which the metal dissolves with the evolution of hydrogen, and the ions of organic bases, as we have seen, fulfil this condition. Other things being equal, a substance of high molecular weight will be adsorbed to a greater extent than substances of lower molecular weight.[71] Perschke and Vinogradova [72] found that some reducible compounds, e.g. nitro-compounds, benzoquinone, increase the rate of corrosion, because they remove the film of hydrogen on the surface of the metal and so allow further reaction to take place.

Electrification at Solution-gas Interfaces. A potential difference at an interface may also arise from the orientation of dipoles

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[68] Speller and Chappell, *Chem. Met. Eng.*, **34**, 421, 423, 1927 ; Chappell, Roetheli and McCarthy, *Ind. Eng. Chem.*, **20**, 582, 1925 ; Forrest, Roberts and Roetheli, *ibid.*, **20**, 1369, 1928 ; Ardagh, Room and Owen, *ibid.*, **25**, 1116, 1933.

[69] *Ibid.*, **21**, 1066, 1929.

[70] *Ibid.*, **28**, 159, 1048, 1936.

[71] See also W. Machu, *Korrosion u. Metallschutz*, **13**, 1, 1937.

[72] *Chim. et Ind.*, **36**, 1101, 1936.

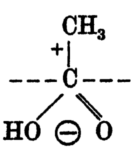
at or near the interface. If μ is the dipole moment of each molecule in the direction vertical to the plane of the surface, and n is the number of such molecules in 1 cm.^{2}, the potential difference is

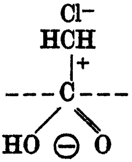
$$\Delta V = 4\pi n\mu / D,$$

where D is the effective dielectric constant.

Numerous measurements of potential differences at solution-air interfaces have been made. Bichat and Blondlot,[73] Kenrick,[74] and later Frumkin and collaborators [75] used a method in which a stream of the solvent flows down the centre of a cylindrical tube, while a stream of solution flows down the walls. The two solutions are connected, by means of calomel electrodes, to a quadrant electrometer and the natural ionisation of the air is sufficient to permit a measurement of the potential difference across the air gap.* The potential difference measured is, of course, the difference of the two interface p.d's, at the surface of solvent and solution respectively.

It was found by this method that aliphatic acids generally produce a positive potential, i.e. the air side of the interface is positive, relative to the surface of water, but their salts produce a small negative effect. The substitution of halogens in the hydrocarbon residues of the aliphatic acids makes the potential progressively more negative, which is regarded as due to the relatively negative halogen atom pointing outwards from the surface :





The effects are approximately proportional to the amounts of the substances adsorbed. Inorganic salts produce small changes of potential difference, usually of negative sign, i.e. the outer part of the surface is relatively negative, indicating that the anions approach the surface more closely than the cations. The valency

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[73] *J. physique*, **2**, 533, 1883. [74] *Z. physikal. Chem.*, **19**, 625, 1896.

[75] *Ibid.*, **109**, 34, 1924; **111**, 190, 1924; **123**, 321, 1926; *Acta Physicochim.*, **1**, 883, 1934; **2**, 1, 1935.

* Does the streaming cause a slight ionisation of the surrounding air ? Falling water, as in waterfalls, becomes electrified by friction.

of the ions has no great effect, e.g. although thorium nitrate reverses the sign of the electrokinetic potential of gas bubbles (p. 106), it has no effect on the total potential difference.

Another method, which can be used at stationary surfaces, was developed by Guyot[76] and Frumkin.[77] A wire or plate, which is coated with polonium or other radioactive material, is placed above the solution and confers a sufficient conductivity on the air in its vicinity to permit measurements of the potential difference between the plate and a standard electrode connected with the solution. The measured potential difference includes the p.d. at the surface of the metal plate, which is unknown and may be variable. Williams and Vigfusson[78] made a critical comparison of this method with that of Kenrick, using various inorganic salt solutions, and found that although there was a qualitative resemblance between the results, there was no quantitative agreement at all and the values obtained depended on the distance between the plate and the surface. The method has been widely used for studying the potential differences at water surfaces covered with insoluble surface films.[79] In this case the potential difference at the surface of the metal plate may be kept uncharged, and the effects produced by changes of concentration of the molecules in the surface film, changes of p_H of the underlying liquid, etc., can be studied. For a full account of this work, which cannot conveniently be described without dealing with other properties of the surface films, see N. K. Adam's *Physics and Chemistry of Surfaces.*[80]

In another method, which has been developed and used by Garrison,[81] Zisman and Yamins,[82] and Porter,[83] the plate and the surface of the water form a condenser. If the distance between the plate and the surface is varied the capacity changes and a current

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[76] *Ann. physique*, **2**, 506, 1924.

[77] *Z. physikal. Chem.*, **116**, 485, 1925; cf. Sawai, *Trans. Faraday Soc.*, **31**, 765, 1935.

[78] *J. Physical Chem.*, **35**, 345, 1931.

[79] E.g. Schulman and Rideal, *Proc. Roy. Soc.*, **130**A, 259, 1931; Harding and Adam, *Trans. Faraday Soc.*, **29**, 837, 1933; Harkins, *J. Chem. Physics*, **1**, 852, 1933; **3**, 693, 1935.

[80] Oxford Univ. Press, 2nd edition, 1938.

[81] *J. Physical Chem.*, **29**, 1517, 1925.

[82] *J. Chem. Physics*, **1**, 1656, 1933; *Rev. Sci. Inst.*, **3**, 7, 1932.

[83] *J. Amer. Chem. Soc.*, **59**, 1884, 1937.

flows between the plate and the liquid. If the plate is charged so that no current flows when it is moved, it is taken to be at the same potential as the solution.

APPENDIX

THE THERMODYNAMICS OF ELECTROCAPILLARY CURVES

As pointed out above (p. 80) the difficulty of a thermodynamic theory is the uncertainty whether equilibrium at the interface is effectively maintained or rather, since irreversible processes obviously occur at a polarised electrode, whether these are immaterial. The theory has been discussed at length by Koenig,[84] Rice [85] and particularly by Craxford, Gatty and Philpot.[86] Broadly speaking, the conclusion of these authors is that the equation given (p. 58) is justified. It is not possible to summarise these lengthy arguments, but the following derivation and discussion may be useful.

The thermodynamic condition of equilibrium between two phases is

$$\bar{F}_1 = \bar{F}_1' \quad . \quad . \quad . \quad . \quad (1)$$

for every neutral component which is common to both phases, and

$$M_1 = M_1' \quad . \quad . \quad . \quad . \quad (2)$$

for every charged component (ion) which is common to both phases. Here $\bar{F}_1$, $\bar{F}_1'$ are the partial free energies (Gibbs's chemical potentials) of a given substance in the two phases, and $M_1 = \bar{F}_1 + z\epsilon V$; $M_1' = \bar{F}_1' + z\epsilon V'$, where V, V' are the electric potentials of the two phases and $z\epsilon$ the charge on unit mass (usually the mol) of the substance.

Now, if we consider a mercury electrode in contact with an aqueous solution containing mercurous ions, which we shall represent for simplicity as Hg^+. The only component common to both phases is Hg^+ and the only condition of equilibrium which is required is

$$(\bar{F}_{Hg^+} + z\epsilon V)_{\text{solution}} = (\bar{F}_{Hg^+} + z\epsilon V')_{\text{metal}} \quad . \quad . \quad (3)$$

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[84] *Z. physikal. Chem.*, **154**, 421, 454, 1931; **156**, 38, 1931; **157**, 96, 1931; *J. Physical Chem.*, **38**, 111, 339, 1934.

[85] *Ibid.*, **30**, 1348, 1926.

[86] *Phil. Mag.*, **16**, 849, 1933; **17**, 54, 1934; **19**, 965, 1935; **22**, 359, 402, 1936.

If the mercury is polarised, while the electric potential of the solution remains constant (i.e. V' changes by an amount $\Delta V'$, while V remains constant), the chemical potential of mercury ions in the solution must change by the amount $\Delta\bar{F}_{Hg^+} = z\epsilon\Delta V'$. As pointed out previously it is very doubtful if equilibrium is actually maintained with respect to mercury ions, for the concentration of mercury ions corresponding to appreciable negative polarisations of the mercury is extremely minute.

For such a surface the Gibbs adsorption equation can be written as

$$\Gamma_\epsilon dM_\epsilon + \Gamma_{Hg^+}dM_{Hg^+} + \Gamma_1 d\bar{F}_1 + \Gamma_2 d\bar{F}_2, \text{ etc.}, \quad + d\sigma = 0, \quad (4)$$

where Γ_ϵ, Γ_{Hg^+} are the surface excesses of electrons and mercury ions and Γ_1, Γ_2, etc., the surface excesses of other components. The surface excess of any substance is defined as the difference between the amount actually present in a region which includes the interface and that which would be present if the phases were completely homogeneous up to a specified dividing surface. The values of these quantities thus depend on the position chosen for the dividing surface.

Various choices have been made. Gibbs and earlier authors in effect placed the dividing surface so that $\Gamma_\epsilon = 0$, and identified Γ_{Hg^+} as determined on this supposition with the charge on the mercury. Schofield [87] chose to place the dividing surface so that $\Gamma_{Hg^+} = 0$, when (4) becomes

$$\frac{d\sigma}{dM_\epsilon} = \frac{d\sigma}{\epsilon dV} = -\Gamma_\epsilon.$$

Butler pointed out [88] that the Γ_ϵ so obtained is not necessarily equal to the amount of electrons which corresponds with the charge on the mercury side of the double layer. For example, if the double layer consists of an excess of electrons on the metal facing an excess of mercury ions in the solution, this definition will require the dividing surface not to coincide with the surface of the metal but to be placed in the solution a small distance from the actual surface of the metal. Measured with respect to this surface Γ_ϵ will be less than corresponds to the actual charge on the metal and may in fact

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[87] *Phil. Mag.*, **50**, 641, 1926.

[88] *Proc. Roy. Soc.*, **113A**, 594, 1927.

be zero. If there are no, or practically no mercury ions in the solution, and the solution side of the double layer consists of ions of other species, this difficulty disappears and the dividing surface so defined will be coincident with the actual surface of the electrode.

Alternatively we may postulate that the dividing surface is so placed that Γ_s is the amount of electrons which corresponds with the charge on the mercury side of the double layer, which will generally make it coincide with the actual surface of the metal. Then we may conclude that

(1) If there is no excess of mercury ions on the solution side of the double layer, Γ_{Hg^+} will be zero ;

(2) If the concentration of mercury ions in the solution is very small, equilibrium of mercury ions between the phases may not be maintained, and in that case $dM_{Hg^+} = 0$.

In either case the electrocapillary equation becomes

$$\epsilon\Gamma_s \,.\, dV + \Gamma_1 d\bar{F}_1 + \Gamma_2 d\bar{F}_2, \text{ etc.,} \quad + d\sigma = 0.$$

CHAPTER V

ELECTROKINETIC PHENOMENA

The Zeta-Potential. It is obvious that only the diffuse part of the double layer is free to move relative to the surface, and consequently electrokinetic phenomena will be determined only by that part of the potential difference which is produced by the diffuse layer. That the electrokinetic potential difference was not necessarily the same as the whole potential difference between two phases was clearly realised by von Smoluchowski,[1] Freundlich [2] and Gyemant.[3] Freundlich called this potential difference the ζ-potential.

It has been pointed out that cataphoresis and electro-endosmose are two different aspects of the same phenomenon—the relative motion in an electric field of two phases between which there is a potential difference.[4]

The velocity of this relative motion was first calculated by Helmholtz [5] and the theory was subsequently improved by Lamb,[6] Perrin,[7] von Smoluchowski,[8] without any essential modification of the result which may be expressed as

$$v = K \, . \, (ED \, . \, \zeta/\eta), \quad . \quad . \quad . \quad (1)$$

where D is the dielectric constant of the medium, ζ the effective potential difference, E the applied electric field (fall of the potential difference in unit length) and η the viscosity.

The following simple derivation, due to Briggs [9] illustrates the ideas involved.

[1] *Graetz' Handbuch der Elect. und d. Magnet*, **2**, 366, 1914; *Physikal Z.*, **17**, 557, 583, 1916; *Z. physik Chem.*, **92**, 129, 1918.

[2] Freundlich and Rona, Sitz., *Preuss. Akad. Wiss.*, 397, 1920.

[3] *Z. Physik*, **17**, 190, 1923.

[4] See McBain and Laing, *J. Physical Chem.*, **33**, 673, 706, 1929.

[5] *Ann. Physik*, **7**, 337, 1879.

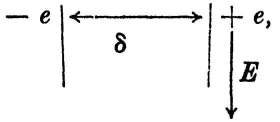
[6] *Phil. Mag.*, **25**, 52, 1888.

[7] *J. Chim. Phys.*, **2**, 601, 1904; **3**, 50, 1905.

[8] *Loc. cit.*

[9] *J. Physical Chem.*, **32**, 641, 1928.

Suppose the charge per unit area on the side of the double layer which is free to move is e, and the distance from the surface δ. If the potential difference per unit length is E, the electrical force on this charge is Ee. At equilibrium this is equal to the frictional force which must be overcome, which can be expressed as $\eta v/\delta$,



where η is the viscosity of the liquid and v the velocity produced. Hence we have

$$v = Ee\delta/\eta,$$

or, writing the potential difference as

$$\zeta = 4\pi\delta e/D,$$

we have

$$v = ED\zeta/4\pi\eta.$$

According to this calculation K in (1) is equal to $1/4\pi$. This applies to flat surfaces or, at least, to surfaces in which the radius of curvature is large compared with the thickness of the double layer. Debye and Hückel,[10] who were primarily concerned with the cataphoretic mobility of ions in their ionic atmosphere, i.e. with cases in which the thickness of the double layer (ionic atmosphere) is large compared with the radius of the particle, found that $K = 1/6\pi$. Henry [11] took account of the conductivity of the two phases and obtained

$$K = 1/6\pi(3\kappa/2\kappa + \kappa'),$$

where κ, κ' are the conductivities of the liquid and solid. If the latter is zero, this reduces to $K = 1/6\pi$. The influence of the shape and size of the particles is rather obscure, and reference may be made to the following summaries.[12] Bull and Gortner [13] have suggested that it is better to regard electrokinetic measurements

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[10] *Physikal Z.*, **25**, 49, 205, 1924. [11] *Proc. Roy. Soc.*, **133A**, 106, 1931.

[12] Articles in Discussion on Colloidal Electrolytes, *Trans. Faraday Soc.*, **31**, 1 *seq.*, 1935; E. J. W. Verwey, *Chem. Revs.*, **16**, 363, 1935; Abramson, *Electrokinetic Phenomena*, Chem. Cat. Co., 1934. Articles on *Colloid Symposium Monographs*, VI, 1928; VII, 1931. For electrokinetics at metallic surfaces, see Kruyt and Oosterman, *Kolloid Z.*, **48**, 377, 1938. [13] *Physics*, **2**, 21, 1932.

as a means of determining (δe) rather than ζ. δe, the product of the electric charge by the thickness of the double layer, may be regarded as the electric moment of the double layer.

Cataphoresis. The fundamental equation for cataphoretic velocity, if the radius of the particle is not too small, is

$$v = \frac{\zeta DX}{4\pi\eta} = \frac{\zeta DRi}{4\pi\eta},$$

where X = electric field, which can be expressed as $X = E/l = Ri$, where E = potential difference in liquid column of length l, R = specific resistance of liquid and i = current through it. ζ is usually given in multivolts and X in volts/cm.[2] To convert these to electrostatic c.gs. units, we divide the value of ζ by 300×10^3 and X by 300. For aqueous solutions $D = 80$ and $\eta = 0{\cdot}01$. Hence for unit field (1 volt/cm.).

$$v = \frac{\zeta \times 80}{4 \times 3{\cdot}14 \times 0{\cdot}01 \times 300 \times 10^3 \times 300} \text{ cm./sec.}$$

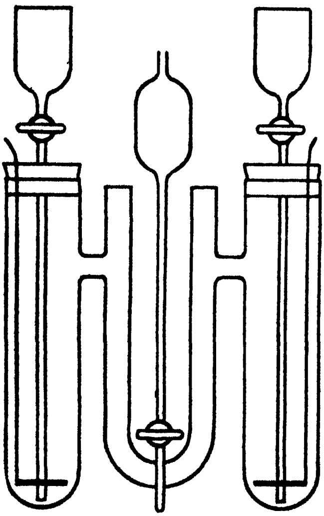
or

$$v = 7 \times 10^{-6}\,\zeta.$$

For glass in water, Quincke found $v = 3 \times 10^{-4}$ cm./sec., hence $\zeta = 40$ millivolts.

It is to be noted that in this calculation the velocity is independent of the radius of the particle and is of the same order as the mobility of the larger ions.

Cataphoretic mobility can be determined by observation of the movement of a boundary of the particles in an apparatus similar to that used for the direct observation of ionic mobilities by the moving boundary method. For example, Fig. 1 shows an apparatus used by Svedberg and Tiselius.[14] Tiselius has made a careful study



V. 1.—Cataphoreses apparatus of Svedberg and Tiselius. (*J. Amer. Chem. Soc.*)

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[14] *J. Amer. Chem. Soc.*, **48**, 2272, 1926; cf. Scott and Svedberg, *ibid.*, **46**, 2700, 1924; Svedberg, *Trans. Faraday Soc.*, **26**, 737, 1930.

of the main sources of error and has produced an apparatus which is capable of great precision.[15] It is necessary that the liquid in which the colloidal particles are suspended should have the same composition as the solution in which it is in contact at the boundary, otherwise anomalous movements at the boundary will occur. In circular tubes the liquid in the middle loses heat less rapidly than the liquid near the walls and therefore gets hotter during the passage of the current. This causes a difference of density which gives rise to convection currents. Tiselius gets over this partly by making measurements near the temperature of maximum density of water (4°), and partly by using rectangular tubes, 3 mm. × 25 mm. in cross-section, built up of plate glass.[16]

The apparatus is shown in Figs. 2 and 3.[17] The U-tube is divided into four sections I, II, III, IV, of which II and III can be slid horizontally by means of the gears (*g*), which are operated by the knobs *k*, *k′* (Fig. 3). The boundary is initially formed by filling the channel up to section II with the colloidal solution and the section III is then slid horizontally, while the excess of the solution in II is removed and replaced by the contact solution. This portion is then slid into place again. The electrodes *E*, *E′* in the large vessels are of silver, silver chloride and must have a sufficiently large capacity, and they are surrounded, in the smaller portions of the vessels, with a strong chloride solution.

This apparatus has been used with great success to study the mobilities of proteins. Since solutions of these substances are colourless, it is not easy to make the boundary visible. In the earlier experiments Svedberg made use of the fluorescence produced by ultraviolet light, but this necessitates using quartz apparatus. Tiselius has made use of the refractive index change at the boundary, which is utilised in Töpler's *schlieren* technique[18] to give a

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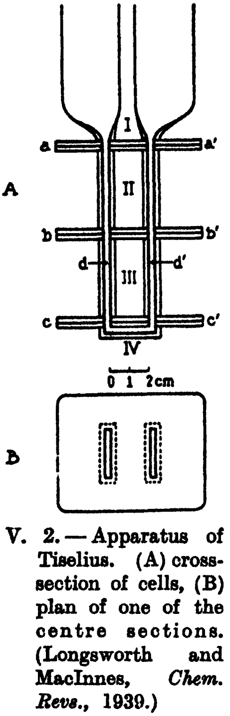
[15] *The Moving Boundary Method of Studying the Electrophoresis of Proteins*, Uppsala, 1930.

[16] *Trans. Faraday Soc.*, **33**, 524, 1937; *Kolloid Z.*, **85**, 129, 1938; *Svensk Kemesk Tidskrift*, **50**, 58, 1938.

[17] This is a slightly modified form of the apparatus, described by Longsworth and MacInnes, *Chem. Revs.*, **24**, 271, 1939.

[18] Longsworth (*J. Amer. Chem. Soc.*, **61**, 529, 1939) gives an improved photographic recording method; cf. Philpot, *Nature*, **141**, 283, 1938; Andersson, *ibid.*, **143**, 720, 1939.

photographic record of the boundary. With mixtures of proteins a series of boundaries can be seen, and proteins which were thought to be single compounds have been shown to be complex. For example, Fig. 4 shows successive photographs of the boundaries obtained with human blood serum, showing at least three components.



V. 2.—Apparatus of Tiselius. (A) cross-section of cells, (B) plan of one of the centre sections. (Longsworth and MacInnes, *Chem. Revs.*, 1939.)

Separations of two proteins can be effected in this way. If the two boundaries move in the same direction they will probably not be far apart before they have moved completely out of the U-tube. To overcome this Tiselius has added a device which causes a slow flow of the liquid to take place through the tube, by which means one boundary may be kept stationary with respect to the walls. The faster moving component can then be isolated by sliding compartment II of the vessel to the side.[19]

Proteins are amphoteric electrolytes, and the charge on the molecule depends on the ionisation equilibrium of the various acid and basic groups, and is therefore determined by the p_H of the solution. The mobility of proteins in solution is therefore a function of the p_H, usually not far off from linear, at least in the neighbourhood of the isoelectric point (zero mobility). Fig. 5 shows the mobilities of the components of horse serum at constant ionic strength.

Apparatus for measuring the mobility of individual particles which are sufficiently large to be visible in the microscope have been described by a number of authors, of which examples are listed below.[20] It is found that the velocity varies with the distance of

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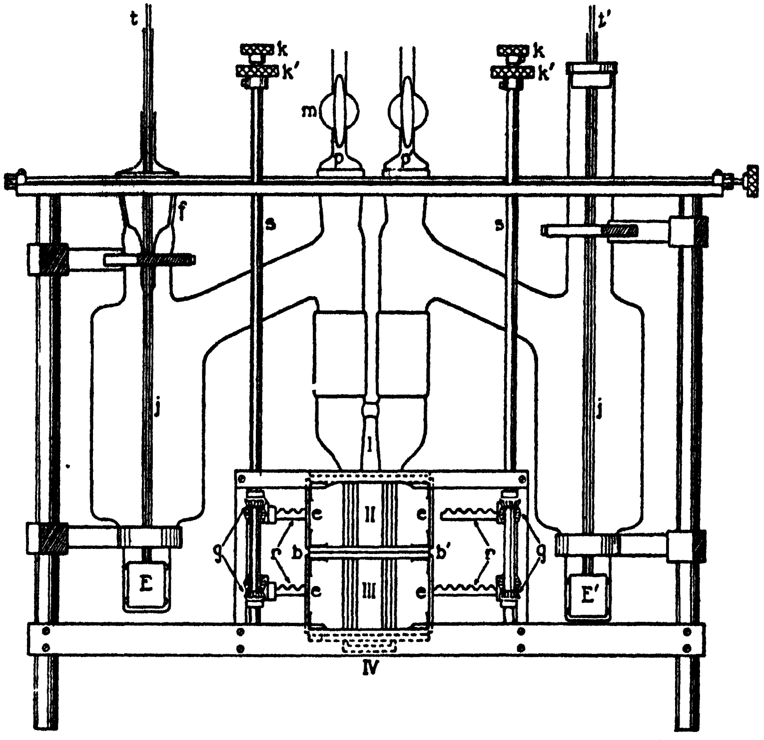
[19] Studies with this apparatus: *Biochem. J.*, **31**, 313, 1464, 1937; **32**, 1814, 1938; *Science*, **87**, 416, 1938; Tiselius and Horsfall, *J. Exp. Med.*, **69**, 83, 1939.

[20] J. H. Northrop, *J. Gen. Physiol.*, **4**, 629, 1921; Kunitz, Northrop and Kunitz, *ibid.*, **6**, 413, 1923; **7**, 729, 1924; Bull, *J. Physical Chem.*, **39**, 577, 1935; Mattson, *ibid.*, **32**, 1532, 1928; **37**, 223, 1933; Abramson, Moyer and Voet, *J. Amer. Chem. Soc.*, **58**, 2362, 1936; Moyer, *J. Bact.*, **31**, 531, 1936; Gils and Kruyt, *Kolloid Z.*, **45**, 60, 1937.

the particle from the sides of the tube and may in fact be of opposite sign in the centre of the tube and very near the walls. This is due to the fact that an endosmotic flow takes place at the walls and there is therefore a circulation of the liquid along the walls in one direction, and since the whole apparatus is closed a reverse flow must take place in the centre. The theory was given by Smoluchowski,[21] who showed that the true cataphoretic velocity could be observed (in flat tubes) at two levels, which lie at 21 per cent. of the whole thickness of the cell, from the top and bottom respectively.[22] Fig. 6 shows an observed distribution of velocities.



V. 3.—Apparatus of Tiselius, with electrode vessels and support. (Longsworth and MacInnes, *Chem. Revs.*, 1939.)

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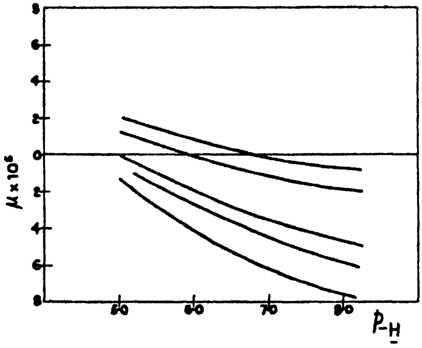
[21] *Handbuch d. Elekt. u. d. Magnet.*, V, II, 366 (1921); see Abramson, *Electrokinetic Phenomena*, Chap. III.

[*For footnote* 22 *see page* 98.

A comparison of the moving boundary and microscopic methods of determining mobilities has been made by Moyer,[23] who compared the mobility of horse serum pseudoglobulin, as determined by Tiselius, with that of collodion particles covered with the same protein. Fig. 7 shows the result.



V. 5.—The mobilities of different components in four times diluted horse serum at constant ionic strength 0·1. (Tiselius, *Biochem. J.*, 1937.)

Electroendosmose. If the double layer is on the surface of a stationary cylindrical capillary, the whole of the liquid inside the capillary moves with the velocity v, when an electric field is applied. The volume which passes through a capillary of radius r in unit time is therefore

$$V = \frac{\pi r^2 \zeta D X}{4\pi\eta} = \frac{\pi r^2 \zeta D E}{4\pi\eta l},$$

where E is the electromotive force applied between the ends of the capillary of length l. For a bundle of capillaries of cross-section Q, this becomes

$$V = \frac{Q \, . \, \zeta D E}{4\pi\eta l},$$

or, if χ is the specific conductivity of the liquid and i the current flowing through the diaphragm, we have $i = \chi Q E / l$, and

$$V = \frac{\zeta D i}{4\pi\eta\chi}.$$

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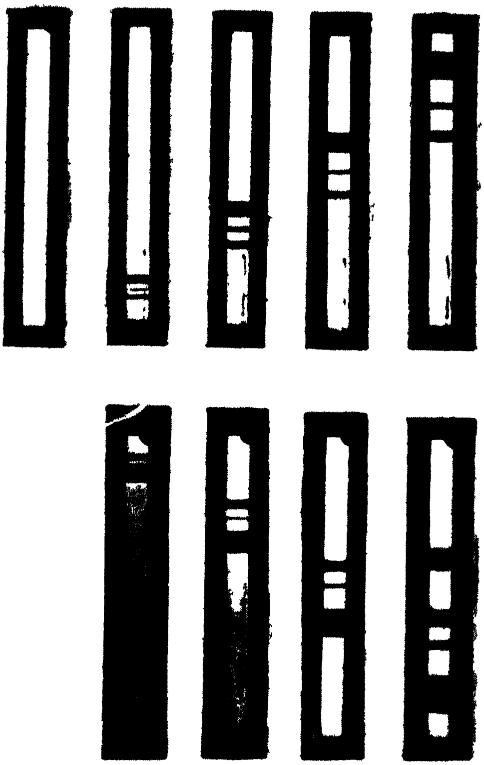
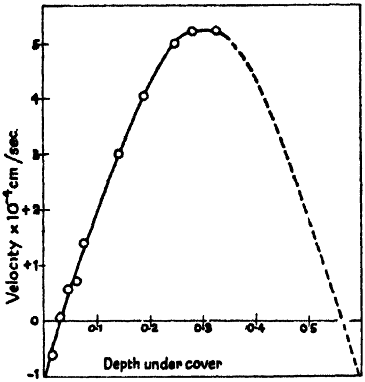
[22] For possible errors see D. C. Henry, *J. Chem. Soc.*, 997, 1938. The distribution of velocities was first studied by R. Ellis (*Z. physikal. Chem.*, **78**, 321, 1912). Newton (*Phil. Mag.*, **9**, 769, 1930) found that the distribution of velocities s parabolic in tubes 0·8 cm. wide, and Currie (*ibid.*, **12**, 429, 1931) found that the distribution in a cylindrical tube does not depend on the diameter. Alty and Johnson (*ibid.*, **20**, 129, 1935) studied the cataphoresis of fatty acid particles, taking electro-osmotic flow into account.

[23] *J. Biolog. Chem.*, **122**, 641, 1938.

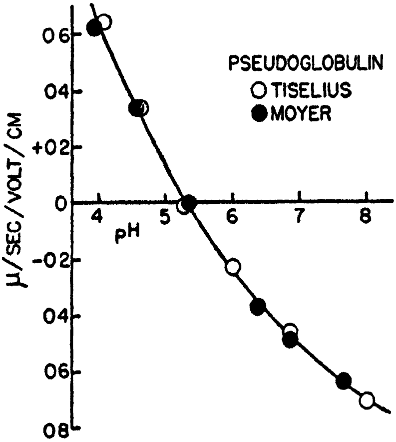


V. 4.—Cataphoretic analysis of blood serum in phosphate buffer of $p_H = 8 \cdot 06$. Voltage 7·25 volts per cm. Photographs at time intervals of 20 mins. Fastest component is serum albumin, the other two, serum globulin fractions. The upper and lower sets of photographs show the upward and downward movements of the boundaries in the two limbs of the U-Tube. (Tiselius.)

It has been shown, however, that the conductivity of the liquid as it exists in the diaphragm may differ from the normal conductivity,[24] and it is desirable to use the actual specific conductivity χ_s, as it exists in the diaphragm, which can be measured in the course of the experiment.



V. 6.—Variation of velocity with distance from walls in flat cell 0·6 mm. thick. (Ellis.)



V. 7.—Mobilities of horse serum pseudoglobulin at 20° C. Data of dissolved protein by Tiselius, adsorbed protein on collodion particles by Moyer.

The hydrostatic pressure required to prevent this flow is $P = V\sigma$, where σ is the resistance of the diaphragm to flow. For a single capillary this is $\sigma = 8\eta l/\pi r^4$. Hence

$$P = 2\zeta ED/\pi r^2 \quad \text{or} \quad 2\zeta ED/Q.$$

Streaming Potentials. When a liquid is forced through a capillary or a diaphragm a potential difference is established between the two ends. This was studied first, using a single glass capillary, by Kruyt,[25] Freundlich and Rona,[26] and Kruyt and Willigen.[27] More recent forms of apparatus for diaphragms have been described

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[24] Fairbrother and Martin, *J. Chem. Soc.*, **125**, 2319, 1924; Briggs, *J. Physical Chem.*, **32**, 641, 1928; *Coll. Symp. Monograph*, VI, 41, 1928; McBain, *Trans. Faraday Soc.*, **16**, 150, 1921.

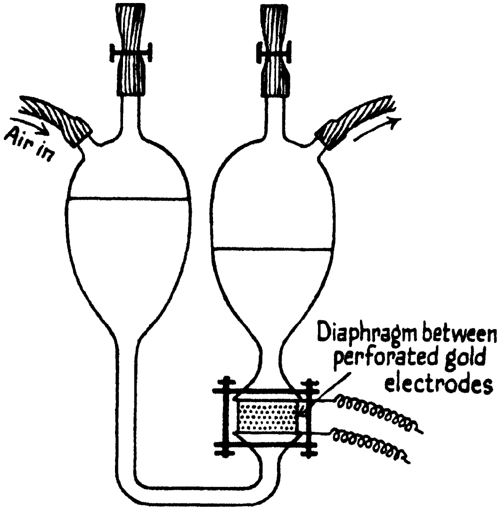
[25] *Kolloid Z.*, **22**, 81, 1918.

[26] *Sitz. preuss. Akad. Wiss.*, **20**, 397, 1920.

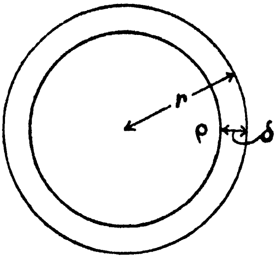
[27] *Kolloid Z.*, **45**, 307, 1928.

by Briggs,[28] Martin and Gortner,[29] and Gortner and Lauffer.[30] An apparatus is shown in Fig. 8.

The following equation between the electromotive force produced and the pressure applied was first given by Helmholtz.[31] Consider a single cylindrical tube of radius r through which the liquid is forced by the hydrostatic pressure P (Fig. 9). Let ρ be the charge density of the mobile side of the double layer at a distance δ from the side of the tube. If the velocity of the liquid at the wall of the tube is zero, the velocity at a distance δ can be written as



V. 8.—Apparatus for streaming potentials. (Martin and Gortner.)



V. 9.

$$v = \frac{\partial v}{\partial \delta} \cdot \delta,$$

assuming a constant velocity gradient. The quantity of electric charge transported in unit time by the flow of liquid through an annular ring of thickness $d\delta$, and length approximately $2\pi r$, is

$$di_0 = \rho \frac{\partial v}{\partial \delta} \cdot \delta \cdot 2\pi r \cdot d\delta.$$

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[28] *J. Physical Chem.*, **32**, 641, 1928.

[29] *Ibid.*, **34**, 1509, 1930.

[30] *Ibid.*, **42**, 641, 1938.

[31] *Wied. Ann.*, **7**, 337, 1879 ; cf. Briggs, *loc. cit.*

$\rho\delta \,.\, d\delta$ is the electric moment of the element of the double layer considered, and as in Helmholtz's theory we have

$$\int \rho\delta \,.\, d\delta = \zeta D/4\pi.$$

The total charge transported by the flow in unit time is thus

$$i_0 = \frac{\zeta D}{4\pi} \cdot \frac{\partial v}{\partial \delta} \,.\, 2\pi r.$$

By Poisselles' theory of flow in capillary tubes we have

$$\frac{dv}{dr} = -\frac{dv}{d\delta} = -\frac{rP}{2l\eta}.$$

Hence,

$$i_0 = \frac{\zeta D}{4\pi} \cdot \frac{PA}{l\eta},$$

where $A = \pi r^2$ is the cross-section of the tube. This movement of charge must be opposed by the potential difference between the ends of the capillary. If the latter is E the amount of charge which is carried back through the area A is

$$i_1 = EA/\chi l,$$

where χ is the specific conductivity of the liquid. For equilibrium, to prevent any accumulation of charge at one end of the capillary i_0 and i_1 must be equal, and therefore

$$E = \frac{\zeta D}{4\pi} \cdot \frac{P}{\eta\chi}.$$

Units.—P is usually stated in cms. of mercury, and to convert to dynes/cm.^{2} must be multiplied by 13·6, the specific gravity of mercury, and by the gravity constant 981 dynes. As before for water, D can be taken as 80 and η as 0·01. If χ is in reciprocal ohms it must be multiplied by 9×10^{11} to convert to c.gs. units. Hence, if ζ is in volts ($\zeta/300$ c.gs. units) we have

$$E = \frac{\zeta P}{\chi} \times \frac{13{\cdot}6 \times 981 \times 80 \times 300}{300 \times 9 \times 10^{11} \times 4 \times 3{\cdot}14 \times 0{\cdot}01} \text{ volts.}$$

For a given surface and solution, E should therefore be proportional to P. The following table gives (A) a series of measurements by Kruyt and Willigen with a glass capillary in dilute KCl;

(B) measurements by Briggs with a cellulose diaphragm in conductivity water:—

TABLE I. EFFECT OF PRESSURE ON STREAMING POTENTIALS

A			B		
P cms. of Hg.	*E* Millivolts.	*E*/*P*	*P* cms. of Hg.	*E* Millivolts.	*E*/*P*.
40	486	12·15	55·2	141	2·56
50	605	12·10	47·9	122	2·55
60	725	12·08	38·7	100	2·58
70	834	11·91	28·2	75	2·66
80	943	11·79	17·8	48·6	2·79
			7·5	21·5	2·86

Briggs pointed out that where the surface conductivity is not negligible, χ_S as defined above (p. 98) must be used. He found that $E\chi_S/P$ was a constant with diaphragms of cellulose fibres of widely varying densities.

These equations are only valid, however, for capillaries having a radius above a certain critical value.[32] This is partly due to the necessity of the radius being greater than the thickness of the double layer, and partly owing to the fact that the streaming potential itself induces an endosmotic flow opposite to the direction of streaming, which decreases the effective hydrostatic pressure. Some anomalous results obtained have been due to the use of capillaries below the critical radius.[33]

Some Results. Comparison of ζ-Potentials Measured by Different Methods. It would not perhaps be very surprising if the ζ-potentials determined by different methods at the same surface did not agree, for the ζ-potential being the " diffuse " part of the whole potential difference is not a very clearly defined quantity, and it is not at all impossible that the fraction of the whole potential difference which is operative would depend on the method of experiment. For the purpose of comparison it is necessary that the surfaces should be in the same state. Van der Grinten [34] compared cataphoresis and electro-osmose at glass surfaces and found a distinct difference. It is doubtful, however, if the surface of powdered

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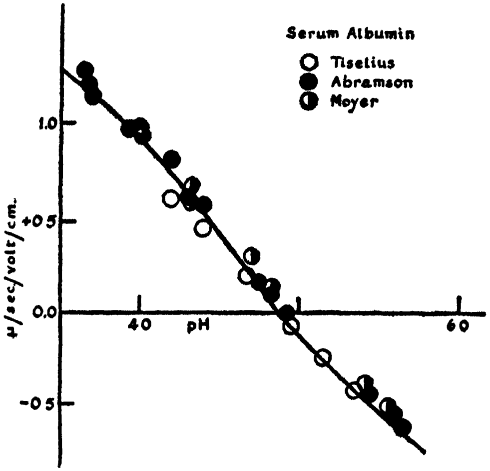
[32] Bull and Moyer, *J. Physical Chem.*, **40**, 9, 1936; Bull, *Kolloid Z.*, **60**, 130, 1932.

[33] See White, Urban and van Atta, *J. Physical Chem.*, **36**, 3152, 1932.

[34] *J. Chim. Phys.*, **23**, 209, 1926.

glass is identical with that of sheet glass. Henry[35] compared the cataphoresis of wax particles with electro-osmosis at wax-coated surfaces and found good agreement, using Smoluchowski's equation. Other authors have coated glass surfaces with proteins in order to bring them into identical states.

Abramson[36] found that the mobility of dissolved proteins was practically the same as that of quartz particles, 1000 times as large, on which the proteins have been adsorbed. A considerable amount of work has since been done with more accurate techniques,[37] and it has been found that in some cases there is perfect agreement between the mobilities of the protein molecules themselves and that of various particles on which the protein has been adsorbed. Fig. 10 shows a recent comparison of the mobilities of horse serum albumin over a range of p_H, in solution and on quartz (Abramson) and collodion (Moyer) particles respectively. Perfect agreement has also been found in the case of horse pseudoglobulin. In such cases it may be concluded that the adsorption of the protein brings about no important changes in the orientation or activity of the carboxyl and amino groups.



V. 10.—Electric mobility of horse serum albumin as a function of p_H in 0·02 μ acetate buffers at 20° C. (Abramson, Gorin and Moyer, *Chem. Revs.*, 1939.)

In other cases, e.g. egg albumin, the cataphoretic behaviour of the adsorbed film differs slightly but definitely from that of the

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[35] *Proc. Roy. Soc.*, **133A**, 106, 1931; cf. Dummelt and Bowden, *ibid.*, **142A**, 382, 1933.

[36] *J. Amer. Chem. Soc.*, **50**, 390, 1928; *J. Gen. Physiol.*, **15**, 575, 1932.

[37] For summary see Abramson, Gorin and Moyer, *Chem. Revs.*, **24**, 345, 1939.

dissolved molecules.[38] Protein films on a variety of surfaces, quartz, glass, oil, collodion and carbon, gave the same mobility curve (isoelectric point at $p_H = 4{\cdot}82$), but it was intermediate between that of the dissolved protein (4·55) and that of particles of denatured protein (5·0). It therefore appears that in such cases the protein is partly denatured in becoming adsorbed.

The mobility of particles coated with protein seems to be quite independent of their size, and further evidence of this is given by a comparison of the cataphoretic mobility with the electro-osmotic mobility at flat, or at least coarse-grained surfaces. Abramson [39] found a good agreement between the two methods. Briggs [40] had also studied the streaming potentials at similar surfaces and found that the ζ potential agreed well with that calculated from the mobility.

Bull [41] compared the three methods with protein-covered Pyrex surfaces and found very good agreement, the average ratio of the ζ's by cataphoresis, C, and electro-endosmose, E, being 0·99, by S (streaming potentials) and C 0·97, and by S and E 0·99. But the agreement was bad with bare quartz surfaces and cellulose fibres.

Monoghan, White and Urban [42] found that at Pyrex in the presence of gelatine, there is good agreement in the isoelectric concentrations of hydrogen ions (i.e. the concentrations of salts required to produce zero mobility) determined by the three methods. On the other hand, without gelatine, the S method does not give rise to the same isoelectric concentration of thorium, ferric and aluminium salts as C and E. They suggest that while only the diffuse part of the double layer is moved by streaming, the application of an electric field (as in the C and E methods) affects the outer parts of the Helmholtz layer also. White, Monoghan and Urban [43] further found that at glass and gelatine surfaces the C and E values only agree when the salt concentration is greater than 10^{-3} M. With lower concentrations the value of the ratio of E to C may

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[38] Moyer, *J. Physical Chem.*, **42**, 71, 1938.

[39] *Ibid.*, **35**, 289, 1931 ; cf. Daniel, *J. Gen. Physiol.*, **16**, 457, 1933 ; Moyer and Abramson, *ibid.*, **19**, 727, 1936 ; *J. Biol. Chem.*, **123**, 391, 1938.

[40] *J. Amer. Chem. Soc.*, **50**, 2358, 1928.

[41] *J. Physical Chem.*, **39**, 577, 1935.

[42] *Ibid.*

[43] *Ibid.*, **39**, 611, 1935.

reach 3. Moyer and Abramson,[44] however, were unable to confirm any significant rise of the ratio from unity, provided the gelatine coating was complete. White and Fourt [45] again found a difference when the gelatine concentration was $<$ 0·1 per cent., which has been denied by Moyer,[46] provided the gelatine coating is first deposited from a stronger solution.

Kemp and Rideal used the cataphoretic mobility to study the adsorption of gliadin on quartz particles, and they also used the change of mobility with time to measure the rate of adsorption.[47] Prideaux and Howitt [48] studied the cataphoresis of colloidal gold particles in the presence of increasing concentrations of protein, and found that the "protective action" of the protein manifested itself at the point where the concentration of the protein was just sufficient to form a complete surface film on the particles.

Cataphoresis of Air Bubbles. The air-solution interface offers a very favourable opportunity for electrokinetic measurements, since the results could be correlated with information derived from measurements of the surface-tension and of the total potential difference (p. 87). Owing to practical difficulties, however, not much work has been done. Quincke first observed [49] that in pure water air bubbles moved to the anode, i.e. are negatively charged. More extensive investigations were made by MacTaggart [50] and Alty.[51] The former found that hydrogen, oxygen and illuminating gas had the same mobility, which was the same order as that usually observed with colloidal particles, viz. 4×10^{-4} cm.^{2}/volt/sec. He studied the effect of additions of electrolytes and of some non-electrolytes. Strong acids gradually reduced the mobility to zero, while tri- and quadrivalent cations, e.g. Al^{+++}, Th^{++++}, produced a reversal of the direction of motion at quite small concentrations. Alty confirmed the independence of the mobility on the nature of

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[44] *J. Gen. Physiol.*, **19**, 727, 1936.

[45] *J. Physical Chem.*, **42**, 29, 1938.

[46] *Ibid.*, **42**, 391, 1938; cf. *Trans. Amer. Electrochem. Soc.*, **73**, 215, 1938.

[47] *Proc. Roy. Soc.*, **147**A, 1, 11, 1934.

[48] *Ibid.*, **126**A, 126, 1929; *Biochem. J.*, **25**, 391, 1931.

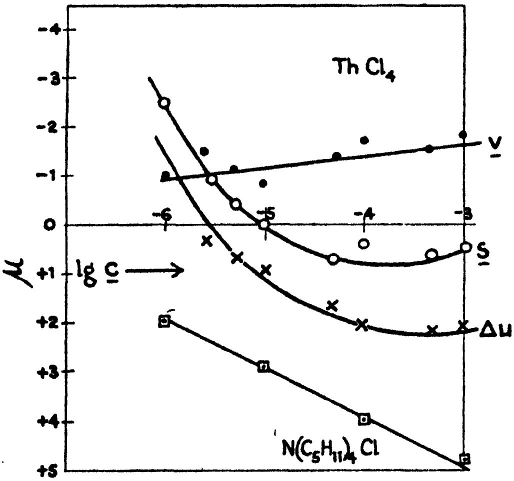
[49] *Pogg. Annalen*, **113**, 513, 186.

[50] *Phil. Mag.*, **27**, 297, 1914; **28**, 367, 1914; **44**, 386, 1922.

[51] *Proc. Roy. Soc.*, **106**A, 315, 1924; **110**A, 178, 1926; **112**A, 235, 1926; Currie and Alty, *ibid.*, **122**A, 622, 1929.

the gas and found that the charge on the particle was small in very pure water.

It is difficult to understand the origin of the charge of the particles and particularly the cause of the reversal of the charge by polyvalent cations, since there is no independent evidence that these cations are adsorbed at the surface. McTaggart used a closed cylindrical tube which was rotated to keep the bubbles at the axis, and the electro-osmotic flow of the liquid, which occurs under these circumstances along the walls of the tube and back along the axis, was not corrected for.



V. 11.—Effect of $ThCl_4$ on the apparent (*s*) and true mobility (*v*) of air bubbles. The squares also show the effect of $N(C_5H_{11})_4Cl$. (Bach and Gilman.)

N. Bach and A. Gilman[52] have re-examined the question and made a careful examination of the effect of the electro-osmotic flow of the liquid. The usual correction is difficult to apply in the case of gas bubbles and special methods were devised. They find that lanthanum and thorium salts cause a reversal of the apparent direction of motion, owing to the fact that the bubbles are carried by the flow of water towards the cathode at a greater rate than that of their own movement towards the anode. Fig. 11 shows *s* the apparent mobility, $\Delta\mu$ the effective velocity of the solution and *v* the true mobility of the particle. In increasing concentrations of thorium salt, the real mobility becomes increasingly negative.

In a further paper[53] the effect of capillary active substances, such as tetraalkyl ammonium salts and sodium palmitate, was

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[52] *Acta Physicochimica*, **9**, 1, 1938.

[53] *Ibid.*, **9**, 27, 1938.

studied. The former produce a positive charge on the surface which increases linearly with the logarithm of the concentration. The latter makes the surface increasingly negative. The ratio of the concentrations tetra-iso-amyl- to tetra-butyl-ammonium chloride which have the same mobility is about 9, which is in agreement with Traube's rule for equal adsorption. Analogous measurements of the total interfacial potential difference show that this increases with concentration considerably more rapidly than the ζ potential.

Other Electrokinetic Phenomena. Dorn discovered in 1878 [54] that potential differences between the top and bottom of a liquid are produced when charged particles fall through it. Stock [55] showed that this potential difference was related to the p.d. between the particles and the liquid. It was further investigated by Billitzer,[56] and Freundlich and Mäkelt.[57] More recently Bull used the method to determine the nature of the charge of galena particles,[58] but the results were not confirmed by cataphoretic measurements.[59] The effect may be of considerable meteorological importance.[60]

Very similar is the "waterfall" or "ballo-electric" effect. When a spray of the liquid is directed against an electrode, the latter acquires a charge (in the case of pure water, positive) while the gas space contains the opposite charge. It was first investigated by Lenard,[61] and has been extensively investigated.[62] The effect appears to be due to the tearing apart of the two sheets of the double layer, whereby the charges of one sign are dispersed in the surrounding atmosphere. The nature of the gas has very little effect on the magnitude of the charge. It can also be observed with non-aqueous liquids, provided they are not completely non-polar. Inorganic electrolytes greatly reduce the effect, but surface-active non-electrolytes, such as alcohol, fatty acids, etc.,[63] may increase the effect and in some cases, e.g. aniline, chloracetic acid, the sign

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[54] *Ann. Physik* (4), **3**, 20, 1878; **9**, 513; **10**, 46, 1880.

[55] *Anz. Akad. Wiss. Wien.*, 131, 1913.

[56] *Ann. Physik*, **11**, 937, 1903.

[57] *Z. Elektrochem.*, **15**, 161, 1909.

[58] *J. Physical Chem.*, **33**, 656, 1929.

[59] *Ibid.*, **38**, 401, 1034.

[60] Cf. Shaw, *Proc. Roy. Soc.*, **122A**, 49, 1929.

[61] *Wied. Ann.*, **46**, 584, 1892.

[62] See A. Becker, *Jahr. d. Radioakt.*, **9**, 52, 1912, for summary to 1912; Bühl, *Kolloid Z.*, **59**, 346, 1932, for more recent summary.

[63] Christiansen, *Ann. d. Physik*, **40**, 107, 233, 1913; **51**, 530, 1916; **59**, 95, 1919.

of the charge may be reversed. A salt and a non-electrolyte together produce an effect which is greater than the sum of their separate effects. It is obvious that the effect is closely related to the electrokinetic phenomena. Bull and Gortner have studied the streaming potentials of aqueous solutions projected into organic liquids.[64]

Another effect is the electroviscous effect predicted by v. Smoluchowski in 1916, according to which the charge on colloidal particles will cause an enhancement of the viscosity.[65] He obtained the expression

$$\frac{\eta}{\eta_0} = 1 + 2{\cdot}5\phi\left[1 + \frac{1}{\chi\eta_0 r^2}\left(\frac{\zeta\epsilon}{4\pi}\right)^2\right],$$

where ϕ is the percentage of the total volume occupied by the disperse phase, η is the viscosity of the suspension, η_0 that of the pure solvent, and χ the specific conductivity. According to Bull, however,[66] the value of the factor in square brackets, which is the correction for the effect of the charges, differs from unity by less than 1 per cent. for protein particles.

The Ionic Atmosphere. The earlier calculations of Gouy and Chapman of the potential difference of diffuse layers (p. 76) were succeeded by the well-known calculation of Debye and Hückel [67] of the distribution of ions in the *ionic atmosphere* round any given ion. This atmosphere arises from the fact that a given ion attracts ions of unlike sign and repels ions of like sign. If n_i is the number per c.c. of ions of valency z_i (and charge $z_i\epsilon$, where ϵ is the electronic charge) in the bulk of the solution, the concentration where the potential is ψ is $n_i\, e^{-z_i\epsilon\psi/kT}$, and the total charge density at this point is

$$\rho = \sum n_i z_i\, \epsilon\, e^{-z_i\epsilon\psi/kT}.$$

Applying Poisson's equation,*

$$\nabla^2\psi = -\,4\pi\rho/D,$$

we have

$$\nabla^2\psi = -\,\frac{4\pi}{D}\sum n_i z_i\, \epsilon\, e^{-z_i\epsilon\psi/kT}.$$

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[64] *Physics*, **2**, 21, 1932.

[65] *Kolloid Z.*, **18**, 190, 1916.

[66] *Z. physik. Chem.*, **161**, 192, 1932.

[67] *Physik. Z.*, **24**, 185, 1923.

* $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

Debye and Hückel solved this equation by making the approximation

$$e^{-z_i\epsilon\psi/kT} \to 1 - z_i\epsilon\psi/kT,$$

which is only valid if $z_i\epsilon\psi/kT \ll 1$. With this assumption we have

$$\nabla^2\psi = \kappa^2\psi,$$

where
$$\kappa^2 = \frac{4\pi\,\epsilon^2}{DkT}\sum n_i z_i^2.$$

Writing

$$n_i = c_i\,N_0/1000,$$

where c_i = concentration in mols./litre, and let $\frac{1}{2}\Sigma c_i z_i^2$ be called the ionic strength μ, we have

$$\kappa^2 = \frac{4\pi\,\epsilon^2}{DkT}\cdot\frac{N_0}{1000}\cdot 2\sqrt{\mu}.$$

The form of the solution of this equation depends on whether it is to refer to a plane or spherical surface.

Spherical surfaces. The general solution can be expressed as

$$\psi = \frac{e}{D}\frac{e^{-\kappa r}}{r},$$

where ψ is the potential at a distance r from the centre of an ion or sphere having the charge e. If ζ is taken as the potential at the surface of a particle, which has a radius a and a charge e, we have

$$\zeta = \frac{e}{Da}e^{\ \kappa a},$$

which may be successively approximated to

$$\zeta \to \frac{e}{Da}\frac{1}{1+\kappa a} \to \frac{e}{Da}\left(\frac{1}{a}+\kappa\right) \qquad . \quad . \quad (1)$$

for small values of κa.

If ρ is the charge density at the surface of the particle we have $e = 4\pi a^2 \cdot \rho$, and therefore

$$\zeta = \frac{4\pi\rho}{D}\cdot\frac{a}{1+\kappa a},$$

and for plane surfaces ($a \to \infty$) this gives *

$$\zeta = \frac{4\pi\rho}{D\kappa}.$$

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* It is not legitimate to apply this to a plane surface, since it has already been assumed that κa is small; but the relation is nevertheless the same as that obtained below.

Plane surfaces. The appropriate solution is

$$\psi = Ae^{-\kappa x},$$

where $x =$ distance from the surface. In order to evaluate the constant A, we notice that the charge density on the surface is

$$e = \int_a^\infty \rho \, . \, dx,$$

where ρ is the charge density (for unit volume) in the ionic atmosphere at a distance x from the surface, and a is the shortest distance of approach of the ions to the surface. Writing

$$\rho = -\frac{D}{4\pi}\nabla^2\psi = \frac{D}{4\pi} \, . \, \kappa^2\psi,$$

we have

$$e = \int_a^\infty \frac{D}{4\pi} \, . \, \kappa^2\psi \, dx = \int_a^\infty \frac{D}{4\pi} \, . \, \kappa^2 A e^{-\kappa x} \, . \, dx,$$

or

$$e = \frac{D\kappa A}{4\pi} e^{-\kappa a}.$$

Introducing this value of A we have

$$\psi = \frac{4\pi e}{D\kappa} \, . \, e^{\kappa(a-x)},$$

or identifying ψ with ζ for $x = a$

$$\zeta = \frac{4\pi e}{D\kappa}.$$

It is to be noted that $1/\kappa$ appears in the role of δ, the thickness of the double layer.

The effect of the approximations made in the Debye-Hückel theory have been discussed by several authors.[68] G. S. Hartley [69] has pointed out that with uni-univalent electrolytes the value of $z_i \epsilon \psi / kT$ does not become less than 1 until $r = 7{\cdot}08 \times 10^{-8}$ cm.^{2} The quantitative success of the theory in accounting for the behaviour of salt solutions is due to the fact that the contribution of the regions close to an ion, where the approximation fails, to the charge of the atmosphere is small, owing to their small volume.

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[68] E.g. Gronwall, La Mer and Svandved, *Physikal Z.*, **29**, 558, 1928 ; *J. Physical Chem.*, **35**, 2245, 1931 ; S. Levine, *Proc. Roy. Soc.*, **146**, 597, 1934 ; Müller, *Physikal Z.*, **28**, 324, 1937.

[69] *Trans. Faraday Soc.*, **31**, 31, 1935.

Another form of the equation, which avoids the approximations of the Debye-Hückel theory, has been given by H. Müller.[70] If the solution contains only two kinds of ions (positive and negative) we have $n_+z_+ = -n_-z_-$. For a plane surface the primary equation becomes

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi}{D} . \sigma = -\frac{4\pi}{D} . n_+ z_+\epsilon \left(e^{-z_+\psi/kT\epsilon} - e^{-z_-\epsilon\psi/kT}\right).$$

The surface charge is given by

$$e = -\int_0^\infty \rho . dx,$$

and the boundary conditions are

$$\psi = 0, \left(\frac{\partial\psi}{\partial x}\right) = 0, \quad \text{when } x = \infty;$$

$$\left(\frac{\partial\psi}{\partial x}\right) = \frac{4\pi e}{D}, \quad \text{when } x = 0.$$

The integration of this equation [71] gives

$$e = \sqrt{\frac{D . RT . c}{2\pi \times 1000}} \sqrt{\frac{1}{z_+}\left(e^{-z_+\epsilon\zeta/kT} - 1\right) + \frac{1}{z_-}\left(e^{-z_-\epsilon\zeta/kT} - 1\right)}, \quad (2)$$

where $c =$ salt concentration in mols./litre and ζ is the value of ψ for $x = 0$. For two ions of equal valency, i.e. $z_+ = z_- = z$, this may be simplified to

$$e = 2\sqrt{\frac{DRTe}{2\pi \times 1000}} \sinh z\left(\frac{\epsilon\zeta}{2kT}\right)$$

$$= 2\alpha\sqrt{c} \sinh\left(\frac{z\zeta}{2\beta}\right),$$

where $\beta = 0{\cdot}025$ volts, and $\alpha = 17{,}650$ at 18° C., for aqueous solutions.

Electrokinetic Potential and the Coagulation of Colloids. The coagulation of lyophobic colloidal sols was first studied quantitatively by Schulze,[72] Linder and Picton [73] and Hardy,[74] who found

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[70] *Kolloidchem. Beihefte*, **26**, 257, 1928; Abramson and Müller, *Bull. Am. Physical Soc.*, **7**, 11, 1932; cf. Verwey, *Chem. Revs.*, *Cold Spring Harbour Symp.*, **1**, 1933.

[71] Cf. a similar calculation by R. Audubert, *J. Chem. Phys.*, **30**, 89, 1933.

[72] *J. prakt. Chem.*, **25**, 431, 1882; **27**, 320, 1883.

[73] *J. Chem. Soc.*, **61**, 148, 1892; **67**, 62, 1895; **71**, 568, 1897.

[74] *Z. physikal. Chem.*, **33**, 385, 1900.

that ions of opposite sign to the charge of the colloidal particles were the effective precipitating agents, and the ionic concentration required for precipitation diminished rapidly as the valency of the ion increased. As a rule the precipitation concentrations for negatively charged sols are of the order of 25-100 milli-equivalents per litre for univalent cations, 1-10 for bivalent, and 0·1 to 1 for trivalent cations. The values for different cations of the same valency do not differ very much, and inorganic anions have only a small influence.

These facts gave rise to the general idea that the coagulation was prevented by the repulsion between the charges carried by the particles, and the effect of the electrolyte was to neutralise the charge by the adsorption of ions of opposite sign. Freundlich[75] accounted for the relative precipitation concentrations of ions of different valencies by supposing that coagulation occurred when the charge was reduced to a certain value. The quantities of uni-, bi- and trivalent ions which must be adsorbed are therefore in the ratios $1 : \frac{1}{2} : \frac{1}{3}$. The relative concentrations of the ions required to produce these adsorptions are now found, assuming that they all have similar adsorption isotherms, and this gives an explanation of the ratios observed. Anomalies can also be accounted for by the assumption of abnormal adsorbability.

However, this view has been abandoned, because it was found[76] that the amounts of different cations carried down in the precipitation of a negative colloid are not equivalent. We have seen that changes in the concentration of the electrolyte may produce changes in the ζ-potential without any alteration in the charge. It has therefore been suggested that coagulation occurs when the ζ-potential is reduced to a certain critical value.[77] Müller[78] applied his theory (p. 111) to calculate the concentration of electrolytes of various types which is necessary to lower the potential of a negative surface to $\zeta = -50$ millivolts, on the assumption that the charge

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[75] *Kolloid Z.*, **1**, 321, 1907; *Z. physikal. Chem.*, **73**, 385, 1910.

[76] Powis, *ibid.*, **89**, 91, 189, 1915; Kruyt and Briggs, *Proc. Akad. Sci. Amsterdam*, **32**, 384, 1929.

[77] Freundlich, Joachimsthal and Ettisch, *Z. physikal. Chem.*, **141**, 249, 1929; Kruyt, *Rec. trav. chim.*, **39**, 618, 1920.

[78] *Loc. cit.*, ref. 70.

on the surface is constant. The following table gives his figures (n_+, n_- = valency of +, − ions):—

n_-	$n_+ = 1$	$n_+ = 2$	$n_+ = 3$	$n_+ = 4$
1	50	10·7	2·06	0·38
2	47	10·5	2·06	0·38
3	46	10·4	2·06	0·38
4	46	10·4	2·06	0·38

The relative concentrations required for 1-, 2-, 3- and 4-valent cations are in the ratios 125 : 25 : 5 : 1, a series somewhat similar to that observed. It must be remembered that in practice a variation of the charge of the particle with the electrolyte concentration would probably also occur, at least in small electrolyte concentrations.

The cause of the comparative stability of lyophobic sols is still uncertain. Earlier ideas concentrated on the lowering of surface energy which would be produced by a double layer at the surface of particles.[79] Under suitable conditions this might be large enough to make the surface energy zero or negative. On this basis a sol might be thermodynamically stable, each value of ζ probably having a preferred particle size. Kruyt, however, denies that lyophobic sols are ever thermodynamically stable, and maintains that there is no degree of dispersion which is more stable than others. In actual sols a coarsening always occurs in time, although sometimes very slowly.

There is no doubt, of course, that the electric fields round the particles prevent their coalescence, or perhaps greatly diminish the chance of a collision between two particles resulting in their coalescence. A. March, however,[80] found that the observed electrokinetic potentials were at least ten times too small to produce a sufficient repulsion between particles, and concluded that stability was due to a protecting skin of solvent round each particle. Müller suggests[81] that such a film is produced by the electric field of the double layer. It is well known that the electric field of an ion produces a considerable hydrostatic pressure close to its surface,

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[79] Donnan, *Z. physikal. Chem.*, **46**, 197, 1903; A. March, *Ann. d. Physik*, **84**, 605, 1927; *Kolloid Z.*, **45**, 97, 1928; W. C. M. Lewis, *Trans. Faraday Soc.*, **28**, 597, 1932; O. K. Rice, *J. Physical Chem.*, **30**, 189, 1348, 1660, 1926.

[80] *Loc. cit.*

[81] *J. Physical Chem.*, **39**, 743, 1935.

which gives rise to a compression or *electrostriction* of the solvent.[82] In the same way Müller calculated that at a plane surface at which $\zeta = 0{\cdot}1$ volts, in a N/1000 solution of an electrolyte, the hydrostatic pressure is 18 atmospheres. At a curved surface the electric field changes more rapidly with distance and considerably greater pressures may be established.

The energy of repulsion between the electric fields of two particles is given by Hamaker [83] as

$$P_e = \frac{e^2}{DR} \cdot \frac{e^{-\kappa R}}{\kappa a + 1},$$

where R is the distance between their centres.[84] Combining this with expressions for the van der Waals' attractions and the short-range repulsive forces between large spheres,[85] curves are obtained which vary in shape according to the magnitudes of e and κ, and permit of an interpretation of the circumstances under which coagulation, peptisation and thixotropy occur.

The Charge of Particles. It is obvious that the mobility of a particle (and its ζ-potential) may be affected in two ways by the concentration of the electrolytes in the solution. (1) The surface charge may be a function of the electrolyte concentration (particularly if the charge is produced by the adsorption of ions on the surface), (2) for a constant charge the mobility will vary with the strength of the ionic atmosphere as previously described. The nature of the variation of mobility therefore depends on the type of surface.

(1) *Inert surfaces.* Fig. 12 shows some measurements of the ζ-potential made by Bull and Gortner [86] at the cellulose-water interface in the presence of various electrolytes. The charge in water itself is negative, and a uni-univalent electrolyte causes at first an increase in ζ, followed by a decrease. Cations of higher valency may cause a decrease from the start and aluminium and thorium

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[82] Cf. T. J. Webb, *J. Amer. Chem. Soc.*, **48**, 2589, 1926; Zwicky, *Physik. Z.*, **27**, 271, 1926.

[83] *Rec. trav. chim.*, **55**, 1015, 1936; **56**, 3, 1937.

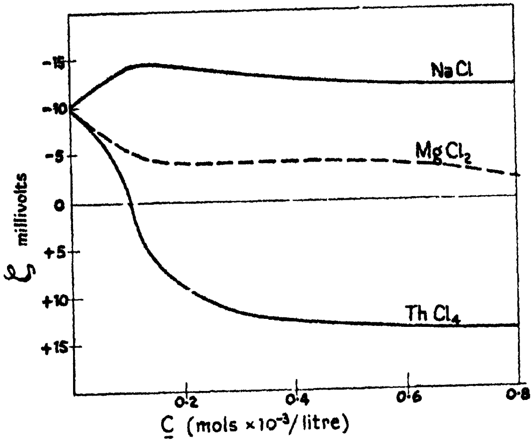
[84] See S. Levine, *Proc. Roy. Soc.*, **146**, 597, 1934, for a solution of the Debye-Hückel equation in the region between two spheres.

[85] Discussed further in *Rec. trav. chim.*, **57**, 61, 1938.

[86] *J. Physical Chem.*, **35**, 309, 1931.

salts cause a reversal of the charge. A similar behaviour has been observed at oil,[87] glass and other surfaces.

Abramson and Müller [88] used Müller's expression (2, p. 111) to calculate the charge density at the surface in the case of salts which do not reverse the sign of the charge, and curves of the type shown in Fig. 13 were obtained not only with the data for glass surfaces, but also for quartz, paraffin oil, charcoal and cellulose in solutions of alkali and alkaline earth metals. A correction is made for the initial charge of the surface in water. The $\rho - c$ curves so obtained are similar in form to the Langmuir adsorption isotherm, the charge density tending to a limiting value ρ_M at the higher concentration, and may be represented by



V. 12.—$\zeta - c$ curves for cellulose-water interface. The $MgCl_2$ curve ha been moved vertically downwards about 5 milli-volts, to correspond with the others, since this series began at a higher water value. (Bull and Gortner.)

$$\frac{\rho}{\rho_M - \rho} = Bc,$$

or

$$\rho = \rho_M \, Bc/(1 + Bc).$$

In the case of glass, the maximum value of ρ was 9000 e.s.u., corresponding to 2×10^{13} ions/cm.^{2}, a number which is sufficient to cover only about 1 per cent. of the surface.

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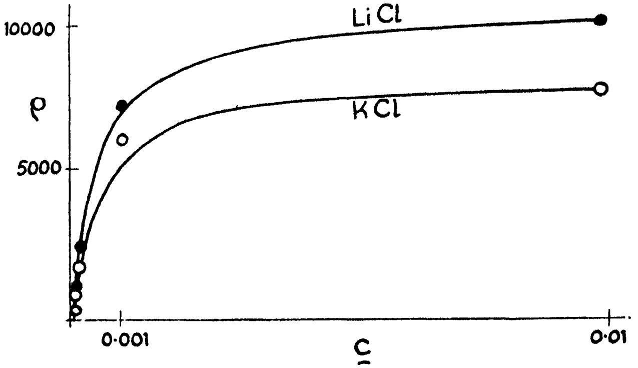
[87] *Z. physikal. Chem.*, **89**, 91, 1915.

[88] *Loc. cit.*, ref. 70; Abramson, *J. Physical Chem.*, **39**, 749, 1935.

Abramson[89] has also used this method to determine the variation of the charge on bacteria with salt concentration.

TABLE II. CHANGES OF CHARGE DENSITY OF TYPHOID BACILLI WITH CONCENTRATION OF NaCl

NaCl Conc. M.	$v\mu$/sec[90].	ζ-Volts.	ρ e.s.u.
0·001	3·9	0·053	1420
0·004	3·6	0·049	2590
0·01	3·2	0·043	3390
0·02	2·4	0·033	3600
0·04	1·6	0·022	3150



V. 13.—Charge on a glass surface. (Abramson.)

It is obvious that the descending part of the $\zeta - e$ curves in these cases does not mean a decrease of the charge density with concentration, but frequently an increase.

Janssen[91] also used Gouy's theory (p. 75) to calculate from ζ the charge of the diffuse layer. Bull and Gortner[92] used a radically different method involving simultaneous measurements of the streaming potential and of the surface conductance. They found with solutions of KCl and $CaCl_2$ at a cellulose surface that in the concentration region between 10^{-4} and 10^{-3}, the decrease of the ζ-potential is accompanied by an increase of charge.

(2) *Proteins.* Abramson[93] used the Debye-Hückel equation

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[89] *J. Bact.*, **27**, 89, 1934.

[90] Data of Mudd and Joffe, *Cold Spring Harbour Symp.*, 1933, p. 71.

[91] *Sow. Phys.*, **4**, 322, 1933; *Dissert.*, Utrecht, 1933.

[92] *J. Physical Chem.*, **35**, 309, 1931.

[93] *J. Gen. Physiol.*, **15**, 375, 1932; **16**, 593, 1933.

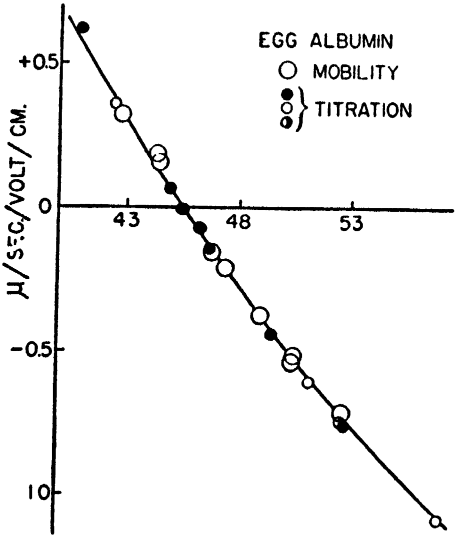
(1, p. 109) to determine the charge of colloidal particles from the mobility. For particles of this size we have

$$v = \frac{1}{6\pi}\frac{\zeta D}{\eta} \quad \text{and} \quad \zeta = \frac{e}{Dr}\left(\frac{1}{1+\kappa r}\right)$$

so that we can obtain the charge e on the particle by the expression

$$e = 6\pi\eta v \, . \, \zeta r(1 + \kappa r).$$

For a given ionic strength the charge is evidently directly proportional to the mobility and is therefore determined by the p_H of the solution (see Fig. 7). Abramson compared the charge so determined with the number of hydrogen or hydroxyl ions bound, as determined by titration. If h is the number of equivalents of H^+ bound per gram of protein (which may be positive or negative), and M the molecular weight of the protein, we have $e = hM\epsilon$, where ϵ is the electronic charge. Quite good agreement between the two methods was found, using molecular weights from other sources (Fig. 14). It was concluded that the mobility of the same protein in solutions of different p_H's was proportional to the number of H^+ or OH^- ions bound.[94] The two equations may also be used to determine the radius r of the protein particle. The results with three proteins are shown in Table III, where the calculated r is compared with that derived from the molecular volumes ($r_{M \cdot V \cdot}$).



V. 14.—Comparison of titration data and mobility for dissolved egg albumin at 25°. (Moyer and Abels.)

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[94] This applies only to solutions containing simple electrolytes, which are not specifically absorbed. Polyvalent ions sometimes influence the charge of proteins, e.g. Loeb, *J. Gen. Physiol.*, 5, 395, 1923.

TABLE III. RADII IN $m\mu$ OF PROTEIN MOLECULES FROM TITRATION AND MOBILITY DATA AT 20° C.

	M	r	$r_{M.V.}$	V_e/V_t
Egg albumin	22,200	3·26	2·32	0·59
Serum albumin	67,000	3·91	2·70	0·46
Pseudoalbumin	165,000	5·22	3·66	0·48

The last column is the ratio of the experimental mobility to that calculated for a sphere having a radius corresponding to the molecular volume. The discrepancy is ascribed at least partly to the non-spherical shape of the molecules.

Moyer and Abels [95] obtained better agreement using the empirical expression

$$v = \zeta Dr(2 + \kappa r), \text{ or, in general,}$$
$$v = \zeta Dr(a + \kappa r).$$

Moyer and Abramson [96] suggest the following method of determining the molecular weight of proteins. The ratio of the mobilities in two solutions of the same p_H, but differing ionic strengths,[97] is

$$\frac{v_1}{v_2} = \frac{\kappa_2 r + a}{\kappa_1 r + a},$$

from which r can be found.[98] The molecular weight is then given by

$$M = \frac{6\pi\eta v_1}{h\epsilon} \cdot (\kappa_1 r + 2).$$

A further elaboration of these equations is used [99] to determine the ratio of length to breadth of the protein molecules.

Heteropolar Surfaces.* In the case of heteropolar solids, certain electrokinetic effects are observed which are specifically determined by the chemical nature of the solid. These effects arise through the adsorption, at the surface of the solid, of ions common to, or compatible with, the crystal lattice of the solid substance. Thus when the solid is brought into contact with a solution of an electrolyte, the surface is positive or negative, depending upon the nature of the ions present in the solution. For instance, small particles of silver iodide move towards the cathode in a dilute solution of silver

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[95] *J. Biol. Chem.*, **121**, 331, 1937.

[96] *Ibid.*, **123**, 391, 1938.

[97] For the effect of salt concentration on the iso-electric p_H, see Smith, *ibid.*, **108**, 187, 1935; **113**, 473, 1936.

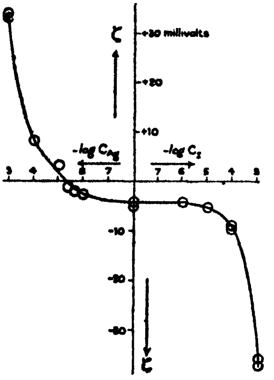
[98] More elaborate equations are given in *Chem. Revs.*, **24**, 362, 1939.

[99] *Loc. cit.*, ref. 98.

* Contributed by Dr. T. R. Bolam.

nitrate, but towards the anode in potassium iodide, silver ions being adsorbed on the crystal surface in the one case, and iodide ions in the other.[100]

Evidence for the existence of the adsorption of a common ion by salt crystals has come partly from analytical investigations [101] and partly from the study of the properties of colloidal suspensions of insoluble salts.[102] In general, a slight excess of a common ion has a stabilising influence upon such suspensions, and the sign of the surface charge is always that of the common ion present in excess. Adsorption of a common ion is to be expected as the result of the operation of the forces responsible for the growth of the crystal.[103] The ions constituting the surface layer of the crystal lattice are in an unsaturated condition as compared with those in the interior of the crystal, and strive to satisfy their valence forces by attaching suitable ions of opposite charge. Since the adsorption forces are identical in nature with the lattice forces, it follows that ions other than those common to the lattice will be adsorbed, provided they are capable of entering the lattice. For example, colloidal suspensions of silver iodide are stabilised by chloride, bromide, cyanide, and thiocyanate, but not by nitrate, sulphate, carbonate, phosphate, or bichromate ions.[104]



V. 15.—ζ-potential of silver iodide diaphragms in potassium iodide and silver nitrate solutions. (Lange and Crane.)

With regard to the quantitative aspects of the relation between the adsorption and the electrokinetic behaviour, the available data have been derived mainly from studies of the silver halides. In Fig. 15 are shown the values of ζ calculated by Lange and Crane [105]

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[100] Lottermoser and May, *Kolloid Z.*, **58**, 176, 1932.

[101] Kellermann and Lange, *ibid.*, **81**, 88, 1937 (a review).

[102] Mukherjee, *Trans. Faraday Soc.*, **16A**, 103, 1920-21.

[103] Fajans and Frankenburger, *Z. physikal. Chem.*, **105**, 255, 1923; Fajans and Erdey-Grúz, *ibid.*, **158**, 97, 1931.

[104] Kruyt and van der Willigen, *ibid.*, **139**, 53, 1928; Kruyt and Cysouw, *ibid.*, **172**, 49, 56, 1935; Basinki, *Kolloid Beihefte*, **36**, 257, 1932.

[105] Lange and Crane, *Z. physikal. Chem.*, **141**, 225, 1929.

from their careful measurements of the rate of endosmotic flow of solutions of silver nitrate and potassium iodide through diaphragms of precipitated silver iodide. The diaphragm possessed a small negative charge when in contact with a saturated solution of the salt ($c_{Ag^+} = c_{I^-} = ca.\ 1{\cdot}6 \,.\, 10^{-8}$ N); and a concentration of silver ion of about $4 \,.\, 10^{-6}$ N was required to attain the isoelectric point ($\zeta = 0$). Earlier and less exact determinations, by Kruyt and van der Willigen,[106] of the influence of dilution on the cataphoretic speed of positively charged colloidal suspensions of silver iodide had indicated that the isoelectric point was reached when the silver ion concentration was reduced to 10^{-5}-10^{-6} N. Verwey and Kruyt[107] measured the adsorption of iodide ions by the particles in dialysed (negative) colloidal suspensions of silver iodide, and found that up to $c = 10^{-4}$ N their data fitted the equation

$$\frac{dx}{d \log c} = \text{constant,*}$$

where $x =$ gram-ions adsorbed by one gram of silver iodide, and $c =$ final concentration of potassium iodide. By an extrapolation based on this equation, it was estimated that there was no excess of silver or iodide ions on the crystal surface when in equilibrium with a solution of the order 10^{-10} N with respect to iodide ion, i.e. of the order 10^{-6} N with respect to silver ion. Kolthoff and Ligane[108] have more recently determined the adsorption of silver and iodide ions on freshly precipitated silver iodide by two independent methods. From electrometric measurements of the desorption which occurred on digesting the precipitate at 90°-95°, it was found that there was no adsorption of either ion when the silver ion was $0{\cdot}89 \,.\, 10^{-6}$ N. On the other hand, the value $1{\cdot}41 \,.\, 10^{-6}$ N was obtained by electrometric titration of silver nitrate with potassium iodide and comparison of the experimental curve with the theoretical curve based on the assumption that the precipitate possessed no adsorptive pro-

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[106] Kruyt and van der Willigen, *Z. physikal. Chem.*, **139**, 59, 1928. See, however, Gorochowsky, *J. Physical Chem.*, **39**, 465, 1935; and Kruyt and van Gils, *Kolloid Z.*, **78**, 32, 1937.

[107] Kruyt and Verwey, *Z. physikal. Chem.*, **167A**, 149, 1933.

* This equation has been found to hold in a number of cases (see Kellermann and Lange, *loc. cit.*).

[108] Kolthoff and Ligane, *J. Amer. Chem. Soc.*, **58**, 1531, 1936.

perties. Taken together, the foregoing results suggest that the negative charge on the surface of small silver iodide crystals in contact with saturated silver iodide solution is due entirely to the adsorption of iodide ions,* these being more readily adsorbed than are silver ions. The tendency of the iodide ion to go from the aqueous phase to the silver iodide phase is so much greater than that of the silver ion that a 10,000 fold excess of the latter is required to reach the point at which they counterbalance each other. It is to be expected that in general the concentrations of the lattice ions will not be equivalent at the isoelectric point.

The work of Kruyt and others has shown that the electrokinetic behaviour of insoluble salts is more complicated than originally appeared to be the case. Kruyt and Ruyssen [109] have studied the streaming potentials produced by diaphragms prepared from different samples of barium sulphate. Precipitated barium sulphate, of particle size about 10 μ, was found to be slightly negative in pure water, more negative with solutions of sodium sulphate, and positive with barium chloride, the charge increasing, in both cases, with increasing concentration of electrolyte. Similar specific effects of sulphate and barium ions were observed by Gyemant [110] and Michaelis and Dokan.[111] According to Kruyt and Ruyssen, however, a diaphragm of material (particle size about 150 μ) obtained by pulverising crystals of natural barytes behaves in a very different fashion. The negative charge is not reversed by barium chloride, and the ζ-concentration curve for this salt closely resembles that obtained with an "inert" surface of paraffin wax,[112] as shown in Fig. 16. In an investigation of streaming potentials with silver bromide as solid phase, Julien [113] found that the negative charge on a capillary of the fused insoluble salt was not reversed by silver

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* Lange and Crane (*loc. cit.*) observed that the rate of flow of a saturated solution of silver iodide did not change when the solution was freed from carbon dioxide. This supports the view that the negative charge on the diaphragms was not due to the adsorption of HCO_3^- or OH^--ions.

[109] Kruyt and Ruyssen, *Proc. Akad. Wetenschappen Amsterdam*, **37**, 624, 1934.

[110] Gyemant, *Z. physikal. Chem.*, **103**, 260, 1922.

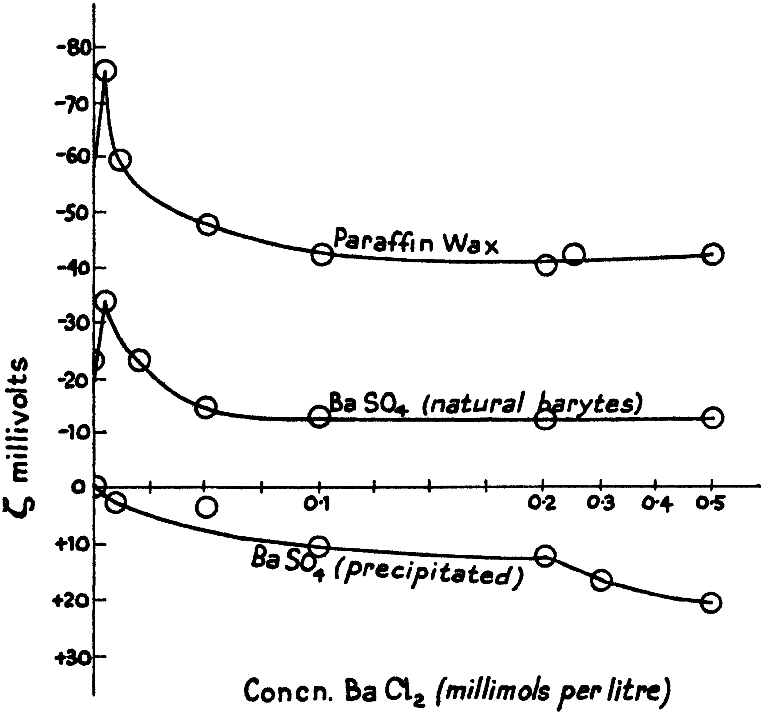
[111] Michaelis and Dokan, *Kolloid Z.*, **37**, 67, 1925.

[112] Kruyt and Ruyssen, *Proc. Akad. Wetenschappen Amsterdam*, **37**, 498, 1934.

[113] Julien, Thesis (1933), Utrecht; Kruyt, *Bull. Soc. Chim. Belgique*, **43**, 571, 1934.

nitrate. On the other hand, reversal was obtained when the capillary was coated with a layer of colloidal silver bromide.

Examination by means of X-rays showed that the effects observed by Kruyt and Russyen were not due to differences in the crystal structure of the different samples of barium sulphate. Kruyt has therefore put forward the following interpretation. The adsorption of a common ion is probably restricted to certain "active" areas of the crystal surface, namely, the edges and corners characteristic of the crystal, and also regions where the lattice is imperfectly formed. It is also reasonable to suppose that large crystals of natural barytes are more perfect than the smaller ones obtained by precipitation. Hence the retention, by the larger crystals, of a negative charge in the presence of barium chloride may be attributed to their possessing such a small active surface that the adsorption



V. 16.—ζ-potential of natural and precipitated barium sulphate. (Kruyt.)

of barium ions is insufficient to make the surface positive. This interpretation is in line with the results of some experiments by Verwey [114] on the "ageing" of colloidal silver iodide. Adsorption of silver or iodide ions on the surface of freshly formed particles was found to be followed by desorption, which proceeded the more rapidly the higher the temperature. The desorption was not accompanied by change in the crystal structure, and the degree of coarsening of the particles under the given conditions was quite inadequate to account quantitatively for the desorption on the basis of decrease in the *total* area of the crystal surfaces. Julien (*loc. cit.*) has also established that when insoluble silver salts are allowed to age in contact with dilute silver nitrate, they tend to lose their initial positive charge and become negative.

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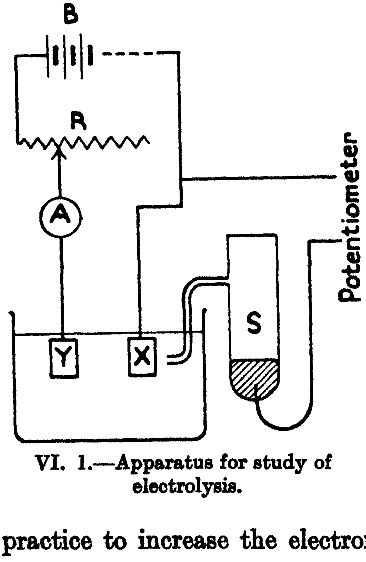
[114] Kruyt and Verwey, *Z. physikal. Chem.*, **167**A, 1933; see also Kolthoff, *J. Physical Chem.*, **40**, 1027, 1936.

CHAPTER VI

ELECTRODE REACTIONS AND OVERVOLTAGE

WE now pass to the consideration of the phenomena which occur at electrodes during the passage of a current. The potential difference at an electrode when a current is passing may be observed by an arrangement such as that shown in Fig. 1. The current from the battery B passes *via* the resistance R and ammeter A between the electrodes X and Y. The potential of X, with reference to the standard electrode S, is measured by means of a potentiometer. The electrode vessel S is provided with a capillary tip, which is brought very close to the electrode under observation, so that no appreciable part of the fall of potential, which occurs in the solution during the passage of the current, is included in the measured electromotive force of the cell SX. In earlier years it was usually the practice to increase the electromotive force applied by the battery by means of a sliding potentiometer until electrolysis began. The total electromotive force required to initiate steady electrolysis was called the *decomposition voltage* of the solution; and the potential of an electrode when electrolysis begins, the *decomposition potential* at that electrode. Recently it has usually been found more convenient to pass *constant currents* between the electrodes, which can be done by using a battery of fairly high voltage (when changes



VI. 1.—Apparatus for study of electrolysis.

in the resistance of the cell will be of small importance), together with a suitable high resistance. The potential of the electrode X can then be observed as a function of the current passing between the electrodes.

In some cases the potential of an electrode during the passage of a current in either direction remains near to its value when no current is passing. For example, if a metal in a solution containing its ions is made the anode or cathode, so that the metal dissolves or is deposited, the potential usually remains quite near the reversible potential of the electrode, if the current is not too large and if the electrolysis is not continued so long that significant changes of concentration take place. Overbeck also showed that when metals are cathodically deposited[1] on platinum electrodes, the electrode potential approximates to the reversible potential of the metal as soon as a few atomic layers of the latter have been deposited.

In other cases, however, there is a considerable difference between the potential of the electrode when electrolysis is taking place and the corresponding reversible potential. Thus, when hydrogen is being liberated at metallic cathodes, the cathode potential is usually considerably more negative than the reversible hydrogen potential of the solution. Again, the liberation of oxygen at the anode takes place at an appreciable rate only when the anode potential is considerably more positive than the (calculated) reversible potential of oxygen in the solution. When the potential of an electrode through which a current is passing differs from its value at open circuit, the electrode is said to be *polarised*. The difference between the potential of the electrode at which the electrolysis takes place and the reversible potential of the same process in the given solution is called the *overvoltage* or *overpotential*.

Hydrogen and Oxygen Overvoltages. The method of the earlier experimenters was gradually to increase the applied electromotive force, observing the cathode potential at which the steady formation of hydrogen first occurs, as detected either by the current passing or by the appearance of a visible bubble of gas. The values determined in this way varied a good deal according to the method

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[1] *Ann. Physik*, **31**, 337, 1887; cf. Tödt, *Z. Elektrochem.*, **34**, 591, 1928; Nichols, *J. Amer. Chem. Soc.*, **57**, 267, 1935.

used and the state of the electrode. Some representative values are given below :—

TABLE I. HYDROGEN OVERVOLTAGES

	(2)	(3)	(4)
Platinised Pt	0·0	0·05	—
Smooth Pt	—	0·09	0·0
Iron	0·03	0·08	0·17
Silver	0·07	0·15	0·10
Nickel	0·14	0·21	0·14
Copper	0·19	0·23	0·13
Tin	—	0·53	0·40
Lead	0·36	0·64	0·40
Mercury	0·44	0·78	0·57

In 1905 Tafel,[5] experimenting with solutions which had been freed from oxygen and in which the anode and the cathode were so arranged that the oxygen liberated at the former could not reach the cathode, made the important observation that the overvoltage varies with the current, and gave the relation

$$i = k\,e^{-bV}, \qquad . \quad . \quad . \quad . \quad (1)$$

where i is the current and V the potential of the electrode and k and b are constants. Tafel noticed that the constant b was approximately half the factor $\mathbf{F}/RT$.* The variation of the overvoltage with the current density can thus be expressed as

$$\frac{dV}{d\log_{10} i} = -\frac{2{\cdot}303}{b} = ca\,.\,\frac{2 \times 2{\cdot}303\,RT}{\mathbf{F}}.$$

The value of this expression at 18° is about 0·116 volts, i.e. the overvoltage should increase by 0·116 volts for each 10-fold increase of current density. This relation has been confirmed with a number of metals by Harkins and Adams,[6] Lewis and Jackson[7] and by Bowden and Rideal.[8] The observed values of $dV/d\log_{10}i$ show

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[2] Coehn and Dannenberg, *Z. physikal. Chem.*, **38**, 601, 1901; from current-voltage curves.

[3] Caspari, *ibid.*, **30**, 89, 1899; first gas bubbles.

[4] Thiel *et al.*, *Z. anorg. Chem.*, **83**, 329, 1913; **132**, 15, 1923; gas bubbles.

[5] *Z. physikal. Chem.*, **50**, 641, 1905.

* The factor 2·303 $RT/\mathbf{F}$, which occurs in many electrochemical calculations has the value 0·058 volts at 18° C.

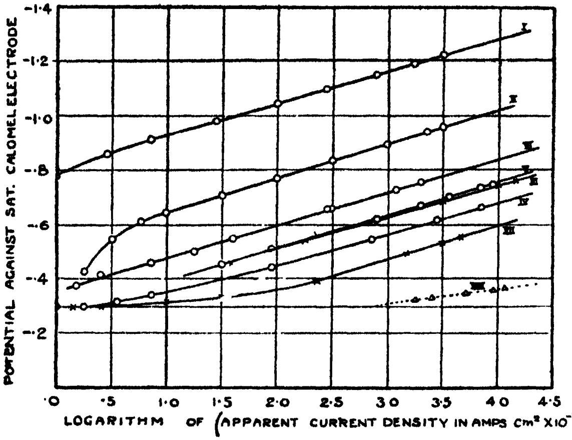
[6] *J. Physical Chem.*, **29**, 205, 1925.

[7] *Z. physikal. Chem.*, **56**, 207, 1906.

[8] *Proc. Roy. Soc.*, **120A**, 59, 1928.

some variation, but are usually between 0·10 and 0·12 volts. A greater range of values was given by Baars.[9]

The relation, however, does not hold at electrodes, such as platinised and " active " platinum, having a very low overvoltage,[10] and in some cases at very small current densities and usually at high current densities there are also deviations. Some examples of V plotted against $\log_{10} i$, taken from Bowden and Rideal's work, are shown in Fig. 2. Tafel noticed that b decreased with rise of temperature, as it should if it is identified with $F/2RT$. In the more exact experiments of Bowden it was shown that b varies inversely with T as this expression requires.[11]



VI. 2.—Curve I, mercury ; curve II, platinised mercury, 1/100 covered ; curve III, platinised mercury, thin film of Pt ; curve IV, etched silver, new ; curve V, etched silver, old ; curve VI, polished silver ; curve VII, bright platinum ; curve VIII, spongy platinum. (In curve VIII the current density is expressed in amps. × 10^{-6} in order to bring it on the figure. It should be displaced two divisions to the right.) (Bowden and Rideal, *Proc. Roy. Soc.*, vol. 120, 1928.)

The characteristics of the overvoltage curves of various metals are shown in Table II, which is taken from a summary by Bowden and Agar.[12]

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[9] *Ber. Ges. Förd Naturwiss. Marburg*, 63, 213, 1928.

[10] Cf. Knorr and Schwartz, *Z. physikal. Chem.*, 176, 161, 1936 ; *Z. Elektrochem.*, 40, 38, 1934 ; Wirtz, *Z. physikal. Chem.*, 36B, 435, 1937.

[11] Bowden, *Proc. Roy. Soc.*, 126A, 107, 1929.

[12] *Ann. Rep. Chem. Soc.*, 35, 90, 1938.

Table II. Overvoltage of Hydrogen on Different Metals

Electrode.	Solution.	α.	i_0.	W.	Remarks.	Reference.
Mercury	$0{\cdot}2N$, H_2SO_4	0·52	6×10^{-12}	18·0		11, 72
	$0{\cdot}1N$, HCl	0·49	$1{\cdot}7 \times 10^{-12}$	—		22
	$0{\cdot}2N$, NaOH	0·24	$6{\cdot}9 \times 10^{-9}$	8·65		9, 72
Gallium	$0{\cdot}2N$, H_2SO_4	0·5	$1{\cdot}6 \times 10^{-7}$	15·2	87°	13
Wood's alloy	,,	0·4	1×10^{-8}	16·4	87°	13
Polished Ag	,,	0·5	$3{\cdot}2 \times 10^{-8}$	—	25°	8
Nickel	,,	0·52	6×10^{-7}	—	25° (dependent on state of surface)	8
Bright Pt	,,	0·75-0·3	$1{\cdot}4\text{-}6 \times 10^{-6}$	9·5-11·5	α (decreases with time)	11, 15
Palladium	,,	0·5	2×10^{-5}	9	{Electrode flamed}	12
	$0{\cdot}2N$, NaOH	0·4-0·5	1×10^{-5}	10		16
Lead	$2N$, H_2SO_4	0·3	—	—	—	17
Tantalum	$2N$, H_2SO_4	0·28	—	—	—	14
Copper	—	0·8-0·5	10^{-5} to 10^{-6}	—	(Wirtz)	10
Bismuth	$2N$, H_2SO_4	0·5-0·4	5×10^{-12} to 8×10^{-11}	—	variable	14
Cobalt	,,	0·5	10^{-8}	—	,,	14
Antimony	,,	0·2 (variable)	2×10^{-6}	—	,,	14

Representing the *overvoltage* by V_h, the current as may be expressed by

$$i = i_0 \, . \, e^{+\alpha F V_h / RT}, \qquad . \quad . \quad . \quad . \quad . \quad (2)$$

or,

$$i = \text{const.} \times e^{-(W - \alpha F V_h)/RT}, \qquad . \quad . \quad . \quad (3)$$

where i_0 is the extrapolated value of the current at zero overvoltage, i.e. at the reversible hydrogen potential, and α is Tafel's factor $\alpha = b \, . \, \frac{RT}{F}$. In (3), i_0 is represented as const. $\times \, e^{-W/RT}$, where W is the activation energy for $V_h = 0$.

The influence of the p_H of the solution on the overvoltage has been the subject of considerable differences of opinion,[18] which

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[13] Bowden and O'Connor, *Ann. Rep. Chem Soc.*, **128**A, 318, 1930.

[14] Quoted by Bowden and Agar, ref. 12, p. 99.

[15] Volmer and Wick, *Z. physikal. Chem.*, **172**, 429, 1935.

[16] Knorr and Schwarz, *Z. Elektrochem.*, **40**, 38, 1934; *Z. physikal. Chem.*, **176**, 161, 1937.

[17] Erdey-Grúz and Wick, *ibid.*, **162**, 53, 1932.

[18] Glasstone, *J. Chem. Soc.*, **125**, 2414, 2646, 1924; Lloyd, *Trans. Faraday Soc.*, **25**, 525, 1929; Heyrovski, Heyrasymenko, *Rec. trav. chim.*, **44**, 499, 503, 1925 (dropping electrode); *Z. physikal. Chem.*, **149**A, 123, 1930; *Z. Elektrochem.*, **34**, 129, 1928.

appear, however, to be due mainly to differences of the conditions under which the measurements were made. Bowden [19] determined the whole log $i - \Delta V$ curve in solutions of various p_H's and found very little difference except at high current densities and low hydrogen-ion concentrations, where curves having approximately twice the normal slope were obtained. These changes are probably due to (1) changes of concentration of hydrogen ions near the electrode produced by the electrolysis,[20] (2) the inclusion under these conditions in the measured potential of an appreciable fall of potential in the solution. Kabanow [21] found that when a correction was made for the latter, linear log $i - V$ curves having the normal slope (0·12-0·14) were obtained with current densities extending from 10^{-3} to 10^1 or 10^2 amps./cm.^{2} Lewina and Sarinsky [22] found that the log $i - \Delta V$ curves were independent of the HCl concentration, but small concentrations of lanthanum chloride caused appreciable displacements of the curves, which are ascribed to changes of the ζ-potential in accordance with Frumkin's theory.[23] It is shown that an increase of slope at higher current densities could be produced by organic contamination of the electrode.

Very little work has been done on overvoltage in non-aqueous solutions. Lewina and Silberfarb find [24] that Tafel's relation holds for mercury in alcoholic solutions of HCl, and Novoselski [25] finds that it holds at mercury electrodes in methyl and ethyl alcohol and in ether.

A similar phenomenon occurs in the liberation of oxygen at anodes. The reversible oxygen potential cannot usually be realised, but from calculations of the free energy change in the reaction $H_2 + \frac{1}{2}O_2 = H_2O$, it is found that it should be 1·22 volts more positive than the hydrogen electrode potential in the same solution. On this basis Coehn and Osaka [26] obtained the following values for

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[19] *Trans. Faraday Soc.*, **24**, 473, 1928 ; *Proc. Roy. Soc.*, **126**A, 107, 1932.

[20] Cf. Agar and Bowden, *ibid.*, **169**A, 206, 1938.

[21] *Acta Physicochimica, U.R.S.S.*, **5**, 193, 1936.

[22] *Ibid.*, **6**, 491, 1937 ; **7**, 485, 1937.

[23] *Z. physikal. Chem.*, **164**A, 121, 1931 ; *Acta Physicochimica*, **7**, 475, 1937.

[24] *Ibid.*, **4**, 275, 1936.

[25] *J. phys. Chem. Russ.*, **11**, 369, 1938.

[26] *Z. anorg. Chem.*, **34**, 86, 1903 ; cf. Caspari, *Z. physikal. Chem.*, **30**, 89, 1899; Westhauer, *ibid.*, **51**, 65, 1905.

the minimum overvoltages required for oxygen evolution in normal potassium hydroxide :—

TABLE III. OXYGEN OVERVOLTAGES IN N-KOH

Nickel	0·06	Silver	0·41
Cobalt	0·14	Cadmium	0·43
Platinised Pt	0·25	Palladium	0·43
Iron	0·25	Platinum (smooth)	0·45
Lead	0·31	Gold	0·53

On the whole, metals with a low hydrogen overvoltage tend to have a high oxygen overvoltage. But the figures of different investigators do not agree very well; the overvoltage depends on the state of the surface, it frequently increases as the duration of the electrolysis is increased, and it increases with the current density.[27] Bowden found [28] that Tafel's equation applies to the discharge of oxygen at platinum electrodes in dilute sulphuric acid, the exponent b in $i = ke^{+bV}$ having the same value as for hydrogen liberation, i.e. $b = \mathbf{F}/2RT$.

Theories of the Hydrogen Overvoltage.[29] Numerous theories have been suggested to account for the overvoltages required for the liberation of hydrogen and other gases. It would appear that the formation of hydrogen must occur in two stages: (1) the discharge of hydrogen ions, with formation of some kind of *atomic* hydrogen; (2) the combination of two hydrogen atoms to form a molecule, viz.

$$(1)\ H^+ + \epsilon \rightarrow H, \quad (2)\ 2H \rightarrow H_2.$$

The overvoltage might arise from either of these stages. If the reaction (2) were the slower stage, atomic hydrogen would accumulate at the electrode surface during the passage of current until its concentration was such that the hydrogen atoms would combine to molecules at the same rate as they are formed in the discharge process. Under these conditions the electrode potential would not have its normal value, but that corresponding to an excess of atomic hydrogen. It was thought that the latter would

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[27] Foerster, *Z. Elektrochem.*, **8**, 527, 1902; **10**, 714, 1904; *Z. physikal. Chem.*, **69**, 236, 1909.

[28] *Proc. Roy. Soc.*, **126**A, 107, 1929.

[29] For a recent survey, see K. Wirtz, *Z. Elektrochem.*, **44**, 303, 1938.

be more "electromotively active" than molecular hydrogen, and therefore the electrode potential would become more negative than the reversible potential during the passage of current.[30] Metallic hydrides have also been suggested as possible electromotively active substances.[31]

Among other suggestions which have been made are: (1) the overvoltage is connected with the additional energy which may be required to form small bubbles of the gas in the solution. If this were the case substances which lower the surface tension might be expected to reduce the overvoltage. However. these substances frequently increase the overvoltage[32] through being adsorbed on the surface and therefore reducing the available area; (2) the hydrogen forms an obstructive film on the surface of the electrode, which offers a considerable "transfer resistance" to the passage of current, and the fall of potential in this film is included in the measured potential difference.[33] The existence of "transfer resistance" has, however, been fairly convincingly disproved.[34]

More recently it has been realised that the overvoltage might also arise from the process of discharge of the hydrogen ions. In aqueous solutions, hydrogen ions exist in the hydrated form H_3O^+, and it could be supposed that the discharge process takes place in either of the following ways:—

(*a*) electrons escape from the metal and become attached to nearby hydrogen ions in the solution;

(*b*) the protons of hydrogen ions (H_3O^+) come into contact with, or are adsorbed on, the metal and are then neutralised.

Both of these views have been advocated. In classical electron theory the rate of escape of electrons from a metal having a thermionic work function ϕ is expressed as $i = ke^{-\phi/kT}$. If there is

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[30] Cf. Tafel, Lewis and Jackson, *loc. cit.*

[31] Newbery, *J. Chem. Soc.*, **109**, 1359, 1916; Heyrovski, *Rec. trav. chim.*, **44**, 499, 1925; **46**, 582, 1927.

[32] Thiel and Breuning, *Z. anorg. Chem.*, **83**, 329, 1913.

[33] Newbery, *J. Chem. Soc.*, **105**, 2422, 1914; *Trans. Faraday Soc.*, **15**, 126, 1919; *Proc. Roy. Soc.*, **107A**, 486, 1925; **111A**, 182, 1926.

[34] Ferguson and others *J. Physical Chem.*, **38**, 1117, 1934; **39**, 191, 1935; **42**, 171, 1938.

a potential difference V at the surface of the metal, the work done by electrons in escaping is increased to $\phi + \epsilon V$, and the rate of escape becomes

$$i = k\, e^{-(\phi+\epsilon V)/kT}.$$

The rate of escape of electrons may thus be greatly increased by giving V a negative value, and the overvoltage might be regarded as the displacement of V required to enable electrons to escape from the metal at the required rate. Since ϕ is constant for each metal, the relation between i and V is $i = k'e^{-\epsilon V/kT}$, which is of the same form as Tafel's experimental equation, except that the exponent of the latter is about half this value. Gurney and Fowler[35] have applied the methods of quantum mechanics to this process and find that a factor of this magnitude appears in the result of the calculation (see below).

That the primary process is the transfer of protons from hydrogen ions (H_3O^+) in the solution to adsorption positions on the electrode was suggested by Erdey-Grúz and Volmer.[36] They supposed that a fraction α of the whole potential difference was effective in modifying the activation energy of this process, and then its rate could be written as $Z_{H^+} = kC_{H^+} \,.\, e^{-\alpha VF/RT}$. If $\alpha = \frac{1}{2}$ the Tafel relation is accounted for.

Frumkin[37] modified this by supposing that the concentration of hydrogen ions in the double layer was given by

$$C_{H^+} = (C_{H^+})_e e^{-\zeta F/RT},$$

where $(C_{H^+})_e$ was the concentration in the interior of the solution and ζ the electrokinetic p.d. of Stern between the solution and the inside of the diffuse double layer. Then

$$Z_{H^+} = k(C_{H^+})_e \,.\, e^{-\alpha\psi F/RT}\, e^{-\zeta F/RT},$$

where $\psi = V - \zeta$ is the potential difference of the Helmholtz double layer. When $\alpha = 0{\cdot}5$ this becomes

$$Z_{H^+} = k(C_{H^+})_e \,.\, e^{-FV/2RT} \,.\, e^{-\zeta F/2RT},$$

or
$$V + \zeta = \frac{2RT}{F}\log [\mathrm{H}^+] - \frac{2RT}{F}\log i + \text{const.}$$

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[35] See ref. 43.

[36] *Z. physikal. Chem.*, **150**, 203, 1930; **162**, 53, 1932; M. Volmer, *Phys. Z. d. Sowjetunion*, **4**, 346, 1933.

[37] *Z. physikal. Chem.*, **160**, 116, 1932; **164**, 121, 1933.

By Stern's theory of the double layer, it is shown that under certain conditions[38]

$$\zeta = \text{const.} + \frac{RT}{F} \log [\mathrm{H}^+],$$

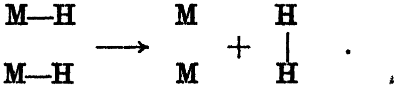
therefore, for a constant current, we obtain

$$V = \frac{RT}{F} \log \mathrm{H}^+ + \text{const.},$$

i.e. the overvoltage varies with the hydrogen-ion concentration in the same way as the potential reversible hydrogen electrode.

If hydrogen is first formed in the adsorbed state it must be desorbed before it can be liberated. In some theories this is considered to be the rate-determining step. Bowden and Rideal[39] thought that adsorbed hydrogen atoms would be deformed by the forces near the surface of the metal in such a way as to form orientated dipoles. The activation energy required for the escape of these dipoles from the surface would then depend on the electric field near the surface, and could be expressed as a linear function of the potential difference between the metal and the solution, viz. $W = w - \alpha V$, where $W =$ activation energy for p.d. V. In another paper[40] Bowden suggested that the dipole arises because the adsorbed hydrogen atom, which on account of its electron affinity attracts negative electricity from the metal, is virtually a negative hydrogen ion. This attracts positive hydrogen ions from the solution, forming an electrical "doublet," which on neutralisation gives rise to molecular hydrogen. Heyrovski also suggested[41] that molecular hydrogen is formed by the union of positive hydrogen ions from the solution with negative hydrogen ions at the electrode.

Molecular hydrogen could also be formed by two adjacent adsorbed atoms of hydrogen leaving the surface as a molecule :



$$\begin{array}{c}\mathrm{M{-}H}\\ \mathrm{M{-}H}\end{array} \longrightarrow \begin{array}{c}\mathrm{M}\\ \mathrm{M}\end{array} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H}\end{array} \quad . \quad . \quad . \quad (a)$$

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[38] Cf. *Acta Physicochimica*, **6**, 502, 1937.

[39] *Proc. Roy. Soc.*, **120**A, 59, 1928.

[40] *Ibid.*, **126**A, 107, 1929.

[41] *Rec. trav. chim.*, **44**, 499, 1925; **46**, 582, 1927; *Coll. Czech. Chem. Comm.*, **9**, 273, 345, 1937.

Horiuti and Okamota [42] found that when the electrolytic separation coefficients of hydrogen and deuterium at metal electrodes were determined, they fell into two classes and suggested that there were two distinct mechanisms of liberation of hydrogen. The first was the "catalytic mechanism" represented by (*a*) above. The second was an "electrochemical mechanism," somewhat similar to those of Bowden and Heyrovski, in which it was supposed that if a hydrogen ion is neutralised at a surface covered with adsorbed hydrogen, a molecule of hydrogen is formed by the combination of the neutralised ion with an adsorbed atom, viz.

$$\mathrm{M{-}H} + \mathrm{H^+} + \epsilon \rightarrow \mathrm{M} + \mathrm{H_2} \quad . \quad . \quad . \quad (b)$$

After this short survey of the various mechanisms which have been proposed, we will now proceed to discuss the mechanisms of the various stages, so far as they have been worked out, in greater detail.

Gurney and Fowler's Theory. The conditions imposed by quantum mechanics on the transfer of electrons from a metal to hydrogen ions in a solution have been investigated by Gurney and Fowler.[43] It is supposed that in a metal there are a large number of separate energy levels, each of which is capable of accommodating two electrons. In the first place we may suppose that the electron levels of the metal are completely filled up to the level having the energy ϕ and completely unoccupied for levels having a greater energy.* This case is shown diagrammatically in Fig. 3 (*a*), where the fraction of the available energy levels which are occupied by electrons is indicated by the breadth of the shaded part.

A hydrogen atom also has a number of energy levels in one of which the electron is present. The energy required to remove it from the lowest level is the ionisation potential $\mathfrak{T}$. According to quantum mechanics electrons are not definitely localised, but are capable of passing at a finite rate through a "potential barrier," i.e. a region through which, according to classical mechanics, they

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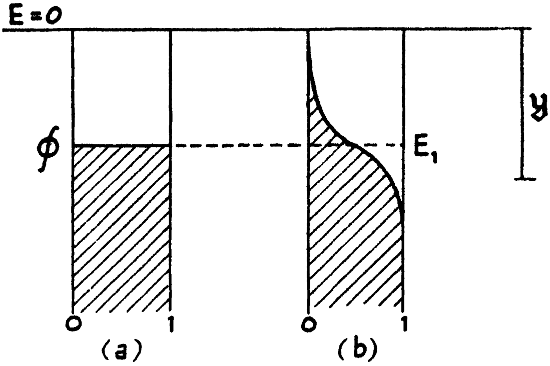
[42] *Sci. Pap. I.P.C.R. Tokyo*, **28**, 231, 1936; *Bull. Chem. Soc. Japan*, **13**, 216 228, 1938.

[43] *Proc. Roy. Soc.*, **134A**, 137, 1931; *Trans. Faraday Soc.*, **28**, 368, 1932.

* The energy of an electron in free space is taken as zero, and *E* represents the loss of energy when the electron passes from free space into the state in question.

have insufficient energy to penetrate to neighbouring energy levels of equal energy. Thus if hydrogen ions are near the surface of the metal, it will be possible for electrons to pass from occupied levels of the metal to unoccupied levels of the ion, if there are any of equal energy. This condition will be fulfilled if $\phi < \mathfrak{T}$. Similarly, a transfer of electrons from hydrogen atoms to the metal will be possible if the *occupied* levels of the atom are of the same energy as unoccupied levels of the metal, i.e. if $\mathfrak{T} < \phi$. The ionisation potential of the isolated hydrogen atom is 13·5 electron-volts, while the thermionic work functions of metal are *ca.* 5 volts, so that at the surface of a metal *in vacuo* the neutralisation of hydrogen ions, but not the ionisation of hydrogen atoms is possible. Certain atoms, such as Cs and Rb, have much lower ionisation potentials and the ionisation process can occur.



VI. 3.

This picture is not quite accurate except at absolute zero. At higher temperatures some electrons are able to pass from the occupied levels below to levels above ϕ, so that there is then a range of levels which are partly filled with electrons, as in Fig. 3 (*b*). The number of electrons in levels above ϕ, however, decreases very rapidly with decrease of E and the conditions stated above remain approximately true.

In aqueous solutions we have to deal not with the isolated hydrogen ion, but with the hydrated form H_3O^+. When this is neutralised we get the unstable molecule H_3O, and the energy change in the process

$$H_3O^+ + \epsilon \rightarrow H_3O$$

can be seen from the accompanying scheme to be

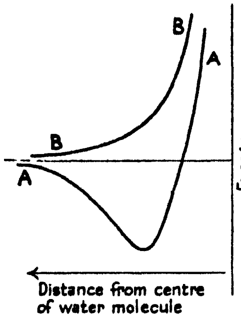
$$N^+ = \mathfrak{T} - H - R,$$

where H is the hydration energy of the hydrogen ion and R the energy required to form the unstable molecule H_3O from H and H_2O. Gurney calls N^+ the neutralisation energy of the ion. It has the

$$\begin{tikzcd}
H^+ + \epsilon & H \arrow[l, "\mathfrak{T}"'] \arrow[d, "R"] \\
H_3O^+ + \epsilon \arrow[u, "H"] & H_3O \arrow[l, "\mathfrak{T} - H - R"]
\end{tikzcd}$$

same function in the solution as the ionisation energy $\mathfrak{T}$ has for an isolated hydrogen ion, and the condition of neutralisation at an electrode is $\phi < N^+$. If there is a potential difference V at the surface of the metal, the energy levels of the metal will be depressed by the amount eV, and condition becomes $\phi + eV < N$.

Now all the hydrogen ions are not in exactly the same state of hydration. The potential energy of H^+ varies with its distance from the centre of gravity of the water molecule to which it is attached, as shown by AA in Fig. 4. The energy between H and H_2O, which is repulsive at all distances, is shown by the curve BB.



VI. 4.—Potential energy of H^+ (AA) and of H (BB) as function of distance from centre of water molecule.

The condition $\phi + \epsilon V < \mathfrak{T} - H - R$ may be written $\phi + \epsilon V + R < \mathfrak{T} - H$, and this can be represented diagrammatically as in Fig. 5.[44] The curve of H is raised a distance $\mathfrak{T}$, and we get AA which represents $\mathfrak{T} - H$. Similarly, BB is the curve of R raised a distance $\phi + \epsilon V$. At the point of intersection X, $\phi + \epsilon V + R = \mathfrak{T} - H$, and for states represented by points on the curve to the left of X, the condition of transfer is satisfied. If E_0 is the energy of the ions in their ground state and E' the energy corresponding to the point X, the probability of an ion having the

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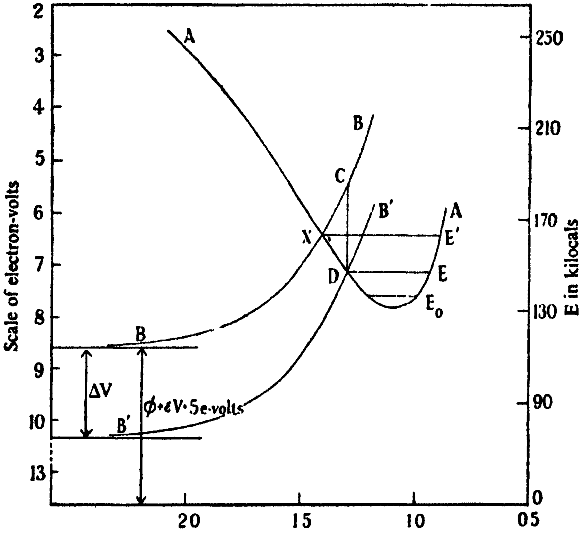
[44] See ref. 46.

energy E' is proportional to $e^{-(E'-E_0)/kT}$ and the current will be proportional to this quantity. If the potential difference at the surface of the metal changes by ΔV, the curve to BB is displaced a distance $\epsilon\Delta V$ and becomes B′B′ and the new intersection point is at D, which represents ions of energy E. The probability of ions having this energy is $e^{-(E-E_0)/kT}$ and the current is now proportional to this factor. The vertical distance between X and D is less than the displacement $\epsilon\Delta V(= \text{CD})$. Since the curves are approximately linear in this region, we may write $\gamma(E'-E) = \epsilon\Delta V$, and the ratio of the currents for the two values of V shown is



VI. 5.—Distance from centre of water molecule (A°). Discharge of proton in H_3O^+. AA, curve of I − H; BB, curve of $\phi + \epsilon V + R$. (*Proc. Roy. Soc.*, vol. 157, 1936.)

$$i'/i = e^{-(E'-E)/kT} = e^{-\epsilon\,.\,\Delta V/\gamma kT},$$

or

$$\log i = \text{const.} - \epsilon\,.\,\Delta V/\gamma kT.$$

If the two curves AA and BB are equally steep near the point of intersection $\gamma = 2$ and we get the experimental relation.

This is a rather rough version of Gurney's calculation, which is only intended to indicate the physical principles involved. A more exact treatment is as follows: Let BB be the curve of $E_1 + \epsilon V + R$, where

E_1 is the energy of the electron level of the metal which is half occupied by electrons. Let B′B′ be the corresponding curve of a lower level $E_1 - \Delta E_1$, while V now remains the same. The probability of finding an electron of this energy is $e^{\ \Delta E_1/kT}$, if ΔE_1 is not too small. An electron in this level can neutralise an ion in the ionic level E_1 which passes through the intersection point D. The probability of an ion having this energy is $e^{(E_0\ \ E)/kT}$. The rate of neutralisation of ions is obtained by summing all the rates of transfer between electronic and ionic levels of equal energy. The transfers which occur above the point X can, however, be neglected, because the number of ions in these levels fall off rapidly with increasing energy, and the number of occupied electronic levels of the metal also decreases. An approximately correct result can be obtained by considering only transfers to ions in the region between E_0 and the intersection point X, having energy E'. Multiplying the probability of an ion having the energy E, by the probability of an electron having the same energy, and integrating between E_0 and E we obtain

$$i = \int_{E_0} e^{(E_0\ \ E)/kT} \,.\, e^{-\Delta E_1/kT} \,.\, \text{const.}\, dE,$$

and
$$\Delta E_1 = \text{CD} = \gamma(E' - E),$$

where γ may be taken as a constant, as before. Hence

$$i = \int_{E_0} e^{(E_0\ \ E)/kT} \,.\, e^{-\gamma(E'-E)} \,.\, \text{const.}\, dE,$$

and we obtain

$$\log i = \text{const.} + (E_0 - E')/kT.$$

From this it follows that

$$-\frac{d \log i}{dV} = \frac{1}{kT}\left(\frac{dE'}{dV}\right) = \frac{\epsilon}{\gamma kT},$$

which is the experimental relation if $\gamma = 2$.

If the constant terms are supposed to be independent of the temperature, we also find that

$$\frac{d \log i}{dT} = \frac{E' - E_0}{kT^2} = \frac{\Delta}{kT^2}.$$

Δ, i.e. the height of the intersection point X above the ground level E_0, can evidently be regarded as the *activation energy* of the process. Since the position of X varies with V, it is evident that Δ changes with the potential difference at which it is measured. Bowden found[45] that at a mercury electrode, when $V = -1{\cdot}0$ volts as

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[45] *Proc. Roy. Soc.*, 126A, 107, 1930.

measured against the saturated calomel electrode, $\Delta = 0{\cdot}43$ electron-volts, or 9·9 kcals. per equivalent. Butler made calculations[46] of $\Delta = E' - E_0$, according to Fig. 5, using the best available information as to the shape of the curves, and found the following values :—

$E_1 + \epsilon V$	3	4	5	6	electron-volts
Δ	8	16	27	38	kilocals.

Bowden's experimental result thus corresponds to $E_1 + \epsilon V = 3{\cdot}2$ volts, or, if the absolute value of V is taken as $- 0{\cdot}5$ volts, to $E_1 = 3{\cdot}7$ volts. The thermionic work function of mercury, as determined by the photoelectric threshold, is 4·5 volts,[47] which is in quite reasonable agreement with the former figure. The calculated value depends on the shapes assumed for the curves, but so far as can be judged from our present knowledge, Gurney's mechanism thus not only gives an approximately correct value of the factor γ, but also appears to be capable of giving rise to an overvoltage, which is quantitatively of the right order of magnitude.

The Reversible Hydrogen Electrode. The mechanism described above is essentially irreversible, for the reverse process, $H_2 \rightarrow H \rightarrow H^+$, cannot take place at an appreciable rate. This can be seen from Fig. 5. The discharge of hydrogen ions occurs at a measurable rate when $E - E_0$ is comparatively small (*ca.* 10 kcals. = 0·4 volts). It can be seen that when $E - E_0$ is small, the height of D above the beginning of the curve B′B′, which represents the energy an isolated hydrogen atom must gain before it can become an ion, is large (*ca.* 60 kcals.). The rate of the process $H \rightarrow H^+$ under these conditions would thus be very small. It could be increased by raising the curve B′B′ considerably, i.e. by increasing $E_1 + eV$ by giving the electrode a more positive potential. If the curves of Fig. 5 are correctly placed, there is no position of B′B′ at which the activation energy is small from both sides at one and the same time, i.e. there is no potential at which *both* processes can occur at an appreciable rate. The same applies with greater force to molecular hydrogen H_2, which has a considerably lower energy than H.

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[46] *Proc. Roy. Soc.*, **157A**, 423, 1936.

[47] H. Cassel and A. Schneider, *Naturwiss.*, **22**, 464, 1934.

This is in accordance with the behaviour of non-reversible electrodes. Armstrong and Butler [48] found that at ordinary platinum electrodes no continuous ionisation of hydrogen occurs, at any rate within 1 volt of the reversible hydrogen potential.

On the other hand, it has been known for a long time that the reversible hydrogen potential is readily established at electrodes which have been platinised or covered with similar active material, which must be the result of a reversible discharge process, which at the reversible potential takes place at equal rates in both directions. Butler and Armstrong [49] also showed that bright platinum could be brought by alternate anodic and cathodic polarisation into an " active " condition, in which it behaves as a reversible electrode. At such electrodes the hydrogen overvoltage is very low, and at low current densities varies at first *linearly* with the current. The process is quite reversible. An anodic current causes the ionisation of hydrogen, viz. $H_2 \rightarrow 2H^+$, so long as there is any molecular hydrogen near the electrode, and the potential is similarly displaced in a positive direction.

The linear relation between the current and the potential difference has been explained [50] as the effect of displacing the potential difference on the two opposing processes which occur at equal rates at the reversible potential. When the potential difference is altered the rate of the process in one direction is increased and that of the other decreased exponentially, and the result is, for small displacements of the potential, a linear relation between the potential and the current (see below).

In order to explain the occurrence of the reversible electrode, we have to find a process which will take place at equal and not insignificantly small rates in both directions at the reversible potential. A process which may have this property, viz. the transfer of protons from the solution to adsorption places on the surface of the electrode, where they become neutralised and may then be desorbed as molecular hydrogen, was first explored by Erdey-Grúz

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[48] *Proc. Roy. Soc.*, **137**A, 604, 1932.

[49] *J. Chem. Soc.*, 743, 1934:

[50] Butler, *Trans. Faraday Soc.*, **28**, 379, 1932 ; Hammett, *ibid.*, **29**, 770, 1933 ; Hoekstra, *Z. physikal. Chem.*, **166**, 77, 1933. Hammett gave the equation

$$E = a + b \log I + cI.$$

and Volmer[51] (see p. 132), and Horiuti and Polanyi[52] showed how Tafel's factor could arise by the modification of the activation energy of the process by changes of the potential difference. These authors, however, regarded the process mainly as an alternative mechanism for the irreversible formation of hydrogen,* which gives rise to Tafel's relation and the latter considered it to have a high activation energy of 20-30 kcals.

Butler[53] showed that when all the factors are taken into account, this process may have a low activation energy, such that it fulfils the conditions of a reversible electrode. Suppose that the energy of interaction (adsorption) of hydrogen atoms with the metal surface is A. Taking this into account, the neutralisation energy of the hydrated hydrogen ion becomes $\mathfrak{T} - H - R + A$ and the condition of neutralisation for an electrode at which the potential difference is V is

$$\phi + eV > \mathfrak{T} - H - R + A,$$

or

$$\phi + eV - A + R > \mathfrak{T} - H.$$

The forces acting on a hydrogen atom or ion in the region between the metal and the nearest water molecules are shown in Fig. 6. AA is the curve of $\mathfrak{T} - H$ as in Fig. 5. BB is the curve of R, the repulsive energy between a hydrogen atom and the water molecule,

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[51] *Z. physikal. Chem.*, **150**, 203, 1930; **162**, 53, 1932.

[52] *Acta Physicochimica, U.R.S.S.*, **2**, 505, 1935.

* Erdey-Grúz and Volmer, in their original paper, give the rate of transfer of hydrogen ions from the solution side of the double layer to the electrode as

$$Z_{H^+} = k_2' C_{H^+} e^{-\frac{V - \alpha VF}{RT}} = k_2 C_{H^+} e^{\alpha VF/RT},$$

and the rate of the reverse process as

$$Z_H = k_3' C_H e^{-\frac{W + \beta VF}{RT}} = k_3 C_H e^{-\beta VF/RT},$$

and they define the reversible potential V_r as that at which the rates in the two directions are equal, i.e. $Z_{H^+} = Z_H$ and then

$$(\alpha + \beta) V_r = \frac{RT}{F} \log \frac{C_H}{C_{H^+}} + \text{const.}$$

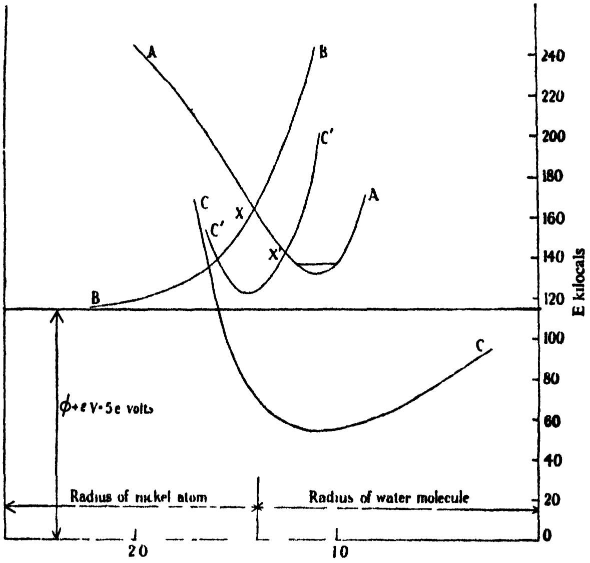
The current i is then given by

$$i = Ae^{\alpha . \Delta V/RT} - Be^{-\beta . \Delta V/RT},$$

where ΔV is the overvoltage, but they only considered the case in which ΔV is so large that the second term is negligible and $i = Ae^{\alpha . \Delta V/RT}$. The linear relation of i, and ΔV, is mentioned by Volmer in *Phys. Z. d. Sowjetunion*, **4**, 346, 1933.

[53] *Loc. cit.*, ref. 46.

raised a distance $\phi + eV$. CC is the energy of interaction of the hydrogen atom with the metal surface, i.e. the adsorption energy. Combining BB and CC we get C′C′, which represents the energy of the hydrogen atom under the combined action of A and R in this region. The condition of neutralisation is satisfied by ions having energy greater than that represented by the point X′. This is considerably lower than X, which represents that required for the formation of the free hydrogen atom. If the adsorption energy is



VI. 6.—Distance from centre of water molecule (A°). Formation of adsorbed hydrogen. AA, curve of I − H; BB, curve of $\phi + \epsilon V + R$; CC, curve of A; C′C′, curve of $\phi + \epsilon V + R - A$. (*Proc. Roy. Soc.*, **157A.**, 1936.)

of the order of 50 kcals. or 2ε-volts, it is estimated that X′ is about 1 ε-volt lower than X, so that adsorbed hydrogen atoms can be formed at a given rate when the potential is 1 volt less negative than is required for the formation of free hydrogen atoms at the same rate in Gurney's scheme.

The potential difference at a reversible electrode is that at which the process occurs at the same rate in both directions. This will be the case when the minima of the curves C′C′ and AA are at approximately the same level. For a practical reversible electrode it is also necessary for the rates of the two opposing processes to be reasonably great, so that the passage of a small current will not upset their balance greatly. This will be the case when the activation energy from both sides is sufficiently small. The activation energy of the reversible process at a nickel surface was estimated as about 8 kcals., taking the radius of the nickel atom as 1·25 Å., and that of the water molecule as 1·38 Å., so that the total distance between the centres, as shown in the diagram, was 2·63 Å. This would permit of a rate of transfer of electrons in both directions of $2{\cdot}5 \times 10^{-4}$ amps./cm.^{2}, and the passage of currents of the order of 10^{-5} amps./cm.^{2} would not disturb the equilibrium potential appreciably.

The desorption of hydrogen. So far only part of the process has been described, since adsorbed hydrogen when formed must leave the surface in the molecular form. The rate of formation of hydrogen is determined by the rate of desorption. At a reversible electrode there must be not only an equilibrium between adsorbed hydrogen atoms and hydrogen ions in the solution, but also between the former and the atmosphere of molecular hydrogen. These equilibria may be represented by the following scheme :—

$$\begin{array}{ccccc} H_2 & \underset{k_3x^2}{\overset{k_4p_{H_2}(1-x)^2}{\rightleftarrows}} & [H] & \underset{k_1(1-x)}{\overset{k_2x}{\rightleftarrows}} & H^+ \\ \text{Gaseous hydrogen} & \text{I} & \text{Absorbed hydrogen} & \text{II} & \text{Hydrogen ions } (H_3O^+) \end{array}$$

Suppose that a fraction x of all the available adsorption positions on the surface of the electrode is occupied by hydrogen atoms. The rate of desorption of hydrogen in the form H_2 may be expressed as k_3x^2 (since two *adjacent* atoms must leave the surface simultaneously and the probability of finding two adjacent places occupied is x^2. The rate of adsorption of hydrogen is proportional to the probability of finding two adjacent places unoccupied by hydrogen atoms, and to the pressure of the hydrogen gas, i.e. $k_4(1-x)^2p_{H_2}$. The adsorption equilibrium I is thus defined by

$$k_3x^2 = k_4(1-x)^2p_{H_2}.$$ [*]

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[*] There are other possibilities, cf. Roberts, *Proc. Camb. Phil. Soc.*, **132**, 152, 1936 ; but the argument is not thereby affected in any essential way.

When hydrogen is being liberated at the electrode, this equilibrium is disturbed and the rate of formation of hydrogen is the difference between the rates of desorption and adsorption, or

$$i = k_3x^2 - k_4(1-x)^2p_{H_2}.$$

It is evident from this that i cannot be greater than k_3, i.e. the maximum rate of formation of hydrogen by this process is limited by the rate of desorption from a completely covered surface. When i is small, the value of x will not differ much from its equilibrium value.

The equilibrium II between adsorbed hydrogen atoms and the ions in the solution depends of course on the potential difference. At the equilibrium potential difference V_0, let the rate of transfer of protons to a completely unoccupied surface ($x = 0$) be k_1 and the rate of transfer from a completely occupied surface ($x = 1$) be k_2; then the equilibrium at V_0 is defined by

$$k_1(1-x) = k_2x.$$

If the potential difference is displaced by the amount ΔV from V_0, these rates become $k_1(1-x)e^{-\epsilon\Delta V/\gamma kT}$ and $k_2\,xe^{\epsilon\Delta V/\gamma kT}$, and the current is

$$i = k_1(1-x)e^{-\epsilon\Delta V/\gamma kT} - k_2\,xe^{\epsilon\Delta V/\gamma kT},$$

where x is determined by the adsorption relation.

When i is small, we have seen that x does not differ much from its equilibrium value, and writing $i_0 = k_1(1-x) = k_2\,x$, we find that approximately

$$i/i_0 = -\,2e\,.\,\Delta V/\gamma kT.$$

For small values of $i(< k_3)$ we therefore have a linear relation between i and V. With greater currents, x will no longer remain at the equilibrium value, but will diminish, and therefore ΔV will increase more rapidly. If i_0 is greater than the maximum rate of desorption, this mechanism is no longer adequate and the potential will rise until some other discharge process can come into action.

According to this the behaviour of electrodes depends largely on the rate at which hydrogen is adsorbed and desorbed.[54] Sherman

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[54] Cf. Náray-Szabó, *Z. physikal. Chem.*, **178**, 355, 1937; *ibid.*, **181**, 367, 1938.

and Eyring[55] calculated the activation energy for the adsorption of H_2 on carbon as a function of the spacing of the carbon atoms, and found that it was a minimum for a certain spacing (3·5 Å.), which is considerably greater than the normal C—C distance. It is thus likely that for each metal there is an optimum spacing and the catalytic activity will depend on whether a suitable spacing is actually present at the surface. Okamoto, Horiuti and Hirota calculated[56] that with nickel the optimum spacing is 3·52 Å., which is present in the 110 plane of the crystal.*

There are several alternative processes which might come into operation when the current exceeds the maximum rate of catalytic desorption. Hydrogen ions may be discharged at such a surface by a process similar to Gurney's, except that it takes place not at a bare metallic surface but at a surface saturated with adsorbed hydrogen. Molecular hydrogen may then be formed in three ways :—

(1) The hydrogen atom so formed is effectively free and remains so until it encounters and combines with another similar hydrogen atom.

(2) The hydrogen atom is loosely attached to the surface. It may migrate over the surface until it encounters a similarly attached atom, with which it forms a molecule, viz. :

$$\begin{array}{l} \mathrm{M{—}H\ldots H} \\ \\ \mathrm{M{—}H\ldots H} \end{array} \longrightarrow \begin{array}{l} \mathrm{M{—}H} \\ \\ \mathrm{M{—}H} \end{array} + \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H} \end{array}$$

(3) Molecular hydrogen is formed by the combination of a discharged atom with an adsorbed atom ; or by the discharge of the molecular ion H_2^+ (cf. Bowden, Heyrovski, Horiuti), viz. :

$$\mathrm{M{—}H\ldots H} \rightarrow \mathrm{M} + \mathrm{H_2},$$

or

$$\mathrm{M{—}H\ldots H^+} + \epsilon \rightarrow \mathrm{M} + \mathrm{H_2}.$$

(1) must be regarded as rather improbable, since it is unlikely that a hydrogen atom will long remain free. There appear to be no reliable criteria for distinguishing (2) and (3), and the energy

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[55] *J. Amer. Chem. Soc.*, **54**, 2661, 1932.

[56] *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **29**, 223, 1936.

* For a discussion of the state of hydrogen adsorbed on zinc, see M. Satô, *Sci. Rep., Tôhoku Imp. Univ.*, **25**, 829, 1937.

required to remove a molecule of hydrogen by (3) is not known. Hirota and Horiuti have given evidence for the existence of molecular ions at the surface of mercury.[57] Barclay and Butler[58] investigated the cathodic polarisation of freshly made mercury surfaces and were unable to detect any sign of the deposition on mercury of adsorbed hydrogen at any potential below the usual overvoltage (see p. 74, the experiments do not indicate what process occurs at the normal overvoltage—only that adsorbed hydrogen is not previously deposited).

Summary. It is evident that no single mechanism of hydrogen liberation is adequate in all circumstances, and of the various reaction paths which have been proposed that which is the easiest in any given circumstances will be followed. The only distinction that can be drawn in practice is between reversible and irreversible electrodes. In the former case the overvoltage is small and with small currents, at least, varies linearly with the current. In the latter, the overvoltage is comparatively high, and Tafel's relation is obeyed with a constant which probably does not differ greatly from $F/2RT$ at uncontaminated surfaces.

If the metal has no affinity for atomic hydrogen the only available mechanism appears to be the formation of " free " hydrogen by Gurney and Fowler's process. This may be the case with mercury. At most metals the energy of binding of atomic hydrogen is probably quite considerable, and in the first place adsorbed hydrogen will be deposited on the electrode. If the rate of desorption is great this deposition will be the rate determining process (Volmer, Erdey-Grúz), but under these circumstances the electrode is probably reversible. If the rate of desorption is small, the electrode surface will be saturated with hydrogen and with greater currents another process must come into operation. The possibilities depend again on the strength of the metal-hydrogen binding. If the adsorbed hydrogen is very firmly bound, hydrogen molecules may be formed by the combination of two free or loosely attached hydrogen atoms; if less firmly bound, the molecule of hydrogen may be formed by the combination of a discharged atom with an adsorbed atom.

[57] *Bull. Chem. Soc. Japan*, **13**, 228, 1938.

[58] *Trans. Faraday Soc.*, Jan. 1940.

The Oxygen Electrode. The possible mechanisms of the liberation of oxygen at anodes are very similar to the mechanisms of hydrogen formation discussed above. Gurney and Fowler[59] showed that their theory, when applied to the discharge of negative ions, was capable of giving the factor $b = F/2RT$ in Tafel's equation. The discharge process can most simply be regarded as the neutralisation of negative oxygen ions,* $\mathrm{O}^{=}$. The process of neutralisation can then be represented as follows. If $\mathfrak{T}$ is the energy required to remove the two electrons from the isolated $\mathrm{O}^{=}$ ion, the *neutralisation energy* in solution can easily be seen from the following scheme, where the arrows indicate the directions in which energy is absorbed, to be

$$N^{-} = \mathfrak{T} + H + R.$$

$$\begin{tikzcd}
\mathrm{O}^{=} \arrow[r, "\mathfrak{T}"] & \mathrm{O} \arrow[d, "R"] \\
(\mathrm{O}^{=})\mathrm{H_2O} \arrow[u, "H"'] \arrow[r, "N^{-}"'] & \mathrm{O}(\mathrm{H_2O})
\end{tikzcd}$$

H and R are the energies of interaction of the oxygen ion $\mathrm{O}^{=}$ and the oxygen atom O, with water. (The latter is assumed to be a repulsion, but it may perhaps be a weak attraction.) The condition of transfer of electrons from the oxygen ions in the solution to the electrode is thus

$$2(\phi^{0} + \epsilon V) > \mathfrak{T} + H + R.$$

Writing this as $$2(\phi^{0} + \epsilon V) - R > \mathfrak{T} + H,$$

this condition is represented by Fig. 7, where the energies are plotted against a co-ordinate representing the position of the $\mathrm{O}^{=}$ ion with respect to neighbouring water molecules. AA is the curve of H displaced downwards a distance $\mathfrak{T}$, i.e. the distance downwards

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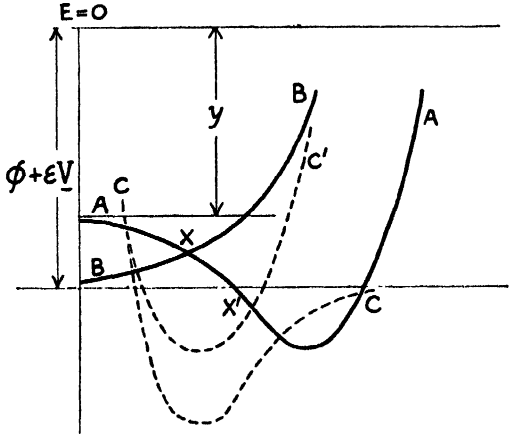
[59] *Loc. cit.*, ref. 43.

* The hydroxyl ion $\mathrm{OH^{-} = O^{=} + H^{+}}$ is to be regarded as a hydration product of the oxygen ion; $\mathrm{O^{=} + H_2O \rightarrow 2OH^{-}}$, and the energy of formation of $\mathrm{OH^{-}}$ from $\mathrm{O^{=}}$ and $\mathrm{H^{+}}$ can be included in the hydration energy. The discharge of $\mathrm{OH^{-}}$ can be supposed to take place by $\mathrm{OH^{-} = O + H^{+}} + 2\epsilon$. There is no convincing evidence that the intermediate product OH is formed.

from $E = 0$ represents $\mathfrak{T} + H$. BB is the curve of R displaced downwards a distance $2(\phi^o + \epsilon V)$ so that the distance downwards of this curve represents $2(\phi^o + \epsilon V) - R$. The condition of neutralisation is satisfied by ions having energy greater than that represented by the intersection point X of the two curves. If V is increased positively, X moves downwards and the probability of an ion having the necessary energy is increased. By the same arguments that were used in connection with the hydrogen overvoltage it can be shown that

$$\frac{d \log i}{dV} = \frac{\epsilon}{\gamma kT}.$$

The adsorption of oxygen and the reversible oxygen electrode. The researches of Langmuir [60] on gas adsorption on metal filaments has shown that oxygen is adsorbed as atoms and very tenaciously held on tungsten, carbon and metals of the platinum type. The film of oxygen on tungsten is so stable that it will not react with hydrogen or carbon monoxide even at 2800° K. Langmuir and Villars [61] found that the heat of evaporation of this adsorbed oxygen from tungsten was 160 kcals. The conditions required for the electrochemical deposition of adsorbed oxygen at a metal at which the energy of adsorption is considerable are shown in Fig. 7. CC represents the energy of adsorption of oxygen atoms as a function of the distance from the metal surface. Combining this with BB, we get C′C′ which represents the energy of the oxygen atoms



VI. 7.—Conditions for discharge of oxygen ions and deposition of oxygen.

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[60] E.g. *J. Amer. Chem. Soc.*, **37**, 1139.

[61] *Ibid.*, **53**, 486, 1931.

in the region between the metal and the nearest water molecules. The new intersection point X′ of this curve with AA is considerably lower than X, so that in this case adsorbed oxygen is formed more easily than free oxygen. This scheme is similar to that already described (p. 142) for the formation of adsorbed hydrogen. It was shown that this process may be reversible, and if the adsorbed hydrogen is also in reversible equilibrium with the molecular hydrogen in the gas, a reversible hydrogen electrode results. A reversible oxygen electrode would similarly depend on the realisation of the two equilibria

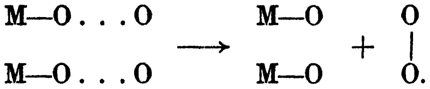
$$O_2 \rightleftharpoons [O] \rightleftharpoons O^{=}(aq.).$$

It is however well known that the reversible oxygen electrode cannot be realised. This might be due to the failure of either of these equilibrium, but it will be shown below that the deposition of oxygen from the solution and the ionisation of oxygen adsorbed on the electrode can easily be observed, and there does not appear to be any reason why the two processes should not occur together at a sufficient rate for reversibility at a single potential. It is more likely that the failure is due to the non-establishment of the adsorption equilibrium. Oxygen adsorbed on the surface of non-attackable metals has a very low potential energy, and although adsorption may occur easily enough, desorption is difficult and may be very slow, so that a reversible equilibrium between the gas and the adsorbed oxygen is not realisable.

When the rate of deposition of oxygen on the electrode by an anodic current exceeds the rate of desorption, the electrode will quickly become completely covered by adsorbed oxygen, and if the current is to continue the discharge of oxygen ions by some other process must take place. The possibilities are similar to those considered in the case of hydrogen, but since the adsorbed oxygen atoms are very firmly held to the metal, it is unlikely that molecular oxygen could be formed by the combination of a discharged atom with an adsorbed atom; viz.

$$M - O + O^{=} + 2\epsilon \rightarrow M + O_2.$$

It is more probable that the oxygen now formed is loosely attached to the surface, and molecular oxygen is formed by the combination of two such atoms, viz.



$$\begin{array}{c}\text{M—O}\ldots\text{O}\\ \text{M—O}\ldots\text{O}\end{array} \longrightarrow \begin{array}{c}\text{M—O}\\ \text{M—O}\end{array} + \begin{array}{c}\text{O}\\ |\\ \text{O.}\end{array}$$

The Decay of Overvoltage. If B is the double layer capacity of an electrode, the rate of change of the potential, with a current i, when there is no transfer of charges across the double layer (p. 70), is

$$B\frac{dV}{dt} = i \qquad . \quad . \quad . \quad . \quad (a)$$

If electric charges (i.e. electrons or ions) cross the double layer at the rate i', of the total current i only the part $i - i'$ is available for changing the charge of the double layer, and the rate of change of the potential is then given by

$$B\,.\frac{dV}{dt} = i - i' \qquad . \quad . \quad . \quad . \quad (b)$$

When electrolysis occurs at a *constant* potential, it is evident that $i' = i$, i.e. the current is equal to the rate of transfer of charge across the double layer.

Now suppose that hydrogen is being liberated at a metallic cathode and the potential of the electrode has reached the constant value of the overvoltage for which $i = i'$, and the current is then stopped. The rate of change of the potential is now given by putting $i = 0$ in (b), i.e.

$$B\,dV/dt = -\,i'.$$

If the neutralisation process continues, after the stoppage of the current, at the rate corresponding to the electrode potential given by $i' = ke^{-aV}$, we shall have

$$-\frac{dV}{dt} = \frac{k}{B}e^{-aV},$$

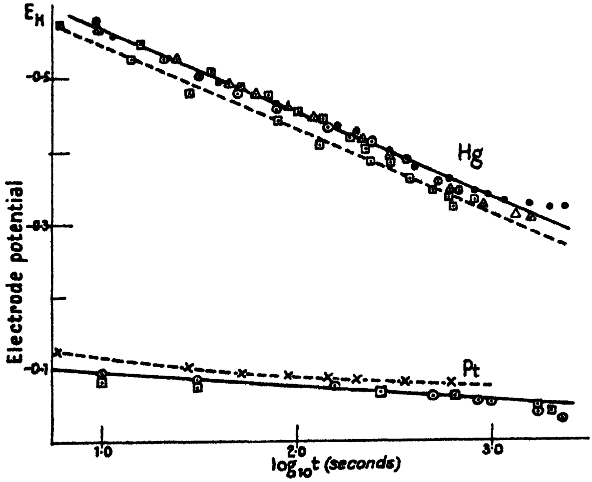
which, on integration, gives

$$e^{aV_t} - e^{aV_0} = akt/B,$$

where V_t is the potential at the time t and V_0 its value at the instant the current is stopped ($t = 0$). For times greater than a few seconds e^{aV_0} is small compared with e^{aV_t} and may be neglected, and then

$$\frac{aV_t}{2\cdot303} = \log_{10}\left(\frac{ak}{B}\right) + \log_{10} t,$$

i.e. after the first few seconds the potential varies linearly with the logarithm of the time, and the slope $\Delta V/\Delta \log t$ is $2\cdot303/a$, the same as the slope of the $V - \log_{10} i$ curve. This is 0·116 volts at 15°, and the result of the calculation therefore is that the potential should become 0·116 volts more positive for each ten-fold increase of the time.



VI. 8.—Decay of hydrogen overvoltages at mercury and platinum electrodes. (Armstrong and Butler, *Trans. Faraday Soc.*)

Bowden[62] observed marked discontinuities in the decay of hydrogen voltages, which he attributed to minute traces of metallic impurities which are not removed from the solutions by ordinary methods of purification. Armstrong and Butler[63] observed the rate of decay of the hydrogen overvoltage at mercury electrodes in highly purified solutions, and obtained rates which agreed with this calculation (Fig. 8), when the initial potential of the electrode was not more negative than $E_h = -1\cdot0$ volt. Under these conditions

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[62] *Trans. Faraday Soc.*, **23**, 671, 1927. [63] *Ibid.*, **29**, 1261, 1933.

they concluded that the transfer of charges across the double layer continues at the rate $i' = ke^{-aV}$, where a has the usual value after the stoppage of the current. If the hydrogen formed or any other product of the electrolysis were electromotively active under these conditions, i.e. could yield electrons to the metal at any appreciable rate, the rate of transfer of charge from the metal to the solution would be less than that assumed in the calculation and the rate of decay would be less than that observed. This is the most direct proof yet obtained that under these conditions, at least, the products of the electrolysis are not electromotively active. If the initial potential of the electrode was about — 1·4 volts, much slower rates of decay were observed which were attributed to the deposition of traces of the alkali metals at the electrode during the passage of the current. At platinum electrodes, having a much lower overvoltage, the rate of decay was appreciably smaller, indicating an appreciable activity of hydrogen under these circumstances.

The rate of decay of oxygen overvoltage at platinum electrodes obeys a similar relation, except during the first minute, when it is somewhat slower. This apparently indicates the formation during the electrolysis of a product having a transient activity, which disappears in about a minute.

The Electrolytic Separation of Hydrogen and Deuterium. After the discovery by Urey of the heavy isotope of hydrogen called deuterium, it was found by Washburn and Urey and by G. N. Lewis and Macdonald that it could be concentrated in aqueous solutions by electrolysis.[64] The hydrogen liberated at the cathode contains a smaller proportion of deuterium than the water undergoing electrolysis, so that the solution remaining in the electrolytic cell gets continuously richer in deuterium. The separation effected is usually expressed as the ratio of the proportions of hydrogen and deuterium in the gas and in the liquid, viz.

$$\alpha = (\mathrm{H/D})_{\mathrm{gas}}/(\mathrm{H/D})_{\mathrm{liquid}}.$$

The facts found in numerous investigations may be summarised as follows :—

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[64] Washburn and Urey, *Proc. Nat. Acad. Sci.*, **18**, 496, 1932; Lewis and Macdonald, *J. Chem. Physics*, **1**, 341, 1933.

(1) In the earlier investigations the separation factor was determined usually by analysing the deuterium content of the electrolyte after a considerable amount of electrolysis. It is obvious the state and purity of the electrode might change very considerably during the electrolysis, so that only rough average values were to be expected. Generally, values between 5 and 10, largely independent of the electrode material, current density and acidity of the solution were obtained.[65] Topley and Eyring [66] found $\alpha = 5\text{-}7$ for Fe, Ni, Cu, Ag, Pb, Pt, but only 2·9 for Hg and 3·4 for an active platinum electrode.

(2) Greater accuracy is obtained by analysis of the liberated gas. Using this method, Horiuti and Okamoto [67] found that the metals were divided into two groups having the following factors :—

Ni 6·7, Au 6·4, Ag 6·0, Cu 7·4, Pt 6·9, Pb (alk.) 6·8, Sn 3·1, Hg 3·1, Pb (acid) 3·0.

This has been confirmed by Walton and Wolfenden,[68] who also found that in the first group the temperature coefficient of α was large and negative, and in the second group about zero or positive.

Eucken and Bratzler [69] found that the variable factors obtained with a single metal, and very high values (10 to 17) could be obtained with many metals if they were " activated " by anodic polarisation. Mercury always has a low value of 3 to 4. In general the separation factor was lower, the higher the overvoltage. The addition of adsorbable substances which raise the overvoltage, presumably by covering part of the surface, diminishes the separation factor.

(3) At catalytically active electrodes, the gas first formed may undergo the exchange reaction

$$HD + H_2O = HDO + H_2,$$

so that the observed gas composition may not represent the primary result of the electrolytic process. The equilibrium constant of this

[65] Bell and Wolfenden *et al.*, *Proc. Roy. Soc.*, **144A**, 22, 1934 ; *J. Chem. Soc.*, 286, 1936 ; Tronstadt and Brun, *Z. Elektrochem.*, **40**, 556, 1934 ; Brawn and Dagget, *J. Chem. Physics*, **3**, 218, 1935.

[66] *Ibid.*, **2**, 217, 1934 ; *J. Amer. Chem. Soc.*, **55**, 5058, 1933.

[67] *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **28**, 231, 1936.

[68] *Trans. Faraday Soc.*, **34**, 436, 1938.

[69] *Z. physikal. Chem.*, **174A**, 273, 1936.

reaction is *ca.* 4,[70] and this is the value which the separation factor should have if the gas reaches equilibrium before leaving the electrode. Values of about this magnitude have been obtained at catalytically active electrodes, such as platinised platinum.[71]

(4) This complication is avoided in the experiments of Bowden and Kenyon,[72] and Heyrovski,[73] who made a direct comparison of the hydrogen overvoltage under similar conditions in H_2O and almost pure D_2O. The former found the difference of overvoltage at a mercury electrode to be 0·13 volts, and the slope of the $\log i - V$ curves was the same in the two cases, from which it followed that the rate of discharge of hydrogen ions was 13·8 times as great as that of deuterium ions at the same electrode potential. The latter gives 0·087 volts as the difference of overvoltage.

Various explanations of the separation have been suggested according to the author's views as to the mechanism of electrolysis. They may be classified as follows :—

(1) The significant process is the transfer of electrons from the electrode to hydrated ions in the solution, as in Gurney's theory. Bell [74] pointed out that the only significant difference between hydrogen and deuterium in this theory was the zero point energy of the hydrated ion, i.e. in the value of E_0 (p. 136). On this view it follows that [75]

$$\log \frac{i_H}{i_D} = \frac{E_0{}^H - E_0{}^D}{kT} = \frac{\Delta E}{kT}.$$

Taking ΔE as 1·4 kcals.,[76] this gives $\alpha = i_H/i_D = ca.\ 12$. Lange,[77] from the difference of hydration heat of H^+ and D^+, estimates ΔE as *ca.* 1 kcal., which gives $\alpha = ca.\ 5$.

(2) The formation of hydrogen takes place by the transfer of

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[70] Bonhoeffer and Rummel, *Z. Elektrochem.*, **40**, 469, 1934; Farkas, A. and L., *J. Chem. Physics*, **2**, 468, 1934.

[71] Farkas, A. and L., *loc. cit.; Proc. Roy. Soc.*, **146**, 623, 1934; Washburn, Smith and Fransden, *Bur. Standards. J. Res.*, **11**, 453, 1933.

[72] *Nature*, **135**, 105, 1935; Kenyon, *Diss.*, Camb., 1937.

[73] *Coll. Czech. Chem. Comm.*, **7**, 281, 1935; **9**, 207, 273, 344, 1937; *Nature*, **140**, 1022, 1937; *Chem. List.*, **31**, 440, 1937; *Chem. Reviews*, **24**, 125, 1939.

[74] *J. Chem. Physics*, **2**, 164, 1934.

[75] Butler, *Z. Elektrochem.*, **44**, 55, 1938; Bell's expression was $\Delta E/\gamma kT$, which appears to the author to be incorrect.

[76] Eyring and Sherman, *J. Chem. Physics*, **1**, 345, 1933.

[77] *Z. Elektrochem.*, **44**, 31, 1938.

protons from the ions of the solution to adsorption places on the metal (Volmer and Erdey-Grúz), where they are neutralised and desorbed as molecular hydrogen. The separation might then arise from either of the following effects :—

(*a*) The difference of the rates of transfer of protons and deutons over or through a potential barrier to the electrode surface.[78] If the barrier were of considerable height an appreciable part of the current might be contributed by protons passing *through* it at energies below the summit. In such a case the difference of permeability to the two isotopic particles would be considerable and large factors might be expected.[79] There is no experimental evidence, however, of large factors. Appleby and Ogden [80] obtained factors as high as 100, but Walton and Wolfenden were unable to confirm this.[81] Topley and Eyring [82] used the transition state method, and on the assumption that there is no tunnelling and that atoms are " quasi-free " in the transition state, found a maximum separation factor of 19.

(*b*) Differences of the rates of desorption of the various possible hydrogen molecules from the electrode, on account of the smaller zero point energy of adsorbed deuterium, or the greater moments of inertia of HD and D_2.[83]

Halpern and Gross [84] calculated that factors of 11 to 13 would arise if this were the rate-determining step. On the other hand, Okamoto, Horiuti and Hirota [85] calculate a factor of 7·1 for their " catalytic " process. Walton and Wolfenden have suggested [86] that the fact that the ratio of the discharge rates in pure H_2O and D_2O is 13·5, while the separation factor in dilute solutions of deuterium in water is only about 3, is due to the circumstance that in the former case we are comparing the rates of formation of D_2 and H_2 and in the latter the rates of HD and H_2; and on any " transition state " theory involving an interaction of two atoms,

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[78] Cf. Topley and Eyring, *J. Chem. Physics*, **2**, 217, 1934.

[79] Ogden and Bawn, *Trans. Faraday Soc.*, **30**, 432, 1934.

[80] *J. Chem. Soc.*, 163, 1936.

[81] *Ibid.*, 1677, 1937.

[82] *J. Chem. Physics*, **2**, 217, 1934.

[83] Eyring and Sherman, *ibid.*, **1**, 345, 1933.

[84] *Ibid.*, **3**, 452, 1935.

[85] *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **29**, 223, 1936.

[86] *Loc. cit.*, ref. 68.

the latter ratio will be equal to the square root of the former. The separation factor in the latter case should be $\sqrt{13\cdot5} = 3\cdot7$, which is close to that observed.

The Catalysed Exchange Reaction $HD + H_2O = H_2 + HDO$. It was first shown by Polanyi and Horiuti [87] that this reaction is catalysed by platinum black and similar materials, and since then it has been extensively studied with finely divided catalysts and at electrodes by these authors and others,[88] for it was realised that its mechanism must be intimately connected with that of the reversible hydrogen electrode, since in the reaction molecular hydrogen passes into solution and the rate must be that of the slowest of the interchanges by which this occurs. The following facts have been established :—

(1) It is a first order reaction with respect to the partial pressure of HD, and the rate of exchange varies inversely with the pressure of the gas, according to $k \propto p^{1/n}$, where n varies from 0·6 to 0·85.
(2) The rate is somewhat greater in acid than in alkaline solutions.
(3) The activation energy of the process is 5 to 8 kcals.
(4) The exchange is inhibited by the cathodic polarisation of the electrode, but anodic polarisation does not affect the rate until the oxidation of the electrode material begins.[89]

Eley and Polanyi, and Farkas, A. and L., also studied [90] the *para*-hydrogen conversion, and Calvin and Dyas [91] the reaction $H_2 + D_2 = 2HD$ at similar catalysts. These reactions involve only the adsorption of the hydrogen and its subsequent desorption, and it was found that

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[87] *Mem. Proc. Manchester Lit. Phil. Soc.*, **78**, 47, 1934.

[88] Eley and Polanyi, *Trans. Faraday Soc.*, **32**, 1388, 1936; Farkas, A. and L., *ibid.*, **30**, 1671, 1934; **32**, 922, 1936; **33**, 678, 1937; Bonhoeffer and Rummel, *Naturwiss.*, **22**, 45, 1934.

[89] Calvin, *Trans. Faraday Soc.*, **32**, 1428, 1936 (the reaction employed was $D_2 + H_2O \rightarrow HD + HDO$).

[90] *Loc. cit.*

[91] *Trans. Faraday Soc.*, **33**, 1492, 1937.

(5) The conversion rate was somewhat greater (2 to 3 times) than the rate of the exchange reaction under similar circumstances.

(6) Calvin and Dyas reported that the $H_2 + D_2$ reaction is accelerated by cathodic polarisation of the catalyst.

From (1) and (3) Eley and Polanyi concluded that the slower step was the adsorption process, and since this rate is influenced by the nature and acidity of the liquid and by the polarisation of the electrode, it has been suggested that the metal-hydrogen binding (M . . . H) is electrically unsymmetrical or polar, so that the rates of adsorption and solution would be influenced by the electrical conditions at the interface. In order to account for (6) also, Calvin and Dyas suggested that both molecularly and atomically adsorbed hydrogen are polar, and that when the catalyst is cathodically polarised the reaction

$$M - H_2 + M \rightarrow 2M - H$$

is accelerated, while the ionisation reaction, which may be represented as

$$M - H - H_2O \rightarrow M^- + H_2O^+,$$

on which the exchange depends, is inhibited. A. and L. Farkas[92] suggested that the effects (4) could be explained by a change of the water content of the adsorption layer with increasing cathodic polarisation.

Butler[93] showed that the phenomena (4) could easily be explained on the basis of his theory of the reversible hydrogen electrode. It is shown that under certain circumstances the exchange rate is determined by the rate of adsorption of HD, which is proportional to (1) the pressure of HD in the gas; (2) the square of the fraction of the surface of the catalyst which is unoccupied by adsorbed hydrogen, i.e. $(1 - x)^2$, where x is the fraction of surface covered by adsorbed hydrogen.

The effect of polarising the electrode under these circumstances is as follows. The exchange rate is unaffected by polarisation so

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[92] *Trans. Faraday Soc.*, **33**, 678, 1937.

[93] *Z. Elektrochem.*, **44**, 55, 1938.

long as the current is so small that x remains unchanged. When the currents passed are sufficiently great to modify the adsorptive equilibrium, we see that (1) x is decreased by anodic polarisation, but if x is small, $1 - x$ cannot change very much and then anodic polarisation will not influence the rate of exchange ; (2) x is increased by cathodic polarisation and the rate of exchange is then diminished. This mechanism thus appears to be capable of accounting for the effects of polarisation (4), but not that reported under (6).

Hirota and Horiuti [94] found that the catalytic activities of different metals for the exchange reaction were in the order

$$\mathrm{Pt} > \mathrm{Ni} > \mathrm{Fe} > \mathrm{Cu} > \mathrm{Au} > \mathrm{Ag}.$$

The activity of the last three is, however, so small as to be observable only at higher temperatures. This order is the same as that found by Bonhoeffer [95] for the rates of recombination of atomic hydrogen at surfaces of the metals, and on the whole is the reverse of the order of the overvoltages. It is obvious that the exchange reaction requires at least some degree of reversibility at the electrode. K. Wirtz [96] found that at copper, which has the lowest overvoltage of irreversible electrodes, no exchange occurs at overvoltages between 0·1 and 0·2 volts.

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[94] *Sci. Pap. I.P.C.R. Tokyo,* **30,** 151, 1936.

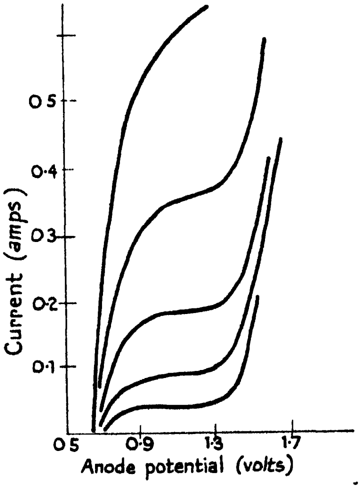
[95] *Z. physikal. Chem.,* **118,** 199, 1924.

[96] *Ibid.,* **36**B, 435, 1937.

CHAPTER VII

CONCENTRATION POLARISATION AND THE DEPOSITION OF METALS

Concentration Polarisation. Changes of concentration may occur in the vicinity of electrodes when a dissolved substance is removed in an electrolytic process faster than it can reach the electrode by diffusion, or when it is formed faster than it can diffuse away from the electrode. Changes of the electrode potential produced by such changes of concentration are said to be the result of concentration polarisation. This phenomenon frequently occurs in electrolysis, especially when the substance taking part in the electrolytic process is present at a comparatively small concentration, and may obscure the primary process so that it is desirable to be able to recognise its characteristics.



VII. 1.—Potential-current curves for anodic oxidation of ferrous chloride solutions. (Wilson and Youtz.)

When an electrode at which a reversible oxidation potential, e.g. the ferrous-ferric potential, is established is made the cathode, electrolysis occurs and reduction of the ferric salt takes place with small currents at potentials which are not greatly different from the reversible potential. If the electrolysing current is gradually increased a point is reached (Fig. 1) at which a transition occurs, the potential rising to near the potential required for the liberation of hydrogen. A similar phenomenon is observed if the electrode is made the anode and, in fact, very frequently occurs in the electrolysis of solutions. The current at which the transition occurs evidently represents the maximum rate at which the depolariser can reach the electrode by diffusion. When this limit is exceeded some other discharge process, such as the liberation of hydrogen at cathodes and the liberation of oxygen at anodes, must come into operation. The transition current is approximately proportional to the concentration of the depolariser.[1] It is greatly increased by stirring the electrolyte and to some extent by increase of temperature.[2]

Nernst[3] applied to electrolytic processes the diffusion layer theory previously put forward for heterogeneous reactions, such as the rate of solution of solids by Noyes and Whitney.[4] It is supposed that at the electrode surface there is a diffusion layer of thickness δ, outside which the concentration is that of the bulk of the solution. In order to simplify the treatment it is supposed the concentration gradient of the depolariser (dc/dx) is constant throughout the diffusion layer. Then if c_0 is the concentration in the bulk of the solution and c_e the concentration at the surface of the electrode, the concentration gradient is $(c_0 - c_e)/\delta$, and the rate of diffusion for an area of 1 cm.^{2} is

$$\frac{D(c_0 - c_e)}{\delta}.$$

where D is the diffusion coefficient. It is obvious that this cannot be greater than its value when $c_e = 0$; hence the maximum rate of diffusion is Dc_0/δ. This is to be identified with the rate of removal of the depolariser by the transition current. If i is the current in amps., and $\mathbf{F}$ is Faraday's constant (96490) coulombs and n the number of Faradays required for the electrolysis of 1 mol. of the depolariser, the rate of removal of the depolariser in mols./sec. is $i/n\mathbf{F}$. Hence the transition current i_0 is

$$\frac{i_0}{n\mathbf{F}} = \frac{Dc_0}{\delta}.$$

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[1] Wilson and Youtz, *J. Ind. and Eng. Chem.*, **15**, 603, 1923; Goldschmidt, *Z. f. Elektrochem.*, **7**, 267, 1900; Nernst and Merriam, *Z. physikal. Chem.*, **53**, 235, 1905.

[2] Glasstone and Reynolds, *Trans. Faraday Soc.*, **29**, 399, 1933.

[3] *Z. physikal. Chem.*, **47**, 52, 1904.

[4] *Ibid.*, **23**, 689, 1897.

If c_0 is expressed in mols./c.c. and D in cm.^{2}/sec., then δ is in cm. (Dc_0/δ = mols./cm.^{2} × secs.).

This calculation assumes that the depolariser reaches the electrode solely by diffusion. If it is an ion which takes part in the electrolytic transport through the solution, let $\alpha i_0/\mathbf{F}$ be the number of equivalents of the ion so transported through the diffusion layer per second. α is the transport number of the ion; and if z is the number of equivalents in 1 mol., the total rate at which the substance reaches the electrode, in the limiting case, is

$$\frac{Dc_0}{\delta} + \frac{\alpha i_0}{zF}, \text{ which is equal to } i_0/nF,$$

and therefore,
$$\frac{i_0}{nF}\left(1 - \frac{n\alpha}{z}\right) = \frac{Dc_0}{\delta}.$$

When the ion is completely discharged at the electrode $n = z$.[5]

Wilson and Youtz[1] found that in the oxidation of ferrous ions at 27°, the value of δ so found from i_0 was about 0·05 cm. and independent of the concentration. For reasonably small molecules, $D = ca.\ 10^{-5}$, so that with this value of δ,

$$i_0 = \mathbf{F} \,.\, Dc_0/\delta = 10^5 \,.\, 10^{-5}\, c_0/0{\cdot}05 = 20c_0 \text{ amps.},$$

where c_0 is the concentration in mols./c.c. When the solution is stirred, δ decreases and under conditions of violent stirring reaches a thickness of 10^{-3} cms.[6] These are of the same order as the values of δ determined under similar conditions from the dissolution of solids.[7]

The transition current is not, however, a very definite quantity for it depends on the interval which elapses between the starting of the current and the time at which the observation of the potential is made. This is evident if the change of potential with time is examined.[8] Fig. 2 shows some typical curves obtained for the

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[5] For theory of limiting currents at dropping mercury electrode and polarograph, see MacGillivry and Rideal, *Rec. trav. chim.*, **56**, 1013, 1937; MacGillivry, *ibid.*, **57**, 33, 1938; see also Lingane and Kolthoff, *J. Amer. Chem. Soc.*, **61**, 825, 976, 1045, 1939.

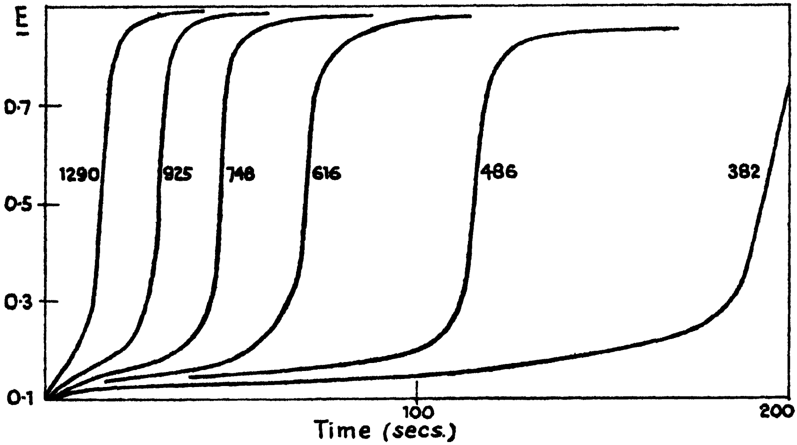
[6] Nernst and Merriam, *loc. cit.*; cf. Eucken, *Z. Elektrochem.*, **38**, 341, 1932. For photographic demonstration of diffusion layer, see Antweiler, *ibid.*, **43**, 596, 1937; **44**, 719, 831, 1938.

[7] Brunner, *Z. physikal. Chem.*, **47**, 56, 1904.

[8] Butler and Armstrong, *Proc. Roy. Soc.*, **139A**, 406, 1933.

cathodic reduction of solutions of quinhydrone. The potential remains near the reversible electrode potential until all the depolariser near the electrode has been used up, when a transition occurs and the potential rises to the region of hydrogen liberation. The time interval between the start of the current and the transition is called the transition time.

The transition time increases rapidly as the current is decreased and it can easily be seen that if the potential is measured at a constant time interval (e.g. 100 secs.) potentials on the first stage of the curves are obtained with currents having transition times > 100 secs., while potentials on the final stage are obtained with currents having transition times < 100 secs. In fact the " transition current " of the first stage is the current which has a transition time equal to the interval between the starting of the current and the observation of the potential, which is roughly the same in a series of experiments.



VII. 2.—Variation of cathode potential with time in cathodic reduction of 0·05 per cent. quinhydrone solution. Numbers are currents in amps. × 10^{-6}, for electrode of 4·3 cm.^{2} (Armstrong and Butler.)

Sand,[9] following Weber,[10] applied Fick's diffusion equation,

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2},$$

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[9] *Phil. Mag.*, **1**, 45, 1900; *Z. physikal. Chem.*, **35**, 641, 1900; *Trans. Faraday Soc*, **1**, 1, 1905.

[10] *Wied. Ann.*, **7**, 536, 1879.

($c =$ concentration at a distance x from electrode at time t), to determine the concentration changes in the vicinity of electrodes in the course of electrolysis. This can be solved, giving c as a function of x and t, on the assumption that the rate of diffusion of the depolariser at the electrode surface ($x = 0$) is equal to the rate at which the depolariser is used up in the electrolytic process, i.e.

$$D\left(\frac{dc}{dx}\right)_{x=0} = \frac{i}{n\mathbf{F}}.$$

This implies that the rate of change of the concentration at the surface is small compared with the rate of diffusion, and the expression obtained is therefore only applicable to small currents. The result, for $x = 0$ and neglecting ionic migration, can be approximated to

$$c_e = c - k\frac{i}{n\mathbf{F}}\sqrt{\frac{t}{D}}.$$

If the transition time, $t = \tau$, is identified with the time in which c_e becomes equal to zero, we have

$$\tau = k'(c/i)^2.$$

A more elaborate treatment, with similar assumptions, was given by Rosebrugh and Lash Miller,[11] who give the following expression for the concentration at the electrode at the time t for the case in which ionic transport may be neglected :

$$\frac{D(c_e - c_0)}{\delta} = \frac{i}{nF}(1 - \zeta),$$

where
$$\xi = \frac{8}{\pi^2}\sum_{m=1,3,5}\frac{1}{m^2}e^{-m^2\alpha t},$$

where $\alpha = \pi^2 D/4\delta^2$ and $m =$ odd integers 1, 3, 5, etc.,

or
$$\frac{c_e}{c_0} = 1 - \frac{i}{i_0},$$

where $i_0 = n\mathbf{F}Dc_0/\delta$ is the rate of diffusion when $c_e = 0$.

Similarly, for the case in which the concentration of the depolariser is greater at the electrode than in the solution we have

$$\frac{c_e}{c_0} = 1 + \frac{i}{i_0}.$$

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[11] *J. Physical Chem.*, **14**, 816, 1910.

Agar and Bowden[12] have used these equations to determine the displacement of the potential during the passage of current, writing

$$\Delta V = \frac{RT}{n\mathbf{F}} \log \left(\frac{c_e}{c_0}\right).$$

For *small values* of αt this can be reduced to

$$c_e - c_0 = \frac{i}{nF} \cdot \frac{\delta}{D} \cdot \frac{4}{\pi^{3/2}} \sqrt{\alpha t} \text{ (approx.)}$$

$$= 1{\cdot}129 \frac{i}{nF} \sqrt{\frac{t}{D}},$$

which is the same as Sand's equation; and it would appear that the latter is only valid for small values of t.*

For large values of t, ξ approaches zero, and therefore the steady state reached after a long time is represented (in the case where the depolariser is used up at the electrode) by

$$\frac{D(c_0 - c_e)}{\delta} = \frac{i}{nF}.$$

We have then $$\Delta V = \frac{RT}{n\mathbf{F}} \log \left(1 \pm \frac{i}{i_0}\right).$$

The rate of change of the concentration polarisation with time is given by using the expression

$$c_e/c_0 = 1 - (1 - \xi)(i/i_0),$$

and $$\Delta V = \frac{RT}{n\mathbf{F}} \log \frac{c_e}{c_0} = \frac{RT}{n\mathbf{F}} \log \left\{1 - (1 - \xi)\frac{i}{i_0}\right\}.$$

Agar and Bowden also show that the resistance of the diffusion layer gives rise to an ohmic potential drop which is normally

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[12] *Proc. Roy. Soc.*, **169A**, 206, 1938.

* For larger values of αt, Rosebrugh and Miller gave the approximation

$$c_e - c_0 = \frac{i}{n\mathbf{F}} \cdot \frac{\delta}{D}\left\{1 - \frac{8}{\pi^2} e^{-\alpha t}\right\},$$

i.e. $c_e = 0$, when $$-\frac{c_0 n\mathbf{F}D}{i\delta} = 1 - \frac{8}{\pi^2} e^{-\alpha t},$$

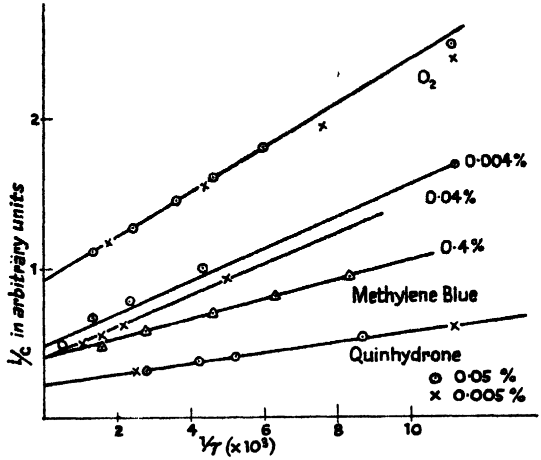
or writing $-i_0 = c_0 n\mathbf{F}D/\delta$ for the limiting current, we have

$$1 - i_0/i = \frac{8}{\pi^2} e^{-\alpha t},$$

or $$\log (1 - i_0/i) = \log (8/\pi^2) - \alpha t.$$

This indicates that $t \rightarrow \infty$ when $i = i_0$.

included in the measured electrode potential and which is of the same order and varies with the current in the same way as the concentration polarisation proper.



VII. 3.—Relation between current and transition time for cathodic processes. Upper line, oxygen in acid (circles) and in alkaline solution (crosses). Lower lines, methylene blue and quinhydrone at marked concentrations.

In Sand's experiments[13] on the deposition of metals, and Karnoglanoff's[14] on the oxidation of ferrous ions and the reduction of ferric ions, approximate agreement with Sand's formula for transition time was found. This formula, however, indicates that an infinite value of τ is not reached until i approaches zero. Butler and Armstrong[8] found that for the reduction of methylene blue and quinone solutions and the oxidation of hydroquinone solutions, the transition time s appeared to tend to infinity as the current approached a limiting value i_0, below which the transition does not take place. For the longer transition times the data are in good agreement with the equation

$$(i - i_0)\tau = \alpha,$$

where i_0 is the limiting current and α a constant for a given solution. Fig. 3 shows i plotted against $1/\tau$ in a number of cases.[*] A

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[13] Sand and Cottrell, *Z. physikal. Chem.*, **42**, 385, 1903.

[14] *Z. Elektrochem.*, **12**, 5, 1906.

[*] It is difficult to determine, with the available data, whether this equation or $(i - i_0)\sqrt{\tau} = \alpha$ is more in accordance with the facts. Probably $(i - i_0)\,\tau = \alpha$ holds better for the longer transition times and $(i - i_0)\sqrt{\tau} = \alpha$ is better for the shorter times. For the cathode reduction of quinhydrone solutions the latter fits all the data very well, but very long times were not observed. Further observations are required to determine which is the limiting case with small currents. Occasionally i_0 is small and the second relation then approximates to Sand's equation.

relation of this kind has also been found under similar circumstances for the cathodic reduction of oxygen,[15] nitrobenzene[16] and the anodic solution of gold in hydrochloric acid.[17] Both i_0 and α are approximately proportional to the concentration.

Butler and Armstrong[18] suggested the following explanation of this relation. Suppose that initially there is an amount q_o of the depolariser (measured as the quantity of electricity required to reduce it) within a certain short distance of the electrode. The amount after the time t will be equal to the original amount, less the amount removed in the electrolytic process and plus the amount which has diffused into this region from the bulk of the solution, and the latter may be expected to be a function of the concentration in the bulk of the solution and of the time t. Thus we can write

$$q_t = q_o - it + f(c, t).$$

It is now supposed that in the initial stages of the electrolysis a concentration gradient is established, through which the depolariser then diffuses at a constant rate. Then $f(c, t)$ may be written as

$$f(c, t) = \alpha' + \beta t,$$

where α' is the amount of diffusion in the initial stages and β the ultimate constant rate of diffusion. Therefore

$$q_t = q_o + \alpha' - (i - \beta)t.$$

The transition time τ is identified with the time required to reduce q_t to zero, and is therefore given by

$$(i - \beta)\tau = q + \alpha' = \alpha,$$

i.e. the limiting current i_o is the constant diffusion rate β. Both β and α would be expected to be proportional to the concentration.

The Electrolytic Deposition of Metals. The experiments of Le Blanc[19] showed that the deposition and solution of metals usually takes place quite near to the reversible potential of the metal in the same solution. At higher current densities some displacement of the electrode potential from the reversible value occurs, but the investigation of the current-voltage relationship presents difficulties which do not occur, or are less acute in the observation of overvoltages of gas evolution. These are, (1) the

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[15] *Proc. Roy. Soc.*, 143A, 89, 1933.

[16] *Trans. Faraday Soc.*, 32, 989, 1936.

[17] *Ibid.*, 30, 1173, 1934.

[18] *Loc. cit.*, ref. 8.

[19] Abh. Bunsen-Ges., 1910, No. 3.

area of the electrode may change continuously during the deposition or solution of a metal; (2) concentration polarisation, i.e. changes in the concentration of ions near the electrode, readily occurs when the current is continued; (3) when the displacement of the potential is small it is not easily distinguished from the ohmic fall of potential in the solution between the tip of the reference electrode (see Chap. VI, Fig. 1) and the electrode under investigation. The latter can be diminished by bringing the tip very close to the metal surface, or by measuring the potential during a very short intermission of the polarising current.[20]

Lakhani[21] found that with a mercury electrode in mercurous nitrate solutions the displacement of the potential varied with the distance between the tip and the mercury surface, and could be made to disappear entirely, within the range of currents which could be passed through the apparatus, when the tip was practically in contact with the mercury, if the solution was stirred to prevent concentration polarisation. In many cases, however, it appears that a real displacement of the potential (or overvoltage for metal deposition) occurs. This is particularly large for iron, cobalt and nickel.[22] It is possible that the real displacement (apart from concentration polarisation) is small with soft metals with which the reversible potential is easily established, and large with hard metals with which a reversible potential can only with difficulty be realised.

The mechanism of the electrolytic deposition of metals has been discussed by numerous workers,[23] whose views fall under two headings: (1) the deposition occurs in two stages, the metal ion first being discharged and then finding its place in the metal lattice; (2) the processes of neutralisation and deposition are simultaneous. In (1) it is supposed that the metal atoms formed are at first in an intermediate state between the original state and that which they will eventually take up in the lattice. Le Blanc[24] thought the first step to be the dehydration of the ion, which might be a slow process

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[20] Cf. Glasstone, *J. Chem. Soc.*, 250, 1924. [21] *Thesis*, Edinburgh.

[22] Schweitzer, *Z. Elektrochem.*, 15, 602, 1909; Schildbach, *ibid.*, 16, 967, 1910; Glasstone, *J. Chem. Soc.*, 2887, 1926; Foerster, Abh. Bunsen-Ges., No. 2, 1911.

[23] For general review, see F. Müller, *Z. Elektrochem.*, 43, 812, 1937; also discussion on Structure of Metal Coatings, *Trans. Faraday Soc.*, 31, 1043 *seq.*, 1935.

[24] *Loc. cit.*; *Trans. Faraday Soc.*, 9, 251, 1914.

giving rise to an overvoltage. Hughes[25] assumed by analogy with other kinds of crystallisation that a metal atom concentration occurs at the cathode surface, with more or less supersaturation, and attempted to correlate the degree of supersaturation in the intermediate state with the size of the crystals formed. A similar idea was elaborated by Aten and Boorlaage.[26] On the other hand, Blum and Rawdon,[27] and also Fröhlich and Clark[28] regarded the deposition as a single simultaneous process, the ion being discharged at the points of the cathode surface at which the lowest discharge potential is required. Volmer[29] thought that the deposition would take place layer by layer, and until any layer is complete a certain proportion of the ions will be in an "intermediate state," which is not their final lattice positions. Brandes[30] extended this and from the temperature coefficient of the (linear) i-V curves made an estimate of the activation energy of the diffusion process along the surface, by which atoms were supposed to reach their final lattice positions. Hunt, who gives a very good review of the situation,[31] suggests alternatively[32] that the ions accumulate in the double layer until a complete layer of the lattice can be formed.[33]

Erdey-Grúz and Volmer[34] studied the deposition of Zn, Cd, Ni, Pb, Cu and Ag from their salt solutions and found that at low current densities the displacement of the potential was proportional to the current, but with greater currents the latter increases more rapidly and tends to the relation $\log i \propto V$. Lakhani obtained similar results[35] with both the anodic and cathodic processes at silver and zinc electrodes, the magnitude of the displacement being about the same in either direction.

Erdey-Grúz and Volmer discuss the mechanism of the deposition process and state the following possibilities :—

(1) If the discharge of cations is the rate-determining process, the relation between i and V will be of the form

$$V = a - b \log i \qquad . \quad . \quad . \quad (\alpha)$$

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[25] D.S.I.R., *Bull.* No. 6, 1922.

[26] *Rec. trav. chim.*, **39**, 720, 1920.

[27] *Trans. Amer. Elect. Soc.*, **44**, 397, 1923.

[28] *Z. Elektrochem.*, **31**, 649, 1925.

[29] *Z. physikal. Chem.*, **139**, 597, 1928.

[30] *Ibid.*, **142**, 97, 1929.

[31] *J. Physical Chem.*, **36**, 1006, 2259, 1932.

[32] *Trans. Amer. Elect. Soc.*, **65**, 95, 413, 1934.

[33] Cf. Hoekstra, *Rec. trav. chim.*, **50**, 339, 1931.

[34] *Z. physikal. Chem.*, **157**, 165, 182, 1931.

[35] *Loc. cit.*, ref. 21.

(2) If, however, the discharge process is very rapid, the relation will depend on the method and growth of the metal crystals. They suppose that in this case the ions would pass over the double layer into a state intermediate between that of the hydrated ion and the crystalline metal, in which they would remain until they can find positions where they can attach themselves to the growing metal. There are then two possibilities :—

(*a*) The rate of growth is determined by the abundance of crystallisation nuclei. The potential will then be determined by the degree of supersaturation necessary in the intermediate state for the formation of crystallisation nuclei. From this they obtain the relations

$$\log i \propto 1/V, \text{ for two-dimensional nuclei} \quad . \quad . \quad (\beta)$$

$$\log i \propto 1/V^2, \text{ for three-dimensional nuclei} \quad . \quad (\gamma)$$

(*b*) If growth takes place at the edges of incomplete layers, and the transport of ions over the surface is the determining factor, then as shown by Brandes,[36] the relation should be $i \propto V$ (δ).

The experiments mentioned caused the authors to decide in favour of case 2(*b*). Erdey-Grúz [37] has, however, more recently studied the deposition of silver from various complex ion solutions and obtained the relations α, β, δ in different cases, and therefore he concluded that the rate determining step varies from case to case. Experiments have also been made on the deposition of zinc [38] and copper [39] on the respective metals, in which expressions of type (1) were obtained.

The conclusion (1) is, however, not necessarily correct. When a reversible potential is established between a metal and its ions in solution, there must be a simultaneous transfer of ions from the solution to the metal and *vice versa*, the reversible potential being that which is required to effect equality of the rates of transfer in the two directions. If the potential difference is varied, e.g. making the metal more negative, the rate of transfer of ions from the solution to the metal surface will be increased and that in the reverse

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[36] *Loc. cit.*, ref. 30.

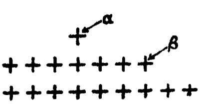
[37] *Z. physikal. Chem.*, **172**, 157, 1935.

[38] Essen and Levin, *J. Gen. Chem. Russ.*, **6**, 1539, 1936.

[39] Essin, Antropov and Levin, *Acta Physicochimica, U.R.S.S.*, **6**, 447, 1937; *J. Gen. Chem. Russ.*, **7**, 2719, 1937.

direction decreased, and the result is (see p. 140) a *linear* relation between the current and the electrode potential when the current is not great enough to disturb the reversible equilibrium very much.[40] The range of currents over which a linear relation may be expected to hold is therefore determined by the rates of transfer of ions across the double layer at the reversible potential. With currents which are large compared with the rates of transfer at the reversible potential, the relation becomes an exponential one of type α.

However, only liquid and soft metals such as sodium or lead actually give rise to well-defined potentials. With hard metals the reversible potential has usually been measured on a finely divided material and massive pieces of the metal do not usually have exactly the reversible potential, at least without careful preparation. At such electrodes the transfer rate of the reversible potential may be very small and the linear relation may be practically absent. At such electrodes the rate of deposition of metal atoms may well be influenced by the circumstances of crystalline growth.



VII. 4.

At the surface of a hard metal the potential energy probably varies from point to point. Isolated atoms (α) on the surface of a completed plane will have a higher energy than those (β) which are partly surrounded by others at the edge of an incomplete plane (Fig. 4). At a given V, deposition will take place preferentially at the positions of lowest energy available, i.e. at the edge of growing layers rather than haphazardly over the surface. An increase of V may make a great range of points at which deposition could occur accessible to the ions, and the form of the $i - V$ relation under these circumstances would depend on the numbers of deposition sites having the given energies.

The deposition of a metal on an electrode of a different kind has been studied by Erdey-Grúz with Volmer[41] and Wick.[42] They found that in some cases, e.g. silver on platinum, mercury on platinum and tantalum, an initial deposition potential considerably more negative than the reversible potential was required, but

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[40] Butler, *Trans. Faraday Soc.*, **28**, 379, 1932.

[41] *Z. physikal. Chem.*, **157**, 182, 1931.

[42] *Ibid.*, **162**, 63, 1932.

in others, e.g. mercury on gold, this was not the case. The current-potential curves show characteristic kinks. These authors interpret their observations as meaning that in some cases a considerable degree of supersaturation is required to start the formation of crystallisation nuclei on foreign surfaces. Samartzev and Evstropov [43] made similar observations and Essin, Antropov and Levin [44] observed a similar effect in the deposition of copper on copper.

It is well known that metals are deposited in a smooth and fine-grained state from solutions of complex ions, e.g. cyanides, and this is made use of in electroplating. The cause of the phenomenon is not well understood. Kohlschutter [45] thought that insoluble cyanides were deposited on the electrode and prevented the growth of the crystals. Other authors have thought that the decomposition of the complex ion was a necessary preliminary to the deposition, and the minute concentration of simple ions favoured the formation of small crystals. Under these conditions a considerable displacement of the potential may occur, but Glasstone [46] showed that in the case of silver in argenticyanide solutions, this is due almost entirely to concentration effects. This is in agreement with more recent work on the deposition of zinc [47] and cadmium [48] from cyanide solutions.

The deposition of metals on mercury has been very extensively studied. Heyrovský used a dropping mercury electrode in which the electrode surface is being continuously renewed.[49] He invented an apparatus called a polarograph for automatically recording the current-potential curves. This has been used for the study of not only metal deposition, but also for electrolytic reductions, hydrogen overvoltage, etc. The number of published papers is so large it is impossible to refer to them here, but reference can be made to excellent summaries in *Chemical Reviews*.[50] The cathode ray

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[43] *J. Phys. Chem. Russ.*, **5**, 854, 1934; cf. Obrutscheva, *ibid.*, **11**, 473, 1938; *Acta Physicochimica, U.R.S.S.*, **8**, 679, 1938; cf. Abramson, *Bull. Acad. Sci., U.R.S.S., Ser. Chim.*, 1197, 1938.

[44] *Acta Physicochimica, U.R.S.S.*, **6**, 447, 1937.

[45] *Z. Elektrochem.*, **19**, 181, 1913.

[46] *J. Chem. Soc.*, 690, 1929.

[47] Essin and Alfimeeva, *J. Phys. Chem. Russ.*, **8**, 137, 1936.

[48] Essin and Beklemischeva, *J. Gen. Chem. Russ.*, **6**, 1602, 1936.

[49] *Phil. Mag.*, **45**, 303, 1923.

[50] *Ibid.*, **24**, 125, 1939.

oscillograph has also been used for the rapid recording of these curves.[51] Since metals dissolve in the mercury, giving amalgams, they are deposited at more positive potentials than at solid electrodes, and a separation can sometimes be observed which is impossible at solid cathodes. The deposition of alkali metals at a stationary or stirred mercury cathode has been studied by Essin, Loschkarev and Sofcysky,[52] who conclude that the polarisation observed is probably due to the hindered diffusion of the metal into the mercury.

Dissolution of Metals in Acids. The dissolution of impure metals in acids, etc., which is of great importance in connection with corrosion, has been much studied and usually interpreted in terms of the theory of local galvanic elements. For example, if zinc contains fragments of a more noble metal, when immersed in a liquid a galvanic cell or couple is formed, of which the zinc forms the negative pole. The zinc therefore passes into solution, and hydrogen is formed at the relatively positive noble metal. For this work reference may be made to books on corrosion.[53]

Not much information is available about the solution of undoubtedly pure metals. In strong acids the velocity of solution is often so rapid that the observed rate is the rate of diffusion of hydrogen ions to the surface. The reactions between the metals and dissolved halogens are similar. van Name[54] studied the reaction between numerous metals and iodine and found that at a given temperature mercury, cadmium, zinc, copper and silver react at practically the same rate, and the temperature coefficient is that to be expected for a diffusion process (activation energy = *ca.* 4000 cals.). On the other hand, the rates of solution of some metals are not entirely determined by the diffusion rate. For example, Centnerszwer found that cadmium and tin dissolve in hydrochloric acid more slowly than zinc by a factor of 10^3, and the rate is proportional to a high order of the hydrogen-ion concentration.[55]

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[51] Matheson and Nichols, *Trans. Amer. Elect. Soc.*, **73**, 193, 1938.

[52] *Acta Physicochimica*, **6**, 447, 1937. For discharge of NH_4^+ ions, see Loschkarev and Essin, *J. Gen. Chem. Russ.*, **8**, 510, 1938.

[53] E.g. U. R. Evans, *Metallic Corrosion : Passivity and Protection* (E. Arnold).

[54] *J. Amer. Chem. Soc.*, **38**, 253, 1916 ; *Amer. J. Sci.*, **32**, 207, 1911 ; **36**, 543, 1913 ; **42**, 301, 1916 ; **43**, 453, 1917.

[55] *Z. physikal. Chem.*, **137**, 352, 1928 ; **141**, 167, 1929 ; **161**, 124, 1932 ; **167**, 221, 1934 ; *Z. Elektrochem.*, **37**, 598, 1931.

These observations have been interpreted in terms of a theory in which one of the factors determining the rate is the adsorption of hydrogen ions.[56]

Kilpatrick and Rushton [57] studied the solution of magnesium in solutions containing weak acids and found specific rate constants (distinct from the effect of the hydrogen-ion concentration in equilibrium with the acid) by the undissociated acid molecules. Brönsted and McCane [58] studied the solution of sodium from sodium amalgams in various buffer solutions containing sodium dehydrogen phosphate, glycocoll, and phenol. They also found specific effects by the individual acids, similar to those observed in general acid catalysis, and they conclude that the rate determining step in the reaction is the transfer of an electron from the metal to a molecule of the acid. The rate in solutions of strong acids would be so great that diffusion would be the determining factor.

The rate was also proportional to the square root of the sodium concentration. Hammett and Lorch [59] suggested that this means that the potential difference between the metal and solution is determined by the sodium concentration and the transfer of electrons then takes place at the normal rate (as in electrolysis) for the potential difference.

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[56] Centnerszwer and Hellier, *J. Chim. Phys.*, **34**, 217, 1937.

[57] *J. Physical Chem.*, **34**, 2180, 1930.

[58] *J. Amer. Chem. Soc.*, **53**, 3624, 1931.

[59] *Ibid.*, **54**, 2128, 1932.

CHAPTER VIII

SOME ELECTRODE PROCESSES

The Adsorption of Oxygen at Anodes. The phenomena which occur at platinum electrodes when they are forced with comparatively large currents to pass from the region of (cathodic) potentials at which hydrogen evolution occurs to the (anodic) region at which oxygen is liberated, and *vice versa*, was first studied by Bowden.[1] He found an almost linear change of potential between these regions requiring about 3×10^{-3} coulombs in either direction. In addition " arrests " were observed, i.e. the potential remained constant for a time (1) in the anodic curve at active electrodes near the reversible hydrogen potential, (2) in the cathodic curve at a potential which depended on whether the solution was saturated with hydrogen or oxygen. The former was ascribed to depolarisation by hydrogen and the latter to the reduction of a platinum oxide formed at the anode. The constant quantity required for the linear changes was attributed to the removal in the anodic process of a layer of adsorbed hydrogen and its replacement by adsorbed oxygen on the electrode, and *vice versa*.

Butler and Armstrong studied the behaviour of platinum electrodes under similar circumstances in greater detail.[2] The main features observed are shown in Fig. 1. The potential of a platinum electrode in an aqueous solution containing oxygen is usually $+ 0{\cdot}8$ to $+ 0{\cdot}9$ volts, with reference to a hydrogen electrode in the same solution. When the electrode is polarised anodically, the potential falls comparatively slowly (curve I) and about 1×10^{-3} coulombs (per cm.^{2})[3] must be passed before the constant value is

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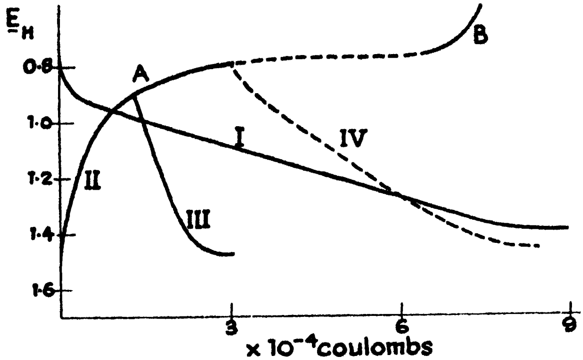
[1] *Proc. Roy. Soc.*, 125A, 446, 1929.

[2] *Ibid.*, 137A, 604, 1932; Armstrong, Himsworth and Butler, *ibid.*, 143A, 89, 1933.

[3] The first anodic curve is often appreciably slower than this. Probably the additional amount of electricity is used in removing impurities on the surface.

reached at which oxygen is continuously liberated. If the current is now stopped the potential rises slowly (towards more negative values) as the overvoltage decays, and if the current is started again *cathodically*, curve II is obtained. The potential rises rapidly and at first linearly to about $E_h = +0{\cdot}7$ volts (or a somewhat more negative potential if the current is large) and then remains nearly constant for some time between A and B. Finally it begins to rise again, and if the current is not stopped it ultimately reaches the value at which hydrogen is liberated. If the current is reversed again (making it anodic) at the point B, curve I is obtained again; but if the reversal is made before the beginning of the arrest AB, the



VIII. 1.—Behaviour of a 1 cm.² platinum electrode in dilute H_2SO_4; current, $3{\cdot}1 \times 10^{-6}$ amps. (Armstrong, Himsworth and Butler.)

potential falls much more rapidly, but still linearly to the oxygen liberation potential (curve III). Between A and B, curves intermediate in slope, such as curve IV, are obtained. These curves can be observed with quite small currents, and then the changes take place comparatively slowly. The quantity of electricity passed during the linear part of curve I is usually about 10^{-3} coulombs for a bright platinum electrode having an apparent area of 1 cm.², and is independent of the current density. This amount is sufficient for the liberation of 10^{-8} equivalents or 3×10^{15} atoms of oxygen. It is estimated that at a platinum surface there are $1{\cdot}2 \times 10^{15}$ atoms/cm.², so that if the real area of the electrode is three times its apparent area, this quantity is sufficient to form a complete layer of adsorbed oxygen on the surface, in which each platinum atom is covered by an oxygen atom. We have seen (p. 147) that from energetic considerations, it would be expected that adsorbed oxygen may be formed at a more negative potential than " free " oxygen. These experiments provide fairly conclusive evidence that the formation of adsorbed oxygen actually occurs.

When such an adsorbed layer has been formed, the changes of potential are much more rapid. Provided that the electrode is not allowed to pass along the slow stage AB, the same rate of change is observed on both cathodic (curve II) and anodic (curve III) polarisation. In these changes it is probable that the oxygen layer remains intact and the process which occurs is the charging and discharging of the double layer, the capacity being about 1×10^{-4} coulombs/volt.

When the electrode has been cathodically polarised to the point B, the anodic curve again has the slower rate (I). It follows that the adsorbed layer of oxygen is removed as the electrode passes along the slow stage AB. The quantity of electricity passed in this stage is, however, much greater than that which would be required to remove the adsorbed layer, and under some conditions it may amount to 1 coulomb. Bowden suggested[1] that this stage marks the reduction of a layer of *oxide* formed at the surface of the platinum. Armstrong, Himsworth and Butler[2] showed, however, that the process which occurs here is the reduction of *oxygen* present in the solution, for the length of the arrest AB, (1) depends on the current by $(i - i_0)\tau = \alpha$, which is characteristic of cases of concentration polarisation by dissolved substances, (2) is greatly influenced by stirring the solution; and a similar process occurs, without the necessity of a previous anodic polarisation, when a platinum electrode is cathodically polarised in a solution containing dissolved oxygen. Nevertheless, as mentioned above, the adsorbed oxygen is also reduced as the electrode passes along the arrest AB.

The Electrolytic Behaviour of Hydrogen. We must now consider whether the cathodic formation of adsorbed hydrogen and its anodic removal from an electrode can be demonstrated by similar experiments. The behaviour of platinum electrodes in the neighbourhood of the reversible hydrogen potential is much more complicated than at anodic potentials. When an ordinary bright platinum electrode, which has previously been the cathode or is in contact with a solution containing hydrogen, is made anodic, no depolarisation usually occurs at or near the reversible hydrogen potential, and the potential changes rapidly to about $E_h = +0{\cdot}5$, at which some electrolysis occurs. Butler and Armstrong showed[4] that this is due to the ionisation of hydrogen which was either dissolved in or firmly bound to the electrode in an adsorbed state. Comparison of the amount of anodic polarisation required to remove this hydrogen, with the amount of the previous cathodic polarisation, and the behaviour on successive anodic polarisations suggested that some solution in the metal occurs.

If the electrode is now "activated"[5] by alternate anodic and cathodic polarisations the potential remains, on anodic polarisation with small currents, for some time quite close to the reversible hydrogen potential, and the ionisation of hydrogen in fact goes on at this potential until all the hydrogen which can reach the electrode by diffusion has been used up. At such an electrode it is impossible to determine the amount of adsorbed hydrogen by anodic polarisation with small currents. Pearson and Butler[6] attempted to reduce the importance of the diffusion of hydrogen to the electrode by the use of large currents, and recorded the rapid changes of potential so produced by means of a cathode ray oscillograph. Fig. 2 shows their results with platinum electrodes in dilute sulphuric acid. With a fresh electrode, which had previously been cathodically polarised, curve I was obtained on anodic polarisation with a large current (*ca.* 1 amp.). This electrode was inactive, but after anodic polarisation it becomes active and curve II is then obtained. This consists of two slow stages α and γ, joined by a more rapid change β. On the average stage α required $4{\cdot}8 \times 10^{-4}$ coulombs/cm.^{2}, and stage γ $10{\cdot}2 \times 10^{-4}$ coulombs/cm.^{2} The process γ is evidently the deposition of a monatomic layer of adsorbed oxygen as previously observed (p. 175), and process α, which is half the length of γ, must evidently be the removal from the electrode, by ionisation, of an equal number of adsorbed hydrogen

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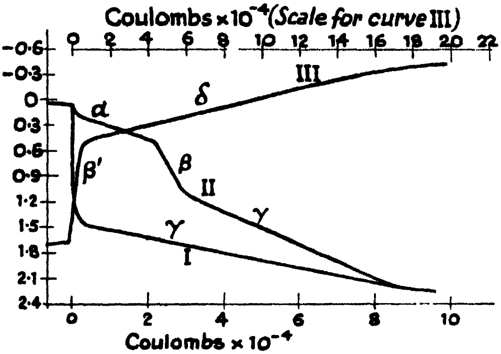
[4] *J. Chem. Soc.*, 743, 1934.

[5] Beans and Hammett, *J. Amer. Chem. Soc.*, **47**, 1215, 1925; Hammett, *ibid.*, **46**, 7, 1924.

[6] *Trans. Faraday Soc.*, **34**, 1163, 1938.

atoms. When this is completed the potential falls more rapidly along β, where the only process occurring is the charging of the double layer, until the potential, at which oxygen is deposited, is reached.

If the electrode is now cathodically polarised, curve III is obtained. At the beginning there is a stage β_1' having the same slope as the capacity change β and then a single approximately linear stage δ, which flattens out towards the end, is observed. The length of this is rather greater than the sum of α and γ. Thus in the cathodic curve the removal of the adsorbed oxygen and the deposition of adsorbed hydrogen cannot be distinguished, but the total passage of current is sufficient for both processes. The two processes therefore appear to be contiguous under these conditions, but in alkaline solutions they are distinct.



VIII. 2.—Typical anodic and cathodic oscillograms in sulphuric acid. (Pearson and Butler, *Trans. Faraday Soc.*, 1938.)

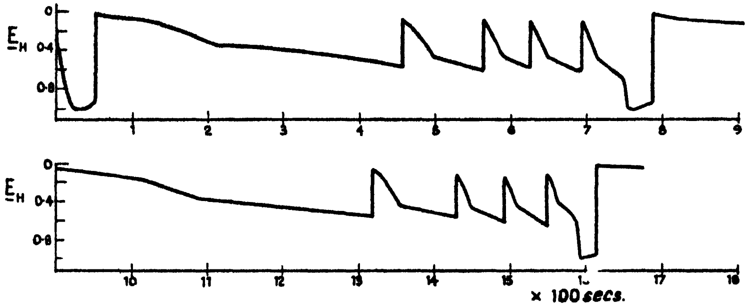
The length of process γ at inactive electrodes is the same as the sum of α, β and γ at the active electrodes. The changes produced by "activation" are not very well understood. The most likely cause of the activation of an electrode is the removal of a film of metallic or other impurities from the surface. Volmer and Wick [7] found that the activity of platinum electrodes was decreased by increasing concentrations of arsenious oxide. Erschler, Deborin and Frumkin,[8] who eliminated the effect of diffusion to the electrode by using platinum electrodes in contact with very small quantities of the solution, obtained curves very similar to I (Fig. 2) with electrodes which were "poisoned" with arsenic, and with increasing

[7] *Z. physikal. Chem.*, 172A, 429, 1935.

[8] *Acta Physicochimica*, 8, 565, 1938.

amounts of arsenic a gradual transition from curves of type II to type I was observed. A quantity of sodium arsenate, sufficient to deposit a monatomic layer covering only 1/6th of the electrode surface, caused the almost complete disappearance of process α. On the other hand, Armstrong and Butler[9] found that the deposition of oxygen on an electrode was an essential part of the process of activation.

The activity of an electrode is gradually lost on standing in the solution and more rapidly when cathodically polarised. This is probably due to the deposition of metallic impurities, and accounts for the rise of overvoltage with time, which has frequently been observed at platinum electrodes. Hammett and Lorch, however, found[10] that the activity also decays with time when the electrode is kept in hydrogen gas. It is suggested that in this case the loss of activity is due to sintering (or increase of crystal size), and not to poisoning.



VIII. 3.—Periodic oscillations of potential of platinum electrode on anodic polarisation in a solution containing hydrogen. (Armstrong and Butler.)

When active platinum electrodes are anodically polarised with small currents in solutions containing hydrogen, periodic oscillations of the electrode potential are often observed.[11] They generally belong to one of two types, (1) the potential returns suddenly to near the reversible hydrogen potential from $E_h = +0{\cdot}4$ to $0{\cdot}5$; (2) the return occurs from near the potential at which the deposition of adsorbed oxygen begins, i.e. *ca.* 1·0 volts. Fig. VIII. 3

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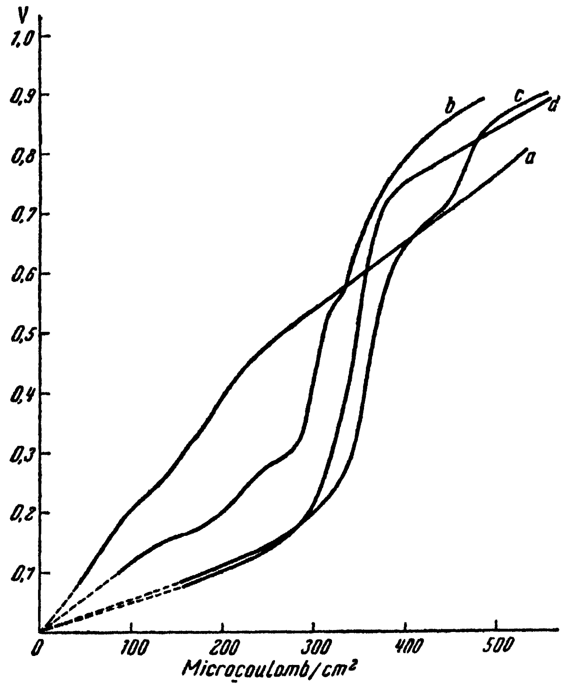
[9] *Loc. cit.*, ref. 4.

[10] *J. Amer. Chem. Soc.*, **55**, 70, 1933.

[11] Thalanger and Volmer, *Z. physikal. Chem.*, **150**, 401, 1930; Butler and Armstrong, *Nature*, **129**, 613, 1932.

is an example which shows both types. A possible interpretation is as follows. At an active electrode process, (1), viz. the ionisation of the dissolved hydrogen occurs and the potential remains near the reversible hydrogen potential for some time, until the hydrogen near the electrode has been used up. The potential then falls gradually to $E_h = 0{\cdot}4$, where another process (2) occurs. This appears to be the ionisation of hydrogen dissolved in or firmly bound to the metal. This keeps the potential again constant for a time and gives the hydrogen of the solution an opportunity to reach the electrode, by diffusion, when process (1) can occur again. The sequence is repeated until the gradual loss of activity of the electrode, caused perhaps by the deposition of metallic impurities, brings it to an end. The potential then falls to near the oxygen deposition potential, where it is reactivated and the whole series begins again.



VIII. 4.—Charging curves. (*a*) 1*n* Na_2SO_4 + 0·02*n* NaOH; (*b*) 1*n* Na_2SO_4 + 0·02*n* H_2SO_4; (*c*) 1*n* HCl; (*d*) 1*n* KBr + 0·02*n* HCl. (Erschler, Deborin and Frumkin.)

Slygin and Frumkin[12] have made extensive experiments on the adsorption of hydrogen on platinised platinum electrodes. Capacity measurements show that the area of these electrodes may be some thousand times that of similar smooth electrodes, and the potential

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[12] *Acta Physicochimica, U.R.S.S.*, **3**, 791, 1935; **4**, 911, 1936; **5**, 819, 1936.

changes occur quite slowly even with comparatively large currents. The electrode is cathodically polarised, so as to liberate hydrogen, and the excess of hydrogen in the solution is removed by bubbling nitrogen. On anodic polarisation, " charging curves " are obtained between the potential and the quantity of electricity passed, of which typical examples are shown in Fig. VIII. 4. These curves are reproducible, and if the current is stopped at any point and reversed, the curve is usually followed in the reverse direction with only slight modifications.

These curves consist of three portions, (1) a comparatively slow change in which the main process is the ionisation of adsorbed hydrogen. This is linear in HCl and HBr solutions, but in dilute H_2SO_4 and KOH there are well-defined " kinks," the origin of which is not well understood. (2) The potential then falls rapidly (a " double layer " change) to the point at which (3) either the oxidation of the electrode or, in the case of halide solutions, the liberation of halogen begins. From the capacity in the double layer region the surface area is estimated as 2700 times the apparent surface, and using this figure the quantity of hydrogen adsorbed, which is removed along stage 1, is $1{\cdot}2 \times 10^{15}$ atoms/cm.^{2}, which is in good agreement with the estimated number in a complete monatomic layer.

Frumkin represents these changes as follows. If A is the quantity of hydrogen adsorbed on the electrode and E the free charge of the double layer, the quantity of electricity passed from the initial state in which these quantities are A_0, E_0, is

$$Q = (A_0 - A)\mathbf{F} - (E_0 - E).$$

The changes in the charge of the double layer can also be found by measuring the changes in the adsorption of hydrogen ions between two potentials. In practice this is more conveniently effected by carrying out measurements in which the hydrogen-ion concentration is low compared with other cations. Then practically all the hydrogen ions which might be present in the double layer are replaced by these cations and appear in the bulk of the solution. In hydrochloric acid and similar solutions the changes of adsorbed hydrogen ions are in good agreement with the double layer capacity in stage (2), i.e. the double layer change accounts for the whole of the electricity passed in this stage; but in alkaline solutions this is not the case. The quantities of electricity required in stage (2) are definitely greater than corresponds to the double layer capacity, and it appears that the deposition of oxygen begins before all the hydrogen has been removed from the surface.

In later papers of this series[13] bright platinum electrodes have been studied. Erschler obtained charging curves, similar to those of platinised electrodes, but rather less reversible, at electrodes which were in contact with extremely small quantities of solution, from which all the oxygen could be removed by cathodic polarisation. Erschler, Deborin and Frumkin studied the effect of various treatments on the charging curves. After heating in hydrogen, the quantity of easily removable hydrogen is 40 per cent. of that obtained after heating in air, followed by cathodic polarisation, and a quantity of very firmly bound hydrogen, removable at about + 0·5 volts, is present on the electrode. When platinum is heated in oxygen at 900° for 10 secs., an atomic layer ($1{\cdot}3 \times 10^{15}$ atoms/cm.^{2}) of oxygen is formed.

Formation of Oxide Films on Noble Metals. The study of the anodic behaviour of gold,[2] and of some metals of the platinum group[14] has given an interesting insight into the early stages of the oxidation of metals. When all these metals are anodically polarised a layer of adsorbed oxygen atoms, such as has been described in the case of platinum, is formed before oxygen is freely evolved. When rhodium and palladium are anodically polarised with comparatively large currents for some time, small quantities of a distinct "oxide" are also formed. This can be demonstrated by cathodically polarising an electrode which has been so treated, when a new stage appears in the cathodic curve before the potential reaches the point at which the reduction of *adsorbed* oxygen occurs (e.g. Fig. VIII. 5). This marks the reduction of the "oxide," and the amount of oxide present after the anodic treatment can be measured by the length

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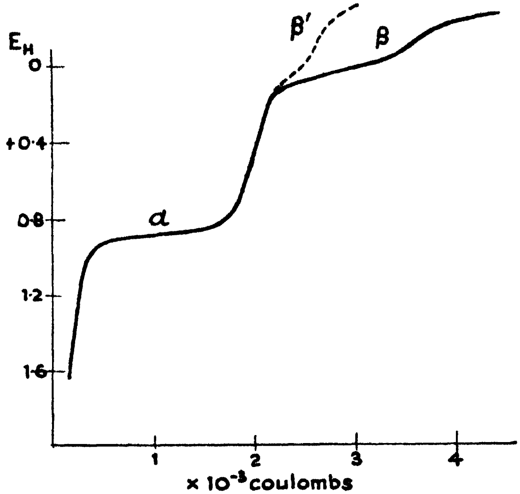
[13] Erschler and Proskurnin, *Acta Physicochimica*, 6, 195, 1937; Erschler, *ibid.*, 7, 327, 1937; Erschler, Deborin and Frumkin, *ibid.*, 8, 565, 1938; *Trans. Faraday Soc.*, 35, 464, 1939.

[14] Butler and Drever, *ibid.*, 32, 427, 1936.

of this cathodic stage. The method is very sensitive and quantities of oxide which are otherwise undetectable can be determined, e.g. with a current of 5 × 10^{-6} amps. an arrest of 10 secs. is equivalent to 5 × 10^{-10} equivalents of oxide or 1·5 × 10^{14} atoms of oxygen. This method has also been used for measuring the amount of oxide formed in the thermal oxidation of copper.[15]

With rhodium the amount of oxide formed even after long anodic treatment is of the order of one molecular layer, but with palladium appreciably greater quantities are formed, and after a long time there is sufficient to be visible as a black coating on the electrode. If there is an interval between the anodic treatment and the subsequent cathodic, the length of the cathodic break is less, i.e. the oxide dissolves or decomposes. This is particularly the case in acid solutions where, with palladium, it was found that half the amount of oxide originally present disappeared in an interval of 20 secs.; but in alkaline solution it is much more stable, the loss being only 8 per cent. in five minutes. On account of this behaviour it was suggested that the oxide is "peroxidic" in nature.



VIII. 5.—Cathodic polarisation of a gold electrode which has previously been anodically polarised. Stage α, reduction of the oxide; stage β, reduction of adsorbed and free oxygen; β′, solution stirred to remove excess of oxygen near electrode.

With new electrodes the formation of the oxide occurs very slowly. The following table shows the amounts of oxide formed (as measured

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[15] Miley, *J. Amer. Chem. Soc.*, **59**, 2626, 1937; Carnegie Schol. Mem., *Iron and Steel Inst.*, **25**, 197, 1936; 5th Report of Corrosion Committee (*J. Iron and Steel Inst.*), Section D3, 243, 1938.

by the cathodic coulombs required to reduce it) at palladium electrodes in successive experiments :—

OXIDATION OF PALLADIUM IN N/5 NaOH WITH $8{\cdot}5 \times 10^{-3}$ AMPS.

Anodic coulombs	*Cathodic coulombs*	*Anodic coulombs*	*Cathodic coulombs*
(1) 510×10^{-3}	14×10^{-4}	(4) $76{,}500 \times 10^{-3}$	85×10^{-4}
(2) 1020	19	(5) 1020	70
(3) 5100	35	(6) 8·4*	48

It can be seen that when a comparatively large amount of oxide has been formed by long anodic treatment and reduced, it is re-formed much more quickly, and in fact a considerable amount of oxidation now occurs even with very small anodic currents. This effect, however, disappears when the electrode is left untreated for a few days, when the electrode reverts to its original condition.

It was found that in this case the oxide began to be formed at the very earliest stages of the anodic treatment simultaneously with the deposition of adsorbed oxygen. The following table shows observations with a rhodium electrode, which had previously been anodically oxidised with a large current and then reduced. A current of 10^{-5} amps. was now passed anodically, taking the potential in successive experiments to increasingly positive values. Q_1 is the quantity of electricity required to take the electrode to the given potential, and Q_2 the quantity required at an untreated electrode in forming the adsorbed oxygen layer. The difference $Q_1 - Q_2$ is presumably the quantity of electricity used in the formation of peroxide along this stage. It agrees quite well with Q_3, the amount of electricity actually required to reduce the peroxide formed.

ANODIC OXIDATION OF A PREVIOUSLY OXIDISED AND REDUCED RHODIUM ELECTRODE

Potential reached	*Coulombs required* $\times 10^{-4}$			
	Q_1	Q_2	$Q_1 - Q_2$	Q_3
+0·18	3·1	1·5	1·6	1·5
0·28	7·7	3·0	4·7	2·4
0·38	9·9	4·5	5·4	3·7
0·48	13·0	6·0	7·0	6·0
0·58	18·2	7·5	10·7	9·2
0·68	22·9	9·0	13·9	13·8
0·78	36·5	9·0	27·5†	19·3

* With 28×10^{-4} amps.

† The evolution of oxygen has begun at this point, and this figure includes current employed in the liberation of oxygen.

After anodic polarisation of gold electrodes in dilute sulphuric acid the cathodic curve also shows two breaks.[16] The length of the one at more negative potentials is greatly influenced by stirring the solution and is therefore due to depolarisation by dissolved oxygen. The more positive break is quite unaffected by stirring and must be caused by the reduction of an oxide. After a long continued anodic polarisation the electrode becomes covered with a black film which is probably an oxide of gold, and this disappears again at this stage of the cathodic process. The composition of the black substance has been investigated. Jirsa and Buryànek[17] found that after drying over sulphuric acid its composition was close to $Au(OH)_3$, and after drying at 142° and over phosphorus pentoxide, the proportion of gold was somewhat less than that required for Au_2O_3. As in the former cases the effect of consecutive oxidations and reductions is cumulative, i.e. when the oxide has been formed and reduced, it is reformed with an efficiency practically 100 per cent. at the beginning of the next anodic treatment. The oxide formation begins simultaneously with the deposition of adsorbed oxygen. As the amount of oxide increases the efficiency of its formation decreases and finally, when the current is continued for a long period, it remains constant at about 1 per cent. In alkaline solutions, however, gold resembles the platinum metals, and even after long anodic treatment the amount of oxide formed hardly exceeds that which might be expected to form a layer a molecule thick.

No oxide formation could be detected with platinum and iridium by similar methods,* but since, as pointed out previously (p. 152), the oxygen overvoltage of platinum decays abnormally slowly during the first 100 secs. after the stoppage of the anodic current, it is possible that a small amount of peroxidic oxygen is formed which decomposes in this period.

Returning to palladium and rhodium it is clear that since the rate of oxidation is so small that it takes a considerable time to form

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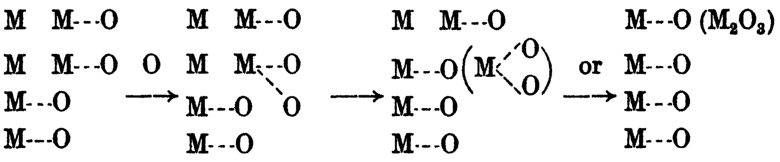
[16] *Loc. cit.*, ref. 2.

[17] *Chem. Listy.*, **16**, 189, 299, 329, 1922; Jirsa and Tellinck, *Z. Elektrochem.*, **30**, 286, 1924.

* Platinum oxide can, however, be formed by strongly heating platinum in oxygen.

even a single molecular layer of oxide, some parts of the surface must be more readily oxidised than others, and it must be supposed that the oxidation begins at exposed atoms or edges and gradually spreads over the surface. A reasonable explanation of the observed facts is given if it be supposed that such exposed atoms are able to take up a second oxygen atom as in (*a*), which will be peroxidic in character.



(*a*) (*b*) (*c*)

The attachment of the exposed atom to the surface may be so weakened by this that it is pulled out from the metal forming a peroxide or oxide as in (*b*) or (*c*), while the underlying metal atoms now take up adsorbed oxygen. The stage (*a*) has not been directly observed, but indications of it are to be found in the slight electromotive activity observable at platinum after the stoppage of the current. This may be due to a slight peroxidation as in (*a*), without any distinguishable oxide formation, like (*b*) or (*c*).

The attack of an insoluble metal at the anode by oxygen thus takes place in the following stages. The formation of an adsorbed layer of oxygen atoms is probably followed by the addition of peroxidic oxygen at exposed parts of the surface. With the more inert metals, platinum and iridium, the process stops here, but if the forces between the metal atoms are not so great the attachment of the "peroxidised" atoms to the surface may be so weakened that distinct molecules of an oxide are formed, and the neighbouring atoms are then left open to attack. This occurs very slowly with palladium and rhodium, but more rapidly with gold. The extent to which it goes will depend on the porosity of the oxide layer; if the latter adheres firmly to the surface the oxidation soon comes to a stop, as with gold in alkaline solutions. If the oxide forms porous masses the oxidation can continue indefinitely, as with gold in sulphuric acid. When the surface oxide is reduced the atoms are probably redeposited in a chaotic condition and are readily reoxidised, but if the electrode is left standing for a few days a process akin to crystallisation takes place and the electrode reverts to its original inactive state.

The Anodic Passivity of Metals. Passivity was independently discovered by Bergmann[18] and by Keir[19] about 1790, who found that iron on being dipped in strong nitric acid lost its activity, in that it would no longer dissolve in acids or precipitate silver from silver nitrate. It is rediscovered by Wetzlar[20] in 1827 and in 1836 Schönbein[21] began his investigations, in which he found that the phenomenon, which he called passivity, could also be produced by making the metal the anode in oxy-acid solutions. Faraday expressed the opinion[22] that the phenomenon was due to a protective oxide film on the metal. In reply to a letter from Schönbein he says:—

> "My strong impression is that the surface of iron is oxidised or that the surface *particles* are in such relation to the oxygen of the electrolyte as to be equivalent to oxidation; and having thus their affinity for oxygen satisfied and not being dissolved by acid under the circumstances, there is no renewal of the metallic surface and no reiteration of the successive particles of iron on the elements of successive particles of the electrolyte."

Very little progress in understanding passivity was made during the nineteenth century. In 1898 Hittorf[23] sharply criticised the oxide theory on the grounds that (1) the existence of new and very unstable oxides must be assumed, (2) chromium, which in the active state goes into solution in the divalent form, does not cease to dissolve when it becomes passive, but dissolves in the form of chromate.

Many investigations have since been made and numerous theories as to the cause of passivation and the nature of the passive state have been put forward. It is impossible to discuss these in any

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[18] *De diversa phlogisti quant. in metallis* (*Opuscula phys. et chem.*).

[19] *Phil. Trans.*, **80**, 374, 1790.

[20] Schweizer's *J. f. Chem. u. Phys.*, 1827.

[21] *Pogg. Ann.*, **37**, 390, 590, 1836.

[22] *Phil. Mag.*, **9**, 122, 1836; **10**, 175, 1837.

[23] *Z. physikal. Chem.*, **25**, 729, 1897; **30**, 481, 1899; **34**, 385, 1900; *Z. f. Elektrochem.*, **14**, 482, 1898; **6**, 6, 1899; **7**, 168, 1900.

detail, but the following, without being exhaustive, will give a general idea of the various points of view suggested :—[24]

(1) The metal undergoes a kind of allotropic charge, which has been pictured variously as a change of valency,[25] of electron density,[26] of internal equilibrium between possible ionic states.[27]

(2) Passivity is brought about by the retardation of the solution of metal ions by one of the following effects :—

(*a*) The formation at the surface of the metal of a coherent "oxygen gas charge,"[28] or a metal-oxygen alloy,[29] which hinders the solution of metal ions.

(*b*) The absence of a positive catalyst (hydrogen) which is supposed to be required for the solution process.[30]

Foerster later combined this[31] with the oxygen charge theory. Both hydrogen and oxygen were supposed to have a negative catalytic effect on the anodic solution of metals, but hydrogen can also act as an activator by combining with oxygen and oxides.[32]

The existence of oxide films on passive metals is now widely accepted.[33] On some metals thick visible films of insoluble salts, and of oxides, may be formed at the anode under suitable circumstances. For example, gold and lead are oxidised in dilute sulphuric acid, and many metals give oxide or hydroxide films in alkaline solution. These films may cover a considerable part of the surface

[24] For general surveys, see *Trans. Faraday Soc.*, **9**, 203, 1914 ; **19**, 748, 1924.

[25] Krüger, *Z. physikal. Chem.*, **39**, 104, 1902 ; Finkelstein, *ibid.*, **39**, 91, 1902.

[26] W. J. Müller, *ibid.*, **48**, 577, 1904.

[27] A. Smits, *Theory of Allotropy* (Longmans, Green, 1922) ; Smits and Aten, *Z. physikal. Chem.*, **88**, 743, 1914 ; **90**, 723, 1915 ; Smits, *Trans. Faraday Soc.*, **19**, 772, 1924.

[28] Foerster, Abh. Deutsch. Bunsen-Ges., No. 2, 1909 ; Grave, *Z. physikal. Chem.*, **77** 513, 1911 ; Adler, *ibid.*, **80**, 835, 1912 ; Rathert, *ibid.*, **86**, 567, 1914 ; Schmidt, *Trans. Faraday Soc.*, **9**, 257, 1914.

[29] Fredenhagen, *Z. physikal. Chem.*, **43**, 1, 1903 ; **63**, 1, 1908 ; *Z. f. Elektrochem.*, **11**, 857, 1905 ; **12**, 797, 1906 ; Jordis, *ibid.*, **11**, 787, 1905 ; Muthmann and Frauenberger, *Z. Elektrochem.*, **10**, 929, 1904 ; Flade, *Z. physikal. Chem.*, **76**, 513, 1911 ; Allmand and Puri, *Trans. Faraday Soc.*, **21**, 1, 1925.

[30] Le Blanc, *Z. physikal. Chem.*, **6**, 472, 1900.

[31] *Z. f. Elektrochem.*, **22**, 95, 1916 ; *Elektrochem. wassrig. Lösungen*, 1915.

[32] Other theories were suggested by Le Blanc, *Z. f. Elektrochem.*, **6**, 472, 1900 ; Sackur, *ibid.*, **14**, 612, 1908 ; Reichenstein, *ibid.*, **17**, 699, 1911 ; **19**, 672, 1913 ; **30**, 238, 1924 ; *Trans. Faraday Soc.*, **9**, 228, 1914.

[33] See U. R. Evans, *Metallic Corrosion, Passivity and Protection* (E. Arnold) ; E. S. Hedges, *Protective Films on Metals* (E. Arnold).

and give rise to a certain degree of passivity (mechanical passivity), but usually the protection is incomplete. On the other hand, passive iron, nickel, etc., do not differ in appearance or in brightness from the active metal. U. R. Evans [34] isolated an invisible oxide film from passive iron by dissolving away the underlying metal. Evidence (not always unambiguous) has also been obtained as to the existence of such films on passive metals by the reflection of polarised light,[35] by the change of photoelectric properties on passivation,[36] by electron diffraction.[37]

It is obvious that the greater the protection conferred by a film the thinner it will be, and it is probable that a completely protective film need only be a single molecule thick and that the films of an appreciable thickness often observed are of a secondary character. The difficulty that known oxides do not usually have the necessary resistance to acids, etc., may be overcome by supposing that the oxygen is adsorbed, rather than united with the metal as definite molecules of an oxide. Bennett and Burnham [38] considered that unstable oxides may be adsorbed on the metal and thereby stabilised. Tammann suggested that oxygen atoms form a kind of alloy with the metal, occupying definite positions in the space lattice.[39] Meunier [40] has also expressed the view that the oxygen is held to the surface in a kind of "Langmuir film." Electrochemical evidence of the existence of such monotomic oxygen films on noble metals has already been given (p. 175).

The important question is not, however, whether such films exist, but how they come to be formed on metals which in the active state readily pass into solution. It has been found that

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[34] *J. Chem. Soc.*, 1020, 1927.

[35] Tronstad, *Z. physikal. Chem.*, **142**, 241, 1929; **158**, 369, 1932; *Trans. Faraday Soc.*, **29**, 502, 1933; **30**, 349, 1934; **31**, 1151, 1935.

[36] H. S. Allen, *ibid.*, **9**, 247, 1914; Becker and Helberg, *Z. Elektrochem.*, **31**, 31, 1925.

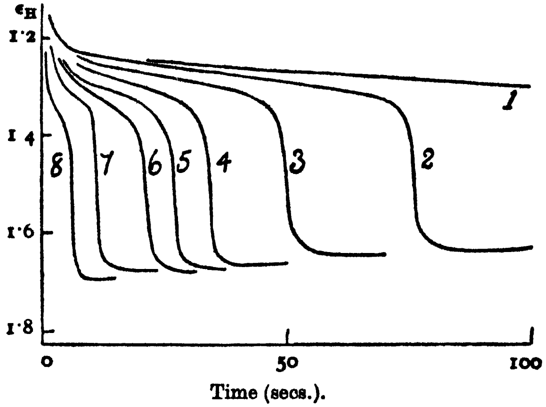
[37] G. P. Thomson, *Proc. Roy. Soc.*, **128**A, 657, 1930; Boas and Rupp, *Ann. Physik*, **13**, 1, 1932; Rupp, *Kolloid Z.*, **69**, 375, 1934; Iitaka, Miyake and Iimora, *Nature*, **139**, 156, 1937; Iimori, *Bull. Chem. Soc. Japan*, **13**, 152, 1938; *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **34**, 60, 1937; Smith, *J. Amer. Chem. Soc.*, **58**, 173, 1936.

[38] *J. Physical Chem.*, **21**, 107, 1917; cf. Bancroft and Porter, *ibid.*, **40**, 37, 1936; Lepin, *Acta Physicochimica, U.R.S.S.*, **8**, 659, 1938.

[39] *Z. anorg. Chem.*, **107**, 103, 1919.

[40] *Bull. Soc. Chem. Belg.*, **36**, 435, 1927.

when a metal which can be passivated, such as iron or nickel, is anodically polarised with small currents it passes into solution. When the current is increased a point is reached at which a transition occurs, and the potential changes to a more positive value at which oxygen is evolved and the metal almost or completely ceases to dissolve.[41] Further, with a given current, which is sufficient to cause passivation, the transition only occurs after a certain time [42] which is shorter the greater the current (Fig. 6).



VIII. 6.—Typical anodic passivation curves of gold in 0·012 *N*, HCl Currents: (1) 0·68, (2) 0·71, (3) 0·81, (4) 0·88, (5) 0·99, (6) 1·01, (7) 1·52, (8) 2·05 × 10^{-3} amps.

In such cases what causes the solution of the metal to cease? In a long series of papers,[43] W. J. Müller and collaborators have developed a "Bedeckungstheorie," according to which the initial cause of the passivity is the accumulation at the electrode of a

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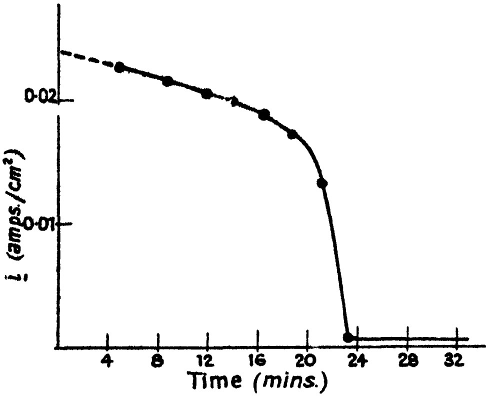
[41] Fredenhagen, *Z. physikal. Chem.*, **43**, 1, 1903; **63**, 1, 1908; Schoch and Randolph, *J. Physical Chem.*, **14**, 719, 1910; *Amer. Chem. J.*, **41**, 231, 1909; White, *ibid.*, **15**, 723, 1911.

[42] Lobry de Bruyn, *Rec. trav. chim.*, **40**, 53, 1921.

[43] Summary, *Trans. Faraday Soc.*, **27**, 736, 1931; "Die Bedeckungstheorie der Passivität der Metalle und ihre experimentelle Begründung" (*Verlag Chemie*, Berlin, 1933); list of papers to 1934 is given by Hedges in *Ann. Rep. Chem. Soc.*, 1934, p. 129. The more important recent papers are: *Z. Elektrochem.*, **40**, 119, 570, 578, 1934; **41**, 83, 641, 1935; **42**, 166, 789, 830, 1936; **43**, 406, 561, 1937; *Monatsch.*, **66**, 35, 1935; **68**, 431; **69**, 1, 437, 1936; **70**, 113, 1937; *Korrosion und Metallschutz*, **11**, 25, 1935; **12**, 132, 1936; **13**, 144, 1937; **14**, 49, 63, 77, 198, 1938 (mainly on corrosion problems); *Ber.*, **68B**, 989, 1935; *Kolloid Z.*, **86**, 150, 1939.

product of the electrolysis, such as a metallic salt or a basic salt formed by hydrolysis, until the solution becomes supersaturated and a solid thereupon crystallises on the electrode surface. This covers up a portion of the surface and so increases the current density on the remainder, and in time the effective current density on the uncovered portions may be 100 to 1000 times the original value. The current may now be great enough to displace the potential into the region in which oxygen can be liberated, or some other change can occur, which brings about passivity. In other cases a natural oxide film is present on the surface of the metal, and the process of passivation consists in the crystallisation of metallic salt in its pores.



VIII. 7.—Passivation at a shielded electrode of iron in $2n$ H_2SO_4. (W. J. Müller.)

Müller used a horizontal electrode carefully shielded from disturbances produced by convection, and under these conditions the behaviour of the electrode was reproducible. He usually kept the applied e.m.f. constant and observed the change of current with time. The onset of passivity is marked by a rapid fall of the current (Fig. 7).

Assuming that the thickness of the film remains constant and that the film grows sideways only, the fall of the current i with the time t is given as

$$t = C - A\left\{\frac{i}{i_0 - i} + \frac{2{\cdot}3}{i_0}\log\frac{i_0 - i}{i - i_R}\right\},$$

where $i_0 =$ initial current, $i_R =$ residual current, and C and A are constants defined by

$$C = \frac{s\delta A}{\mathrm{F}(1-\mu)i_0}; \quad A = \frac{s\delta^2}{\chi\mathrm{F}(1-\mu)w_0},$$

where s is the density of the film material, δ its thickness, A the original anode area ; **F** the electrochemical equivalent, μ the anionic transport number, w_0 the resistance of the boundary layer and χ the conductivity of the solution in the boundary layer. C is practically equal to the time in which the rapid fall of the current occurs, i.e. the passivation time τ, hence

$$\tau = C = k\left(\frac{\delta}{i_0}\right).$$

This equation suggests that if δ is independent of the current, $\tau i_0 = \text{const.}$ Müller and his collaborators found, however, that in numerous cases a linear relation is obtained when log τ is plotted against log i_0, the slope being 2 in many cases, i.e. the results can be represented by

$$\tau = \mathrm{B}i_0^{-n},$$

where $n = 2$. For example, with iron in sulphuric acid this holds for currents between 3×10^{-3} amps. and 3·5 amps., with passivation times from 100 to 0·1 secs. The constant B (which represents the passivation time for a current of 1 amp.) was found to be approximately proportional to the solubility of the salt formed at the anode, with copper and iron in sulphuric acid solutions.

In order to account for this relation, it is suggested that the thickness of the film varies inversely with the initial current. This may reasonably be supposed to be the case, since the film thickness is determined by the size of the crystals which separate from the supersaturated solution, and the size will be greater the smaller the degree of supersaturation which is proportional to the current.

Reasonably constant values of A were obtained until the surface was nearly completely covered by the film. A then begins to change and it is suggested that the film now grows in thickness, the later stages of the process are represented by

$$t_2 - t_1 = B\left(\frac{1}{i_1^2} - \frac{1}{i_2^2}\right),$$

where i_1, i_2 are the currents at times t_1, t_2.

The anodic behaviour of gold in chloride solutions was studied by Shutt and collaborators[44] under very different experimental

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[44] Shutt and Stirrup, *Trans. Faraday Soc.*, **26**, 635, 1930 ; Shutt and Walton, *ibid.*, **28**, 741, 1932 ; **29**, 1210, 1933 ; cf. J. W. Müller, *ibid.*, **28**, 471, 1932.

conditions, viz. with violent agitation produced by causing a stream of the solution from a centrifugal pump to impinge on the surface of the electrode. Under these circumstances they found[45] that there was a limiting current i_0, below which passivation does not occur, and that the passivation times, which ranged in the experiments from 0·03 to 1 sec., could be represented by

$$(i - i_0)\tau = \alpha,$$

where i_0 and α are constants for a given solution and are proportional, in hydrochloric acid and potassium chloride solutions, and in mixtures of them, to the chloride-ion concentration. They suggested that the solution of gold can only occur if chloride ions are adsorbed on the electrode and i_0 represents the rate of adsorption.

Armstrong and Butler[46] found that for passivation times greater than about 10 secs. a similar equation holds in *unstirred* solutions. Since the same relation was obtained under similar circumstances in cases of concentration polarisation (p. 165), it was suggested that both in unstirred and stirred solutions the onset of passivity is due to the depletion of chloride ion near the electrode and that i_0 represents the *rate of diffusion* of chloride ions to the surface. It was calculated that the thicknesses of the diffusion layer required to account for the limiting currents observed are of the order of 10^{-3} cms. in stirred solutions and 10^{-2} cms. in unstirred solutions, which are of the same order as the values obtained from other processes, such as the dissolution of solids.

Pearson and Butler,[47] in an attempt to eliminate diffusion effects, studied the passivation of gold with very large current densities, using a cathode ray oscillograph to record the short passivation times, extending from 10^{-1} to 10^{-3} secs. They found that the relation

$$(i - i_0)\tau = \alpha$$

holds up to the shortest times which could be observed. With the larger currents the effect of the term $i_0\tau$ is small, and effectively the condition $i\tau = \alpha$ was realised (Fig. 8) and showed no signs of

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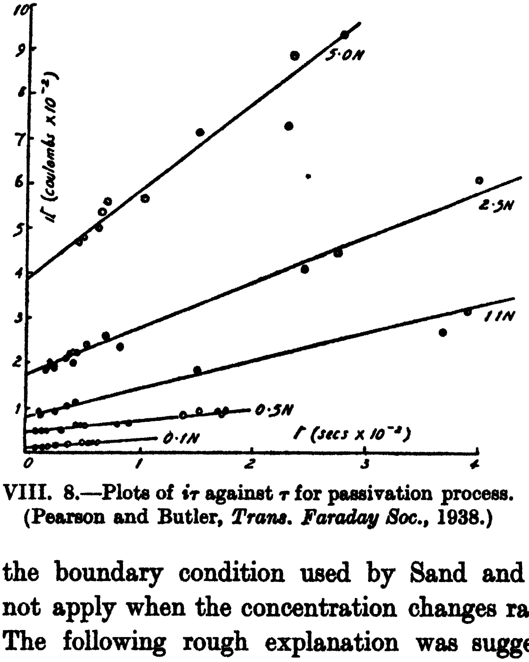
[45] Shutt and Walton, *Trans. Faraday Soc.*, **30**, 914, 1934; cf. J. W. Müller, *ibid.*, **31**, 1291, 1935.

[46] *Ibid.*, **30**, 1173, 1934; cf. Shutt, *ibid.*, **31**, 636, 1935.

[47] *Ibid.*, **34**, 806, 1938.

being departed from as the current density increased. Thus the quantity of electricity which produces passivation approaches, with large currents, the constant value α, which is proportional to the chloride-ion concentration. It is equivalent to the amount of chloride in 2×10^{-4} cms. of solution.



VIII. 8.—Plots of $i\tau$ against τ for passivation process. (Pearson and Butler, *Trans. Faraday Soc.*, 1938.)

α was considered to be the quantity of electricity used in setting up the diffusion layer, through which diffusion takes place at the rate i_0. In order to explain its constancy under these conditions it is necessary to consider the process of setting up the diffusion layer in greater detail than previously (p. 166). The exact calculation by Fick's equation of concentration changes near an electrode when ions are removed at a high constant rate presents great difficulties, for the boundary condition used by Sand and others (p. 162) does not apply when the concentration changes rapidly at the electrode. The following rough explanation was suggested by Pearson and Butler :—

At the electrode ions are used up in the process

$$Au + 4Cl^- \rightarrow AuCl_4^- + 3\epsilon$$

at the rate $4i/3F$ equivts./sec., while they are brought up by ionic transport at the rate $n_a i/F$, where n_a is the anionic transport number. The net rate of depletion of chloride ions at the electrode can thus be taken roundly as i/F equivts./sec. and the total amount of the ions used up in the whole passivation process is $i t/F$. Most of these ions must have arrived at the electrode by diffusion, so that the diffusion rate during the setting up of the diffusion layer must approximate to $i/\mathbf{F}$. We therefore need to consider for how long ions can reach the electrode at this rate.

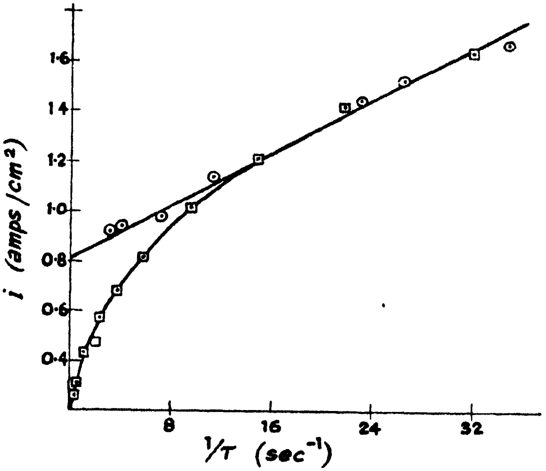
The rate of diffusion near the electrode is Ddc/dx. If chloride ions were suddenly removed from a thin film near the electrode, the immediate result would be a very large gradient over a thin layer of the solution. At the beginning of the process the concentration gradient may therefore easily be sufficiently great to enable ions to flow in as fast as they are removed by the electrolytic process. But as the diffusion goes on the diffusion layer is bound to broaden, and the maximum possible gradient will diminish. If it is assumed for simplicity that the gradient is uniform from one side of the diffusion layer to the other, we see that the condition under which ions can arrive at a rate approximating to $i/\mathbf{F}$ is $D\Delta c/\Delta x = i/\mathbf{F}$. Taking D as 2×10^{-5} and $\mathbf{F}$ as 10^5, and since the maximum possible value of Δc is c, we see that the maximum value of the diffusion layer is $\Delta x = 2c/i$. Taking c as 10^{-4} to 5×10^{-3} mols./c.c. and $i = 1$ to 20 amps./cm.^{2}, we see that the maximum thickness which will enable diffusion to occur at a rate not much different to $i/\mathbf{F}$ is 10^{-3} to 10^{-4} cms., which corresponds with the values of α observed.

With large current densities, stirring has no effect on the passivation time (Fig. 9), and it would therefore appear that the diffusion layer comes within a region close to the electrode which is not much disturbed by the agitation of the solution. With smaller current densities, however, the passivation time is increased by stirring, and with sufficiently small currents the relation $(i - i_0)\tau = \alpha$ again holds in the absence of stirring. The following table shows the values of i_0 and α under the two conditions. It appears from these figures that with small currents the diffusion layer is broader in unstirred solutions and the effect of stirring is therefore to narrow the diffusion layer:—

CONSTANTS i_0 AND α IN $0{\cdot}05N$, HCl

	Unstirred solutions	*Violent stirring*
i_0	$3{\cdot}6 \times 10^{-3}$	80×10^{-3}
α	34×10^{-3}	$0{\cdot}6 \times 10^{-3}$

It is clear that in the case of gold in chloride solutions, passivation is the result of the depletion of chloride ions at the electrode. What is the role of the chloride ions in bringing about or facilitating the solution of gold? It is obvious that in the absence of chloride ions the soluble ion $AuCl_4^-$ cannot be formed, and if Au^{+++} ions pass into solution, they will be hydrolysed to an oxide. It is not clear, however, whether, in the absence of chloride ions, the auric ions actually pass into solution and undergo hydrolysis to an oxide of gold which is deposited on the electrode, or whether under such conditions gold ions cannot detach themselves from the metal, so that the oxide is formed primarily by the deposition of oxygen on the electrode.



VIII. 9.—Effect of stirring on the passivation times of gold in 1*n* HCl. (Shutt and Walton.)

Shutt and Stirrup showed [48] that passivated gold electrodes are covered with an oxide two or three molecules thick. This can be removed by cathodic polarisation which reactivates the electrode. The electrode also recovers its activity spontaneously in the presence of chlorides, the activation time being approximately inversely proportional to the chloride-ion concentration.

Roberts and Shutt [49] have also found that the anodic behaviour

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[48] *Trans. Faraday Soc.*, **26**, 635, 1930.

[49] *Ibid.*, **34**, 1465, 1938. The passivity of chromium has also been studied by E. Müller, *Z. Elektrochem.*, **36**, 963, 1930; **37**, 185, 1931; **43**, 42, 1937; *Z. physikal. Chem.*, **159**, 68, 1932; **176**, 273, 1936; **181**, 89, 1937; and by W. J. Müller and Briggs, *Monatsch.*, **70**, 113, 1937.

of chromium is, in many respects, similar to that of gold. With small anodic currents chromium dissolves as chromium ions, but when the anodic current is increased a transition occurs and the potential becomes much more positive. The solution of the chromium does not cease, but it now dissolves mainly in the form of chromate. The transition times are related to the current by

$$(i - i_0)\tau = \alpha,$$

and it was found that in hydrochloric acid solutions the limiting current i_0 is inversely proportional to the hydrogen-ion concentration and to the square root of the chloride-ion concentration. α increases to some extent with the concentration. The same relation holds in sulphuric acid and sulphite solutions, but i_0 and α are much smaller than in hydrochloric acid. It is concluded that the first stage in the passivation consists in a reduction of the concentration of hydrogen ions near the electrode, which it is suggested is produced by the ionic transport of the ions away from the electrode. When this layer has become sufficiently alkaline, oxygen is deposited and the chromium now dissolves as chromate.

To sum up, it appears that anodic passivity may be produced in two ways: (1) by the separation on the electrode of a product of the electrolysis, which may cover a considerable part of the surface and so increase the current density on the uncovered portions to an extent sufficient to cause the deposition of oxygen or other processes which are responsible for passivity; (2) by concentration polarisation (depletion) of a substance in solution, such as Cl^- in the case of gold, which is necessary for the continued solution of the metal ions.

Electrolytic Reduction and Oxidation. When a reversible oxidation-reduction electrode is made the anode oxidation occurs, and when made the cathode reduction occurs, and with small currents the displacement of the potential from the reversible potential is usually comparatively small. We have seen (p. 159) that, with currents above a certain limiting value, a transition from the oxidation or reduction process to the liberation of oxygen or hydrogen occurs, which is due to concentration polarisation. The displacements of the potential with smaller currents were also originally ascribed to concentration polarisation.[50] Haber and Russ, however,[51] as the result of their work on electrolytic reduction of nitrobenzene, etc., suggested that the displacement of the potential was due to the inherent slowness of some stage of the electrochemical process. In the case of reductions, it was postulated that hydrogen was first formed and reacted with the depolariser. If this reaction is "slow," there will be an accumulation of free hydrogen at the electrode, which will give rise to a displacement of the electrode potential, according to

$$E = E^{o} + \frac{RT}{F} \log \frac{[H^{+}]}{[H]}, \qquad . \quad . \quad . \quad (\alpha)$$

where [H] is the concentration of "free" hydrogen at the electrode. If the reaction is represented by

$$X + nH \rightarrow XH_{n},$$

the rate of reduction will be $k[X][H]^{n}$, and in the steady state this will be equal to the rate of formation of hydrogen by electrolysis, i.e. $i = k[X][H]^{n}$. Substitute in (2) the value of [H] so obtained, we get

$$E = E^{o} + \frac{RT}{F} \log [H^{+}] + \frac{RT}{nF} \log \frac{k[X]}{i}.$$

This equation was found to represent the dependence of E on the current and depolariser concentration fairly well, when n was taken as $2/x$ (where x is usually about 2) instead of the stoichiometrical value 2.

Rosenthal, Lorch and Hammett[52] have recently investigated the reduction and oxidation of quinhydrone solutions at platinum electrodes under conditions of rapid stirring. Under these conditions the concentration polarisation was believed to be small, which was borne out by the fact that the current-potential curves varied considerably with the *state* of the electrode. At a given potential it was found that the rate of reduction was proportional to the

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[50] Nernst, in discussion of paper by Goldschmidt, *Z. Elektrochem.*, **7**, 267, 1900; *Z. physikal. Chem.*, **47**, 52, 1904; Brunner, *ibid.*, **47**, 56, 1904.

[51] *Ibid.*, **47**, 257, 1904; also *ibid.*, **32**, 193, 271, 1901; Russ, *ibid.*, **44**, 641, 1903.

[52] *J. Amer. Chem. Soc.*, **59**, 1795, 1937.

quinone concentration, and the rate of oxidation to the hydroquinone concentration and the effect of acidity, etc., could be represented bv

$$i = k_a\frac{[\mathrm{HQ}]}{[\mathrm{H}^+]^p}\, e^{E/a} - k_c[\mathrm{Q}][\mathrm{H}^+]\, e^{-E/c}.$$

where HQ = hydroquinone, Q = Quinone, p = constant. The two terms are equal at the reversible quinhydrone potential, and at potentials which differ from the reversible potential by more than 0·1 volt, one term becomes negligible and i varies exponentially with E. This equation is of the type to be expected if the rate-determining processes are the transfers of electrons to and from the electrode, but the influence of the hydrogen-ion concentration is obscure.[53]

Haber and Russ's theory has also been applied to the interpretation of reversible reductions.[54] It does not seem, however, to be compatible with many of the facts of hydrogen overvoltage. For example, in the case discussed above the reduction of quinone occurs with great rapidity at blank platinum electrodes at + 0·65 volts, at which the discharge rate of hydrogen ions is completely negligible, and the same is the case with irreversible reductions, e.g. of nitrobenzene. It is difficult to see how in such cases hydrogen can be the primary product. It is also based on the assumption that the electrode potential is a reversible one, determined by the concentration of "free" hydrogen. The reversible hydrogen potential is the exception rather than the rule, and at most electrodes hydrogen is liberated irreversibly and the potential at which this occurs is not influenced by the hydrogen present.

It has been suggested[55] that electrolytic reductions may be effected in the following ways :—

A. By the direct transfer of electrons from the electrode to the depolariser.

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[53] See also V. Čupr, *Coll. Czech. Chem. Comm.*, **11**, 14, 1939; who gives the relation $i = \frac{\Delta_e}{R} - \frac{0{\cdot}058}{R}\log\left\{1 + \frac{ik}{[\mathrm{HQ}][\mathrm{Q}]}([\mathrm{HQ}] + [\mathrm{Q}] + ik)\right\}$.

[54] See Foerster's, *Elektrochemie wässeriger Löseingen*; Brookman's, *Electro-organic Chemistry*; Glasstone and Hickling's, *Electrolytic Oxidation and Reduction.*

[55] Leslie and Butler, *Trans. Faraday Soc.*, **32**, 989, 1936.

B. By a secondary reaction of the hydrogen primarily liberated with the depolariser. The hydrogen may be in one of the following states :—

(1) Free (atomic) hydrogen, or hydrogen which is only loosely attached to the electrode, e.g. when attached to a surface which is already saturated with adsorbed hydrogen, as M—H . . . H.

(2) Adsorbed hydrogen (attached directly to the metal).

These can be distinguished in some cases by studying the circumstances of the reduction. The reduction of unsaturated compounds, such as cinnamic acid, can usually be effected only at reversible electrodes, such as platinised platinum. At these electrodes the adsorbed hydrogen is easily desorbed and is therefore more reactive than molecular hydrogen. It is likely that processes of this type only differ from catalytic hydrogenations in that the hydrogen is produced *in situ.*

For the reduction of other compounds, such as pyridine and ketones, a high overvoltage cathode is necessary. At such electrodes it is probable that the hydrogen formed is either free or at most loosely attached to the surface. The reaction is then a purely secondary combination of hydrogen with the reducible substance, and the electrode potential should be the same as that which is required for the liberation of hydrogen at the same rate in the absence of the depolariser. This has been observed to be the case in the reduction of acetone and pyridine at lead electrodes. Sometimes the depolariser may be adsorbed on the electrode, and by reducing the effective area for hydrogen liberation may cause a displacement of the potential in the negative direction.

It has been frequently suggested that hydrogen is more reactive and has a greater " potential energy " the greater the overvoltage at which it is formed. There does not seem to be any clear basis for this belief. Free hydrogen formed at high overvoltage electrodes may be expected to be more reactive than the adsorbed hydrogen which is to be expected at low overvoltage electrodes. But the negative potential is merely that which is necessary to raise the electronic energy levels of the metal to a point at which the neutralisation process can occur at the desired rate and there is no reason to expect that the energy of the hydrogen formed will be directly influenced by this factor. Of course the concentration of the hydrogen will be increased when the potential is made more negative by a greater current.

When the reduction takes place below the reversible hydrogen potential, it most probably occurs by the direct transfer of electrons to the depolariser, e.g. this is probably the case in the reduction of nitrobenzene. It may be asked why, in such a case, the substance and its reduction product do not give rise to a reversible oxidation-potential. The reason presumably is that the ion formed by the initial step in the reduction is unstable and changes irreversibly into the stable reduction product. The first stage of the reduction of nitrobenzene may therefore be given as

$$C_6H_5NO_2 \overset{2\epsilon}{\rightleftarrows} C_6H_5NO_2^{=} \xrightarrow[\text{irreversible}]{2H^+} C_6H_5NO + H_2O.$$

Electrolytic oxidations appear to be much more complicated, since even in simple cases there is rarely one product of the oxidation. For example, sodium sulphite is oxidised partly to sulphate ($SO_4^{=}$) and partly to dithionate ($S_2O_6^{=}$). This reaction, which has recently been re-studied, may be taken as an example. The earlier workers [56] found that the yield of dithionate was influenced by the nature and previous treatment of the electrode and for this reason rejected a simple electrochemical mechanism and suggested that the oxidation was effected by oxygen. It was suggested that dithionate cannot be formed until a certain pressure of oxygen is reached,[57] but this has been disproved by Glasstone and Hickling,[58] who found that although a transition to a more positive potential occurs in the course of the electrolysis, the nature and efficiency of the oxidation process, which yields 40 to 50 per cent. of dithionate and 50 to 60 per cent. of sulphate was unaffected. The transition occurs more quickly when certain electrode poisons, such as mercuric cyanide, are present, and when the electrode has had previous anodic

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[56] Foerster and Friessner, *Ber.*, **35**, 2515, 1902; *Z. physikal. Chem.*, **47**, 659, 1904; *Z. Elektrochem.*, **10**, 265, 1904.

[57] Essin, *ibid.*, **34**, 78, 1928.

[58] *J. Chem. Soc.*, 829, 1933.

treatment. Salts of Mn, Fe, Co, Cu, etc., decrease yield of the dithionate as well. Similar observations have been made on the oxidation of thiosulphate[59] (to tetrathionate and sulphate).

These authors suggest[60] that the primary anode process is the formation of hydroxyl radicals by the neutralisation of hydroxyl ions, and their subsequent irreversible combination to hydrogen peroxide:

$$2OH^- \rightarrow 2OH \rightarrow H_2O_2.$$

The hydrogen peroxide may then decompose in either of two ways: (1) giving oxygen and water, (2) effecting the oxidation. It is supposed that dithionate is formed by the action of hydrogen peroxide alone, while sulphate may be formed by either oxygen or the peroxide. Any circumstance which favours the decomposition of hydrogen peroxide would thus increase the yield of sulphate. The action of salts of Mn, Co, Fe, Cu, etc., are therefore attributed to their ability to catalyse the decomposition of hydrogen peroxide. The electrode potential itself is regarded as determined by the oxygen present and as having no influence on the course of the reaction. Similar observations and interpretations have been made on the liberation of the halogens at anodes,[61] on the Kolbe synthesis,[62] and on the oxidation of chromic salts to chromates.[63]

In the case of the Kolbe synthesis, O. J. Walker and Weiss[64] found that in the presence of salts of Mn, Co, etc., oxide films were deposited on the electrode, and attributed the change in the product to this alteration of the electrode.

Butler and Leslie[65] list the possible processes by which electrolytic oxidation can be effected as follows:—

A. A primary electrochemical oxidation by the direct transfer of electrons to the electrode from the substance in solution or adsorbed on the electrode surface.

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[59] Glasstone and Hickling, *J. Chem. Soc.*, 2345, 2800, 1932.

[60] For summaries of this theory, see *Ann. Rep. Chem. Soc.*, **34**, 110, 1937; *idem.*, *Electrolytic Oxidation and Reduction* (Chapman & Hall).

[61] *J. Chem. Soc.*, 10, 1934.

[62] *Ibid.*, 1878, 1934; 820, 1936.

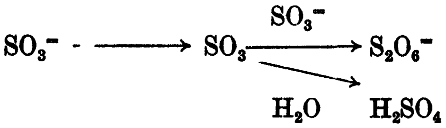
[63] Gross and Hickling, *ibid.*, 325, 1937.

[64] *Trans. Faraday Soc.*, **31**, 1011, 1935; cf. Glasstone and Hickling, *ibid.*, **31**, 1656, 1935; Bancroft, *Trans. Amer. Elect. Soc.*, **71**, 53, 1937.

[65] *Trans. Faraday Soc.*, **32**, 435, 1936.

B. A secondary oxidation brought about by a primary product of the electrolysis, such as
   (1) Atomic oxygen;
   (2) Adsorbed oxygen;
   (3) Any other primary product of the electrolysis, e.g. superficial peroxides.

In the case of sulphites, they found that in neutral solution the oxidation begins at a more negative potential than that at which adsorbed oxygen begins to be formed, and since no other primary process is observed at this potential in the absence of sulphite, it is concluded that the oxidation takes place by the direct discharge of the sulphite ions, which may then give rise either to sulphite or dithionate, as in the following scheme:—



$$SO_3^{=} \longrightarrow SO_3 \xrightarrow{SO_3^{=}} S_2O_6^{=}$$

$$SO_3 \xrightarrow[H_2O]{} H_2SO_4$$

In more alkaline solutions, however, oxidation occurs in the same region as that in which adsorbed oxygen is deposited on the electrode. Then oxidation can be brought about either by the simple electrochemical discharge or by the adsorbed oxygen. Since the latter will yield sulphate only, the increase in the proportion of sulphate formed in alkaline solutions can be understood.

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