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ELECTRICAL PHENOMENA AT INTERFACES

ELECTRICAL PHENOMENA AT INTERFACES

IN CHEMISTRY, PHYSICS AND BIOLOGY

EDITED BY

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PREFACE

THIS volume, a successor to *Electrocapillarity—The Chemistry and Physics of Electrodes and Other Charged Surfaces* is, as can be seen from the title page, largely a new work. I have been fortunate in being able to enlist the co-operation of a number of friends and colleagues, who have written entirely new chapters on subjects on which they have expert knowledge. Some of my own chapters have been reprinted, with additions to bring them up-to-date, but to make room for much new material, without unduly increasing the size of the book, the sections dealing with the thermodynamics and energetics of electrode potentials have been omitted.

As a result the book now covers most of the basic researches on electrical phenomena at interfaces, with a full account of their applications in colloid science, electrochemistry, biochemistry and physiology. It is believed that it will be helpful to many to find in one volume both the physical chemistry and the biological and other applications. Physicists and physical chemists will thus have brought to their notice, perhaps more directly than might otherwise be the case, the more complicated systems which occur in nature towards the elucidation of which their work is progressing. The biological scientists will, it is hoped, be better able to judge the nature of the physical concepts which enter into their interpretations. It will be obvious that much remains to be done in the biological field before the problems themselves are clearly defined, and also that the interfacial potential differences are only one aspect of the behaviour of these very complex systems and cannot be studied in isolation.

J. A. V. B.

February, 1951

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We are also indebted to Professors A. J. Rutgers and Washburn for communicating unpublished data in advance of publication.

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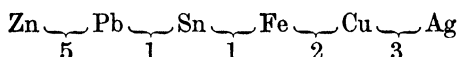
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CHAPTER I

ELECTRICAL POTENTIAL DIFFERENCES AND THEIR ORIGIN

J. A. V. BUTLER, D.Sc., F.R.I.C.

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 :—



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.

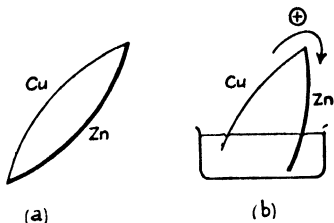
It was soon found that the voltaic pile was capable of producing chemical actions. Nicholson and Carlisle found that if two wires from the pile were placed in water, decomposition occurred ; hydrogen being liberated at the wire connected with the zinc and oxygen at that connected with the copper pole. 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



I 1.

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

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 Pellat¹ and Ayrton and Perry,² together with the electromotive forces of

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 .	0.25	0.35	0.28	0.46	0.62
Lead .	0.15	0.31	0.20	0.35	0.64
Iron .	0.56	0.70	0.60	0.74	0.32
Nickel .	0.47	0.63	—	—	0.51
Copper .	0.71	0.86	0.75	0.89	1.1
Silver .	0.91	1.12	—	—	1.56
Platinum	—	—	0.98	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

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 acquired 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

⁵ See *Phil. Mag.*, **21**, 51, 1886.

moderate vacuum 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

* "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.*

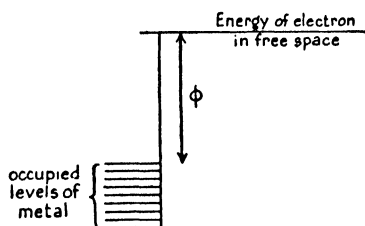
In the more recently developed formulation in terms of quantum mechanics, there are in a piece of metal a large number of *energy-levels* each of which can accommodate two electrons. The electrons of the metal which give rise to its metallic conduction are distributed among these levels in such a way 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.

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

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

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 $\frac{1}{2}mv^2$. At the threshold frequency $\frac{1}{2}mv^2 = 0$ 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



I 2.

* 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-workers⁷ 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

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

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

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

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

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

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

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

contact potential difference between two metals, the magnitude of which is given by (2), was conclusively proved by these experiments.

TABLE II. CONTACT P.D.S 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 Langmuir⁸ 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,⁹ is that the energy of transfer of electrons from one metal to another is itself an important part of the cell reaction.

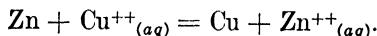
Consider the Daniell cell in its simplest form (Fig. 3). When the cell yields current, zinc dissolves from the negative pole

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

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

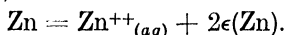
⁹ *Phil. Mag.*, **48**, 927, 1924.

and copper is deposited at the positive pole and the whole cell reaction is

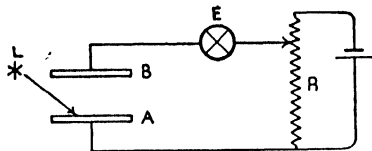


Different component parts of this reaction occur at different parts of the cell. At the zinc electrode zinc ions pass into the solution, leaving their complement of electrons in the metal, i.e. representing

an electron in metallic zinc as $\epsilon(\text{Zn})$, the reaction here is

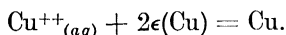


The electrons pass round the external circuit from the zinc to the copper, passing over the junction



I 3.

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.



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.

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.*

* E.g. *Chemical Thermodynamics* by J. A. V. Butler (Macmillan & Co.).

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 EF .

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

$$zFE = -\Delta F.$$

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

$$\Delta S = -d(\Delta F)/dT = zF(dE/dT).$$

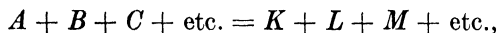
Thus we have

$$zEF = -\Delta H + zTF(dE/dT).$$

Electrical energy obtained. Heat evolved in reaction. Heat absorbed in working of the cell.

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



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 $\alpha_B, \alpha_C, \dots \alpha_L, \alpha_M \dots$ are the activities of the various dissolved substances, the free energy in the reaction can be expressed as

$$\Delta F = \Delta F^0 + RT \log_e \frac{\alpha_L \cdot \alpha_M \cdot \dots}{\alpha_B \cdot \alpha_C \cdot \dots},$$

where ΔF^0 is the free energy change when all the dissolved substances are at unit activity. Since $zE\mathbf{F} = -\Delta F$, we thus have

$$E = -\frac{\Delta F^0}{z\mathbf{F}} + \frac{RT}{z\mathbf{F}} \log_e \frac{\alpha_B \cdot \alpha_C \cdot \dots}{\alpha_L \cdot \alpha_M \cdot \dots} \quad (3)$$

where $-\Delta F^0/z\mathbf{F}$ is a constant for the given reaction at a given temperature which may be written as E^0 . If one of the substances taking part in the reaction is a gas, the activity may be replaced by the pressure.

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

$$\bar{F}_1' = \bar{F}_1'' \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the same applies to each component which is present in both of the phases. This means that a small quantity of the substance in question can be transferred from the one phase to the other without changing the free energy of the system as a whole, which is thus in a state of minimum free energy at the given temperature and pressure.

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 ¹⁰

$$\bar{F}_1' + eV' = \bar{F}_1'' + eV'' \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where V' , V'' are the electrical potentials of the two phases and e is the charge carried by a mol of the substance. Guggenheim ¹¹ 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 II. 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

$$\left. \begin{aligned} \bar{F}'_{\text{Ag}^+} + \mathbf{F}V' &= \bar{F}''_{\text{Ag}^+} + \mathbf{F}V'' \\ \bar{F}'_{\text{Cl}^-} - \mathbf{F}V' &= \bar{F}''_{\text{Cl}^-} - \mathbf{F}V'' \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the single dash refers to the solid and the double dash to

¹⁰ Butler, *Proc. Roy. Soc.*, **112A**, 129, 1926.

¹¹ *J. Physical Chem.*, **33**, 842, 1929; **34**, 1540, 1930; cf. Brønsted, *Z. physikal. Chem.*, **143**, 301, 1929.

the solution. The charge (e) on a mol of silver ions in $+F$ and that on a mol of chloride ions $-F$.

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

$$\begin{aligned}\bar{F}'_{Ag^+} + \bar{F}'_{Cl^-} &= \bar{F}''_{Ag^+} + \bar{F}''_{Cl^-}, \\ \bar{F}'_{AgCl} &= \bar{F}''_{AgCl};\end{aligned}$$

or

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

$$\begin{aligned}\bar{F}''_{Ag^+} &= \bar{F}^o_{Ag^+} + RT \log \alpha_{Ag^+} \\ \bar{F}''_{Cl^-} &= \bar{F}^o_{Cl^-} + RT \log \alpha_{Cl^-}\end{aligned}\quad . \quad . \quad (7)$$

where $\bar{F}^o_{Ag^+}$, $\bar{F}^o_{Cl^-}$ 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 (6) is

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

or, using (4), $V' - V'' = \text{const.} + \frac{RT}{F} \log \alpha_{Ag^+}$

or, alternatively,

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

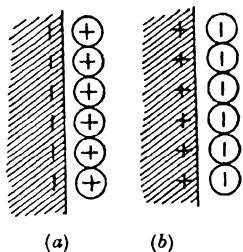
We thus see that the potential difference between silver chloride and its saturated solutions varies with the silver ion concentration in the same way as that of a metallic silver electrode.

A form of this expression was first used by Haber,¹² who made some exploratory measurements. Kolthoff and Sanders¹³ 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.

¹² *Ann. Physik*, **26**, 927, 1908.

¹³ *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.*).

The Electrode Potentials of Metals. We now turn to the consideration of the mechanisms whereby potential differences arise at the various junctions. In 1889 Nernst¹⁴ 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



I 4.

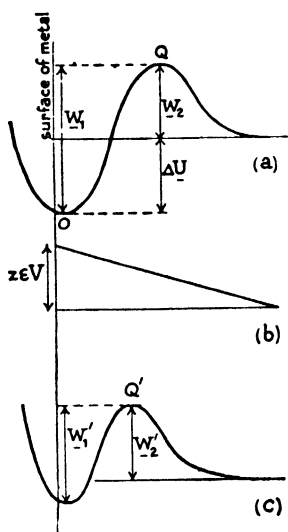
acquires a positive charge. The positive charges of the ions which have passed into the solution and the negative charges on the metal form an "electrical double layer", Fig. 4 (a), which ions must now cross in their passage into the solution. This double layer tends to prevent the solution of ions, 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 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

¹⁴ *Z. physikal. Chem.*, **4**, 129, 1899.

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. 4 (b)).

A more definite physical picture of the process was given in 1924¹⁵ 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



I 5.

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. 5 (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

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

¹⁵ *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.

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 $\theta_2 = c\sqrt{TA}e^{-W_2/kT}$. 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. 5 (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. 5 (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

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

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

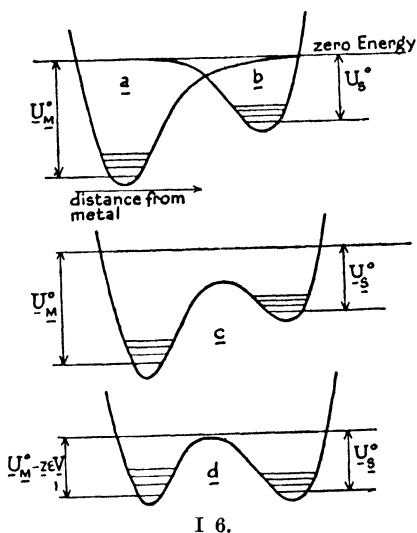
$$V = \frac{\Delta U}{z\epsilon} + \frac{kT}{z\epsilon} \log c + \frac{kT}{z\epsilon} \log \left(\frac{A}{N_1A'} \right).$$

Writing the more familiar RT/zF instead of $kT/z\epsilon$, we obtain the Nernst expression

$$V = V^\circ + RT/zF \log c,$$

where V° is given as $\Delta U/z\epsilon + kT \log (A/N_1A')$. The normal potential difference V° 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 Fowler¹⁶ 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. 6 (a). The horizontal line represents the energy of the isolated ion *in vacuo*, and U_M° 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



I 6.

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.

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. 6 (b)). Here U_s° is the hydration energy of the ion. Combining these two curves we obtain Fig. 6 (c), for representing the

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. 6(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

¹⁶ Gurney and Fowler, *Proc. Roy. Soc.*, **136A**, 378, 1932.

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. 6 (d). The energy of lowest metal level is now $U_M^0 - z\epsilon V$.

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

$$F(U)dU = 1/kT \{ e^{-(U_M^0 - z\epsilon V - U)/kT} \cdot dU \},$$

where $U_M^0 - z\epsilon V$ 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 $1/kT(e^{-(U_s^0 - U)/kT})$, where U_s^0 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

$$N_w e^{-(U_M^0 - z\epsilon V - U)/kT} = \beta N_s e^{-(U_s^0 - U)/kT},$$

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

$$V = \frac{U_M^0 - U_s^0}{z\epsilon} + \frac{kT}{z\epsilon} \log \left(\frac{\beta N_s}{N_w} \right),$$

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,

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

Mechanism of Oxidation-Reduction Electrodes. Nernst and others¹⁷ regarded these electrodes as gas electrodes, the oxidation-

¹⁷ Nernst and Lessing, *C. Zent.*, **2**, 241, 1902; Friedenhausen, *Z. anorg. Chem.*, **29**, 396, 1902.

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 Butler¹⁸ 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 $Ae^{-(\phi_M + eV)/kT}$. 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.

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

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.

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

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

$$A'xe^{-(\phi_M + eV)/kT} = A''yl^{-J/kT},$$

so that

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

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

¹⁸ *Trans. Faraday Soc.*, **19**, 734, 1924.

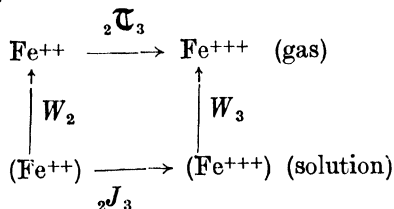
* A more elaborate hypothesis, involving the *adsorption* of the ions on the electrode, was made in the original paper.

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.

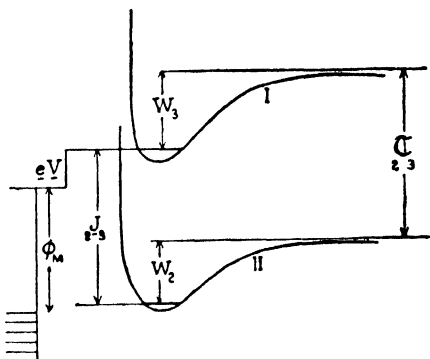
This quantity is not the same as the ionisation potential of the ferrous ion, i.e. the energy required to remove an electron from Fe^{++} *in vacuo*. When a ferrous ion becomes a ferric ion in solution the hydration energy changes and the difference of hydration energy must be included in J . If W_2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

$${}_2J_3 = {}_2\mathcal{T}_3 - (W_3 - W_2) = {}_2\mathcal{T}_3 - \Delta W,^{19}$$

where ${}_2\mathcal{T}_3$ 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^{++} .



A better picture of this process is given by means of the more recently developed potential diagrams. In Fig. 7 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



I 7.

¹⁹ R. W. Gurney, *Ions in Solution* (Camb. Univ. Press, 1938).

hydration energy W_2 . The whole curve is displaced downwards a distance of ${}_2\mathcal{T}_3$, 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.

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 *

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

Potential Differences at the Junction of Two Liquids and the Effect of Membranes. (a) *No membrane separates the liquid.* It has long been recognised that a potential difference can arise at this junction, and a calculation of its magnitude, which has not been improved very much, was given by Nernst. A potential difference will arise if the ions of opposite charge do not have equal mobilities. If, for example, the mobility (or diffusion constant) of the positive ion is greater than that of the negative ion, the weaker solution will tend to become positively charged. It is obvious that, as no real separation of electric charges can occur, a potential difference will arise at the boundary, which will be sufficient to equalise the rate of diffusion of the ions. Most of the calculations which have been made are based on thermodynamics. Nernst, for example, worked out the actual transfer of the ions from one solution to the other (taking the reversible electrodes dipping into the solutions into account) and equated

* 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.

the electrical work done with the osmotic work involved in the transference. The equation obtained for the junction p.d. alone is

$$E_D = \frac{RT}{F} \cdot \frac{u-v}{u+v} \log \frac{c_1}{c_2},$$

where u and v are the respective mobilities of the ions, and c_1 , c_2 the concentrations of the salt at either side of the boundary.

It is obvious that at the junction of two solutions of unequal concentration, equilibrium conditions do not apply and the thermodynamic calculation is not valid. It ought to be possible to calculate the potential difference which will equalise the rates of diffusion kinetically, but the conditions at the boundary are rather difficult to formulate. A large number of variants of the above expression has been given. The most obvious is to allow for variations of the mobilities of the ions, as expressed in the transport number, with concentration. The more general equations, obtained in this way, viz.

$$E_D = \frac{RT}{F} \left(\int_{c_2}^{c_1} \frac{t^+}{z^+} d \ln c_+ - \int_{c_2}^{c_1} \frac{t^-}{z^-} d \ln c_- \right),$$

where t^+ , t^- are the transport numbers of the positive and negative ions, obviously suffer from the same criticism as the special form. Other types introduce the conductivities instead of the concentrations, e.g. Lewis and Sargent's equation

$$E_D = \frac{RT}{F} \ln \Lambda_1/\Lambda_2.$$

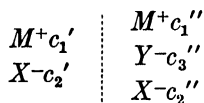
The potential difference also depends to some extent on how the junction is made. Flowing junctions give greater reproducibility than stationary junctions. It has been suggested that the junction potential difference may be eliminated by allowing the two liquids to impinge on each other at a high speed. The maximum value of the junction potential difference, for a tenfold difference of concentration, obtained according to these equations when the mobility of one of the ions is zero, is approximately 0.059 volt at 25° for univalent ions.

(b) *A membrane permeable to both ions separates the solutions.* Even if the membrane is permeable to all the ions, it may modify their relative mobilities and so change the boundary p.d. The

maximum effect produced by a boundary will be when it becomes impermeable to either anions or cations. The potential difference should then approach the theoretical maximum. Michaelis²⁰ investigated dried collodion membranes, which are practically impermeable to water and electrolytes, but apparently permit a slight exchange of cations. The p.d. of the cell

sat. KCl and calomel | KCl 0.1 M | membrane | KCl 0.01 M | sat KCl and calomel
was about 50 mv. If it is assumed that the saturated KCl abolishes the two junction p.d.s with the electrode, this is not far short of the diffusion potential, calculated on the assumption that the anion mobility is zero.

(c) *The membrane is impermeable to one of the ions.* This is the well-known case of the Gibbs-Donnan equilibrium. Suppose a membrane separates a solution containing the salt MX , both of the ions being diffusible through the membrane, from a solution of the salt MY , of which the anion Y^- is unable to pass through. The equilibrium state



is determined by the two conditions :

(1) for the equilibrium of each ion which is able to pass through the membrane, by (5) of page 15 :

$$F' - F'' = ze(V'' - V'),$$

i.e. the potential difference $V'' - V'$ across the membrane is determined by the free energy difference, which is approximately given by

$$\bar{F}' - \bar{F}'' = \Delta F = RT \log \frac{c'}{c''},$$

or more exactly by

$$\Delta F = RT \log \frac{c'f'}{c''f''},$$

where c' , c'' and f' , f'' are the concentrations and activity coefficients of the ions in the two solutions.

²⁰ *J. Gen. Physiol.*, **8**, 33, 1925. See also Labes and Zain, *Arch. exper. Path. u. Pharmacol.*, **126**, 352, 1927; U. Ebbecke, *Z. f. Biol.*, **91**, 247, 1931.

(2) The condition of electroneutrality, by which each phase must remain as a whole electrically neutral.

We must note the following difficulties and qualifications in the application of these equations:

(1) It is not possible to measure the membrane potential difference alone.

(2) If electrodes, reversible to either of the ions M^+ or X^- are placed in both solutions, the e.m.f. of the whole combination will be zero, because the difference of potential at the two reversible electrodes will also be given by

$$ze \cdot \Delta V = RT \log \frac{c'f'}{c''f''},$$

but the sign of this p.d. will be opposite to the sign of the membrane p.d. This is merely an illustration of the fact that no reversible e.m.f. can be obtained from two similar electrodes dipping into two phases which are in equilibrium with each other.

(3) If, however, identical electrodes, such as saturated calomel electrodes dip into the solutions on each side of the membrane, and if the conditions are such that the diffusion potentials between these electrodes and the two membrane liquids are zero, or balance out, then the membrane p.d. will be measured. As has been explained it is impossible to be sure that these conditions are satisfied.

(4) It must be noted that the expression given in this section for an equilibrium p.d. at a membrane at least approximates to the diffusion p.d. under similar conditions, i.e. when the mobility of X^- is zero.

(d) *A membrane having special properties separates the solutions.* Membranes with special properties, e.g. zeolites, ion exchange resins, have been investigated by a number of workers.²¹ These have the property of binding one kind of ion. A theoretical treatment has been given by Meyer (*loc. cit.*), and by Teorell.²²

²¹ K. H. Meyer, *Trans. Faraday Soc.*, **33**, 1073, 1937; K. H. Meyer and J. F. Sievers, *Helv. Chim. Acta*, **19**, 649, 665, 987, 1936; C. E. Marshall, *J. physical Chem.*, **43**, 1155, 1939; **48**, 67, 1944; C. E. Marshall and W. E. Bergman, *J. Amer. Chem. Soc.*, **63**, 1911, 1941; *J. Phys. Chem.*, **46**, 325, 1942; *J. Amer. Chem. Soc.*, **64**, 1814, 1942; C. E. Marshall, *J. physical coll. chem.*, **52**, 1284, 1948; K. H. Meyer and P. Bernfeld, *Helv. Chim. Acta*, **28**, 962, 980, 1945.

²² T. Teorell, *Proc. Soc. Exp. Biol. Med.*, **33**, 282, 1935; *Trans. Faraday Soc.*, **33**, 1054, 1937; see also p. 245.

Fetcher²³ showed that the observed potentials differed considerably from those predicted. Sollner and Carr²⁴ have discussed the discrepancies. Other types of membranes in which the ions were either adsorbed on the pores, or chemically combined have been investigated (cf. ref. 24). Abrams and Sollner²⁵ investigated membranes produced by the adsorption of protamine cations on nitrocellulose. Gregor and Sollner²⁶ used oxidised nitrocellulose membranes, in which a fixed carboxyl group was produced by oxidation and was accompanied by mobile sodium ions. When this membrane separates two sodium chloride solutions, it is more permeable to Na^+ than Cl^- , because the concentration of Na^+ in the membrane is greater than that of Cl^- .

Complex mosaic membranes with parts which are selectively anion-permeable and cation-permeable, have been discussed by K. Sollner.^{26a} Models of these types are provided by "perselective" collodion and protamine collodion membranes,^{26b} which have an appreciable selective permeability. Natural shale membranes and mixtures of ion-exchange resins have been studied by Wyllie and Patwode.^{26c}

(e) *The effect of adsorption at the interface between two phases.* If a dipolar molecule is adsorbed at the interface between two phases, and the molecules are all orientated in the same direction, there will be a potential difference at the interface arising from the dipoles equal to $\Delta V = 4\pi n\mu$ where n is the number of dipoles per unit area and μ their average dipole moment at right angles to the plane of the interface.

If there is an ionic equilibrium across the interface, it will not be affected by the adsorbed layer. The equilibrium will be determined by the equality of the partial free energy of each possible kind of neutral salt molecule in the two phases. It follows that

²³ E. S. Fetcher, *J. physical chem.*, **46**, 570, 1942.

²⁴ K. Sollner, *et al.*, *J. Gen. Physiol.*, **24**, 1, 1940; **25**, 7, 1941; **26**, 17, 1942; **27**, 369, 1943; **28**, 1, 1944.

²⁵ J. Abrams and K. Sollner, *J. Gen. physiol.*, **26**, 369, 1943.

²⁶ H. P. Gregor and K. Sollner, *J. physical chem.*, **50**, 53, 88, 1946.

^{26a} K. Sollner, *Biochem. Z.*, **244**, 370, 1932.

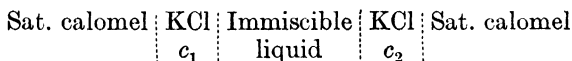
^{26b} K. Sollner, *et al.*, *J. Gen. Physiol.*, **28**, 119, 179, 1944; *J. Amer. Chem. Soc.*, **67**, 346, 1945; *J. Phys. Chem.*, **50**, 470, 1946; **51**, 299, 1947; *J. Phys. and Colloid Chem.*, **54**, 157, 325, 330, 1950.

^{26c} *Ibid.*, **54**, 204, 1950.

the total potential difference across the interface will not in this case be determined by the adsorbed layer. In other words the salts will establish a double layer, which is sufficient to bring the potential difference to the value they require for their own equilibrium.²⁷

If there is no equilibrium across the interface the potential difference may be determined by the adsorbed molecules.

(f) *Oil membranes.* On account of their possible analogy with natural membranes, a great deal of work has been done on "membranes" which consist of a layer of oil, or other immiscible liquid, interposed between two electrolyte solutions.²⁸ The oily layers have usually been liquids, such as guaiacol, salicyl aldehyde, phenol, aniline which have some acidic and basic properties, on account of which they can dissolve either the anion or cation of the aqueous solutions. In the arrangement



the more dilute KCl solution was positive when an acidic liquid like guaiacol was used and negative when a basic liquid like aniline. Dean²⁹ ascribed this to the fact that potassium ions can dissolve in guaiacol, forming potassium guaiacolate, and the liquid then acts as a membrane permeable to K^+ only, while with aniline, chloride ions are soluble as aniline hydrochloride giving a membrane permeable to Cl^- alone.

Osterhout³⁰ used guaiacol interposed between potassium guaiacolate solutions of different concentrations.

²⁷ See Dean, Gatty and Rideal, *Trans. Faraday Soc.*, **36**, 161, 166, 173, 1940.

²⁸ See R. Beutner, *Die Entstehung electrischer Ströme in lebenden Geweben*, Stuttgart, 1920; Ehrensuård and Sillen, *Nature*, **141**, 788, 1938.

²⁹ *Nature*, **144**, 32, 1939; *loc. cit.*, ref. 28.

³⁰ *J. Gen. physiol.*, **26**, 293, 1943; Cold Spring Harbor Symp., **8**, 51, 1940.

CHAPTER II

THE ELECTRICAL DOUBLE LAYER AND ELECTROCAPILLARITY

J. A. V. BUTLER

Potential Differences at Interfaces. A potential difference between two phases arises, as we have seen, if the ions present have an unequal tendency to distribute themselves between the phases. By itself such tendencies would produce unequal distributions of ions in the various phases. The fact that each phase as a whole must be electrically neutral prevents this; and the actual separations of electrical charges which occur are confined to very thin layers in the vicinity of the interfaces. These separations give rise to potential differences at the interfaces which are sufficient to bring the system into equilibrium. It can be shown by thermodynamical reasoning that a single potential difference between two phases is always sufficient to ensure equilibrium, no matter how complex the phases are. This potential difference will arise from an uneven distribution of the electric charges in the boundary region. There will be an excess of positive charges on one side and an excess of negative charges on the other side of the boundary layer, the whole distribution constituting an *electrical double layer*. When an electrically charged particle (or anion) passes from one phase to the other, work is done in passing through the electric field of the double layer, i.e. we say that there is a difference of electric potential between the two phases.

Unfortunately, we have no direct way of directly determining the electrical potential difference between two phases. We cannot take a particle with unit charge and carry it out of one phase into the other, determining at the same time how much electrical work is done. All our measurements of electrical potential differences involve completing a conducting circuit, of which the two phases are a part. This inevitably involves the setting up of two

or more other interfaces, at which electrical potential differences may also occur.

There is thus no way of determining the electrical potential difference at a single interface, and we cannot state what the absolute value of the potential difference is. In many cases, however, it is sufficient and possible to state the potential difference, relative to some electrode which is taken as standard. It is often possible to arrange experiments so that all the interfaces in a circuit remain unchanged (or practically unchanged) except that at which variations of the conditions are being studied.

It has been suggested 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 other components of the Gibbs "chemical potential". This is undoubtedly true, but we shall see that it is possible to learn much about the distribution of electric charges about interfaces. There is no obstacle in theory, although experiment at present is some distance from its achievement, to obtaining a fairly complete knowledge of the charge distribution at an interface, not only of the ions, but also that produced by the orientation of polar molecules. This will be a sufficient knowledge for the solution of the problems which arise in practice. The simplest distribution of charge, which was taken by Helmholtz as a model of actual double layers, is one in which there is a plane with a uniform distribution of charge of density e per unit area, separated by a distance d from a similar plane with charge density $-e$. The product $\tau = ed$ was called the moment of the double layer by Helmholtz. Guggenheim¹ has suggested that a practical unit of τ , viz. 10^{-2} e.s.u. of charge/cm., be called 1 Helmholtz. The usual relation between the potential difference and the moment is

$$\Delta V = \frac{4\pi\tau}{D}.$$

There may be difficulty in applying this owing to ignorance of D in the double layer. Guggenheim suggests that the quantity τ is more useful and unambiguous.

¹ *Trans. Faraday Soc.*, **36**, 139, 1940.

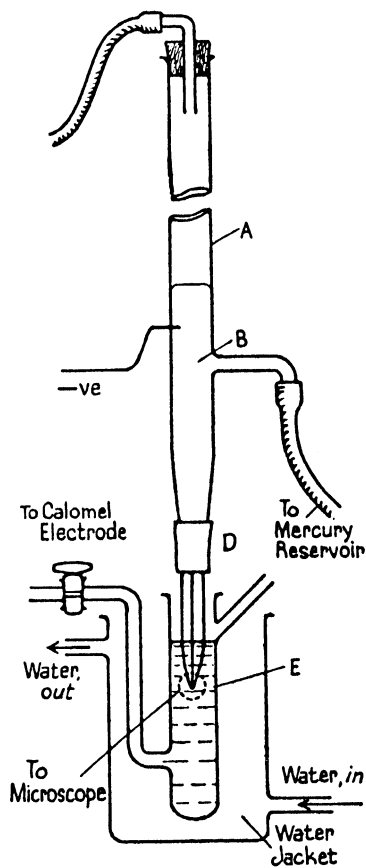
We shall consider in this and succeeding chapters the methods by which information about the distribution of charges at interfaces can be obtained.

We shall first briefly review methods which have been used to

determine qualitatively the sign of the charge of the double layer, i.e. to determine if the solution side is positively or negatively charged. The detailed investigation of the distribution of charge within the double layer will be discussed later.

The Electrocapillary Curve.

When a mercury electrode is polarised its surface tension changes. Lippmann² 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 changes very little, and



II 1.—Apparatus for determining electrocapillary curves.

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

² *Pogg. Ann.*, **149**, 547, 1878; *Ann. d. Chim. et d. Phys.*, **5**, 494, 1875; **12**, 265, 1877.

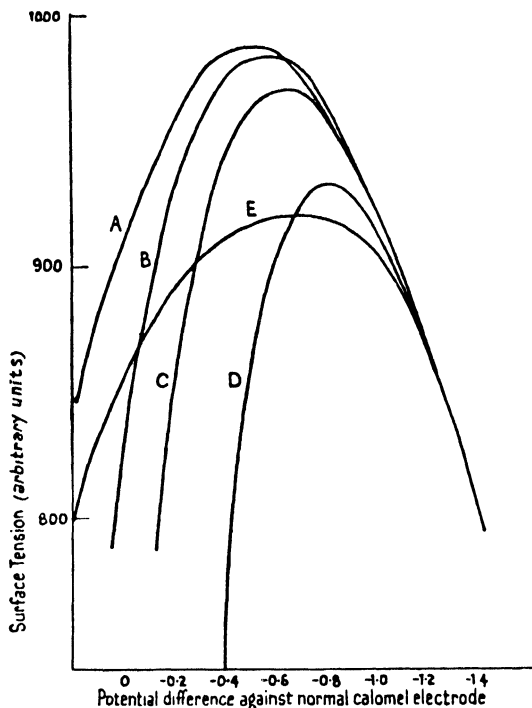
equal to the applied potential difference. The surface tension of the mercury-solution interface is measured by the height of the mercury column required to bring the meniscus to a fixed point in the capillary tube.

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. 58), 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 $d\sigma/dV = 0$,



II 2.—Electrocapillary curves of (A) $N/10$, NH_4NO_3 , (B) $N/1$ KCl , (C) $N/1$ KBr , (D) $N/1$ KI , (E) $N/1$ $\text{KCl} + N/10$ phenol. (Wightman.)

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 $d\sigma/dV = 0$,

³ Kúcera, *Ann. Physik*, **11**, 529, 698, 1903; Craxford and McKay, *J. Physical Chem.*, **39**, 545, 1935. See also Craxford, *Phil. Mag.*, **16**, 66, 268, 1933.

$[e] = 0$ and the potential difference arising from the double layer is therefore zero.

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

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

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 volt with reference to the normal calomel electrode, and the absolute potential difference of the latter is therefore $+0.56$ volt.

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

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.

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. Paschen⁶ found that it 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.

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

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.

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 with metallic amalgams and gallium, which melts at 30° C. Early experiments with amalgams¹⁰ gave curves similar to those obtained with pure mercury, but more recent work by Frumkin and collaborators¹¹ 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

% 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 chloride¹² and its maximum was at — 0.9 volt 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

* See p. 39.

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

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

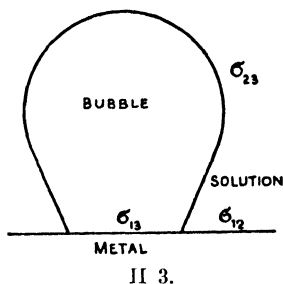
¹² Frumkin and Gorodetskaya, *Z. physikal. Chem.*, **136**, 215, 1928; Muratazejew and Gorodetskaya, *Acta Physicochimica, U.R.S.S.*, **4**, 75, 1936.

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

been developed by Frumkin to determine the capillary curves of solid metals.¹⁴ It is based on the variation of the angle of contact 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 volt 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



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

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

¹⁵ A. Frumkin, A. Gorodetskaya, 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 Gorodetskaya, *Acta Physicochimica*, **9**, 313, 1938.

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:—

(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 volt 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

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

²⁰ McBain and Laing, *J. Physical Chem.*, **28**, 673, 706, 1929.

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

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 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. Garrison²² used a silver needle suspended over a quadrant 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 volt with respect to the N-calomel electrode, in substantial agreement with the electrocapillary maximum. Balaschora and Frumkin²⁵ have also examined the deflection of fine platinum wires in an electric field.

Bennewitz and Schulz²⁶ 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 $+0.19$ volt with respect to the N-calomel electrode.

Other Methods. (1) *Adsorption methods.* M. Proskurnin and A. Frumkin²⁷ found that when a large piece of silver foil is brought

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

²³ *Ann. Physik*, **12**, 1072, 1903.

²⁴ *J. Russ. Phys. Chem. Soc.*, **49**, 207, 1917; *Acta Physicochim.*, **1**, 232, 1934; **9**, 359, 1938; **21**, 193, 1946.

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; V. I. Veselovsky, *Acta Physicochim., U.R.S.S.*, **11**, 815, 1939; cf. Krut and Overbeek, *Trans. Faraday Soc.*, **36**, 110, 1940.

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 silver, the adsorption being positive in the stronger solutions and negative in the weaker ones. At a concentration of about $2 \times 10^{-5} N$, the adsorption was zero, and the authors regarded this as a null solution. The potential of the electrode in this solution is $E_A = 0.51$ volt, which agrees with the value of Billiter and Bennewitz. Similar experiments have been made with charcoal²⁸ and platinum surfaces.²⁹

(2) *The ionisation method.* In any electromotive force measurements 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.³⁰ 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 Lange³¹ 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 $\Delta V_1 = \text{const.} + 0.058 \log c$ (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

²⁸ Frumkin *et al.*, *Acta Physicochim.*, **12**, 795, 1940. •

²⁹ A. Slygin, A. Frumkin, *et al.*, *ibid.*, **4**, 911, 1936; **5**, 819, 1936; see Frumkin, *Trans. Faraday Soc.*, **36**, 117, 1940.

³⁰ *Z. physikal. Chem.*, **125**, 135, 1927; **138**, 357, 1928; Andauer and Lange, **166**, 219, 1933.

³¹ *Z. Elektrochemie*, **43**, 470, 1937; **44**, 542, 562, 1938; cf. Fink and Dehmel, *Trans. Amer. Elect. Soc.*, **70**, 281, 1936.

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

$$\Delta V \text{ (M/solution)} = \Delta V \text{ (M/gas)}$$

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

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 volt. 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 volt with respect to the normal calomel electrode, the absolute potential of the latter will be + 0.56 volt. 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

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 volt
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

* Chalmers and Pasquall (*Phil. Mag.*, **23**, 88, 1937) find the value of the air solution potential difference to be 0.26 volt.

methods. The determinations by electrocapillary and electrokinetic methods for each metal are fairly consistent.

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 -0.56 and that of silver about $+0.2$ volt, with respect to the *n*-calomel electrode, the electromotive force of the cell composed of the two null electrodes is 0.8 volt; 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. Helmholtz³² 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

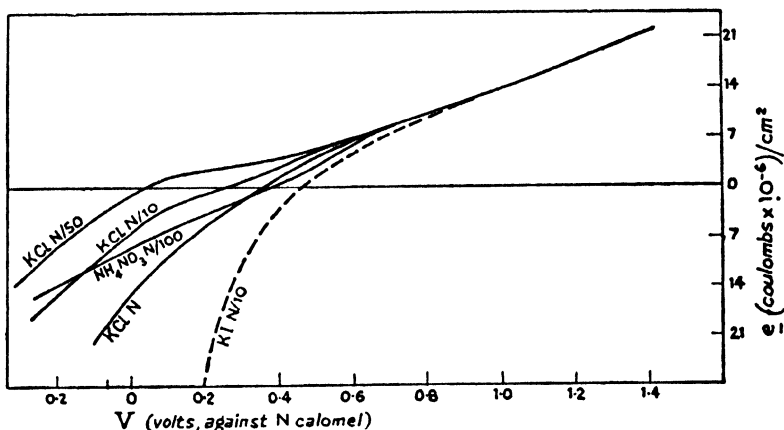
$$e = -d\sigma/dV$$

and

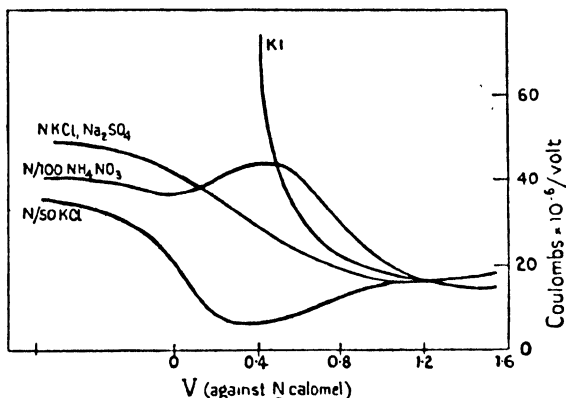
$$\frac{de}{dV} = -d^2\sigma/dV^2.$$

³² *Monats. Preuss. Akad. Sci.*, Nov. 1881; *Wied. Ann.*, 7, 337, 1879.

It is evident that if the capacity were constant, the electrocapillary curves would be exact parabolas. This is, however, only the case in rare instances, such as potassium nitrate solutions³³



II 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 $NKCl$.



II 4 (b).—Types of capacity curves.

which are stated to give an approximately constant capacity of 13 microfarads/cm.² Fig. 4 (a) shows some curves of $-e$ or $d\sigma/dV$, and the shapes of the corresponding capacity curves are indicated

³³ Krüger and Kromreich, *Z. Elektrochem.*, **19**, 620, 1913.

in Fig. 4 (b).³⁴ Since the left-hand branch of the electrocapillary curve is usually steeper than the right-hand branch, the capacity 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.²,³⁵

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:—

$$1 \text{ coulomb} = 300 \times 10^7 \text{ e.s. units,}$$

$$1 \text{ volt} = \frac{1}{300} \text{ e.s. units,}$$

$$1 \text{ farad} = 9 \times 10^9 \text{ e.s. units.}$$

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

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

and

$$\delta = D/4\pi \times 162 \times 10^5 = 0.5 \times 10^{-8} D \text{ e.s. units.}$$

If D is taken as unity, the thickness of the double layer is thus $0.5 \text{ \AA}$.

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

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

and

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

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

Frumkin (*Phil. Mag.*, **40**, 375, 1920) gives for mercury in $2n \text{ H}_2\text{S}_4\text{O}$, 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

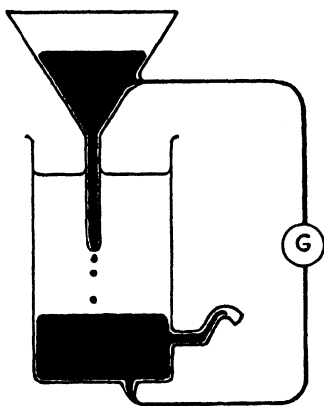
Dropping electrode method. This was initiated by Varley,³⁶ who showed that when mercury flows from a reservoir into a solution forming drops which recombine in a pool at the bottom of the vessel, a current may flow along a wire joining the two masses of mercury (see Fig. 5). However, if the dropping 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

³⁴ Data from Butler and Wightman, *J. Physical Chem.*, **35**, 3293, 1931; see Barclay and Butler, *Trans. Faraday Soc.*, **36**, 128, 1940; Craxford, *ibid.*, **36**, 85, 1940.

³⁵ *Ann. Chim. Phys.* (7), **29**, 159, 1903.

³⁶ *Phil. Trans.*, **101**, 129, 1871.

formation of drops is equivalent to an expansion of the upper mercury surface, and if it were insulated the potential would change until it reached that of the electro-capillary 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,³⁷ and more recently measurements have been made by Frumkin³⁸



II 5.—Dropping electrode.

and by L. St. J. Philpot.³⁹ The former compared the value of e , determined in this way, with that given by $-\frac{d\sigma}{dV}$, 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

	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

$$c = \frac{de}{dV} = \frac{idt}{dV}$$

³⁷ *Loc. cit.*

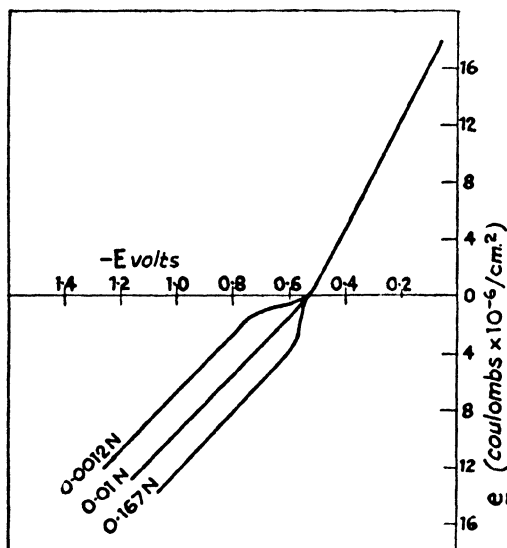
³⁸ *Z. physikal. Chem.*, **103**, 55, 1923.

³⁹ *Phil. Mag.*, **13**, 775, 1932.

The rate of change of the potential difference of electrodes, after starting the current, and also after stopping a steady current, was first investigated by Oberbeck,⁴⁰ Pring,⁴¹ and Le Blanc.⁴² 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. Knobe⁴³ made similar experiments with electrodes at which hydrogen was liberated, and Newbery⁴⁴ also

examined with an oscillograph the changes of potential which occur on stopping and starting the current.

The subject was clarified in 1928 by the careful experiments of Bowden and Rideal,⁴⁵ 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



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

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

⁴⁰ *Wied. Ann.*, **31**, 337, 1887.

⁴¹ *Z. Elektrochem.*, **19**, 255, 1913.

⁴² *Abh. Bunsen-Ges.*, No. 3.

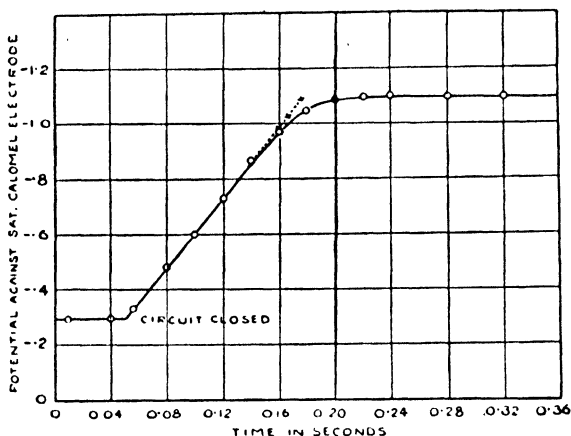
⁴³ *J. Amer. Chem. Soc.*, **46**, 2613, 1924.

⁴⁴ *Proc. Roy. Soc.*, **107A**, 486, 1925; **111A**, 182, 1926; **114A**, 103, 1927; **119A**, 680, 686, 1928.

⁴⁵ *Ibid.*, **120A**, 59, 80, 1928; Bowden and O'Connor, *ibid.*, **128A**, 317, 1930.

of 5×10^{-7} amps./cm.² When the circuit is closed, the potential rises linearly with time, from -0.3 volt to -0.9 volt (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 volt, 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



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

overvoltage, the rate of this process diminishes very rapidly as the electrode potential becomes more positive; and is negligible below -0.8 volt. 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 ($\dot{i}dt/dV$) is the capacity of the double layer.

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.⁴⁶ 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

	<i>Polished</i>	<i>Activated</i>	<i>Annealed</i>	<i>Electroplated</i>	<i>Rolled</i>
B	75	276	65	72	35×10^{-6}
<u>Real Area</u>					
<u>Apparent Area</u>	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,⁴⁷ who obtained values between 7 and 10 microfarads/cm.² M. Proskurnin and A. Frumkin,⁴⁸ using this method more recently, with stringently purified solutions, 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.⁴⁹ 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,

⁴⁶ E. Baars, *Ber. Ges. Förd. Naturwiss.*, Marburg, **63**, 213, 1928; Brandes, *Z. physikal. Chem.*, **142A**, 97, 1929; T. Erdey-Grúz and M. Volmer, *ibid.*, **150A**, 203, 1930; T. Erdey-Grúz and G. G. Kromey, *ibid.*, **157A**, 213, 1931.

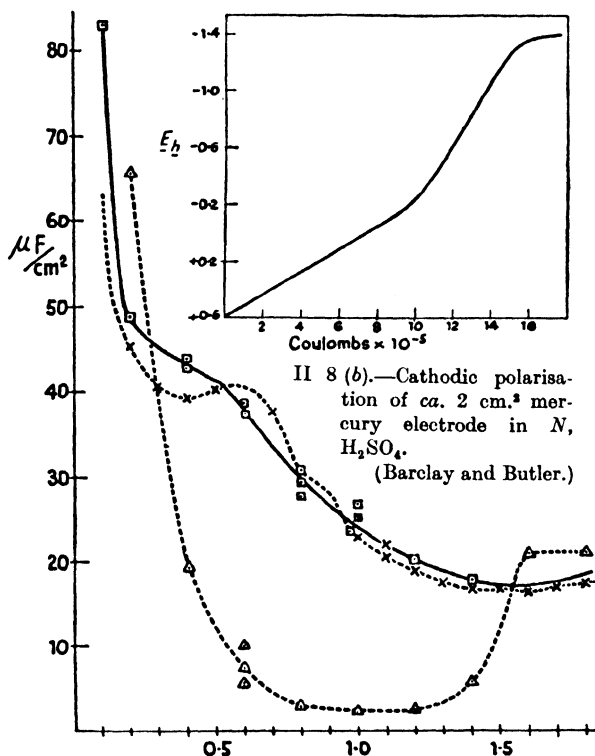
⁴⁷ *Z. physikal. Chem.*, **45**, 1, 1903; *Ann. d. Phys.* [4], **21**, 701, 1906; *Z. f. Elektrochem.*, **19**, 620, 1913.

⁴⁸ *Trans. Faraday Soc.*, **31**, 110, 1935; T. Borissowa and M. Proskurnin, *Acta Physicochim.*, U.R.S.S., **4**, 819, 1936.

⁴⁹ Gorodezkaya and Frumkin, *Acta Physicochim.*, **9**, 45, 1938. See for further measurements by the A.C. method Proskurnin and Vorsina, *C.R. Acad. Sci., U.R.S.S.*, **24**, 915, 1939; Vorsina and Frumkin, *ibid.*, p. 918, 1939; *Acta Physicochim.*, **18**, 242, 1942; Borissowa and Proskurnin, *ibid.*, **11**, 371, 1940 (effect of frequency of A.C.).

etc., greatly reduces the capacity in the middle part of the curve.⁵⁰ It is only in this region that adsorption occurs.

Barclay and Butler⁵¹ have studied the cathodic polarisation of freshly made mercury surfaces, recording the rapid changes of potential with time for constant currents by means of a cathode



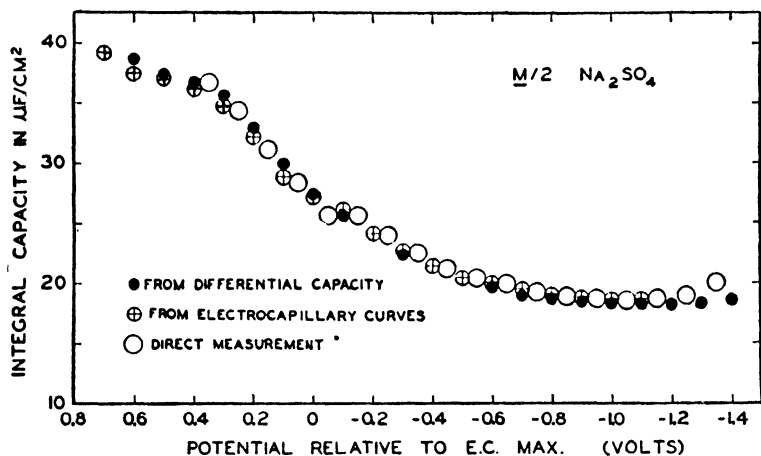
II 8 (a).—Capacities of a mercury surface in N, Na₂SO₄. — from electrocapillary curve; —×— observed at clean surface; —△— after contamination with picein.

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, H₂SO₄. The initial potential is about $E_h = +0.6$ and the

⁵⁰ 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.

⁵¹ *Trans. Faraday Soc.*, **36**, 128, 1940.

curve of potential against charge shows two distinct stages. In the first (α) the capacity is about 60×10^{-6} coulombs/volt/cm.², and at about $E_h = 0.3$ 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.



II 9.—Integral capacities of mercury electrode. (Grahame.)

This is in accordance with the electrocapillary curves (p. 64), which indicate that little adsorption takes place at the initial potential.

D. C. Grahame^{52, 53} has examined the capacity of the double layer at mercury surfaces by an A.C. method. He properly draws a distinction between the "integral" or "static" capacity of the double layer, which is $K = e/V$, and the "differential" capacity $C = de/dV$, which by Lippmann's equation is given by $C = -d^2\sigma/dV^2$. The "integral" charge is obtained from the differential capacity by $e = \int C dV$, from which the integral capacity can be obtained.

Fig. 9 shows the integral capacity at mercury electrodes as

⁵² *J. Amer. Chem. Soc.*, **63**, 1207, 1941; **64**, 1548, 1942. Whitney and Grahame, *J. Chem. Physics*, **9**, 827, 1941.

⁵³ *J. Amer. Chem. Soc.*, **68**, 301, 1946; **71**, 2975, 2978, 1949; *Chem. Revs.*, **41**, 460, 1947.

determined by (a) from the differential capacity determined by A.C. methods, (b) from the electrocapillary curves by Lippmann's equation, and (c) by a direct method, involving the measurement of the charge carried by mercury droplets of known surface area. The agreement is excellent.

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. Gouy⁵⁴ 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. Chapman⁵⁵ 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 that used later by Debye and Hückel to determine the distribution of ions in the ionic atmosphere round a given ion (see p. 54). The result was

$$e \sqrt{\frac{DRT}{2\pi} c} \left(e^{\frac{eV}{2RT}} - e^{-\frac{eV}{2RT}} \right)$$

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.

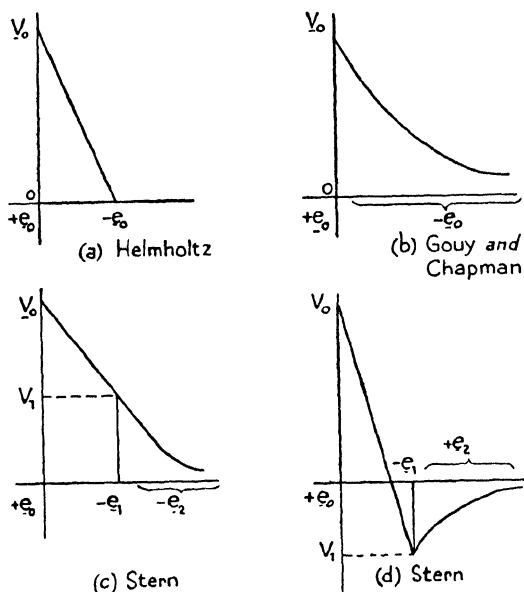
In 1924 Stern⁵⁶ suggested a type of double layer which is a combination of the simple Helmholtz fixed layer with the Gouy-Chapman diffuse layer. If there is a total charge e_0 on the electrode, it is supposed that the corresponding charge $-e_0$ in the

⁵⁴ *J. de physique* (4), **9**, 357, 1910; *Annales de phys.*, **7**, 129, 1917; cf. Bikerman, *Z. physikal. Chem.*, **163**, 378, 1933.

⁵⁵ *Phil. Mag.*, **25**, 475, 1913; cf. Herzfeld, *Phys. Z.*, **21**, 28, 1920.

⁵⁶ *Z. Elektrochem.*, **30**, 508, 1924.

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. 10 (c) and (d).



II 10.—Types of double layer, showing variation of potential with distance from surface and location of charges.

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

$$e_2 = \sqrt{\frac{DRT}{2\pi}} c (e^{\mathbf{F}V_1/2RT} - e^{-\mathbf{F}V_1/2RT}).$$

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 deduced⁵⁷ 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 ,

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

the sign of $RT/F \log c$ 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

$$(2RT/F) \log c.$$

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.⁵⁸

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.

The Ionic Atmosphere. The earlier calculations of Gouy and Chapman of the potential difference of diffuse layers (p. 51) were succeeded by the well-known calculation of Debye and Hückel⁵⁹ 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

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

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

⁵⁷ Cf. Philpot, *loc. cit.*, ref. 37.

⁵⁸ For a discussion of Stern's theory, see Urban and White, *J. Physical Chem.*, **36**, 3157, 1932.

⁵⁹ *Physik. Z.*, **24**, 185, 1923.

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,*

$$\Delta^2\psi = -4\pi\rho/D,$$

we have

$$\Delta^2\psi = -\frac{4\pi}{D} \sum n_i z_i \epsilon e^{-z_i\epsilon\psi/kT}.$$

Debye and Hückel solved this equation by making the approximation

$$e^{-z_i\epsilon\psi/kT} \rightarrow 1 - z_i\epsilon\psi/kT,$$

which is only valid if $z_i\epsilon\psi/kT \ll 1$. With this assumption we have

$$\Delta^2\psi = \kappa^2\psi,$$

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 $\frac{1}{2}\sum c_i z_i^2$ be called the ionic strength μ , we have

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \cdot \frac{N_0}{1000} \cdot 2\sqrt{\mu}.$$

More generally, when $\frac{z\epsilon\psi}{kT} \geq 1$, the exact expression

$$\Delta^2\psi = \frac{8\pi wz\epsilon}{D} \sinh\left(\frac{z\epsilon\psi}{kT}\right)$$

should be used.†

* $\Delta^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. In order to render the dielectric constant dimensionless, Poisson's equation can be written as

$$d^2\psi/dx^2 = -4\pi\rho/DD_0,$$

where D_0 is defined by

$$f = q_1q_2/r_2D_0,$$

in which f is the force acting between charges q_1, q_2 in a vacuum at a distance r . $D_0 = 10^9/c^2 = 1.12 \times 10^{-12}$ coul.volt⁻¹.cm.⁻¹,

has been called the diabattivity of free space (D. C. Grahame, *Chem. Revs.*, **41**, 441, 1947. See Guggenheim, *Trans. Faraday Soc.*, **36**, 139, 1940; Wood, *J. Amer. Chem. Soc.*, **68**, 432, 1946). See p. 89 for a further discussion of this point.

† See Verwey and Overbeek, *Theory of Stability of Lyophobic Colloids*, p. 24.

The form of the solution of this equation depends on whether it is to refer to a plane or spherical surface.

Spherical surfaces. For a spherical particle of radius a , and charge q , the solution of the general equation for ψ can be written as

$$\psi = \frac{q}{Dx} \frac{e^{-\kappa(x-a)}}{1 + \kappa x},$$

which gives the following value for the potential ψ_0 at the surface, where $x = a$:

$$\psi_0 = \frac{q}{Da} \frac{1}{1 + \kappa a},$$

which may be alternately written as

$$\psi_0 = \frac{q}{Da} \cdot \frac{1/\kappa}{1/\kappa + a}.$$

ψ_0 is equal to the zeta potential when a is identical with the radius of shear (see p. 77). This gives explicitly the variation of ψ_0 with the ionic strength; for a uni-univalent electrolyte

$$1/\kappa = 3 \times 10^{-8} / \sqrt{c}.$$

$1/\kappa$ has the significance of the equivalent radius of the ionic atmosphere, i.e. if the whole ionic atmosphere were concentrated at the radius $1/\kappa$, the potential produced would be the same. This follows if one considers a sphere of charge q and radius a , surrounded by a second sphere of charge $-q$ and radius $a + d$. The difference of potential between them is

$$\begin{aligned} \Delta V &= \frac{q}{Da} - \frac{q}{D(a+d)} \\ &= \frac{q}{Da} \frac{d}{a+d}, \end{aligned}$$

i.e. $1/\kappa$ takes the place of d the distance between the concentric spheres.

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

$$e = \int_a^\infty \rho \cdot dx,$$

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

$$\rho = -\frac{D}{4\pi} \Delta^2 \psi = \frac{D}{4\pi} \cdot \kappa^2 \psi,$$

we have

$$e = \int_a^\infty \frac{D}{4\pi} \cdot \kappa^2 \psi dx = \int_a^\infty \frac{D}{4\pi} \cdot \kappa^2 A e^{-\kappa x} \cdot dx,$$

or

$$e = \frac{D\kappa A}{4\pi} e^{-\kappa a}.$$

Introducing this value of A we have

$$\psi = \frac{4\pi e}{D\kappa} \cdot e^{\kappa(a-x)},$$

or identifying ψ with ψ_0 for $x = a$

$$\psi_0 = \frac{4\pi e}{D\kappa}.$$

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.⁶⁰ G. S. Hartley⁶¹ has pointed out that with uni-univalent electrolytes the value of $z_e \psi / kT$ does not become less than 1 until $r = 7.08 \times 10^{-8}$ 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.

Another form of the equation, which avoids the approximations of the Debye-Hückel theory, has been given by H. Müller.⁶² If the solution contains only two kinds of ions (positive and negative)

⁶⁰ 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.

⁶¹ *Trans. Faraday Soc.*, **31**, 31, 1935. See Hartley and Roe, *ibid.*, **36**, 101, 1940.

⁶² *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.

we have $n_+z_+ = -n_-z_-$. For a plane surface the primary equation becomes

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi}{D} \cdot \rho = -\frac{4\pi}{D} \cdot n_+ z_+ \epsilon (e^{-z_+ \psi / kT} - e^{-z_- \psi / kT}).$$

The surface charge is given by

$$e = - \int_0^\infty \rho \cdot dx,$$

and the boundary conditions are

$$\psi = 0, \quad \left(\frac{\partial \psi}{\partial x}\right) = 0, \quad \text{when } x = \infty;$$

$$\left(\frac{\partial \psi}{\partial x}\right) = \frac{4\pi e}{D}, \quad \text{when } x = 0.$$

The integration of this equation⁶³ gives

$$e = \sqrt{\frac{D \cdot RT \cdot c}{2\pi \times 1000}} \sqrt{\frac{1}{z_+} (e^{-z_+ \epsilon \psi_0 / kT} - 1) + \frac{1}{z_-} (e^{-z_- \epsilon \psi_0 / kT} - 1)}, \quad (1)$$

where c = salt concentration in mols./litre and ψ_0 is the value of ψ for $x = 0$. For two ions of equal valency, i.e. $z_+ = z_- = z$, this may be simplified to

$$\begin{aligned} e &= 2 \sqrt{\frac{DRTc}{2\pi \times 1000}} \sinh z \left(\frac{\epsilon \psi_0}{2kT} \right) \\ &= 2\alpha \sqrt{c} \sinh \left(\frac{z\psi_0}{2\beta} \right), \end{aligned}$$

where $\beta = 0.025$ volt, and $\alpha = 17,650$ at 18°C. , for aqueous solutions.

Calculations of the Double Layer Capacity. The contribution of the diffuse double layer to the capacity of the electrode can be calculated from these equations. The integral capacity is

$$K_D = \frac{e}{\zeta} = \frac{2\alpha \sqrt{c}}{\zeta} \sinh (z \epsilon \psi_0 / 2kT)$$

and the differential capacity

$$c_D = \frac{de}{d\zeta} = \frac{z \epsilon}{kT} \alpha \sqrt{c} \cosh (z \epsilon \psi_0 / 2kT).$$

⁶³ Cf. a similar calculation by R. Audubert, *J. Chem. Phys.*, **30**, 89, 1932; *Trans. Faraday Soc.*, **36**, 144, 1940.

The following table shows some of the double layer capacities calculated in this way (for a z - z electrolyte) (D. C. Grahame, *loc. cit.*).^{63a}

Concentration M		Charge $\times \zeta$			
		0.0 v.	0.04 v.	0.08 v.	0.12 v.
1	$\{K_D$	228	252	334	502
	C_D	222	302	568	1200
0.1	$\{K_D$	72.2	79.9	105	159
	C_D	72.2	95.5	180	378
		0.12 v.	0.16 v.	0.20 v.	0.24 v.
0.01	$\{K_D$	50.2	82.9	145	263
	C_D	120	259	565	1233
0.001	$\{K_D$	15.9	26.2	45.8	832
	C_D	37.8	82.2	179	390

The whole capacity of the electrode is equal to the capacity of two condensers of capacities K^0 and K_D , placed in series, K^0 being the capacity of the non-diffuse part of the double layer. There is no clear-cut way of arriving at this quantity. Grahame (*loc. cit.*) has calculated K^0 (and C^0) by subtracting the calculated capacity of the diffuse double layer from the total measured capacity of the electrode. Fig. 11 shows the result for 1 M aqueous sodium fluoride solutions. Assuming then that K^0 and C^0 depend only on the charge of the double layer, the differential capacity of more dilute solutions of sodium fluoride was then calculated. Fig. 12 shows the result of the calculation and the observed values for 0.001 M sodium fluoride.

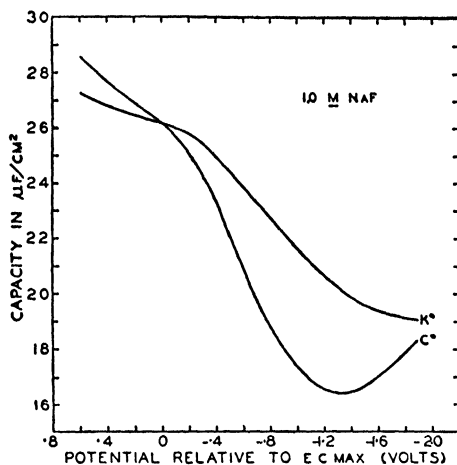
D. C. Grahame^{63b} has considered the effect of a variable dielectric constant, such as might be produced by dielectric saturation, on the diffuse double layer. He finds that the effect on the properties which are experimentally significant is unimportant.

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

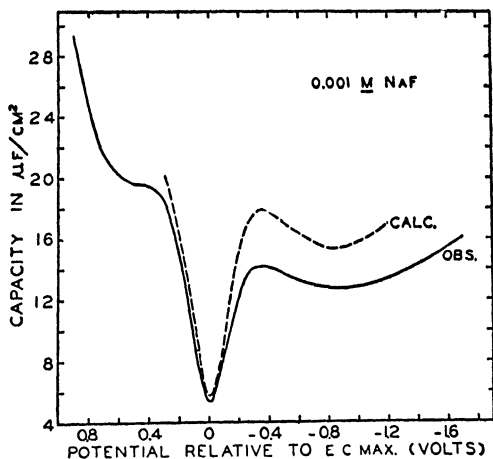
^{63a} See also *J. Amer. Chem. Soc.*, **71**, 2975, 1949.

^{63b} *J. Chem. Physics*, **18**, 903, 1950.

theory of Gibbs. The general adsorption equation of Gibbs, connecting the surface tension and adsorption at an interface



II 11.—Integral and differential capacities of the non-diffuse part of the double layer, calculated from data for 1 *M* aqueous sodium fluoride. This capacity is in series with the capacity of the diffuse double layer. (Grahame.)



II 12.—Calculated and observed differential capacity of mercury in contact with 0.001 *M* sodium fluoride. $T = 25^\circ \text{C}$. Experimental data obtained with 1.0 *M* sodium fluoride enter into these calculations. (Grahame.)

with the concentration of the substances, may be written in the form

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

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

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

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

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

Gibbs⁶⁴ 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 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

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

In accordance with Gibbs's equation, the variation of the surface

⁶⁴ *Scientific Papers*, I, 219.

* 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.

tension with the mercurous ion activity will be given by

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

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. Warbourg⁶⁵ identified $F\Gamma_{Hg^+}$ 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. Lewis⁶⁶ and Patrick⁶⁷ measured the amount of mercurous sulphate carried down when mercury droplets are streamed through a solution. Schofield⁶⁸ 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.⁶⁹ The derivation is unsatisfactory, however, because it assumes that the electrode is always in equilibrium with the solution. 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. 71). Here we shall regard the surface

⁶⁵ *Wied. Ann.* (9), **41**, 1, 1890.

⁶⁶ *Z. physikal. Chem.*, **77**, 129, 1910.

⁶⁷ *Ibid.*, **86**, 545, 1914; Patrick and Bachman, *J. Physical. Chem.*, **30**, 134, 1936.

⁶⁸ *Phil. Mag.*, **1**, 641, 1926.

⁶⁹ 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.

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

$$\sigma = \sigma_0 + \int e dV - \sum \int \Gamma_2 d\bar{F}_2 \quad . \quad . \quad . \quad (2)$$

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

$$\Delta\sigma = \int \Gamma \cdot d\bar{F} \quad . \quad . \quad . \quad . \quad (3)$$

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

$$\Gamma = \Gamma_0 e^{-\alpha e V / kT} \quad . \quad . \quad . \quad (4)$$

and introducing this into (2), we have

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

or

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

i.e.

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

Butler⁷⁰ 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.⁷¹

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 of the curves obtained, which may be called "adsorption curves", are given in Figs. 13 and 14.†

The first theoretical explanation of this phenomenon was given by Frumkin.⁷² 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

⁷⁰ *Proc. Roy. Soc.*, **113A**, 594, 1927.

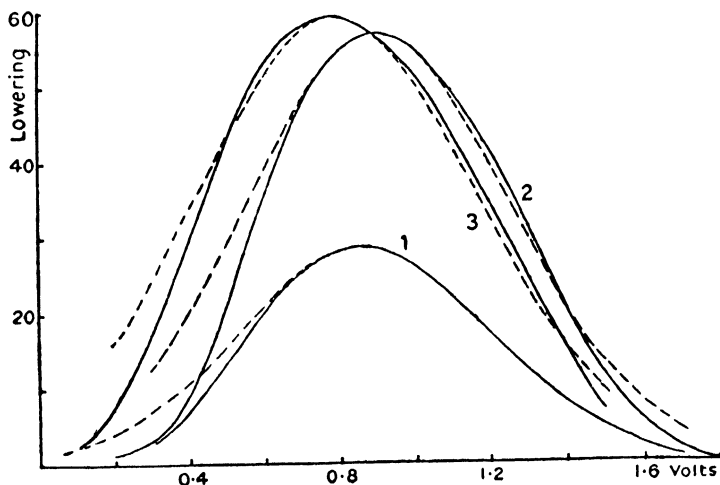
* $\Delta\sigma$ was taken as the difference between σ for KCl and σ for KI for a given value of V . This is not quite accurate, because the chloride also produces a small lowering of surface tension, as compared with the symmetrical nitrate solutions.

⁷¹ The adsorption of anions has also been discussed by Vorsina and Frumkin, *Acta Physicochim.*, U.R.S.S., **18**, 341, 1943; and by Essin and Markov, *ibid.*, **10**, 353, 1939. See also Grahame, *Chem. Revs.*, **41**, 441, 1947.

† 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).

⁷² *Z. physik.*, **35**, 792, 1926.

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



II 13.—Adsorption curves of (1) acetic acid ($M/1$), (2) propionic acid ($M/1$), (3) monochloroacetic acid ($M/1$). (*Proc. Roy. Soc.*)

change of $e^{\phi s/RT}$. This was introduced into rather complicated adsorption equations and accounted for the curves of amyl alcohol solutions.

A somewhat different theory was given by Butler.⁷³ 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

$$w = \delta v \cdot \frac{1}{2} \alpha E^2,$$

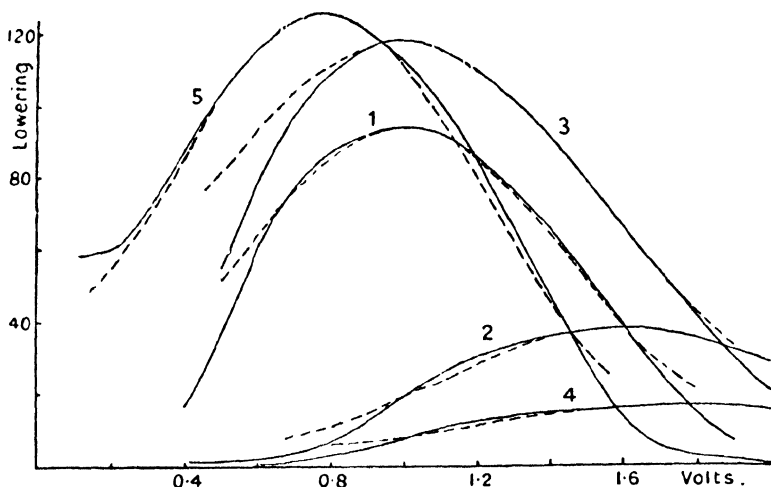
where α = polarisability. Now, consider a solution containing molecules A and B. Suppose that a molecule B of volume δv_B is

⁷³ *Proc. Roy. Soc.*, **122A**, 399, 1929.

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

$$w = \frac{1}{2}(\alpha_A - \alpha_B)E^2 \cdot \delta v_B \quad . \quad . \quad . \quad (5)$$

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



II 14.—Adsorption curves of (1) triethylamine (M/10), (2) triethylamine sulphate (M/10), (3) isobutylamine (M/1), (4) isobutylamine sulphate (M/1), (5) pyrrol (sat.). (*Proc. Roy. Soc.*)

at a surface where the electric field strength is E , and Γ_0 the adsorption for $E = 0$,

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

or by (2),

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

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

$$\Delta\sigma = \Delta\sigma_0 \cdot e^{-aV^2}.$$

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

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

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

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

and therefore, for a given solution,

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

This can easily be transformed * to

$$\Delta\sigma = \Delta\sigma_m e^{-(a(V - V_m)^2)},$$

where $\Delta\sigma_m$ is the maximum lowering of the surface tension and V_m 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 region, which reduces the adsorption of the other solute. Table IV gives the characteristics of the curves of some solutes.

The values of a are of the same order of magnitude as those calculated by the use of (5). 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.

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

TABLE IV. CHARACTERISTICS OF ADSORPTION CURVES

<i>Substance</i>	<i>Concentration</i>	<i>a</i>	<i>V_m</i> *	$\Delta\sigma_m$
CH ₃ OH	M	2.7	- 0.90	7.4
C ₂ H ₅ OH	M	4.1	0.96	27.2
C ₃ H ₇ OH (<i>n</i>)	M	3.3	0.95	79.8
C ₄ H ₉ OH (<i>n</i>)	M/10	5.0	0.92	49.1
C ₆ H ₅ OH	M/10	3.2	0.78	91.3
C ₆ H ₄ · CH ₃ · OH (<i>o</i>)	<i>sat.</i>	1.9	0.78	139.0
C ₆ H ₄ (OH) ₂ (<i>o</i>)	M/10	2.4	0.64	82.6
C ₆ H ₄ (OH) ₂ (<i>p</i>)	M/10	2.6	0.60	82.4
N(CH ₃) ₄ OH	M/10	1.7	1.85	33.7
N(C ₂ H ₅) ₄ OH	M/10	1.7	1.65	63.0
S(C ₂ H ₅) ₃ OH	M/10	1.2	1.74	61.8
N(C ₂ H ₅)(CH ₃) ₃ OH	M/10	1.6	1.80	36.5

* Measured against the electrode Hg, Hg₂, SO₄, Na₂SO₄ (M/2). The potential of this electrode is $E_h = + 0.66$.

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.⁷⁴ The reason for this⁷⁵ 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 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,⁷⁶ especially

⁷⁴ Butler and Ockrent, *J. Physical Chem.*, **34**, 2286, 1930.

⁷⁵ Butler and Wightman, *ibid.*, **35**, 3293, 1931.

⁷⁶ 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.

those of high molecular weight. For example, Rhodes and Kuhn⁷⁷ 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 Hultin⁷⁸ 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.⁷⁹ Perschke and Vinogradova⁸⁰ 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.⁸¹

Electrification at Solution-Gas Interfaces. A potential difference at an interface may also arise from the orientation of dipoles 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,⁸² Kendrick,⁸³

⁷⁷ *Ind. Eng. Chem.*, **21**, 1066, 1929.

⁷⁸ *Ibid.*, **28**, 159, 1048, 1936.

⁷⁹ See also W. Machu, *Korrosion u. Metallschutz*, **13**, 1, 1937.

⁸⁰ *Chim. et Ind.*, **36**, 1101, 1936.

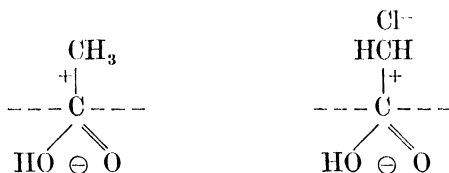
⁸¹ See also Ch'iao and Mann, *Ind. and Eng. Chem.*, **39**, 912, 1947; Bockris and Conway, *Experientia*, **3**, 11, 1947; *idem*, *J. Physical Coll. Chem.*, **53**, 527, 1949.

⁸² *J. physique*, **2**, 533, 1883.

⁸³ *Z. physikal. Chem.*, **19**, 625, 1896.

and later Frumkin and collaborators⁸⁴ 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 of the ions has no great effect, e.g. although thorium nitrate reverses the sign of the electrokinetic potential of gas bubbles it has no effect on the total potential difference.

Another method, which can be used at stationary surfaces, was developed by Guyot⁸⁵ and Frumkin.⁸⁶ A wire or plate, which is

⁸⁴ *Z. physikal. Chem.*, **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.

⁸⁵ *Ann. physique*, **2**, 560, 1924.

⁸⁶ *Z. physikal. Chem.*, **116**, 485, 1925 ; cf. Sawai, *Trans. Faraday Soc.*, **31**, 765, 1935.

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 Vigfusson⁸⁷ 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.⁸⁸ 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 *pH* 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*.⁸⁹

In another method, which has been developed and used by Garrison,⁹⁰ Zisman and Yamins,⁹¹ and Porter,⁹² 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 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.

⁸⁷ *J. Physical Chem.*, **35**, 345, 1931.

⁸⁸ E.g. Schulman and Rideal, *Proc. Roy. Soc. A*, **130**, 259, 1931; Harding and Adam, *Trans. Faraday Soc.*, **29**, 837, 1933; Harkins, *J. Chem. Physics*, **1**, 852, 1933; **3**, 593, 1935.

⁸⁹ Oxford Univ. Press, 2nd edition, 1938.

⁹⁰ *J. Physical Chem.*, **29**, 1517, 1925.

⁹¹ *J. Chem. Physics*, **1**, 1656, 1933; *Rev. Sci. Inst.*, **3**, 7, 1932.

⁹² *J. Amer. Chem. Soc.*, **59**, 1884, 1937.

APPENDIX

THE THERMODYNAMICS OF ELECTROCAPILLARY CURVES

As pointed out above (p. 60) 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,⁹³ Rice⁹⁴ and particularly by Craxford, Gatty and Philpot.⁹⁵ Broadly speaking, the conclusion of these authors is that the equation given (p. 60) 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

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

⁹³ *Z. physikal. Chem.*, **154**, 421, 454, 1931; **156**, 38, 1931; **157**, 96, 1931; *J. Physical Chem.*, **38**, 111, 339, 1934.

⁹⁴ *Ibid.*, **30**, 1348, 1926.

⁹⁵ *Phil. Mag.*, **14**, 849, 1933; **17**, 54, 1934; **19**, 965, 1935; **22**, 359, 402, 1936; Craxford, *Trans. Faraday Soc.*, **36**, 85, 1940; see also Grahame and Whitney, *J. Amer. Chem. Soc.*, **64**, 1548, 1942; Grahame, *Chem. Revs.*, **41**, 441, 1947.

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 $\Delta \bar{F}_{Hg^+} = ze\Delta V'$. 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

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

where Γ_e , 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 $\Gamma_e = 0$, and identified Γ_{Hg^+} as determined on this supposition with the charge on the mercury. Schofield⁹⁶ chose to place the dividing surface so that $\Gamma_{Hg^+} = 0$, when (4) becomes

$$\frac{d\sigma}{dM_e} = \frac{d\sigma}{e dV} = -\Gamma_e.$$

Butler pointed out⁹⁷ that the Γ_e so obtained is not necessarily equal to the amount of electrons which correspond 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_e will be less than corresponds to the actual charge on the metal

⁹⁶ *Phil. Mag.*, **50**, 641, 1926.

⁹⁷ *Proc. Roy. Soc.*, **113A**, 594, 1927.

and may in fact 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_* 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, $\Gamma_{H_g^+}$ 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 $dM_{H_g^+} = 0$.

In either case the electrocapillary equation becomes

$$e\Gamma_* \cdot dV + \Gamma_1 d\bar{F}_1 + \Gamma_2 d\bar{F}_2, \text{ etc.}, + d\sigma = 0. \quad (5)$$

i.e. if e is the electronic charge on the mercury, for a simple salt solution, with two ions, we may write

$$edV + \Gamma_+ dF_+ + \Gamma_- dF_- + d\sigma = 0. \quad (6)$$

An important modification of this equation is obtained,⁹⁸ if we use as the reference electrode, not a fixed electrode of constant composition, but an electrode which is reversible with respect to either the anion or the cation of the solution at the electrocapillary tip. Then

$$dV = dE - dV_{\text{ref.}}$$

where $V_{\text{ref.}}$ is the potential difference of the reference electrode and E the applied e.m.f. If the reference electrode is reversible to the anion, we have $dF = z_e dV_{\text{ref.}}$ and since electroneutrality requires that

$$q + z_+ e \Gamma_+ + z_- e \Gamma_- = 0 \quad (7)$$

we obtain by combining (6) and (7) with the free energy equation,

$$dF = \nu_+ dF_+ + \nu_- dF_-$$

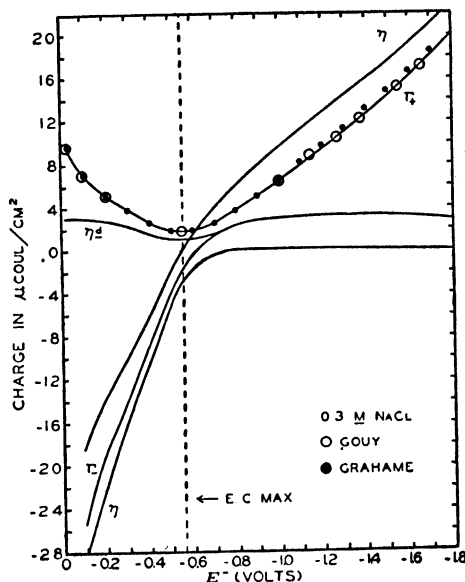
(where ν_+ , ν_- are the number of positive and negative ions in a

⁹⁸ D. C. Grahame and R. B. Whitney, *J. Amer. Chem. Soc.*, **64**, 1548, 1942.

mol. If their charges are z_+ , z_- , obviously $z_+v_+ + z_-v_- = 0$)

$$d\sigma = -edE - \frac{\Gamma_+}{v_+}dF,$$

from which Γ_+ can be obtained unequivocally. A similar equation applies to Γ_- , but in that case the reference electrode is



II 15.—Components of charge of the double layer between mercury and aqueous 0.3 M sodium chloride solution. $T = 25^\circ\text{C}$. Open circles computed from data by Gouy (36). η is total charge. Γ_+ is charge attributable to cations in the double layer; η^d — is charge attributable to anions repelled from the diffuse double layer; η^a — is charge attributable to anions adsorbed on mercury surface. Γ_- is the sum of these two. Potentials measured relative to 0.3 M sodium chloride-calomel electrode. (Grahame and Whitney.)

reversible to the cation. If measurements are made at constant values of E (the actual applied e.m.f.), we shall find

$$\Gamma_+ = -v^+ \left(\frac{d\sigma}{dF} \right)_E$$

$$\Gamma_- = -v^- \left(\frac{d\sigma}{dF} \right)_E.$$

Fig. 15 shows values of Γ_+ , Γ_- obtained in this way for 0.3 M NaCl. It is to be noted that Γ_+ is positive even for positive polarisation.

CHAPTER III

ELECTROKINETIC EFFECTS

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Definitions and Inter-relations. In the previous chapter we have been concerned mostly with those effects occurring in static systems due to the presence of an electrical double layer. When such a layer at a solid-liquid, or liquid-liquid interface is disturbed by the application of external forces, the static equilibrium conditions are destroyed, and a series of *electrokinetic effects* may be observed.

These effects, all fundamentally due to the establishment of thermodynamically irreversible conditions, may be distinguished primarily according to the nature of the disturbing force, which may be mechanical or electrical. Mechanical forces leading to relative motion at the interface can obviously be applied in two ways, either by forcing the liquid phase past a stationary solid surface, or by allowing solid particles to move through a stationary dispersion medium under a gravitational force.

Thus, if a difference of hydrostatic pressure exists between the ends of a capillary containing a liquid, a *streaming potential* is set up between the ends as the liquid flows; the reverse of this phenomenon, the *Dorn effect*, occurs when charged particles are caused to move (by gravitational forces), through a resting liquid; a potential gradient is set up, opposing the motion of the particles.

If the disturbing force producing relative motion is electrical, the converse of these effects occurs. Thus an electric field applied axially to a capillary containing liquid causes the latter to flow, an effect termed *electro-osmosis*; the *electro-osmotic pressure* is that pressure difference at the ends which prevents further flow.

The fourth, and most important, effect is the converse of the Dorn effect: the motion of charged particles through a resting dispersion medium under the influence of an applied electric field.

The effect has been called *cataphoresis* but the more general term *electrophoresis* is now preferred.

It is evident that all these effects are related, being different aspects of the same phenomenon; in the classification adopted here (compare that of Horwitz ¹), an effect is said to be the *converse* of another when the nature of the disturbing force is changed, while the reverse of a given effect is said to occur when a disturbing force of the same kind is applied in a different manner. Thus the converse of the streaming potential is clearly electro-osmosis (electric force producing movement instead of mechanical force a potential), while the reverse is the development of the Dorn potential (mechanical force leading to streaming of solid past liquid instead of liquid past solid).

In addition to these four primary electrokinetic effects, there is a series of subsidiary effects, i.e. modifications to existing properties of the system due to the occurrence of relative motion within the double layer. Chief of these is the *electro-viscous effect*, the increase in viscosity of a solution over and above that required by the Einstein equation, owing to the charge on the solute particles.

The Zeta-potential. Of paramount importance in the quantitative study of electrokinetic effects is the concept of the *electrokinetic*, or *zeta-potential*, ζ . This quantity is defined as the potential at the surface of shear (between, for example, solid particles and the dispersion medium in electrophoresis) due to the combined effect of the charges on the surface and the (equal and opposite) ones of the ionic atmosphere. (The relation of the zeta-potential to the particle or surface charge and the ionic strength of the solution with which the surface is in contact, has been outlined in Chapter II.)

The zeta-potential was introduced by Freundlich ^{2, 3} who also pointed out that it is not necessarily identical with the whole potential difference existing at an interface (see Fig. 1 and pp. 52, 140). The electrochemical potential, μ , of, e.g., a metal in contact with a solution containing its ions, arises by a characteris-

¹ Horwitz, *J. Chem. Ed.*, **16**, 519, 1939.

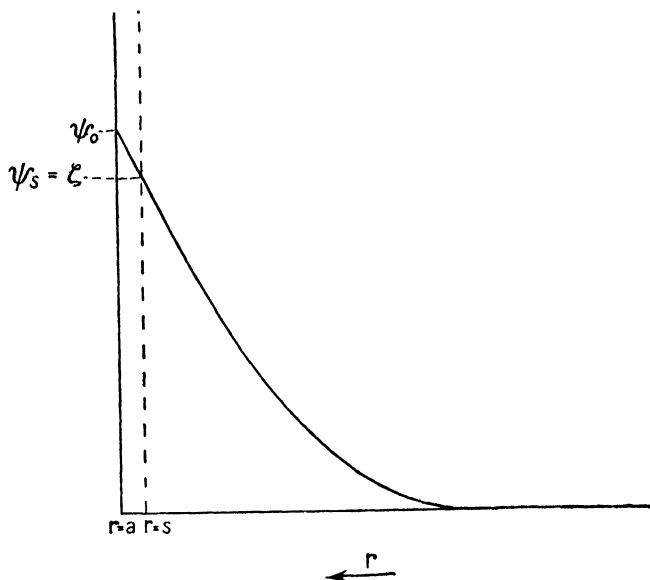
² Freundlich and Rona, *Sitz. Preuss. Akad. Wiss.*, **20**, 397, 1920.

³ Freundlich, *Colloid and Capillary Chemistry*, p. 242, Methuen, 1926.

tically thermo-dynamically reversible process, and the variation of μ with concentration of the ion follows the logarithmic relation demanded by the equation

$$\mu = \mu_0 + \frac{RT}{z_{\pm}F} \ln a$$

where $z_{\pm}$ is the valence and a the activity of the ion in solution. The electrokinetic potential, on the other hand, is determined by the effect of the surface charge on the distribution of electrolyte



III 1.—Diagrammatic representation of the variation of potential with distance from the wall of e.g. a capillary tube. ψ_0 is the phase boundary potential, ψ_s the potential at the surface of shear (the zeta potential).

ions in the neighbourhood of the surface and the position of the surface of shear; the variation of ζ with concentration of electrolyte follows a much more complex course. Freundlich and Ettisch⁴ have measured the two potentials for the same (glass) surface; no dependence or relation was observed between them.

ELECTROKINETIC EQUATIONS. (a) The Streaming Potential. This phenomenon was first reported by Quincke, in 1859,⁵ who

⁴ Freundlich and Ettisch, *Z. physik. Chem.*, **116**, 401, 1925.

⁵ Quincke, *Pogg. Ann.*, **107**, 1, 1859.

observed that the potential developed at the ends of the capillary was directly proportional to the applied pressure for any given solution. This was explained by Helmholtz⁶ who furnished the classical theory for all the primary electrokinetic effects; his equations, derived on the basis of a rigid double layer, have been modified slightly, notably by Smoluchowski^{7, 8}; more recently Bikerman⁹ was able to derive the equations for all the effects on the basis of the diffuse double layer. (See also the derivations published by Rutgers,¹⁰ Porter¹¹ and Wood.¹²)

If a pressure difference P is applied to the ends of a capillary of radius a and length l , the velocity v_r in the tube at any distance r from the centre is given by Poiseuille's theory as

$$v_r = \frac{P}{4\eta l} \cdot (a^2 - r^2). \quad (1)$$

If the electric charge density in the region of the wall is ρ , then the transport of charge per unit time (*current of convection*), i_1 , will be given by

$$i_1 = \int_0^s 2\pi r \cdot \rho \cdot v_r \cdot dr \quad (2)$$

where the limit s corresponds to the radius of the surface of shear (see Fig. 1). Poisson's equation relating the charge density to the potential ψ has, in this case, the form :

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = - \frac{4\pi\rho}{D}. \quad (3)$$

Combining equation (2) with equations (1) and (3) :

$$\begin{aligned} i_1 &= \int_0^s \frac{PD}{8\eta l} \cdot (a^2 - r^2) \cdot \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) \cdot dr \\ &= - \frac{PD}{8\eta l} \int_0^s (a^2 - r^2) \cdot d \left(r \frac{d\psi}{dr} \right). \end{aligned} \quad (4)$$

Integrating by parts :

$$i_1 = - \frac{PD}{8\eta l} \left(\left[r(a^2 - r^2) \cdot \frac{d\psi}{dr} \right]_0^s + 2 \int_0^s r^2 d\psi \right). \quad (5)$$

⁶ Helmholtz, *Wied. Ann.*, **7**, 337, 1879.

⁷ Smoluchowski, *Bull. Acad. Sci. Cracovie, math-nat.*, p. 182, 1903.

⁸ Smoluchowski, in Graetz : *Handbuch der Elektrizität und des Magnetismus II*, 366, Leipzig, 1921.

⁹ Bikerman, *Z. physik. Chem.*, **163A**, 378, 1933.

¹⁰ Rutgers, *Trans. Faraday Soc.*, **36**, 69, 1940.

¹¹ Porter, *ibid.*, **16**, 135, 1921.

¹² Wood, *J. Amer. Chem. Soc.*, **68**, 432, 1946.

When $r = 0$, $\psi = 0$, and $\frac{d\psi}{dr} = 0$; as the surface of shear is situated very near the wall, $s \simeq a$ and the first term within the brackets cancels. When $r = s$, $\psi = \zeta$, by definition: furthermore, since over the region where ψ is varying $r \simeq s$,

$$\begin{aligned} i_1 &= -\frac{DPa^2}{4\eta l} \int_0^s d\psi \\ &= -\frac{\zeta DPa^2}{4\eta l}. \end{aligned} \quad (6)$$

The transport of charge gives rise to a potential difference E at the ends of the tube causing a *current of conduction* i_2 :

$$i_2 = E \cdot \frac{\pi a^2 k}{l}, \quad (7)$$

where k is the specific conductance of the liquid in the tube. Since at the steady state $i_1 = i_2$

$$E = -\frac{\zeta D}{4\pi\eta k} \cdot P, \quad (8)$$

the potential being independent of the dimensions of the tube. (The negative sign is not usually written in equation (8), but it is correct to do so. See Wood.¹²)

From this equation it follows that (E/P) should be constant for a given system, in agreement with Quincke's observation.

Later measurements (e.g. those of Kruyt and van der Willigen¹³) showed that the ratio decreased appreciably with increase of pressure; several workers, e.g. Briggs¹⁴ and especially Bikerman,¹⁵ have shown that this is due to the assumption in equation (11) that the conductance in the capillary is identical with that of the liquid in bulk. With, for example, very dilute aqueous solutions, the contribution of the *surface conductance* increases the current carried; this factor may be allowed for, and correct zeta potentials calculated, by methods such as those of Briggs¹⁴ or Rutgers¹⁰ and Rutgers and de Smet.¹⁶ In the former method, which is now almost standard practice, the electrical resistance of the plug is measured during flow, and the value of the effective conductance

¹³ Kruyt and van der Willigen, *Kolloid Z.*, **45**, 307, 1928.

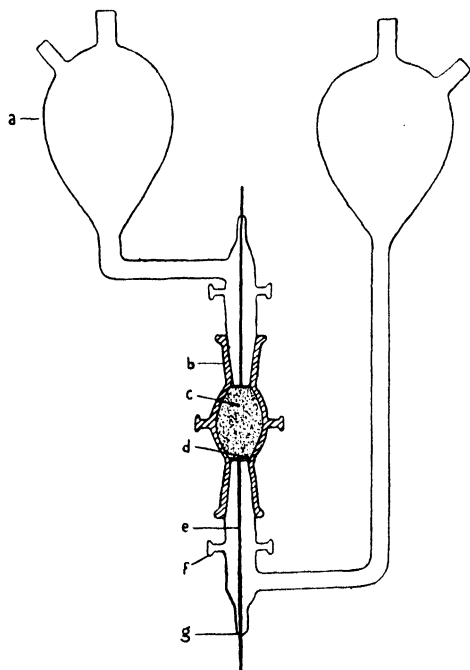
¹⁴ Briggs, *J. Physical Chem.*, **33**, 641, 1928.

¹⁵ Bikerman, *Trans. Faraday Soc.*, **36**, 154, 1940.

¹⁶ Rutgers and de Smet, *ibid.*, **43**, 102, 1947.

(including both bulk and surface conductance) thus obtained is used in equation (8).

Many of the measurements of streaming potentials have been made with porous diaphragms (which behave as a bundle of capillaries) rather than single capillaries: an example of this form of



III 2.—Streaming Potential Apparatus of Gortner.

(a) = Reservoir for liquid, (b) = Ground glass taper joint, (c) = Diaphragm (cellulose or alumina), (d) = Platinum gauze electrodes, (e) = Platinum wire leads, (f) = Binding posts, (g) = Tungsten seal.

e.g. Briggs' figures give a final value of 8.3 mv for the zeta potential of this interface. A great many other systems have been investigated, and the early work has been extensively reviewed by Abramson¹⁸; among the more recent work, that of

apparatus is that developed and extensively used by Gortner,¹⁷ shown in Fig. 2. Some typical results, obtained by Briggs,¹⁴ with a similar but earlier form of apparatus, are reproduced in Table Ia: they refer to a cellulose (bleached sulphite pulp) diaphragm and conductivity water. Values for dilute potassium chloride solution, in a single capillary, obtained by Kruyt and van der Willigen,¹³ are shown in Table Ib.

Both these series of measurements illustrate clearly the diminishing values of (E/P) with increase of pressure, but constant zeta values may be obtained from them,

¹⁷ Gortner, *Trans. Faraday Soc.*, **36**, 63, 1940.

¹⁸ Abramson, *Electrokinetic Phenomena and their Application to Biology and Medicine*, Chemical Catalog Co., 1934. See also Overbeek and Wijga, *Rec. trav. chim.*, **65**, 556, 1946.

TABLE I. EFFECT OF PRESSURE ON STREAMING POTENTIALS

A			B		
<i>P</i> cms. of Mercury	<i>E</i> Millivolts	<i>E/P</i>	<i>P</i> cms. of Mercury	<i>E</i> Millivolts	<i>E/P</i>
7.5	21.5	2.86	40	486	12.15
17.8	48.6	2.79	50	605	12.10
28.2	75	2.66	60	725	12.08
38.7	100	2.58	70	834	11.91
47.9	122	2.55	80	943	11.79

Gortner¹⁷ on the potentials of many organic liquids in contact with an alumina diaphragm is of particular interest in that it provides information on the adsorption and dipolar characteristics of the systems, which may be of great value in the field of heterogeneous catalysis.

In recent years attention has been concentrated on the streaming potentials of dilute aqueous solutions, and many electrolytes have been thus examined; as a result some light has been thrown upon the structure of the double layer, and also upon the role of surface conductance in determining the apparent magnitude of the zeta potentials. This is further discussed in the section on electro-osmosis.

For example, Ruyssen and Loos¹⁹ have used the streaming potential method to investigate the charge on barium sulphate precipitates: fresh material was found to be negatively charged, but the charge was reversed in the presence of barium chloride, due to the adsorption of barium ions. In further work in this field Buchanan and Heymann^{19a, 19b} have shown that the nature of the crystal surface is of some importance in determining the magnitude of the potential: thus ignited crystals of natural barytes were found to have a lower (positive) potential, when in contact with saturated barium sulphate solution, than crystals of precipitated barium sulphate ignited after crystallisation from sulphuric acid.

Eversole and Boardman²⁰ introduced the use of conducting

¹⁹ Ruyssen, *J. Physical Chem.*, **44**, 265, 1940; Ruyssen and Loos, *Nature*, **162**, 741, 1948.

^{19a} Buchanan and Heymann, *ibid.*, **161**, 649, 1948.

^{19b} Buchanan and Heymann, *Proc. Roy. Soc., A* **195**, 150, 1948.

²⁰ Eversole and Boardman, *ibid.*, **46**, 914, 1942.

capillaries in the streaming potential method, so that the "convection current" (see p. 85) could be directly measured. By this means the surface conductance can be determined, and true zeta potentials established.

The re-determination by Wood¹² of the zeta potential at the quartz-conductivity water interface is of considerable importance, as values obtained by previous investigators^{21, 22} had shown much variation, probably due to the slow attainment of equilibrium between solid surface and the liquid. The final value obtained by Wood was -177 millivolts.

An interesting application of streaming potentials is that of Edelberg and Hazel^{22a} who used the method to examine the effect of inorganic salts on the readiness of coating of phosphors on to glass.

(b) The Dorn Effect, Sedimentation Potentials. If the mechanical disturbance of the double layer is brought about by the streaming of solid past liquid (conditions the reverse of those causing the streaming potential), e.g. by allowing charged particles to fall through a column of liquid, then a potential difference is set up between the top and the bottom of the column. This phenomenon was first observed by Dorn²³ in 1878; it was mathematically interpreted by Helmholtz and Smoluchowski by arguments similar to those used in the derivation of the streaming potential. The field X set up by particles of density Δ falling through a medium of density Δ' under a gravitational field g is given by

$$X = \frac{\zeta D(\Delta - \Delta')g}{3\pi\eta k} \quad . \quad . \quad . \quad (9)$$

This equation is subject to the same limitations as the streaming potential equation in that it can only apply to interfaces where the double layer distance is small. Recently Booth,²⁴ in a comprehensive summary to which further reference will be made, has obtained a solution for the general case; a complicated function related to the thickness of the double layer and the size of the particle appears on the right-hand side of equation 9.

²¹ Lachs and Kronman, *Bull. internat. Acad. Polon. Sci.A*, 289, 1925.

²² Lachs and Biczyk, *Z. Physik. Chem.A*, 148, 441, 1930.

^{22a} Edelberg and Hazel, *J. Electrochem. Soc.*, 96, 12, 1949.

²³ Dorn, *Wied. Ann.*, 3, 20, 1878; 10, 46, 1880.

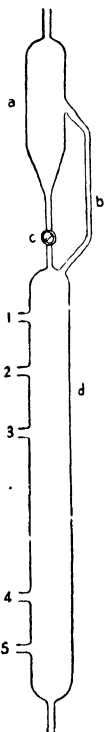
²⁴ Booth, *Nature*, 161, 83, 1948.

Early experimental work by Stock²⁵ showed a correspondence between X and ζ , and the effect was further investigated by Billitzer²⁶ and Freundlich and Mäkelä;²⁷ Bull,²⁸ however, obtained anomalous results with galena particles.

Of the few recent investigations, the most important is that by Quist and Washburn²⁹ who were the first to obtain reliable results with aqueous solutions. They measured, with the apparatus shown in Fig. 3, the potentials brought about

by the fall of Pyrex glass powder through conductivity water, using silver chloride electrodes, and found, in agreement with theory, that E , the potential between the electrodes, was proportional to the rate of flow of the powder and the distance between the electrodes. There was a slight tendency for E to fall off with high values of the rate of flow, indicating the effect of surface conductance. The zeta potential at the glass-water interface was found to be -102 millivolts. The effect of electrolytes on the magnitude of E was found to be in agreement with the Schulze-Hardy rule (see p. 137).

FIG. 3.—Sedimentation Potential Apparatus of Quist and Washburn. (a) = Upper compartment, containing powdered glass, (b) = bypass tube, (c) = stop-cock, (d) = "settling tube". 1, 2, 3, 4, 5, are ground joints for insertion of the electrodes. In use, the apparatus is filled throughout with liquid, the solid powder added to the upper compartment, the stop-cock opened, and the potentials of the electrodes measured after the powder has been flowing for a short time. The bypass tube allows liquid displaced from the settling tube to flow to the upper compartment.



Sedimentation potentials may be of importance in the field of ultracentrifugal investigations; the sedimentation velocity of colloidal particles is one of their most important and useful characteristics, and any factor which may affect the measured velocity is of greatest interest. Tiselius³⁰ showed that the actual

²⁵ Stock, *Anz. Akad. Wiss. Wien*, p. 131, 1913.

²⁶ Billitzer, *Ann. Physik*, **11**, 937, 1903.

²⁷ Freundlich and Mäkelä, *Z. Elektrochem.*, **15**, 161, 1909.

²⁸ Bull, *J. Physical. Chem.*, **33**, 656, 1929.

²⁹ Quist and Washburn, *J. Amer. Chem. Soc.*, **62**, 3169, 1940.

³⁰ Tiselius, *Kolloid Z.*, **59**, 306, 1932.

sedimentation velocity of the particles was the algebraic sum of their sedimentation and electrophoretic motions, and derived an equation allowing for the effect. It is general practice, however, to work at a swamping concentration of electrolyte, when the effect is almost eliminated. (See ³¹, ³².)

(c) **Electro-osmosis.** The flow of water through a porous diaphragm of sand or clay, across which a potential difference is maintained, was first observed by Reuss,³³ in 1809; Wiedemann³⁴ observed that the rate of flow through the diaphragm was proportional to the current, and for a given material, independent of the dimensions. He also observed that the electro-osmotic pressure was proportional to the applied potential difference across the diaphragm.

Helmholtz⁶ calculated the velocity of electro-osmotic flow by treating the charged surface with its attendant double layer (assumed to be rigid) as a parallel plate condenser: if the surface charge density is e (e.s.u. per sq. cm.) and the double layer thickness δ then the zeta potential is given by

$$\zeta = \frac{4\pi e\delta}{D} \quad . \quad . \quad . \quad . \quad (10)$$

where the other symbols have their previous significance.

On the application of a potential gradient X , the liquid in the tube rapidly attains a steady velocity v , when the electrical force Xe is in equilibrium with the viscous retarding force per unit area, expressed as $\eta \cdot \frac{v}{\delta}$. ($\frac{v}{\delta}$ is the velocity gradient, assumed linear).

$$\text{Thus} \quad Xe = \eta \cdot \frac{v}{\delta}$$

$$\text{or} \quad v = \frac{Xe\delta}{\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Combining equations 10 and 11 :

$$v = \frac{\zeta D}{4\pi\eta} \cdot X \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

³¹ Svedberg and Pedersen, *The Ultracentrifuge*, Oxford, 1940.

³² Alexander and Johnson, *Colloid Science*, Oxford, 1949.

³³ Reuss, *Memoires de la Société Imperiale des Naturalistes de Moskou*, **2**, 327, 1809.

³⁴ Wiedemann, *Pogg. Ann.*, **87**, 321, 1852.

Since the mobility u is defined as the velocity (of a particle, or in this case, of a liquid surface) at unit field strength

$$u = \frac{\zeta D}{4\pi\eta} \quad . \quad . \quad . \quad . \quad (13)$$

the Helmholtz-Smoluchowski equation. (For a more rigorous derivation of the electro-osmosis equation, without the restriction of the thin double layer, see Rutgers and de Smet.^{35, 35a})

The relation between the electro-osmotic pressure and the zeta potential may also be obtained. The rate of transport of liquid, V (the *volume* velocity of flow), by electro-osmosis through a single capillary, is

$$V = \pi a^2 v.$$

Substituting for v in equation (12) and rearranging :

$$\zeta = \frac{4\eta V}{a^2 DX} \quad . \quad . \quad . \quad . \quad (14)$$

From Poiseuille's equation, the volume rate of flow through a capillary is given by

$$V = \frac{\pi a^4 P}{8\eta l} \quad . \quad . \quad . \quad . \quad (15)$$

Combining equations (14) and (15) :

$$\zeta = \frac{\pi a^2 P}{2lDX} \quad . \quad . \quad . \quad . \quad (16)$$

and accordingly the electro-osmotic pressure P in equilibrium with a potential difference E between the ends of the tube ($E = lX$) is

$$P = \frac{2\zeta DE}{\pi a^2} \quad . \quad . \quad . \quad . \quad (17)$$

The Relation between Streaming Potentials and Electro-osmosis. The electro-osmotic pressure equation, (17), referring to zero flow, should not be confused with the relation between the streaming potential and the applied pressure, equation (8). The two dynamic effects are, however, related : if equation (12), referring to electro-osmotic flow, written in the form

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

³⁵ Rutgers and de Smet, *Trans. Faraday Soc.*, **41**, 758, 1945.

^{35a} Rutgers, private communication.

(where R is the resistance of the capillary and $+i$ the current) is compared with (8) relating to the streaming potential

$$E = \frac{\zeta DP}{4\pi\eta k},$$

it is at once evident that when applied to the same capillary system

$$\frac{v}{i} = \frac{E}{P} = \frac{\zeta D}{4\pi\eta k}. \quad (18)$$

The determination whether, in practice, the velocity of flow divided by the current in electro-osmosis is equal to the streaming potential at unit pressure forms a convenient test of the theories underlying the effects, and the accuracy of the assumptions involved in the derivation of the equations. In agreement with expectation, the equality was verified by Saxen,³⁶ who used a clay diaphragm and aqueous solutions of copper, zinc and cadmium sulphates. Recently Overbeek and Wijga³⁷ have shown that a diaphragm may be treated mathematically as a system of capillaries, some in series, some in parallel, and that this substitution is the same both for streaming potentials and electro-osmotic flow. They also considered the effect of surface conductance.

There have been many investigations of electro-osmosis since Perrin³⁸ discovered the striking effect of electrolytes on the velocity of flow of aqueous solutions. The electro-osmotic pressure relation was used by Coehn and Raydt³⁹ to determine the dielectric constants of many organic liquids relative to that of acetone (see, for example, Dole⁴⁰), but doubt has recently been cast³⁵ on the reliability of their results.

Among the more important recent investigations are those of de Smet and Delfosse^{41, 42} who worked with solutions of potassium iodide and other salts, in organic liquids such as acetone and the aliphatic alcohols, and of Rutgers and de Smet^{16, 35} who measured electro-osmotic velocities in the same apparatus as was used for

³⁶ Saxen, *Ann. Physik.*, **47**, 46, 1892.

³⁷ Overbeek and Wijga, *Rec. Trav. chim.*, **65**, 556, 1946.

³⁸ Perrin, *J. Chim. Phys.*, **2**, 607, 1904.

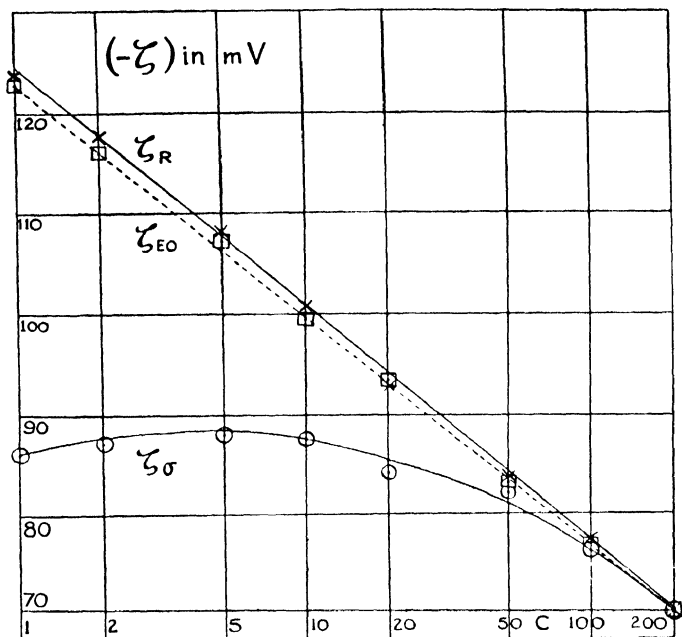
³⁹ Coehn and Raydt, *Ann. Physik* (4), **30**, 777, 1904.

⁴⁰ Dole, *Experimental and Theoretical Electrochemistry*, McGraw Hill, London, 1935.

⁴¹ De Smet and Delfosse, *Bull. Acad. Roy. Belg.*, IV, No. 10, 1942.

⁴² De Smet and Delfosse, *Chem. Zentr.*, II, 1088, 1943.

the determination of streaming potentials, thereby avoiding many of the disadvantages of the latter method. Moreover, the effect of surface conductance could be examined: the zeta-potential, determined from streaming potentials extrapolated to zero surface conductance by Rutgers' method,¹⁰ was found, for salt solutions,



III 4. Zeta Potentials of Aqueous Calcium Chloride Solutions at a Glass Interface. (Rutgers and de Smet, 1947) Ordinate—zeta potential in millivolts, Abscissa—electrolyte concentration in micro-equivalents/litre.

ζ_σ refers to the zeta potentials determined from the classical Helmholtz-Smoluchowski formula for streaming potentials. ζ_{EO} to the values obtained from electro-osmosis, and ζ_R to those calculated from streaming potentials using the actual resistance of the capillary tube instead of the apparent specific conductance of the liquid.

to differ from the potential obtained from the electro-osmotic velocity. The latter potential should be independent of surface conductance, as the actual resistance of the capillary tube was measured. By combining the streaming potential and electro-osmosis equations, the true values of k (the specific conductance in the capillary) were obtained and used to correct the zeta values from streaming potentials to figures (see Fig. 4) almost identical

with those obtained from electro-osmosis. Most accurate results were obtained in the narrowest capillaries, where the surface conductance may account for 60 per cent. of the total. The variation of zeta with the concentration of neutral electrolyte was at first interpreted electrochemically,³⁵ the cation being supposed to take over the role of potential determining ion. Later measurements^{35a} involving the determination of the electrokinetic and electrochemical potentials for the same (glass-water) interface, indicated, however, that the latter potential varied linearly with pH but was almost independent of the concentration of neutral electrolyte. Another explanation, based on Stern's theory of double layer structure (see p. 52), has been proposed.^{35a}

The Physical Significance of the Zeta-potential. The three experimental methods so far described are useful primarily in the determination of zeta-potentials. As electrophoresis measurements may provide results of more extensive significance (electrophoresis thus forming a more or less separate division of the subject), some further aspects of the zeta potential will be discussed here, it being now possible to arrive at a somewhat clearer picture of the significance of the potential and its relation to the experimentally determinable quantities.

Evidently, a common feature in the equations relating to the three effects is the occurrence throughout of the quantity ζD , the fundamental quantity in electrokinetics, and the only one directly determinable by experiment. The particular value of the zeta potential obtained in an experiment will accordingly depend on the value assigned to D , as there is no independent method of measuring ζ . (See, however, ^{20, 46, 47.})

Since there has been in the past no unanimity of opinion as to the value of D to be used (or even in the physical significance of this quantity when applied to systems of molecular dimensions), there must remain a considerable degree of uncertainty as to the actual value of the zeta potential. As Bikerman¹⁵ so clearly pointed out, any value of D may be used without disturbing the agreement between the electrokinetic effects. The problem arose with the original contribution of Helmholtz⁶: in his equations D was omitted entirely; he referred primarily to the *moment of*

the electrical double layer, which he defined as $e\delta$; thus from his equation (without D) for electro-osmosis, the moment M of the double layer is related to the difference in potential ($\psi_1 - \psi_2$) between the two phases (i.e. the zeta potential) by the equation

$$M = e\delta = \frac{\zeta}{4\pi} \text{ (compare with equation (10)).}$$

With the dimensional system then in use, the potential and the moment were thus dimensionally identical (Helmholtz appeared to consider them synonymous); however, with the introduction by Pellat (cited in ref. 38) of the dielectric constant into the equation, the identity is lost, thus:

$$M = \frac{\zeta D}{4\pi}.$$

Among others, Guggenheim⁴³ realised the fundamental character of the moment, and even suggested a new unit for the quantity; his treatment, however, has been criticised by Wood¹² who pointed out, in a comprehensive analysis of the streaming potential method, that the past confusion had arisen directly over the selection of either three or four dimensions for the expression of electrical quantities.

It is evident that the moment may be directly determined from experiment; thus for streaming potentials:

$$M = \frac{\zeta D}{4\pi} = \frac{\eta Ek}{P} \text{ (compare with equation (8)).}$$

Although some investigators have given their results in terms of the moment, the greater convenience and more readily visualised significance of potentials has led to their widespread use; it is essential, of course, as Wood emphasises, that when this is done the value of D used should be quoted.

It is now fairly well established (see Bikerman¹⁵), after much controversy (see, e.g. Horwitz¹), that the value of the dielectric constant approximates to that of the liquid in bulk. Further confirmation of this may be expected from the recently developed static methods, applicable in certain special cases, for the direct

⁴³ Guggenheim, *Trans. Faraday Soc.*, **36**, 139, 1940.

measurement of zeta potentials,^{44, 45} and as a result of some recent theoretical advances, it is possible to derive a more complete interpretation of the zeta potential.

Thus Robinson^{46, 47} has compared the observed relationships between the zeta potential and $\log c$ (c is the concentration of electrolyte) for the quartz-water and glass-water interfaces. Two sets of values of the potentials were obtained independently (by Rutgers and de Smet³⁵ and Jones, Wood, and Robinson^{48, 49}) and showed close agreement; Robinson suggests, following Gurney,^{50, 51} and Fowler^{52, 53} (see also⁴⁰) that the zeta potential in these cases is determined by the equilibrium between anions in solution and those adsorbed on the vitreous surface. From energy considerations, he derived a theoretical ζ - $\log c$ curve which differed from the observed only by the factor 0.6, the deviation of the factor from unity being ascribed to the uncertainty attending the assignment of the conventional values to the dielectric constant and the viscosity within the double layer. The use of the corrected zeta potentials did not affect the earlier quantitative interpretation⁵⁴ of the Jones-Ray effect,⁵⁵ the occurrence of a minimum (at 0.001 N) in the curve of surface tension against concentration of electrolyte. This interpretation of the origin of the zeta potential is reasonably satisfactory for aqueous solutions, and it is no doubt substantially correct; some of the assumptions involved, however, have been criticised by Buchanan and Heymann^{55a} who also emphasised the extreme difficulty of obtaining confirmatory electrode potential measurements under the conditions imposed. The large potentials often encountered with hydrophobic organic liquids were tentatively ascribed by Gortner¹⁷ to "forced dissociation" of the molecules into ions.

⁴⁴ Lewina and Sarinsky, *Acta Physicochim. U.R.S.S.*, **7**, 485, 1937.

⁴⁵ Kruyt and de Bruyn, *Z. Physik. Chem.A*, **186**, 282, 1940.

⁴⁶ Robinson, *J. Chem. Phys.*, **14**, 721, 1946.

⁴⁷ Robinson, *ibid.*, **15**, 113, 1947. ⁴⁸ Jones and Wood, *ibid.*, **13**, 106, 1945.

⁴⁹ Wood and Robinson, *ibid.*, **14**, 251, 1946.

⁵⁰ Gurney, *Proc. Roy. Soc.A*, **134**, 137, 1931.

⁵¹ Gurney, *ibid.*, **136**, 378, 1932.

⁵² Fowler, *ibid.*, **136**, 391, 1932.

⁵³ Fowler, *Trans. Faraday Soc.*, **28**, 368, 1932.

⁵⁴ Wood and Robinson, *J. Chem. Phys.*, **14**, 258, 1946.

⁵⁵ Jones and Ray, *J. Amer. Chem. Soc.*, **59**, 187, 1937.

^{55a} Buchanan and Heymann, *J. Colloid Sci.*, **4**, 137, 151, 157, 1949.

Electrophoresis. The movement of charged particles through a resting dispersion medium under the influence of a potential gradient, the *reverse* of electro-osmosis, is the most practically important electrokinetic effect: it was first observed by Reuss³³ with clay particles.

A quantitative interpretation was given by Smoluchowski⁸ who pointed out that the electro-osmosis equation

$$u = \frac{\zeta D}{4\pi\eta} \quad . \quad . \quad . \quad (13)$$

must also apply to the motion of a cylindrical particle oriented in the direction of the field (or, in general, to any large particle of "easy" shape and small curvature where the distorted electric field is always parallel to the surface of shear), as the relative movement at the solid-liquid surface is identical.

The zeta potential of a sphere of charge Q and radius r is defined (in the absence of other ions) as:

$$\zeta = \frac{Q}{Dr} \quad (\text{cf. p. 55}),$$

(on the assumption that the shear surface coincides with the surface of the sphere) and accordingly we may relate the charge and radius of a particle (two of its most important colloidal properties) to its mobility:

$$u = \frac{Q}{4\pi\eta r} \quad . \quad . \quad . \quad (19)$$

When other ions (generally those of simple electrolytes) are present, the zeta potential is reduced, an effect considered by the Debye-Hückel treatment outlined in the last chapter.

The zeta potential then becomes

$$\zeta = \frac{Q}{Dr} \frac{1}{1 + \kappa r}; \quad . \quad . \quad . \quad (20)$$

combining equations 20 and 13, we obtain for a large sphere:

$$u = \frac{Q}{4\pi\eta r} \frac{1}{1 + \kappa r} \quad . \quad . \quad . \quad (21)$$

For a small sphere, the relative motion within the double layer cannot be considered to be parallel to the direction of the applied field; an alternative solution may then be derived. Thus, in the

absence of other ions, the electrical force QX acting on a small sphere may be equated to the viscous retarding force (given by Stoke's law)

$$QX = 6\pi\eta rv,$$

$$\text{or} \quad u = \frac{Q}{6\pi\eta r}. \quad (22)$$

By analogy with equations (19) and (21), the mobility of the small sphere in the presence of other ions is given by

$$u = \frac{Q}{6\pi\eta r} \cdot \frac{1}{1 + \kappa r} \quad (23)$$

the equation of Hückel.⁵⁶

The confusion that arose over the question of which of these equations (21) and (23) was applicable to a given system was resolved by Henry⁵⁷ who considered the effect of the conductivity of the particle and the distortion of the applied electric field by the charges of the double layer. By combining these equations with those of fluid motion, Henry obtained a general equation for the electrophoresis of spherical particles:

$$u = \frac{\zeta D}{6\pi\eta r} \cdot f(\kappa r) \quad (24)$$

where $f(\kappa r)$ is the function given by Henry as

$$f(\kappa r) = 1 + \frac{(\kappa r)^2}{16} - \frac{5(\kappa r)^3}{48} - \frac{(\kappa r)^4}{96} + \frac{(\kappa r)^5}{96} - e^{\kappa r} \left[\frac{(\kappa r)^4}{8} - \frac{(\kappa r)^6}{96} \right] \int_{\infty}^{\kappa r} \frac{e^{-t}}{t} \cdot dt \quad (25)$$

At low values of κr (the case of the small sphere) the function approximates to unity, so that equation (23) is valid; at large κr values (large sphere) the function is equal to 1.5, so that the modified Helmholtz-Smoluchowski equation (19) applies. For intermediate cases, some value between 1.0 and 1.5 is assumed. Tables of the values of the function against κr have been given by, e.g., Gorin.⁵⁸ (See reference⁵⁹ for a more extensive treatment of this and allied problems.)

⁵⁶ Hückel, *Phys. Z.*, **25**, 204, 1924.

⁵⁷ Henry, *Proc. Roy. Soc. A*, **133**, 106, 1931.

⁵⁸ Gorin, *J. Physical Chem.*, **45**, 371, 1941.

⁵⁹ Abramson, Moyer and Gorin, *The Electrophoresis of Proteins and the Chemistry of Cell Surfaces* (Reinhold, 1942).

A refinement of this electrophoresis equation has recently been suggested by Gorin^{60, 61, 62} who points out that it was assumed, in the derivation of the Debye-Hückel-Henry equation, that the surface of shear of the migrating particle was identical with the shell of nearest ions of the ionic atmosphere. This shell will actually be at a distance $(r + r_i)$ from the centre of the migrating particle; r_i is the "average radius" of the ions comprising the atmosphere. With this correction, the equation for the electrophoresis of spheres becomes

$$u = \frac{Q}{6\pi\eta r} \cdot \frac{f(\kappa r)(1 + \kappa r_i)}{(1 + \kappa r + \kappa r_i)} \quad (26)$$

Limitations of the Electrophoresis Equation. It was assumed in the derivation of this equation (see p. 54) that the electric energy $z_{\pm}\epsilon\psi$ of the ions comprising the atmosphere was small compared with their thermal energy, kT . With highly charged particles, the potential near the surface may be sufficiently large to invalidate this assumption.

It has often been stated (see, e.g.^{58, 59}) that the controlling factor is the magnitude of the term $z_{\pm}\epsilon\zeta$: this, however, represents the electric energy of an ion in contact with the surface of shear, and so can apply to relatively few of the ions of the atmosphere, especially at low ionic strengths. (See⁶³, and Hartley's conclusions on the success of the Debye-Hückel theory when applied to salt solutions, p. 56.) Bjerrum⁶⁴ considers that when the sum of the radii of the gegen- and colloid ion is less than the minimum, r_{min} , given by $r_{min} = \frac{z_+z_- \epsilon^2}{2DkT}$, then the gegenion must be considered as being electrostatically bound to the central particle. This *ion-pair* formation is, of course, the modern equivalent of the older concept of incomplete dissociation (Hartley⁶⁵). An alternative extension of the Debye-Hückel theory is the attempt to solve the complete form of differential equation governing the drop

⁶⁰ Gorin, *J. Chem. Phys.*, **7**, 405, 1939.

⁶¹ Abramson, Gorin and Moyer, *Chem. Rev.*, **24**, 345, 1939.

⁶² Abramson, *Trans. Faraday Soc.*, **36**, 5, 1940.

⁶³ Creeth and Jordan, *J.C.S.*, 1409, 1949.

⁶⁴ Bjerrum, *Ergeb. Exakt. Naturwiss.*, **6**, 125, 1926.

⁶⁵ Hartley, *Trans. Faraday Soc.*, **31**, 31, 1935; *Quarterly Rev.*, **2**, 152, 1948.

of potential through the double layer. This equation has been given by Müller (see p. 56) (see also Gouy⁶⁶ and Mooney⁶⁷), but has so far only been solved directly for flat surfaces; an approximate solution for spherical particles was, however, obtained by Gronwall, La Mer, and Sandved⁶⁸ by calculating the third and fifth order terms in the series. The effect of these corrections is to reduce the predicted mobility of highly charged particles below that required by the Debye-Hückel-Henry equation; Gorin^{58, 59, 69} has attempted to formulate the correction by a modification of equation (26):

$$u = \frac{Q \cdot f(\kappa r)}{6\pi\eta r} \cdot \left[\frac{1 + \kappa r_i}{1 + \kappa r + \kappa r_i} - n \right] \quad (27)$$

where n , the "valence correction" term, is given by

$$n = 6 \left[\frac{r}{r+r_i} \right] \left[\frac{ze^2}{D(r+r_i)kT} \right]^2 \left[\frac{1}{2} X_3(\kappa r + \kappa r_i) - 2 Y_3(\kappa r + \kappa r_i) \right] \quad (28)$$

Here z is the valence of the colloidal ion, and X_3 and Y_3 are the third order correction functions, derived by Gronwall *et al.* and available in their paper (see also Harned and Owen⁷⁰). The validity of this equation has yet to be firmly established, as its derivation has not been published, and there is little evidence as to its use (the correction terms for most practical systems are negligibly small).

Recently, a different approach to this problem has been made by Booth²⁴: he finds a general expression for the mobility of spherical particles, valid for all values of κr and taking into account the fact that $\frac{e\zeta}{kT}$ may attain the value ~ 4 . Moreover his equation, which is an extension of that developed by Henry, was obtained without making Henry's assumption that the charge distribution round the particle remained symmetrical during migration. Some such lack of symmetry must be expected to develop as the particle moves relative to the ionic atmosphere: the latter will tend to

⁶⁶ Gouy, *J. Phys.*, **9**, 457, 1910.

⁶⁷ Mooney, *J. Physical Chem.*, **35**, 331, 1931.

⁶⁸ Gronwall, La Mer and Sandved, *Phys. Z.*, **29**, 358, 1928.

⁶⁹ Gorin, private communication, referred to in (63).

⁷⁰ Harned and Owen, *The Physical Chemistry of Electrolytic Solutions* (A.C.S. Monographs, Reinhold, 1943).

lag behind the particle, causing the region in front to become less dense, and the region behind, of greater density. Booth's equation, together with the somewhat similar one of Overbeek,⁷¹ was the first to take into account this *relaxation effect*; though of great mathematical complexity, it marks a theoretical advance of considerable importance. The relaxation retardation is small for the lower ζ -potentials, so that Henry's equation needs only a small correction. It is, however, important for higher potentials, and may well lead to a limiting value at higher potentials. The effect of surface conductance on the mobility has recently been investigated theoretically by Booth⁷² and Henry.⁷³

Cylindrical Particles. The treatment of spherical particles has thus reached a fairly satisfactory stage; many of the systems encountered in practice, however (especially in the biochemical fields, where so much electrophoretic investigation has been performed), provide indisputable evidence that the particles approximate to the cylindrical, reaching in some cases, very great degrees of asymmetry. The development of a satisfactory mathematical basis by which the observed characteristics of such systems may be interpreted is accordingly of considerable importance.

Following Henry's treatment of spherical particles, Gorin^{59, 61} obtained for the zeta potential of a long cylinder ($l \gg a$):

$$\zeta = \frac{2Q}{D(1+2a)} \cdot \left[\frac{K_0(\kappa a + \kappa r_i)}{(\kappa a + \kappa r_i)K_1(\kappa a + \kappa r_i)} + \ln \left(\frac{a + r_i}{a} \right) \right]. \quad (29)$$

K_0 and K_1 are Bessel functions, a table of values of which has been given.⁵⁹ As the electric force exerted on a cylinder varies with its orientation, the mobility equation becomes

$$u = \frac{\zeta D}{F'(\kappa a) \pi \eta}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (30)$$

where $F'(\kappa a)$ is the function obtained by Gorin.⁵⁹

Applications of Electrophoretic Equations. Following Hartley's classification⁶⁵ we may distinguish between two types of system which may be studied electrophoretically. Firstly there are the lyophobic sols, where the particles are in the same physical

⁷¹ Overbeek, *Kolloid Beiheften*, **54**, 287, 1943.

⁷² Booth, *Trans. Faraday Soc.*, **44**, 955, 1948.

⁷³ Henry, *ibid.*, **44**, 1021, 1948.

state as the bulk solid (with which they are not in thermodynamic equilibrium); here the charge is determined by the surface characteristics, and is due to adsorption or desorption of ions. The charge on the particle is therefore not stoichiometrically related to the mass, and its actual value is, accordingly, not of fundamental significance. The important factor in these systems is the magnitude of the double layer potential, which determines, *inter alia*, the stability of the suspension. Because the particles are generally large and, having similar surfaces, possess similar surface charge densities, they will migrate with the same velocity, even if of different size or shape. The colloidal properties of the solution are thus due not primarily to the nature of the suspensoid, the bulk of which plays little or no part, but rather to the adsorption characteristics of the surface, and the presence of foreign electrolyte.

For such systems, the micro-electrophoresis method is of great value. The method, due originally to Ellis,⁷⁴ has been developed and extensively used, particularly by Abramson and his school, in America; the movement of a single particle is observed microscopically and measurements are rapid and readily reproducible. Many results of interest have been produced, of which only a few may be mentioned. Reference should be to ¹⁸, ⁵⁹ and ⁷⁵ for a more complete survey of this type of work, much of which may be of considerable physiological importance. The investigations with latex particles,⁷⁶ with bacteria in the presence of chemotherapeutic agents⁷⁷ and when sensitised with immune serum,⁷⁸ with milk fat droplets,⁷⁹ with oil drops in aqueous solutions, etc.,⁸⁰, ⁸¹ may be cited as indicating the width of this very fruitful field of research.

The second important class of suspensions is that which Duclaux⁸² defined as *colloidal electrolytes*, where the particles in

⁷⁴ Ellis, *Z. Phys. Chem.*, **78**, 321, 1912.

⁷⁵ "The Electrical Double Layer," Discussion of the Faraday Society, *Trans. Faraday Soc.*, **36**, 1940.

⁷⁶ Moyer, *Trans. Faraday Soc.*, **36**, 248, 1940.

⁷⁷ Bradbury and Jordan, *Biochem. J.*, **36**, 287, 1942.

⁷⁸ Shibley, *J. Exp. Med.*, **40**, 453, 1924; **44**, 667, 1926; **50**, 825, 1929.

⁷⁹ Moyer, *J. Biol. Chem.*, **133**, 29, 1940.

⁸⁰ Powney and Wood, *Trans. Faraday Soc.*, **36**, 57, 1940.

⁸¹ Clayton, *The Theory of Emulsions and their Technical Treatment*, London, 1935.

⁸² Duclaux, *J. Chim. Phys.*, **7**, 405, 1909.

solution, often in a state of molecular dispersion, are made up of an ionising compound which is in true equilibrium with the solution; the charge on the particle, being determined by the extent of ionisation, is stoichiometrically related to the mass.

At one time, the term "colloidal electrolyte" was used almost exclusively to refer to solutions of soaps (and other detergents) and organic dyes. The former have been extensively investigated, especially by McBain *et al.*⁸³ Such solutions, however, form rather a separate division within the class of colloidal electrolytes; the colloidal properties are due to the amphipathic character of the molecules, and the size of the micellar particle in solution is not of direct significance. The proteins, and other water-soluble biocolloids, form the most important division of this class; here the particles are in general much smaller than those of the first class considered, and the colloidal properties of the solution are determined by *all* of the solute (compare lyophobic sols). The micro-electrophoresis method is generally not directly applicable, but these systems may be very conveniently studied by means of the Tiselius moving boundary electrophoresis apparatus, which is fully described in the next chapter. The micro method has, however, been widely used for the investigation of these systems by causing the colloidal electrolyte to be adsorbed on the surface of an inert (e.g. quartz) particle of microscopic dimensions. The mobility of the particle thus obtained will only be identical with the true electrophoretic mobility of the colloid if (a) the surface characteristics (e.g. for proteins, the orientation and availability of the amino and carboxyl groups, etc.) of the colloid are unaffected by adsorption, and (b) the molecular dimensions are large enough to ensure that the value of the Henry function is approximately the same for the colloidal molecule as for the colloid/quartz particle.

For several proteins these criteria appear to be satisfied, and close agreement has been observed between the *pH*-mobility curves obtained by the micro-electrophoresis method and the moving boundary method (see Chapter IV). Further evidence concerning the effect of protein adsorption was obtained by Ghosh and

⁸³ McBain, *et. al.*, *J.C.S.*, **101**, 2042, 1910; **105**, 417, 957, 1914; **113**, 825, 1918.

Roy⁸⁴: they compared, and showed to be identical, the surfaces of small particles (silica and kaolin), and the walls of the experimental cell, when both were coated with protein. This was achieved by constructing, for electro-osmotic measurements, a porous diaphragm composed of the protein covered particles whose electrophoretic mobility was already known.

The moving boundary method is now capable of giving very precise electrophoretic mobility values, which are of especial interest with molecularly-dispersed colloidal electrolytes, where the mobility is directly related to the molecular dimensions and charge. There have, however, been relatively few attempts to obtain such fundamentally significant results, as investigators have been concerned for the most part with the many complex colloidal mixtures of biological origin, especially the proteins (see Chapter IV), where information concerning the number of components and their relative proportions may readily be obtained.

The pioneer attempts in this direction were made by Tiselius and Svensson⁸⁵ and Adair and Adair.⁸⁶ The former investigators determined the mobilities of egg albumin over a wide range of ionic strengths, and compared these values with those predicted by the uncorrected form of Debye-Hückel-Henry equation, the values of the particle charge being obtained from the membrane potential measurements of Adair and Adair.^{86, 87} There was a close agreement between the observed and calculated mobility values over the whole range, but this was somewhat fortuitous (Gorin,⁵⁸ Longworth⁸⁸) as no account had been taken of the effect of the non-spherical shape of the molecule, nor of the effect of the finite size of the ions in the atmosphere. A more complete characterisation of a few proteins was attempted by Gorin and Moyer⁸⁹: values of the particle charge of, e.g., serum albumin B (axial ratio, from sedimentation and diffusion data, about 5) were calculated from the observed mobilities, using the equation for

⁸⁴ Ghosh and Roy, *J. Indian Chem. Soc.*, **16**, 634, 1939.

⁸⁵ Tiselius and Svensson, *Trans. Faraday Soc.*, **36**, 16, 1940.

⁸⁶ Adair and Adair, *ibid.*, **36**, 23, 1940.

⁸⁷ Adair and Adair, *Biochem. J.*, **28**, 199, 1934.

⁸⁸ Longworth, *Ann. New York Acad. Sci.*, **41**, 267, 1941.

⁸⁹ Gorin and Moyer, *J. Gen. Physiol.*, **25**, 785, 1942.

cylindrical particles, and compared with those obtained from the (suitably corrected) electrometric titration curve. Good agreement was obtained for these sets of data over a small range of pH . The practice of obtaining particle charge values from titration curves is, however, susceptible of rather large errors (see ⁵⁹, p. 92). It is possible that the electrophoretic mobility equation may be of use in obtaining an approximate estimate of particle asymmetry when combined with data from other sources (see Gorin ⁵⁹, ⁶¹, ⁶⁹).

An attempt to compare calculated mobilities with those observed, over a wider range of ionic strength, for the highly asymmetric ion of thymus deoxypentose nucleic acid has been made by Creeth and Jordan,⁶³ the charge values being obtained from membrane potential measurements. Close agreement was observed at low ionic strengths (< 0.05) but serious deviations occurred as the latter factor was increased.

It is evident, from the discrepancies observed in the few investigations so far performed, that more rigorous testing of the electrophoresis equations, with a variety of systems, is required; the increasingly widespread use of the Tiselius method may be expected to provide adequate data.

The Electroviscous Effect. This effect, which is of importance mainly with colloidal electrolytes, is of a different kind from the four reviewed above, in that the displacement of the fixed and movable parts of the ionic atmosphere produces a modification of an existing property, the viscosity.

First predicted by Smoluchowski, the resulting increase in viscosity, for spherical particles, can be stated in the form ⁹⁰:

$$\eta/\eta_0 - 1 = \eta_{sp} = 2.5\phi \left[1 + \frac{1}{\eta_0 k r^2} \cdot \left(\frac{\zeta D}{2\pi} \right)^2 \right], \quad (31)$$

where η is the viscosity of the solution, in which ϕ is the volume fraction of solute, η_0 is the viscosity of the solvent (η_{sp} is the specific viscosity), k the specific conductivity of the solution, and r the radius of the particle.

The derivation of this equation was never published, but Krasny-Ergen ⁹¹ reconsidered the problem, and derived an equation

⁹⁰ Smoluchowski, *Kolloid Z.*, **18**, 194, 1916.

⁹¹ Krasny-Ergen, *ibid.*, **74**, 172, 1936.

identical with 31 except that the last term was multiplied by 1.5.

This equation can only apply to systems where $\frac{1}{\kappa} \ll r$, and is also subject to the limitations of the simple Einstein equation. Few attempts at verification of this equation have been made. Bull⁹² observed a pronounced minimum in the intrinsic viscosity (η_{sp}/ϕ) of ovalbumin solutions in the region of the isoelectric point: the increase in viscosity at other pH 's was greatly reduced by low concentrations of sodium chloride. Bull found that the viscosity increments were many times smaller than predicted by the equation, and considered that the validity of the latter was doubtful even though the condition that $\frac{1}{\kappa} \ll r$ was not satisfied. Booth⁹³ considers the equation to be incomplete; by the application of an extended version, he was able to account fairly satisfactorily for Bull's results.

Recently more extensive investigations of the effect have been undertaken by Briggs *et al.*,^{94, 95, 96} giving results more nearly in accordance with the Krasny-Ergen equation: this was tested for the sodium salt of gum arabic and the sodium and calcium salts of casein. In agreement with expectation, a straight line relationship existed between $\frac{1}{\eta_{sp}}$ and $\left(\frac{\xi^2}{k(\eta - \eta_0)}\right)$, but the slope at different colloid concentrations showed an apparent variation of the particle radius, which is, of course, inadmissible.

By extrapolating to zero potential, Hankinson and Briggs⁹⁵ obtained an approximate value of the relative contribution of the electroviscous effect to the total viscosity: for gum arabic, this was 79 per cent. By assuming the factor 2.5 in the Einstein equation to be correct, it is possible to obtain an indication of the amount of water bound to the colloidal particle: this is of great interest in view of the general difficulty of distinguishing between hydration and asymmetry.

⁹² Bull, *Trans. Faraday Soc.*, **36**, 80, 1940.

⁹³ Booth, Private communication.

⁹⁴ Briggs, *J. Physical Chem.*, **45**, 866, 1941.

⁹⁵ Hankinson and Briggs, *ibid.*, **45**, 943, 1941.

⁹⁶ Briggs and Hanig, *ibid.*, **48**, 1, 1944.

Briggs and Hanig⁹⁶ found that the change in viscosity of β lactoglobulin solutions with ionic strength could almost entirely be accounted for by the change in the electroviscous contribution: such a change is probably also the reason for the striking variation of the viscosity of solutions of the sodium salt of thymus deoxypentose nucleic acid with ionic strength^{97, 98}; here the effect of the reduction of the zeta potential is enhanced by a decreased tendency towards particle interaction.

A somewhat different approach to the subject of electroviscosity has recently been made by Elton,⁹⁹ who has considered electroviscous effects in thin liquid films, and calculated the effect on the viscosity of the resistance of the double layer to shear.

In conclusion, it is evident that the theoretical background at present existing for the streaming potential, Dorn, and electroosmotic effects is generally satisfactory, but that further confirmation of the theory, by combination of results obtained by the different methods for the same system, is still desirable. For electrophoresis (and also the electroviscous effect) much wider and more rigorous testing of the present theory over a variety of systems is necessary before further theoretical advances can be made.¹⁰⁰ An excellent general survey is given by Overbeek in a recent review.¹⁰¹

⁹⁷ Greenstein and Jenrette, *J. Nat. Cancer Inst.*, **1**, 77, 1940.

⁹⁸ Creeth, Gulland and Jordan, *J.C.S.*, 1141, 1947.

⁹⁹ Elton, *Proc. Roy. Soc. A*, **194**, 259, 1948.

¹⁰⁰ See also Hermans and Overbeek, *Rec. trav. chim.*, **67**, 761, 1948; Arnold and Overbeek, *ibid.*, **69**, 1923, 1950.

¹⁰¹ Overbeek, *Advances in Colloid Science*, Vol. III, New York, 1950.

CHAPTER IV

THE ELECTROPHORESIS OF PROTEINS AND SIMILAR SUBSTANCES

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1. Methods. Three methods of studying electrophoretic migration, the transference method, the microscopic method, and the moving boundary method have been applied to proteins. Of these the last is of more general application and is by far the most widely used at present.

The transference method is essentially the Hittorf method for the measurement of transport numbers of inorganic ions adapted to the case of proteins. It is usually employed only when the material under examination has some specific biological effect which can be detected or estimated in solutions in which the concentration is too low to allow the use of the moving boundary method. Cohn, Irving and du Vigneaud¹ have used the transference method in their work on the pressor and oxytocic principles of the pituitary gland.

The microscopic method has certain advantages over the moving boundary method, as it requires less elaborate apparatus, only a very small amount of material, and observations are more rapid. However, since the method consists in the observation of microscopically visible particles, it is applicable only to insoluble materials or to such particles coated with an adsorbed layer of an otherwise soluble material. Other disadvantages are that the method is not of much use for mixtures of proteins, and, owing to the motion of the supporting medium due to electro-osmosis in the narrow tubes used, correct mobility values are obtainable only from observations on particles at two particular levels in the cell. When suitable precautions are taken, the microscopic method gives mobility values equal to, or differing by only a small amount

¹ Cohn, Irving and du Vigneaud, *J. Biol. Chem.*, **137**, 635, 1941.

from, the values obtained under identical conditions by the moving boundary method. This is illustrated by the work of Abramson² and Moyer^{3, 4} on horse serum albumin and egg albumin. A new type of micro-electrophoresis cell, in which the electro-osmotic flow is exactly compensated at the centre of the cell, promises to improve this type of measurement.^{4a} The microscopic method is peculiarly suited to the study of bacterial cells, erythrocytes, etc. A full discussion of this and of all other aspects of this method is contained in the monograph by Abramson, Moyer and Gorin.⁵

Since the main purpose of examining many protein systems by electrophoresis is to obtain information regarding the complexity of these systems and its variation in different circumstances, it is the *moving boundary method* which has attracted most interest, with the result that considerable advances have been made during the last ten or twelve years.

The first moving boundary studies of the migration of ions were made by Lodge⁶ in 1886. Application to colloid systems began in 1897 with the work of Picton and Linder.⁷ The important observation of Hardy⁸ was that the rates of movement of the boundaries, which differed in the two limbs of the U-tube, could be made more nearly equal by addition of sufficient salts to the solution. Svedberg and Andersson⁹ pointed out that, to get exact agreement the conductivity should be the same both above and below the boundary (even after the passage of current), which implies that every ion species is present in the same concentration on both sides of the boundary—an impossibility.

Owing to neglect of these points, and consequent inaccuracies and inconsistencies in results, the moving boundary method tended to fall into disrepute until, in 1930, Tiselius¹⁰ published an

² Abramson, *J. Gen. Physiol.*, **15**, 575, 1932.

³ Moyer, *J. Biol. Chem.*, **122**, 641, 1938.

⁴ Moyer, *J. Phys. Chem.*, **42**, 71, 1938.

^{4a} Rutgers, Faq and van der Minne, *Nature*, **166**, 100, 1950.

⁵ Abramson, Moyer and Gorin, *Electrophoresis of Proteins and the Chemistry of Cell Surfaces* (Reinhold Publishing Corporation, New York, 1942).

⁶ Lodge, *Rep. Brit. Assoc.*, 389, 1886.

⁷ Picton and Linder, *J.C.S.*, **71**, 568, 1897.

⁸ Hardy, *J. Physiol.*, **33**, 251, 1905.

⁹ Svedberg and Andersson, *Kolloid Z.*, **24**, 156, 1919.

¹⁰ Tiselius, *Nova Acta Reg. Soc. Sci. Upsal*, IV, **7**, No. 4, 1930.

account of some extremely important work in which he showed that anomalies in the migration rates could be very considerably reduced by maintaining a nearly constant conductivity across the boundary through the use of solutions containing a comparatively low concentration of protein and a relatively high concentration of salts. The fairly uniform conductivity was achieved by previous dialysis of the protein solution against sufficient of the buffer solution to be employed as supernatant. The use of buffer salts was to prevent any significant changes of pH at the boundaries, which would otherwise cause anomalies. The apparatus also included reversible electrodes (introduced in 1909 by Michaelis¹¹) to eliminate the disturbing effects of gas evolution or of the production of hydroxyl or hydrogen ions and subsequent migration into the U-tube. The electrodes were placed in separate vessels, connected to the U-tube by tubes containing the same buffer solution as formed the supernatant to the colloid; the volume of buffer was large enough to prevent the migration into the U-tube of material from the neighbourhood of the electrodes.

The disadvantages of the simple U-tube apparatus of Tiselius were: (a) lack of a good method of forming sharp boundaries; (b) the need for quartz tubing, since the positions of the boundaries formed by colourless proteins were located by the absorption of ultra-violet light; (c) the tedious work necessary to deduce from the photographs the precise location of a boundary; (d) lack of facilities for removal of samples from different parts of the U-tube after electrophoresis; and (e) the production of disturbing heat convection if too high a current was employed.

Theorell^{12, 13} constructed a U-tube in sections for the purpose of removing samples from different layers after electrophoresis. This method was also adopted in the construction in 1937 of a new apparatus by Tiselius,¹⁴ who eliminated or reduced all the points of criticism of his earlier apparatus. The new Tiselius apparatus (as slightly modified by Longworth¹⁵) is shown in Figs. 1, 2.

¹¹ Michaelis, *Biochem. Z.*, **16**, 81, 1909.

¹² Theorell, *ibid.*, **275**, 1, 1934.

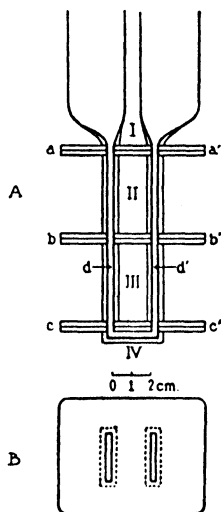
¹³ Theorell, *ibid.*, **278**, 291, 1935.

¹⁴ Tiselius, *Trans. Faraday Soc.*, **33**, 524, 1937.

¹⁵ Longworth and MacInnes, *Chem. Rev.*, **24**, 271, 1939.

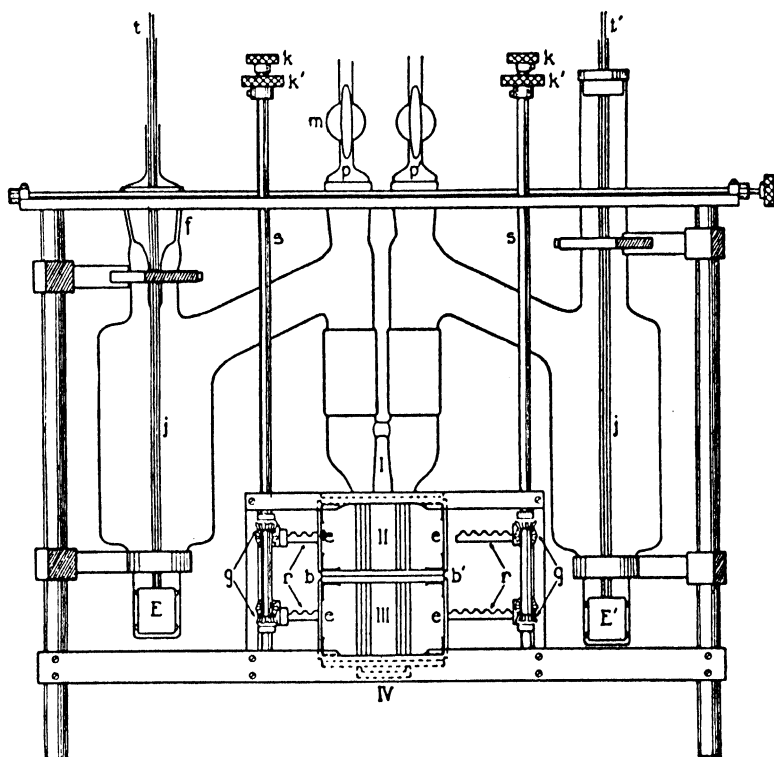
The U-tube is built up of four sections, all except the top section being constructed entirely from rectangular glass plates cemented together. The top section, I, consists of two wide glass tubes, narrowed and flattened at their lower ends and cemented to the flat end-plate coincident with the rectangular holes in that plate. The U-tube is assembled in its holder with sufficient grease (usually vaseline slightly thinned with paraffin) between the end-plates of the sections to prevent leakage. Light springs clamp the U-tube down in its holder. The U-tube channel is filled with the solution of protein (previously dialysed against the requisite buffer) until the level just comes into section II. Section III is slid out of alignment, isolating it from sections II and IV, the slight excess of solution removed from section II, and sections I and II washed out and filled with the buffer solution. During these operations care has to be taken to remove air bubbles and to prevent any grease particles adhering to the cell windows, factors which would affect the observations. The top section is connected to the electrode vessels by glass tubes, the joints being made with tightly fitting rubber tubing. The electrode vessels and connecting tubes are filled with buffer, except for the fact that a small volume must be left for the electrodes and their surrounding solution. The whole apparatus is immersed in a large water-bath thermostated at a temperature just above 0°C . Working near the temperature of maximum density of the solutions, and using a U-tube of narrow rectangular cross-section help to minimise convection and enable rather higher currents to be used.

After the lapse of a period of time for temperature equilibration, the electrodes (silver wire or silver foil coils plated with silver chloride) are placed in the electrode vessels, as shown in Fig. 2, and a layer of potassium chloride solution (saturated at bath



IV 1.—Apparatus of Tiselius. (A) cross section of cells, (B) plan of one of the centre sections. (Longworth and MacInnes, *Chem. Rev.*, 1939.)

temperature) is carefully run to the bottom of the electrode vessel to cover the coil. If both electrode vessels are open at the top it is necessary at this stage to connect the tubes above taps p and p' by a Y-tube into which buffer is sucked up, ensuring a complete liquid connection between the electrode vessels. Before the



IV 2.—Apparatus of Tiselius, with electrode vessels and support. (Longworth and MacInnes, *Chem. Rev.*, 1939.)

boundaries are formed the taps p and p' are closed and the Y-tube removed. If hydrostatic equilibrium were not ensured in this way a sudden displacement of solution would occur as the boundaries were being formed, causing severe disturbances. A single long centre section¹⁶ can replace sections II and III with advantage in

¹⁶ Longworth, Cannan and MacInnes, *J. Amer. Chem. Soc.*, **62**, 2580, 1940.

many analyses. The technique of filling is slightly modified, the bottom section, IV, and one channel of the centre section being filled with protein solution, the other channel of the centre section with buffer. In this case hydrostatic equilibrium cannot simply be ensured before boundary formation, so that a closed electrode vessel system should be used.

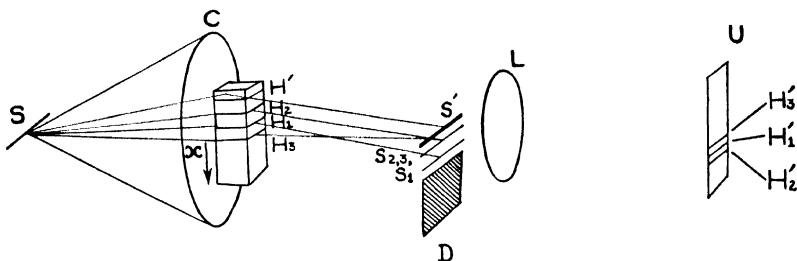
The initial boundaries are formed by sliding the displaced centre section back into alignment, either by means of pneumatic pistons,¹⁴ or by means of a rack and pinion mechanism¹⁵ shown in Fig. 2. A compensating device is necessary to bring into view the initial boundaries from behind the end-plates. In closed electrode vessel systems this consists of a slow injection of buffer on one side of the system by means of a syringe operated by a low-g geared electric motor. When the boundaries in both limbs have thus been brought fully into view (see below the optical systems employed), compensation is stopped and the current switched on. The initial boundaries should always be sharp and free from disturbances as convections are otherwise particularly liable to develop in the early stages.

Under the action of the current two proteins will not in general have identical mobilities (rate of movement per unit potential gradient), and, provided the difference is sufficiently great, the original boundary may split into two or more boundaries moving at different rates. It is then possible to recover samples of some of the components by sliding the U-tube sections out of alignment, removing the assembly from the water-bath, and dismantling the apparatus carefully, emptying the sections one by one in the process. Pure samples of only two components can be thus obtained after a single run, a sample of the fastest component from the ascending limb and a sample of the slowest from the descending. Before sectioning off the U-tube for isolation purposes it is often necessary to operate the compensating device to bring the boundaries to suitable positions in the cell.

2. Optical Systems. The other most important innovation in Tiselius' new apparatus (1937) was the introduction of the schlieren method of Toepler for boundary location. This method, based on refractive index variations, avoided most of the objectionable

features of the light absorption method. The principle of the method is illustrated diagrammatically in Fig. 3.

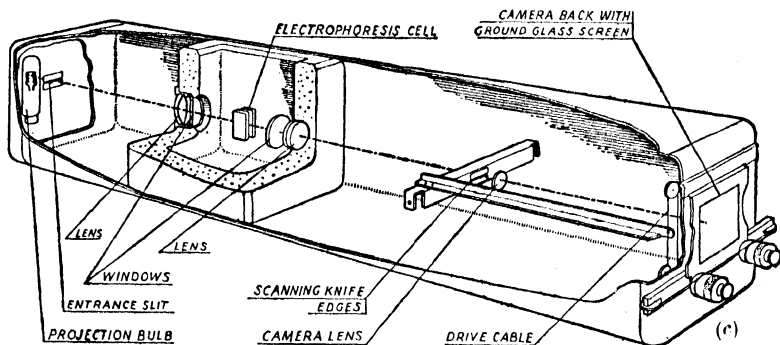
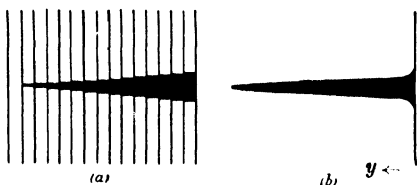
The lens C forms at S' , in the plane of the horizontal straight edge diaphragm D, an image of the narrow horizontal slit S which is brightly illuminated by monochromatic light. The light also passes through the limb U of a cell, which is assumed to contain a medium of uniform refractive index, and consequently does not cause any appreciable deviation of the light. The camera lens L, close behind D, focuses an image U' of the cell U on the camera screen. If D is slowly raised from below S' , the image at U' is not affected until D begins to intercept the light forming the image S' , since all the light from U passes through S' . The intensity of



IV 3.—Diagrammatic representation of the schlieren principle.

light at U' gradually fades until it is zero when D has been raised far enough to intercept completely the light at S' . Suppose, however, that there is a variation of refractive index with height in the cell (although gravity will normally ensure that the refractive index is uniform throughout a thin horizontal layer at any height) so that the light passing through the cell at height H_1 is deflected downwards, producing a fainter image of S at S_1 . If D is slowly raised from below S_1 it will intercept this pencil of light before reaching S' , producing a dark band H'_1 across the image U' in a position conjugate to H_1 . If there are several separate boundaries in the cell each will cause a dark band to appear across U' in the respective conjugate position (provided that D has moved sufficiently far upwards). The larger the gradient of refractive index (dn/dx) at H_1 , the lower is S_1 . In practice the refractive index gradient near H_1 varies continuously with the height

x. If H_1 is the level of maximum refractive index gradient in this region, there will be above and below H_1 two levels, H_2 and H_3 , at which dn/dx is the same, but less than at H_1 . These give rise to an image of S at $S_{2,3}$ between S' and S_1 . Between $S_{2,3}$ and S_1 there will be an infinite number of other images due to the variation of dn/dx at other levels between H_2 , H_3 . As D is raised above S_1 the dark band H_1' will consequently broaden until it covers the region between H_2' and H_3' when D just covers $S_{2,3}$. A series of photographs taken at successive



IV 4.—(a) Schlieren photographs taken with the diaphragm in different vertical positions, (b) Schlieren scanning photograph, (c) Electrophoresis apparatus incorporating the scanning method (Perkin-Elmer Corp.).

vertical positions of D appears as in Fig. 4(a). In the ingenious scanning device of Longworth¹⁷ the vertical movement of D is synchronised with the horizontal motion of a photographic plate past a narrow vertical slit in the plane of U' , giving an automatically recorded plot of dn/dx against x . A pattern obtained by this method is shown in Fig. 4(b). The relative positions of the optical components in this type of system are indicated in Fig. 4(c), which shows the compact apparatus of Moore and White^{17a} which is constructed by the Perkin-Elmer Corporation.

¹⁷ Longworth, *J. Amer. Chem. Soc.*, **61**, 529, 1939.

^{17a} Moore and White, *Rev. Sci. Instr.*, **19**, 700, 1948.

Another modification of the schlieren method, originally devised by Philpot¹⁸ for use with the ultracentrifuge, was soon applied to electrophoretic boundaries. By incorporating a cylindrical lens in the camera (thereby altering the focusing only in a horizontal plane) and substituting a diagonal diaphragm for the horizontal diaphragm D, he obtained curves essentially the same as those given by the scanning method. Later, Svensson^{19, 20} replaced the diagonal diaphragm by a narrow diagonal slit, ob-



IV 5.—Svensson type curve of human serum.

taining his curves as a thin bright line on a dark background (when viewed on the screen) as shown in Fig. 5. Many minor modifications, notably use of almost parallel light through the cell, have been made to increase the precision of the above methods, all of which are in general

use.²¹ Sometimes the cylindrical lens method is used to follow the progress of electrophoresis until a suitable pattern is obtained for recording by scanning, as the scanning method does not allow continuous visual observation of the experiment. Although the scale method of Lamm²² has been used in electrophoretic work (e.g. by Kekwick²³) to give accurate results it also suffers from the disadvantage of not allowing continuous observation and is, moreover, rather tedious.

A drawing of a complete electrophoresis apparatus, not quite to scale is shown in Fig. 6. Based on various assumptions (see below) that may be expected to hold approximately, is the conclusion that the area beneath a peak is a quantitative measure of the component responsible for that peak. If the light passing through the level H_1 in the cell (Fig. 3) is deviated through a small angle θ , $\theta \propto dn/dx$ and the vertical displacement of S_1 from S' is Δ , $\Delta \propto \theta$. Hence $\Delta = k \cdot dn/dx$, where k is a constant, depending on the dimensions of the cell and optical system. In the scanning

¹⁸ Philpot, *Nature*, **141**, 283, 1938.

¹⁹ Svensson, *Kolloid Z.*, **87**, 181, 1939.

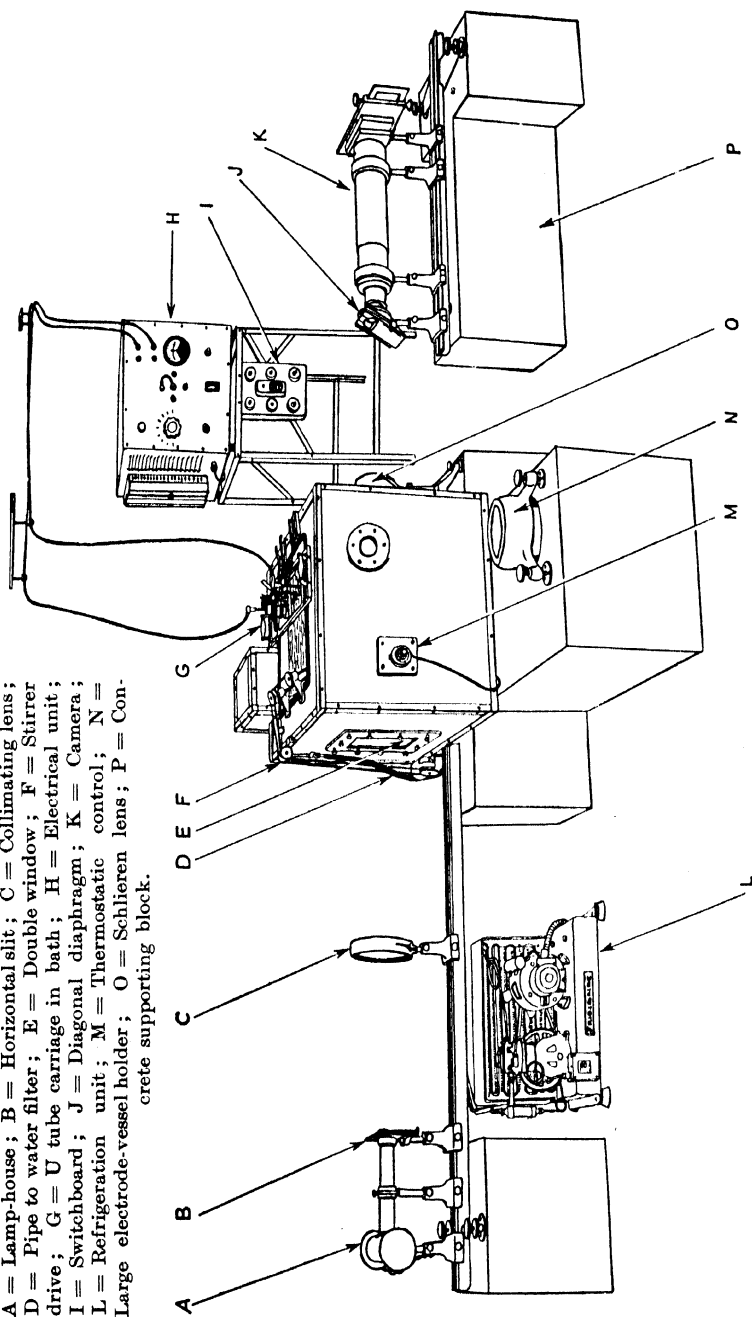
²⁰ Svensson, *ibid.*, **90**, 141, 1940.

²¹ Svensson, *Arkiv. Kemi. Min. Geol.*, **22A**, No. 10, 1946.

²² Lamm, *Nova Acta Reg. Soc. Sci. Upsal.*, IV, 10, No. 6, 1937.

²³ Kekwick, *Trans. Faraday Soc.*, **36**, 47, 1940.

A = Lamp-house; B = Horizontal slit; C = Collimating lens;
D = Pipe to water filter; E = Double window; F = Stirrer
drive; G = U tube carriage in bath; H = Electrical unit;
I = Switchboard; J = Diagonal diaphragm; K = Camera;
L = Refrigeration unit; M = Thermostatic control; N =
Large electrode-vessel holder; O = Schlieren lens; P = Con-
crete supporting block.



IV 6.—General view of a Tiselius apparatus.

method, owing to the synchronised movements, the y values (Fig. 4) are proportional to the corresponding Δ values. Incorporating all constants into one constant K , $y = K \cdot dn/dx$, or, on integration $\int_{x_1}^{x_2} y \cdot dx = K(n_2 - n_1)$. If $(n_2 - n_1)$ is proportional to the concentration of protein, we obtain the result previously stated, which can also be deduced for the cylindrical lens and scale methods.

In future the schlieren methods may be supplemented or even superseded by interference methods.^{24, 25, 25a} Thus Svensson^{25a} obtains his results by replacing the horizontal slit of the schlieren system by a vertical one, and removing the inclined slit, thereby converting the arrangement into a modified Rayleigh interferometer.

3. Errors, Anomalies, etc. Factors which may affect the accuracy of electrophoretic patterns are: (a) defects in the lenses, cell windows, or water-bath windows; (b) errors in focusing; (c) defects in the edges of the slits or diaphragms or incorrect slit-widths; and (d) adventitious refractive index gradients in the water-bath, in the air, or due to moisture condensed on the bath windows. (This condensation can be avoided almost entirely by use of double windows with a drying agent in between and a current of dry air passing over the outer surface.) Most of these points are discussed in detail by Svensson²¹ and by Longworth,²⁶ together with assumptions underlying the optical systems, and other sources of error. Of the latter the chief are due to convections and to conductivity differences. Longworth and MacInnes¹⁵ have calculated the temperature changes which may occur in the cell when current is passing, showing that, for a given rate of migration, more heat is generated in buffers of higher ionic strengths. Since at low ionic strengths boundary anomalies are more pronounced (see below), a compromise is necessary. The maximum current which can be used without producing visible convection is generally about 10-20 mA. for phosphate buffer of ionic strength 0.2 in the ordinary type of cell.

²⁴ Labhart and Staub, *Helv. Chim. Acta*, **30**, 1954, 1947.

²⁵ Lotmar, *ibid.*, **32**, 1847, 1949.

^{25a} Svensson, *Acta Chem. Scand.*, **4**, 399, 1329, 1950.

²⁶ Longworth, *Ind. and Eng. Chem. Anal. Ed.*, **18**, 219, 1946.

One aspect of boundary anomalies has already been mentioned, the unequal rates of migration in ascending and descending limbs. Tiselius²⁷ observed a stationary boundary, formed at the site of the original boundary in the ascending limb during the electrophoresis of horse serum. This, given the name of the δ boundary, was first believed to be due to a slow-moving component of the serum, until Tiselius and Kabat²⁸ concluded that it was an anomaly. The ascending boundaries in electrophoresis experiments have been found to be sharper than the descending. Longsworth and MacInnes,²⁹ discussing this, pointed out that, owing to the Donnan effect,³⁰ there exists a difference in buffer concentration between the protein solution and its supernatant after dialysis. This is accompanied by a difference in their regulating functions, as defined by Kohlrausch.³¹ When migration occurs, a solution of adjusted composition remains, in the ascending limb, between the site of the initial boundary and the moving boundary. The difference in the compositions of the adjusted and original solutions is responsible for the δ boundary. Moreover, it is anticipated that the conductivity of the adjusted solution will be less than that of the supernatant buffer. The ascending boundary moves into a region of higher conductivity (lower potential gradient), with the result that the more slowly-moving protein molecules tend to be overtaken by those behind, producing sharpening and some asymmetry of this boundary. Conversely, in the descending limb, there is a stationary ϵ boundary, and the descending boundary tends to become more diffuse, for reasons similar to those advanced to explain the effects in the other limb. The ϵ boundary, which was first observed by Longsworth and MacInnes, is smaller than the δ boundary, as it does not involve a gradient of protein concentration. The variations of concentration and conductivity throughout the cell, as visualised by Longsworth and MacInnes, are shown in Fig. 7. Their expectations have been confirmed by their own conductivity measurements on samples of solution extracted from

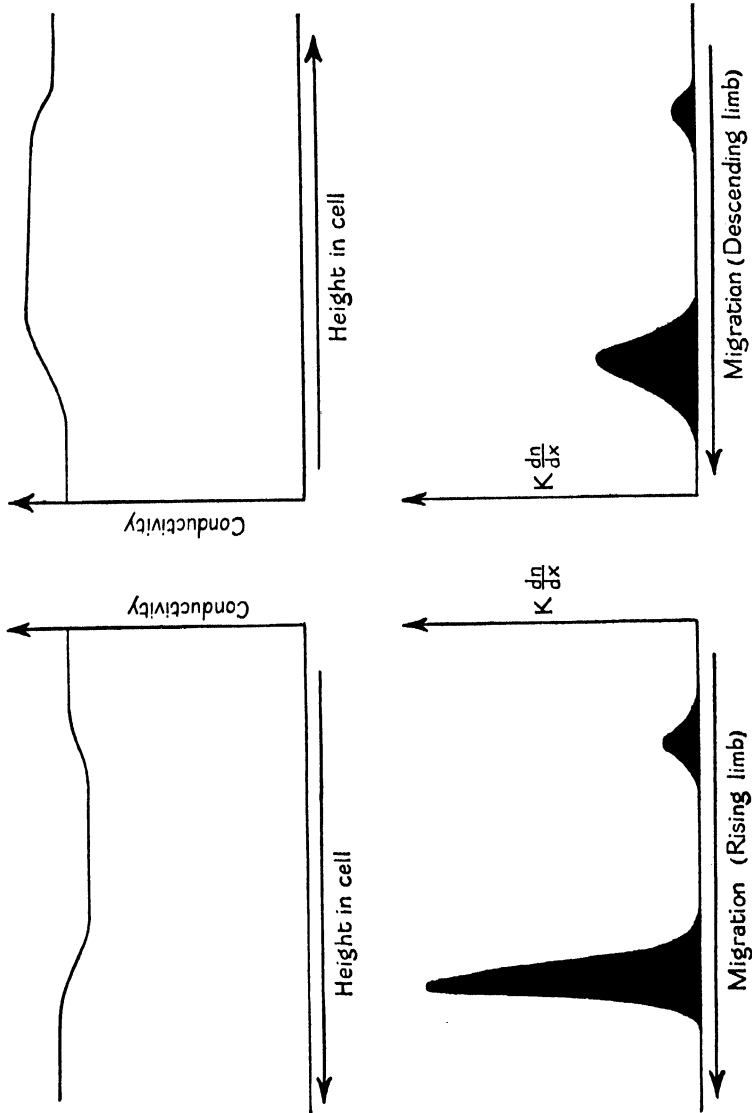
²⁷ Tiselius, *Biochem. J.*, **31**, 1464, 1937.

²⁸ Tiselius and Kabat, *J. Exp. Med.*, **69**, 119, 1939.

²⁹ Longsworth and MacInnes, *J. Amer. Chem. Soc.*, **62**, 705, 1940.

³⁰ Bolam, *The Donnan Equilibria*, Bell, London, 1932.

³¹ Kohlrausch, *Wied. Ann.*, **62**, 209, 1897.



IV 7.—Variations of conductivity and refractive index gradient in the cell at a particular time during an electrophoresis run.

different regions of the U-tube after electrophoresis, and, more recently, by the elegant experiments of Lagercrantz,³² who actually measured the conductivities in the U-tube itself. (Cf. Svensson^{32a}.)

An adequate theory of the moving boundary, taking into account diffusion and other secondary effects, would be extremely complicated mathematically. Consequently most theories propounded have, as a first approximation, neglected these effects. The theory was first developed by Kohlrausch,³¹ and then worked out by Henry and Brittain³³ and by Hacker^{34, 35} for colloid systems containing three ion species. A more comprehensive theory applying first to strong electrolytes was published by Dole,³⁶ together with related experimental work by Longworth.³⁷ Longworth later carried out work on proteins the results of which were considered from the point of view of Dole's theory.³⁸ Svensson²¹ has published a theory, applied particularly to colloids, in which, as well as neglecting secondary effects (see above), he also assumes that the ratio $\left(\frac{u_1}{u_2}\right)$ of the mobilities on either side of a moving boundary is constant for all ions which are present on both sides of that boundary. One important result from this theory is the deduction that, to obtain a correct value of the mobility of an ion not only must it be absent from one side of the boundary, but also the conductivity value used in the calculation must be that prevailing on the side of the boundary on which that ion is present. Svensson's theory predicts the existence of false boundaries, not only the stationary δ and ϵ ones, but also false moving boundaries. He discusses the reasons why few, if any, of the latter have been encountered experimentally. An expression derived for the ratio of the conductivities below and above a boundary respectively is

$$\frac{u_2}{u_1} \left[1 - \frac{C}{B} \right], \text{ where } B = \sum \frac{c_i u_i}{\bar{U}}.$$

³² Lagercrantz, *Arkiv. Kemi Min. G  ol.*, **19A**, No. 7, 1944.

^{32a} Svensson, *J. Amer. Chem. Soc.*, **72**, 1974, 1950.

³³ Henry and Brittain, *Trans. Faraday Soc.*, **29**, 798, 1933.

³⁴ Hacker, *Kolloid Z.*, **62**, 37, 1933. ³⁵ Hacker, *Kolloid Beih.*, **41**, 147, 1935.

³⁶ Dole, *J. Amer. Chem. Soc.*, **67**, 1119, 1945.

³⁷ Longworth, *ibid.*, **67**, 1109, 1945.

³⁸ Longworth, *J. Phys. Colloid Chem.*, **51**, 171, 1947.

The notation used here is as follows :—

u_i = mobility of ion species i above the boundary.

$\bar{U}$ = mobility of boundary $\times \frac{u_1}{u_2}$.

$\frac{u_1}{u_2}$ = ratio of mobilities above and below the boundary for any ion species (assumed constant for all ion species except that which disappears across the boundary, the leading ion).

c_i = ionic concentration of species i above the boundary, expressed in terms of electrochemical equivalents.

C = concentration of the leading ion, in similar units.

All the above are taken with the appropriate positive or negative sign.

To reduce the conductivity differences the value of $\frac{C}{B}$ must be as small as possible. For colloids C is usually very much lower than for a similar weight concentration of a simple inorganic ion, so that colloids are particularly suitable for electrophoresis ; but the lower limit of concentration that can be used is determined by the sensitivity of the optical system and other factors. Generally a protein concentration of about 1 to 2 per cent. is used for analytical work, but lower concentrations for mobility determinations. A large value of B implies a high electrolyte concentration in accordance with the experimental findings of Hardy,⁸ Tiselius,¹⁰ Davis and Cohn,³⁹ Perlmann and Kaufman⁴⁰ and others on the reduction of anomalies ; but B is also affected by the buffer ion mobilities which should be as low as possible, particularly those of ions of the same sign as the colloid. Longworth, Shedlovsky and MacInnes⁴¹ had introduced the use of veronal buffers because of the favourable effects of such conditions.

Another result of Svensson's theory shows that every ion present in the region of the boundary must undergo a concentration change at the boundary, in conflict with the usual practice of attributing

³⁹ Davis and Cohn, *J. Amer. Chem. Soc.*, **61**, 2092, 1939.

⁴⁰ Perlmann and Kaufman, *ibid.*, **67**, 638, 1945.

⁴¹ Longworth, Shedlovsky and MacInnes, *J. Exp. Med.*, **70**, 399, 1939.

the refractive index change solely to the leading ion. The errors thus introduced due to changes of salt concentration may be quite small, whereas other colloid ions may have an appreciable effect; indeed, according to the work of Hoch⁴² the effect may be so great with two colloids of very nearly identical mobilities as to reverse their apparent relative concentrations.

Of secondary effects which have so far been neglected in this discussion one should be mentioned here, namely the necessity of avoiding the use of buffer ions which may have a specific affinity for the protein. This may be difficult since it has been shown that even the chloride ion will combine with negatively charged albumin.⁴³ (See also the work of Davis and Cohn³⁹ regarding phosphates, and of Ballou, Boyer and Luck,⁴⁴ regarding fatty acid salts and their effects in electrophoresis.) Similarly, specific interactions between protein components, particularly when oppositely charged, cause deviations from ideal behaviour, as shown in the work of Tiselius and Horsfall,⁴⁵ Jacob,⁴⁶ and Goldwasser and Putnam.^{46a}

Adair and Robinson⁴⁷ showed that, for the ordinary constituents of serum, refractive increment is proportional to concentration, and the specific refractive increments are the same for all these proteins to a fair degree of accuracy; but this is probably not generally true for other proteins. Thus Armstrong, Budka and Morrison⁴⁸ have shown that the association of lipid material with a protein may considerably alter its specific refractive increment, an observation of particular importance when studying pathological sera. (See also Popjak and McCarthy,⁴⁹ Thorn *et al.*,⁵⁰ and Perlmann and Longworth.^{50a})

⁴² Hoch, *Biochem. J.*, **42**, 181, 1948.

⁴³ Scatchard, Batchelder and Brown, *J. Amer. Chem. Soc.*, **68**, 2320, 1946.

⁴⁴ Ballou, Boyer and Luck, *J. Biol. Chem.*, **159**, 111, 1945.

⁴⁵ Tiselius and Horsfall, *J. Exp. Med.*, **69**, 83, 1939.

⁴⁶ Jacob, *Biochem. J.*, **42**, 71, 1949.

^{46a} Goldwasser and Putnam, *J. Phys. Colloid Chem.*, **54**, 79, 1950.

⁴⁷ Adair and Robinson, *Biochem. J.*, **24**, 993, 1930.

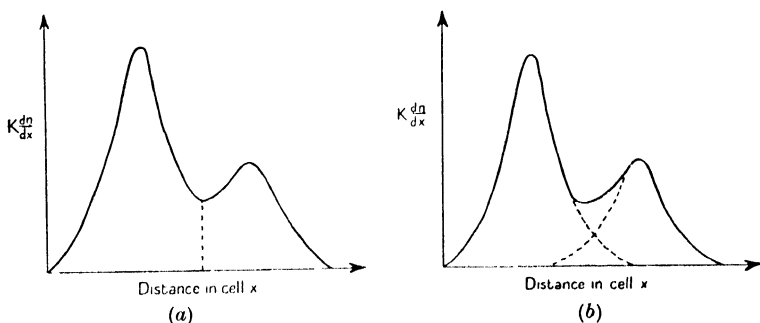
⁴⁸ Armstrong, Budka and Morrison, *J. Amer. Chem. Soc.*, **69**, 416, 1947.

⁴⁹ Popjak and McCarthy, *Biochem. J.*, **40**, 789, 1946.

⁵⁰ Thorn, Armstrong, Davenport, Woodruff and Tyler, *J. Clin. Inv.*, **24**, 802, 1945.

^{50a} Perlmann and Longworth, *J. Amer. Chem. Soc.*, **70**, 2719, 1948.

Estimation of the relative areas of the peaks in a pattern is carried out from traced enlargements, either by the procedure of Tiselius and Kabat,²⁸ who dropped perpendiculars to the base-line from the troughs between the peaks (Fig. 8a), or by that of Pedersen,⁵¹ who reflected the curve of the end peak into the median line, subtracted the ordinates, and proceeded in this way till each peak had been dealt with (Fig. 8b). The first method is the more empirical, but the second cannot be applied very strictly in cases of boundary asymmetry or poorly resolved peaks, so that both methods are employed, and, with reasonably well resolved



IV 8.—Methods introduced by (a) Tiselius and Kabat, and (b) Pedersen for assigning proportions of the total area to different components.

curves, give fairly concordant results. If the δ boundary is not sufficiently well separated from the slowest component, too great an area may be assigned to that component in the anode limb curves.⁵²

The large variation in the mobility of a protein measured at different values of pH , as indicated in Fig. 9, is to be expected since proteins are amphoteric electrolytes, the charge on the molecule depending on the ionisation equilibria of the various acidic and basic groups. The pH of zero mobility, the isoelectric point as defined by this means, is dependent to a comparatively small extent on the ionic strength of the solution used.^{53, 53a} The close relation between the mobility and titration curves of proteins

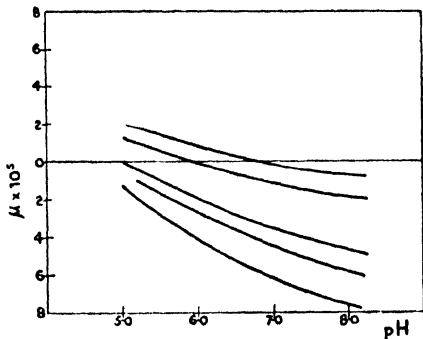
⁵¹ Pedersen, in *The Ultracentrifuge*, by Svedberg and Pedersen, Oxford, 1940.

⁵² Kekwick, *Biochem. J.*, **34**, 1248, 1940.

⁵³ Smith, *J. Biol. Chem.*, **113**, 473, 1936.

^{53a} Scatchard and Black, *J. Phys. Colloid Chem.*, **53**, 88, 1949.

has been shown by Abramson and others.^{2, 54} It should be emphasised here that the fact that a protein preparation shows only one peak on electrophoresis is by no means proof of homogeneity. Measurements must be made over as wide a range of pH as possible, in case the material happens to consist of a mixture of components which possess closely similar mobilities under some conditions.¹⁶ When a single peak is observed over a wide range the rate of spreading may be greater than is accounted for by diffusion, due to the presence of molecular species with mobilities distributed over a narrow range, in



which case reversal of the current causes considerable sharpening of the peaks.⁵⁵

IV 9.—The mobilities of different components in four times diluted horse serum at constant ionic strength 0.1 (Tiselius, *Biochem J.*, 1937.)

Cases in which this is particularly liable to occur are those of the serum globulins in which antibody activity is to be found, such as the human γ globulin studied by Alberty, Anderson and Williams,⁵⁶ and by Alberty.^{56a} Further advances in the study of boundary spreading have been made by Hoch^{56b} and by Brown and Cann.^{56c}

4. Preparative Electrophoresis. When it is desired to find which component or components possess(es) some specific activity it would often be advantageous to carry out a complete separation. In the conventional type of electrophoresis apparatus this is impossible, as such a separation would immediately produce uncontrollable convections due to the formation of unstable density gradients. Attempts to overcome this have been made using:

⁵⁴ Moyer and Abels, *J. Biol. Chem.*, **121**, 331, 1937.

⁵⁵ Sharp, Hebb, Taylor and Beard, *ibid.*, **142**, 217, 1942.

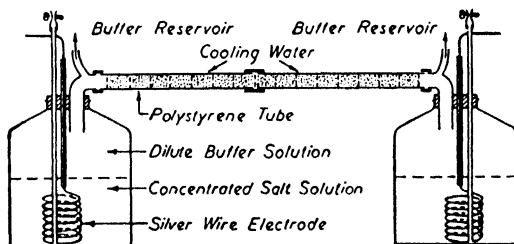
⁵⁶ Alberty, Anderson and Williams, *J. Phys. Colloid Chem.*, **52**, 217, 1948.

^{56a} Alberty, *J. Amer. Chem. Soc.*, **70**, 1675, 1948.

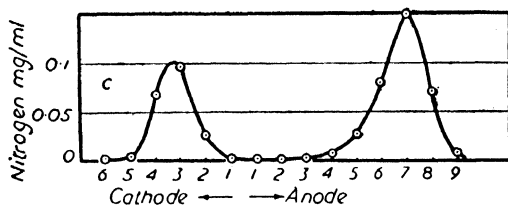
^{56b} Hoch, *Biochem. J.*, **46**, 199, 1950.

^{56c} Brown and Cann, *J. Phys. Colloid Chem.*, **54**, 364, 1950.

(a) diaphragm cells ;^{57, 58} (b) slabs of silica gel ;⁵⁹ (c) a tube with sintered glass packing ;⁶⁰ and (d) a tube with asbestos fibre packing.⁶¹ None of these methods has been unequivocally successful, but useful separations have been achieved, particularly of lower molecular weight substances such as amino acids and peptides.



IV 10.—Apparatus for the electrophoretic separation of amino-acids, peptides, and proteins. (Butler and Stephen, *Research*, 1948.)



IV 11.—Electrophoretic separation of haemoglobin and egg albumin at pH 5.8. (Butler and Stephen, *Research*, 1948.)

The Tiselius¹⁴ apparatus can be used for preparative work, to obtain pure samples, although separation cannot be quantitative. Examples of the use of the ordinary 11 ml. cell are given by Kekwick and Record⁶² and of a larger type cell with more sections by Blix, Tiselius and Svensson,⁶³ and by Thompson and Melnick.⁶⁴

Fig. 10 shows the apparatus of Butler and Stephen,⁶¹ and Fig. 11 an indication of results obtained with it.

Experiments on the electrophoresis of proteins on filter paper have been successfully carried out, but, as with the other procedures listed above, one of the main problems is that of finding a reliable physical method for locating components.^{61a, 61b}

⁵⁷ Gutfreund, *Biochem. J.*, **37**, 186, 1943.

⁵⁸ Hahn and Tiselius, *Biochem. Z.*, **314**, 336, 1943.

⁵⁹ Consden, Gordon and Martin, *Biochem. J.*, **40**, 33, 1946.

⁶⁰ Coolidge, *J. Biol. Chem.*, **127**, 551, 1939.

⁶¹ Butler and Stephen, *Research*, **1**, 525, 1948.

^{61a} Cremer and Tiselius, *Biochem. Z.*, **320**, 273, 1950.

^{61b} Durrum, *J. Amer. Chem. Soc.*, **72**, 2943, 1950.

⁶² Kekwick and Record, *Brit. J. Exp. Path.*, **22**, 29, 1941.

⁶³ Blix, Tiselius and Svensson *J. Biol. Chem.*, **137**, 485, 1941.

⁶⁴ Thompson and Melnick, *Endocrinology*, **28**, 723, 1941.

Several authors ^{21, 65} have produced adaptations of the Tiselius apparatus based on the principle of a semi-continuous operation in which fractions are slowly removed through capillary tubes, fresh material being introduced to the bottom of the cell by similar means.

The electrophoresis-convection technique of Kirkwood ^{66, 67} and the thin flowing layers used by Philpot ⁶⁸ were promising new developments, but the experimental difficulties had prevented exploitation of either until recently. ^{68a}

Svensson ⁶⁹ has recently published a useful survey of preparative electrophoresis methods.

5. Results. The developments in the technique of electrophoresis have resulted in so many applications that several hundred original papers have been published of results obtained. Reviews which may be consulted for the relevant references are given by Abramson, Moyer and Gorin,⁵ Stern and Reiner on "Electrophoresis in Medicine",⁷⁰ Luetscher on "Biological and Medical Applications of Electrophoresis"⁷¹, and Hoch and Marrack.^{71a} The remainder of the chapter will be devoted to a few selected examples illustrating the results of investigations. The principles of the previous sections must be borne in mind when considering such points as homogeneity.

A. Serum and plasma proteins. One of the chief advantages of the method of electrophoretic examination of protein systems is that the conditions of separation are very mild compared with those encountered in fractionation by precipitation with salts or organic solvents, which are liable to lead to undesirable changes such as denaturation, unless special precautions are observed. For this reason many investigations of the blood serum or plasma proteins have been carried out by electrophoresis. Tiselius ²⁷ found (using the simple schlieren optical system) that normal

⁶⁵ MacLagan and Bunn, *Biochem. J.*, **41**, 580, 1947.

⁶⁶ Kirkwood, *J. Chem. Phys.*, **9**, 878, 1941.

⁶⁷ Nielsen and Kirkwood, *J. Amer. Chem. Soc.*, **68**, 181, 1946.

⁶⁸ Philpot, *Trans. Faraday Soc.*, **36**, 38, 1940.

^{68a} Cann, Kirkwood, Brown and Plescia, *J. Amer. Chem. Soc.*, **71**, 1603, 1949.

⁶⁹ Svensson in *Advances in Protein Chemistry*, Vol. 4, Academic Press, New York, 1948.

⁷⁰ Stern and Reiner, *Yale J. Biol. Med.*, **19**, 67, 1946.

⁷¹ Luetscher, *Physiol. Rev.*, **27**, 621, 1947.

^{71a} Hoch and Marrack, *J. Clin. Path.*, **2**, 161, 1949.

horse serum showed four boundaries (besides the δ boundary) at several pH values. Typical patterns of the serum proteins from normal individuals of many species are very similar in general outline, containing an albumin peak and three main globulin peaks α , β , and γ . At most pH values investigated the mobilities decrease from that of albumin in the order given. A normal human plasma pattern (obtained by the scanning technique) is shown in Fig. 12. In some cases the simple nomenclature of Tiselius is inadequate, as in cat sera, where a larger number of peaks is encountered,⁷² so that a more satisfactory way of defining the components is by mobility measurements under controlled conditions with anomalies sufficiently depressed. Often there arises a disturbance in the descending limb at the β -globulin boundary, evident in Fig. 12. The origin of this has been discussed by Moore and Lynn.⁷³ Since different ionic strengths, buffer salts, pH values, etc., affect the results, all experiments for comparative purposes should be carried out under conditions as nearly as possible identical. In America the veronal buffers of Longsworth (e.g. ionic strength 0.1, pH 7.6) are widely used for the analysis of serum and its fractions,^{40, 73} whilst other workers use phosphate buffers or phosphate-chloride mixtures.^{21, 52, 74} Study of human sera and plasmas by many workers (e.g. ^{40, 41, 52, 73-75}) shows that, although the composition is in general reasonably close to an average figure, fairly wide deviations occur in cases of subjects who are apparently quite normal. Table I shows fairly close agreement between the average values obtained by different authors.

Electrophoresis is very useful for examining fractions obtained from serum or plasma by precipitation or other means. Components, such as prothrombin, the presence of which is inferred from other evidence, but which are normally present in amounts too insignificant to appear in the electrophoresis pattern, may be thus concentrated and their purification followed. Comparison of electrophoretic data with salt fractionation methods (such as that

⁷² Deutsch and Goodloe, *J. Biol. Chem.*, **161**, 1, 1945.

⁷³ Moore and Lynn, *ibid.*, **141**, 819, 1941.

⁷⁴ Olhagen, *Acta Med. Scand. Suppl.*, No. 162, 1945.

⁷⁵ Dole, *J. Clin. Inv.*, **23**, 708, 1944.

TABLE I. RELATIVE AMOUNTS OF SOME COMPONENTS OF NORMAL HUMAN SERA AND PLASMAS

Observer(s)	Buffer	Material	Samples	A	α	β	γ
Kekwick . . .	Phosphate	Serum	6	62.5	5.0	11.5	21.0
Olhagen . . .	"	"	10	57.8	7.0	14.5	20.7
Moore and Lynn .	Veronal	Plasma	12	65.1	8.2	14.3	12.4
Taylor and Keys .	Phosphate	Serum	8	65.5	6.8	13.8	13.9

of Howe ⁷⁶) shows that, in neutral solution, the ease of precipitation of the components of serum follows the reverse order of their mobilities (at *pH* values near neutrality). Thus γ globulin tends to precipitate at lower salt concentrations, whilst albumin is brought down only by higher; but in all cases there is much overlapping among fractions and pure components are not obtained by simple fractionation procedures.^{77-82a} It has been shown by the very extensive large scale work of Cohn and his associates,^{83, 84} working at low temperatures (-5°C. to 0°C.) and at carefully controlled values of *pH* and ionic strength, that human plasma can be fractionated without appreciable denaturation, by use of ethanol or methanol. This has enabled the plasma proteins to be prepared in a higher state of purity than previously, giving considerable impetus to the investigation of their physico-chemical properties, and also resulting in the widespread use of plasma fractions for clinical use in cases where this may be more economical than, or preferable to, the use of whole plasma.⁸⁵ Kekwick has followed the course of the low temperature ether fractionation of plasma.⁸⁶

The striking changes that occur in the blood proteins during many diseases were apparent through the comparatively crude

⁷⁶ Howe, *J. Biol. Chem.*, **49**, 93, 1921.

⁷⁷ Svensson, *ibid.*, **139**, 805, 1941.

⁷⁸ Cohn, McMeekin, Oncley, Newell and Hughes, *J. Amer. Chem. Soc.*, **62**, 3386, 1940.

⁷⁹ Cohn, Luetscher, Oncley, Armstrong and Davis, *ibid.*, **62**, 3396, 1940.

⁸⁰ Taylor and Keys, *J. Biol. Chem.*, **148**, 379, 1943.

⁸¹ Majoor, *ibid.*, **169**, 583, 1947.

⁸² Milne, *ibid.*, **169**, 595, 1947.

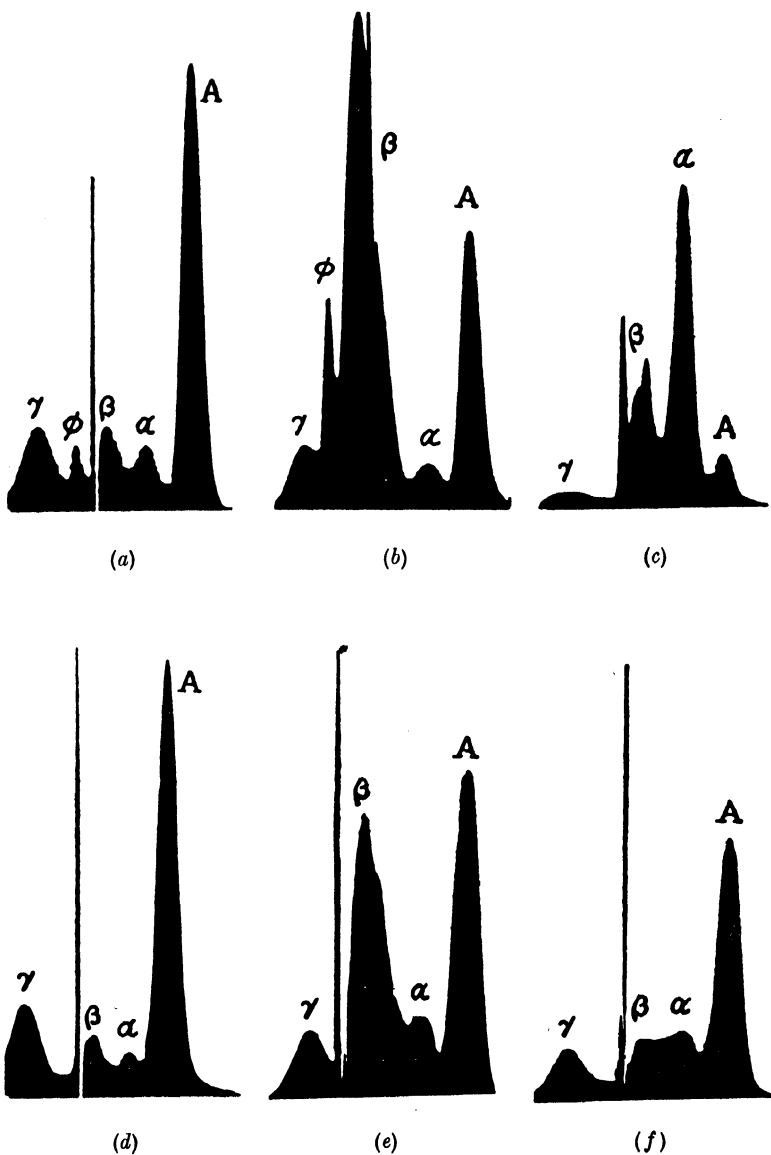
^{82a} Derrien, *Svensk Kem. Tid.*, **59**, 139, 1947.

⁸³ Cohn, Oncley, Strong, Hughes and Armstrong, *J. Clin. Inv.*, **23**, 417, 1944.

⁸⁴ Cohn, Strong, Hughes, Mulford, Ashworth, Melin and Taylor, *J. Amer. Chem. Soc.*, **68**, 459, 1946.

⁸⁵ Edsall, in *Advances in Protein Chemistry*, Vol. 3, Academic Press, New York, 1947.

⁸⁶ Kekwick, Mackay and Record, *Nature*, **157**, 629, 1946.

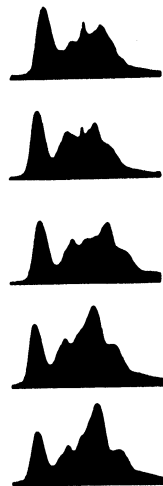


IV 12.—Normal and pathological human sera and plasmas. (Longsworth, Shedlovsky and MacInnes, *J. Exp. Med.*, 1939.)

(a) Normal plasma ; (b) Multiple myeloma plasma ; (c) Nephrosis serum.
 (d) Aplastic anemia serum ; (e) Obstructive jaundice plasma ; (f) Same as (e)
 after other extraction.

salt precipitation methods, which often gave evidence of a significant decrease in the albumin to globulin ratio in such cases. The more accurate picture afforded by electrophoresis has resulted in the study of the patterns given by the serum or plasma in many pathological conditions, some of which are illustrated in Fig. 12.⁴¹ Among the conditions thus studied are scarlet and rheumatic fevers,⁸⁷ nephritis,^{88, 89} and tuberculosis.^{90, 91} The effect of damage to the body tissues, caused by burning and other forms of injury, has formed the subject for work by Chanutin and Gjessing.^{92, 93} Sometimes it is possible to show not only quantitative differences in the proteins, but also qualitative differences, such as alterations in mobilities or association with non-protein substances, such as bilirubin,^{94, 95} lipid material^{48, 96, 97} or carbohydrate.⁹¹ The apparent increase in certain globulin fractions in tuberculosis⁹¹ and nephritis,^{88, 89} has been shown to be due largely to the higher specific refractive increments of the proteins when associated with polysaccharides and lipoids respectively.

Kekwick and Record⁶² showed that, during the immunisation of horses against diphtheria, two types of antibody are produced, included in the β and γ globulin fractions respectively. The progressive rise in these globulins is shown in Fig. 13. That the immune globulins differ from the normal serum globulins is clearly proved by the fact that, in some cases, the



IV 13.—Patterns of horse serum during immunisation against diphtheria toxoid. The first pattern represents the serum prior to the course of immunisation. The others, starting from the second picture, were from sera containing respectively 19.5, 64.5, 800, and 988 units/ml. of antitoxin.

⁸⁷ Dole, Watson, Rothbard, Braun and Winfield, *J. Clin. Inv.*, **24**, 648, 1945.

⁸⁸ Luetscher, *ibid.*, **19**, 313, 1940.

⁸⁹ Luetscher, *ibid.*, **20**, 99, 1941.

⁹⁰ Seibert and Nelson, *J. Biol. Chem.*, **143**, 29, 1942.

⁹¹ Seibert, Seibert, Atno and Campbell, *J. Clin. Inv.*, **26**, 90, 1947.

⁹² Chanutin and Gjessing, *J. Biol. Chem.*, **165**, 421, 1946.

⁹³ Gjessing, Ludewig and Chanutin, *ibid.*, **170**, 551, 1947.

⁹⁴ Gray and Kekwick, *Nature*, **161**, 274, 1948.

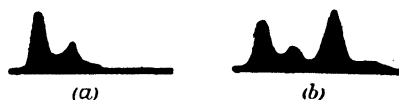
⁹⁵ Martin, *Biochem. J.*, **42**, No. 1, xv, 1948.

⁹⁶ Zeldis, Alling, McCoord and Kulka, *J. Exp. Med.*, **82**, 157, 1945.

⁹⁷ Zeldis, Alling, McCoord and Kulka, *ibid.*, **82**, 411, 1945.

antibody appears as a separate component⁹⁸ and not all of that globulin which contains a particular antibody is precipitated by the corresponding antigen.²⁸ The passive immunisation of young animals which can be brought about by the ingestion of colostrum is correlated with the increase of globulin in the serum, presumably due to direct absorption of colostrum from the intestine^{99, 100} (see Fig. 14).

B. *Other proteins.* The work of Jacob^{46, 101} on the muscle proteins of rabbits gives an indication of some difficulties which may be encountered in a system with a large number of com-



IV 14.—Electrophoretic patterns of lamb serum.
(a) at birth, and (b) after ingestion of colostrum.

ponents prone to be denatured in certain buffers, and to interact among themselves.

The electrophoretic study of the proteins of egg white by Longworth, Cannan and MacInnes¹⁶ has been mentioned already, as it exemplifies one or two points of technique, the variation in the patterns and mobilities at different *pH* values, the phenomenon of reversible boundary spreading, and the effects of interaction between proteins.

Electrophoresis has assisted the examination of several hormones, among them insulin,¹⁰²⁻¹⁰⁴ and the pituitary hormones,^{105, 106} more particularly as an indication of purity; but since, even under fairly favourable conditions, as much as 5 or 10 per cent. of impurity can escape detection, it is not surprising to find that, in the

⁹⁸ Van der Scheer, Wyckoff and Clarke, *J. Immunol.*, **39**, 65, 1940.

⁹⁹ Jameson, Alvarez-Tostado and Sortor, *Proc. Soc. Exp. Biol. Med.*, **51**, 163, 1942.

¹⁰⁰ Charlwood and Thomson, *Nature*, **161**, 59, 1948.

¹⁰¹ Jacob, *Biochem. J.*, **41**, 83, 1947.

¹⁰² Hall, *J. Biol. Chem.*, **139**, 175, 1941.

¹⁰³ Hall, *ibid.*, **140**, 671, 1941.

¹⁰⁴ Sanger, *Nature*, **160**, 295, 1947.

¹⁰⁵ Li, Lyons and Evans, *J. Amer. Chem. Soc.*, **62**, 2925, 1940.

¹⁰⁶ Chow in *Advances in Protein Chemistry*, Vol. 1, Academic Press, New York, 1944.

case of insulin, careful solubility measurements have proved much more useful than electrophoresis as a criterion of purity.

The study of enzymes began before the modern era of refined optical systems, since enzymes such as the yellow respiratory enzyme could be purified in the Theorell type of apparatus.¹⁰⁷ More recently pepsin,^{108, 109} ribonuclease,¹¹⁰ and many other enzymes have been studied. A difficulty met with in the case of taka-diastrase was the tendency for the enzyme to attack the type of membrane normally used for dialysis.¹¹¹ Since an enzyme can often act in concentrations too low to appear in an electrophoretic pattern, it is possible to follow the action of the enzymes on other proteins,^{112, 113} but the smaller fragments produced are often lost if dialysis is performed, so that other methods (e.g. the ultracentrifuge) may yield more information.

As with many enzymes, so with a number of powerful bacterial toxins, the minimum concentration necessary to give detectable biological effects lies far below the limit of detection by the electrophoresis optical system. Consequently preliminary concentration by other methods must be carried out.^{114, 115} Where this has culminated in the isolation of crystalline diphtheria¹¹⁴ and type A botulinum¹¹⁵ toxins, the product has behaved in the electric field as a fairly homogeneous material. Bacterial toxins, treated with formaldehyde, lose their toxicity, but retain their antigenicity. These modified forms, the toxoids, have been examined electrophoretically by a few observers.¹¹⁶⁻¹¹⁸

In their electrokinetic properties viruses behave as typical proteins. Macfarlane¹¹⁹ observed during the electrophoresis of vaccinia virus the development of peculiar streaming effects, which

¹⁰⁷ Theorell, *Biochem. Z.*, **278**, 263, 1935.

¹⁰⁸ Tiselius, Henschen and Svensson, *Biochem. J.*, **32**, 1814, 1938.

¹⁰⁹ Herriott, Desreux and Northrop, *J. Gen. Physiol.*, **23**, 439, 1940.

¹¹⁰ Rothen, *ibid.*, **24**, 203, 1940.

¹¹¹ McFarlane and Rimington, *Proc. Biochem. Soc.*, **38**, xxxiii, 1944.

¹¹² Petermann, *J. Amer. Chem. Soc.*, **68**, 106, 1946.

¹¹³ Petermann, *J. Biol. Chem.*, **162**, 37, 1946.

¹¹⁴ Pillemer and Hutchinson, *ibid.*, **158**, 299, 1945.

¹¹⁵ Abrams, Kegeles and Hottle, *ibid.*, **164**, 63, 1946.

¹¹⁶ Masucci and de Falco, *Proc. Soc. Exp. Biol. Med.*, **58**, 67, 1945.

¹¹⁷ Pillemer, Toll and Badger, *J. Biol. Chem.*, **170**, 571, 1947.

¹¹⁸ Charlwood, *Biochem. J.*, **42**, 425, 1948.

¹¹⁹ McFarlane, *Trans. Faraday Soc.*, **36**, 257, 1940.

were tentatively attributed to electro-osmosis, until Shedlovsky and Smadel¹²⁰ showed that they were due to convections set up by unfavourable density gradients which could be avoided by alteration of the conditions. Interesting because of its highly asymmetric structure is the tobacco mosaic virus.¹²¹

The examination of yeast extracts has revealed a complicated system, the patterns obtained depending on what solution is used for the extraction.^{122, 123}

Irving and Fontaine¹²⁴ have used electrophoresis to characterise the proteins of the peanut, which were previously separated by salt precipitation into ill-defined fractions.

Since the mobility of a particle is determined by its size, shape and charge distribution, as well as by the composition of the supporting medium, it should be possible to calculate one or other of its characteristics provided all the other relevant data are available. Based on certain assumptions regarding the above properties of the particle, efforts have been made to calculate mobilities.^{33, 125, 126} Even for a simple spherical molecule the calculations are not easy, and few examples are available of applications to actual proteins. Tiselius and Svensson¹²⁷ have treated in this way the ovalbumin molecule, which is nearly spherical, and Creeth¹²⁸ has dealt with the highly asymmetric particles of nucleic acids. (See also reference⁵⁴.)

It is clear from the evidence instanced above that, although a tremendous amount of experimental information has already accumulated on the electrophoretic behaviour of a wide variety of proteins, the significance of much of this work cannot yet be fully appreciated, because the theory of the moving boundary method, although considerably advanced by the work of Dole³⁶,

¹²⁰ Shedlovsky and Smadel, *J. Exp. Med.*, **72**, 511, 1940.

¹²¹ Frampton and Takahashi, *Arch. Biochem.*, **4**, 249, 1944.

¹²² Stern, *J. Biol. Chem.*, **152**, 345, 1944.

¹²³ Stern, Schein and Wallerstein, *ibid.*, **166**, 59, 1946.

¹²⁴ Irving and Fontaine, *Arch. Biochem.*, **7**, 475, 1945.

¹²⁵ Smoluchowski, *Bull. Acad. Sci. Cracovie*, 182, 1903.

¹²⁶ Mueller in *Proteins, Amino Acids and Peptides*, by Cohn and Edsall, Reinhold Publishing Corporation, New York, 1943.

¹²⁷ Tiselius and Svensson, *Trans. Faraday Soc.*, **36**, 16, 1940.

¹²⁸ Creeth and Jordan, *J.C.S.*, 1409, 1949.

Svensson²¹, and Alberty¹²⁹, has so far failed to give an adequate representation of the complicated changes which must occur even in relatively simple systems. The derivation of theoretical mobility values and the reverse problem of obtaining information about molecular dimensions are still in an early stage of development. However, the fair degree of success so far attained leads to the hope that it will be possible to circumvent, at any rate to some extent, the mathematical difficulties, so that future developments in theory may make contributions to electrophoresis as important as those which have followed from the practical developments of recent years.

¹²⁹ Alberty, *J. Amer. Chem. Soc.*, **72**, 2361, 1950.

CHAPTER V

THE ELECTROKINETIC BEHAVIOUR OF IONIC CRYSTALS

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IONIC crystals show electrokinetic effects of a special kind which are specifically determined by the structure and chemical composition of the crystal. Certain of these effects arise through the preferential adsorption on the crystal surface of ions common to or at least compatible with the crystal lattice. Adsorption of these ions is due to the operation of forces responsible for the growth of the crystal.¹ The ions constituting the surface layer of the crystal are in an unsaturated condition as compared with those in the interior, and therefore attract and hold suitable ions of opposite charge. Hence when the crystal is brought into contact with a solution of an electrolyte, the surface becomes positive or negative according to the nature of the ions present in the solution. For instance, small particles of silver iodide migrate to the cathode in silver nitrate solutions of appropriate concentrations, but to the anode in solutions of potassium iodide.² Silver ions are adsorbed in the one case, and iodide ions in the other. Ions other than those common to the silver iodide crystal are adsorbed only if they are capable of fitting into the lattice. Thus colloidal suspensions of silver iodide are stabilised by chloride, bromide, cyanide and thiocyanate ions, but not by nitrate, sulphate, carbonate, phosphate or bichromate ions.³

Information regarding the quantitative aspects of the relation between adsorption and electrokinetic behaviour has been obtained mainly from studies of silver halides⁴ and barium sulphate. In

¹ Fajans and Frankenberger, *Z. physikal. Chem.*, **105**, 255, 1923; Fajans and Erdely-Gruz, *ibid.*, **158**, 97, 1931.

² Lottermoser and May, *Kolloid Z.*, **58**, 176, 1932.

³ Kruyt and van der Willigen, *Z. physikal. Chem.*, **139**, 53, 1928; Kruyt and Cysouw, *ibid.*, **172**, 49, 56, 1935; Basinski, *Kolloid Beihefte*, **36**, 257, 1932.

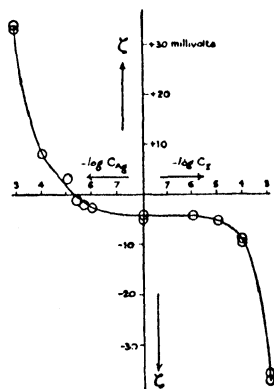
⁴ See review by Kellermann and Lange, *Kolloid Z.*, **81**, 88, 1937.

Fig. 1 are shown the values of the electrokinetic potential calculated by Lange and Crane⁵ from their 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 ($c_{\text{Ag}^+} = c_{\text{I}^-} = \text{ca. } 1.5 \cdot 10^{-8} \text{ N}$); and a concentration of silver ions of approximately $4 \cdot 10^{-6} \text{ N}$ was required to attain the isoelectric point ($\zeta = 0$). Verwey and Kruyt⁶ measured the adsorption of iodide ions by the particles in dialysed sols of silver iodide, and found that up to at least $c = 5 \cdot 10^{-4} \text{ N}$ their data could be expressed by

$$dx = k \cdot d \log c,$$

where x = gram-ions adsorbed by unit mass of silver iodide, c = equilibrium concentration of potassium iodide, and k = constant.* The value of k increased with "ageing" of the sol. By extrapolation it was estimated that there was no excess of silver or iodide ions on the particles 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 Ligane⁷ have measured the desorption of silver and iodide ions from freshly precipitated silver iodide when digested at $90^\circ\text{--}95^\circ$ with dilute solutions of silver nitrate. There was no desorption of either ion when the concentration of silver ions in the solution was $0.89 \cdot 10^{-6} \text{ N}$, while desorption of silver ions occurred at higher concentrations and of iodide ions at lower. In another series of experiments silver nitrate was titrated with potassium iodide by



V 1.— ζ -potential of silver iodide diaphragms in potassium iodide and silver nitrate solutions. (Lange and Crane.)

⁵ Lange and Crane, *Z. physikal. Chem.*, **141**, 225, 1929.

⁶ Verwey and Kruyt, *ibid.*, **167A**, 149, 1933. See also Kruyt and Klompé, *Kolloid-Beihfte*, **54**, 484, 1943; Kruyt and Troelska, *ibid.*, **54**, 262, 1943.

* The expression also holds for the adsorption of lead ions by insoluble lead salts (see Kellermann and Lange, *loc. cit.*).

⁷ Kolthoff and Ligane, *J. Amer. Chem. Soc.*, **58**, 1531, 1926.

the electrometric method. The amounts of silver and iodide ions adsorbed by the precipitate were derived by comparing the experimental curve with the theoretical curve obtained on the assumption that there was no adsorption of either ion. Adsorption of both silver and iodide ions, over considerable concentration intervals, varied according to the equation $dx = k \cdot d \log c$, the value of k being greater for iodide than for silver. The experimental and theoretical titration curves intersect at $1.41 \cdot 10^{-6}$ N silver ion and this, therefore, is the concentration at which neither ion was adsorbed. Taken together, the foregoing results strongly suggest that the electrokinetic behaviour of silver iodide crystals in contact with solutions of silver nitrate or potassium iodide is determined mainly by the excess of silver or iodide ions on the crystals under the given conditions. At a silver ion concentration of about 10^{-6} N neither ion is present in excess and the charge on the crystal, and therefore the value of ζ , is zero. The small negative charge with saturated silver iodide solution is due to preferential adsorption of iodide ions, or to the preferential release of silver ions from the surface layer of the lattice (see below).^{*} Thus the tendency of the silver ions to pass from the crystal to the solution is so much greater than that of the iodide ions, that a 10,000-fold excess of silver over iodide ion must be provided in the solution to ensure that there are equal numbers of these ions on the crystal.

Much further work has been carried out on this subject in recent years by the Kruyt school. A method of determining the electrokinetic potential in AgI sols has been described.^{7a} This is the diffuse part of the double layer potential (see Fig. 10) and is determined by first measuring the potential of a AgI electrode in a concentrated sol of fairly high I concentration, and then that produced in the presence of an indifferent electrolyte. De Bruyn followed up this method^{7b} and found that the effects observed were dependent on the sol concentration.

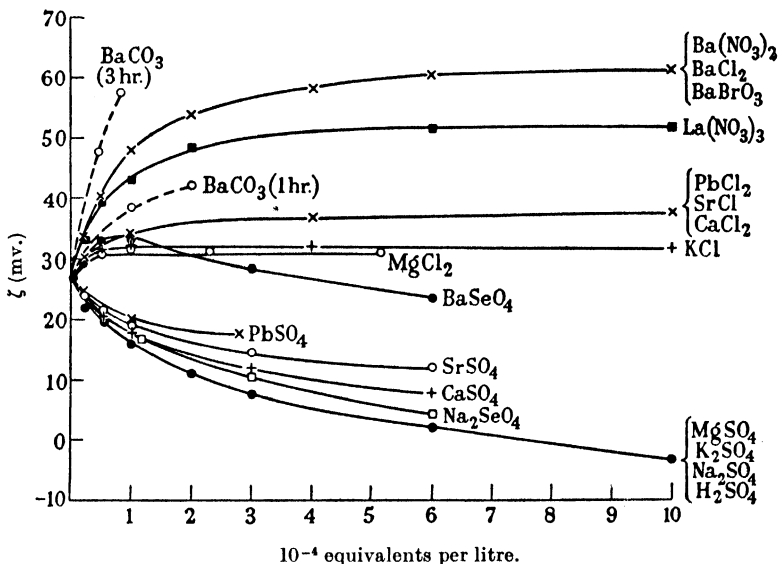
^{*} Lange and Crane (*loc. cit.*) observed that the rate of flow of a saturated solution of silver iodide did not change when the solution was freed from carbon dioxide. This indicates that the negative charge on the diaphragm was not due to the adsorption of bicarbonate or hydroxyl ions.

^{7a} Kruyt and de Bruyn, *Z. physikal. Chem.*, **A186**, 282, 1940; Kruyt and Overbeek, *Trans. Faraday Soc.*, **36**, 110, 1940.

^{7b} de Bruyn, *Rec. trav. chim. Pays-Bas*, **61**, 5, 12, 21, 189, 193, 1942.

The silver bromide sol has been investigated by Basinski^{7c}. He finds that zero charge occurs at 2.4×10^{-7} bromide ions per l. Krut and Klompé^{7d} found that the double layer potential can be changed appreciably by ions which are not potential determining.

Buchanan and Heymann⁸ have recently investigated the potentials produced by streaming electrolyte solutions through diaphragms of barium sulphate. Fig. 2 shows their results for a



V 2.—Influence of electrolytes on ζ -potential of recrystallised barium sulphate (Buchanan and Heymann).

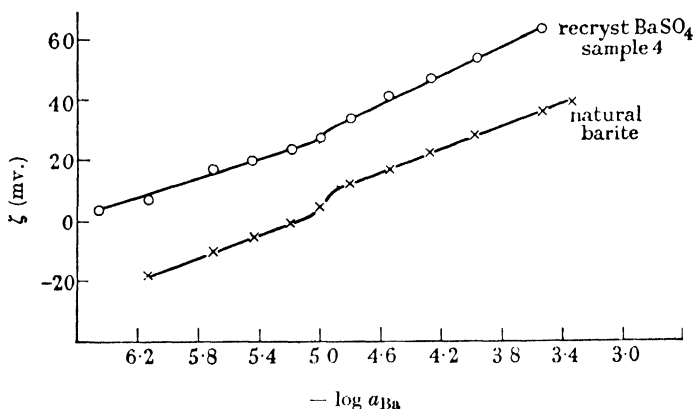
sample of barium sulphate recrystallised from hot sulphuric acid and subsequently ignited. The crystals were positive ($\zeta = +26.6$ mv.) when in contact with saturated barium sulphate solution. It will be seen that ζ is most strongly increased by barium salts, independently of the anion, provided the salt is not sparingly soluble. Similarly, the most marked depression of the potential is effected by the alkali sulphates, magnesium sulphate and sulphuric acid, independently of the cation. In Fig. 3 the

^{7c} Basinski, *Rec. trav. chim.*, **59**, 331, 1940; **60**, 267, 1941.

^{7d} *Proc. Akad. Wet. Amsterdam*, **43**, 975, 1940.

⁸ Buchanan and Heymann, *Proc. Roy. Soc.*, **195A**, 150, 1949; *J. Colloid Science*, **4**, 137, 151, 157, 1949.

ζ -potentials of barium sulphate in solutions of barium chloride and alkali sulphate are plotted against $p_{\text{Ba}} = -\log a_{\text{Ba}}$, a_{Ba} being the activity of the barium ion in the solution. $p_{\text{Ba}} = 5$ corresponds to saturated barium sulphate solution, $p_{\text{Ba}} < 5$ to barium chloride solutions, and $p_{\text{Ba}} > 5$ to sulphate solutions. The curves are straight lines, except for breaks at $p_{\text{Ba}} = 5$, so that $d\zeta = k \cdot d \log a_{\text{Ba}}$ in barium salt solutions, and $d\zeta = k' \cdot d \log a_{\text{SO}_4}$ in sulphate solutions. Data for the adsorption of barium and sulphate ions by barium sulphate are not available, but since the ζ -potential varies



V 3.— ζ -potential, $-\log a_{\text{Ba}}$ curves for recrystallised and natural barium sulphate. (Buchanan and Heymann.)

linearly with $\log a$ it seems highly probable that the potential is determined mainly by the extent to which either ion common to the lattice is present in excess on the crystals forming the diaphragm. Buchanan and Heymann conclude from their data for barium chloride solutions that preferential adsorption of barium ions accounts for only a small fraction of the high positive potential observed with saturated barium sulphate as the streaming solution. They suggest that the chief factor is the preferential release of sulphate ions from the surface layer of the lattice. The much lower value of the positive potential (+5.6 mv.) obtained with natural barium sulphate is ascribed to firmer binding of the sulphate ions as the result of greater orderliness in the structure of the crystal surface.

The observations of Buchanan and Heymann differ in some important respects from those of Kruyt and Ruyssen,⁹ who found that diaphragms of both precipitated and natural barium sulphate were slightly negative when water was forced through them. Moreover, while the precipitated material became positive in solutions of barium chloride, and increasingly so as the salt concentration was increased, no reversal of charge occurred with the natural crystals and the ζ -potential-concentration curve closely resembled that obtained with an "inert" surface of paraffin-wax. Some further observations by Buchanan and Heymann appear to be significant in this connection. One specimen of natural barium sulphate containing organic matter was found before ignition to give a small negative potential (-5.8 mv.) in saturated barium sulphate, but after ignition the potential assumed a considerable positive value ($+11.6$ mv.). It is therefore possible that the unusual behaviour of Kruyt and Ruyssen's natural material was due to contamination with organic matter. Buchanan and Heymann employed diaphragms formed of crystals (100 - $170\ \mu$) much larger than those (about $10\ \mu$) used by Kruyt and Ruyssen in their experiments with precipitated material, but it is difficult to connect the negative charge reported by Kruyt and Ruyssen with this difference in crystal size. Further complications are raised by the later work of Ruyssen¹⁰ who stated that the fine precipitated barium sulphate studied by him was positive against saturated barium sulphate if immediately washed with water, but became negative when allowed to remain in contact with the mother liquor, containing potassium chloride, for twenty-four hours before washing. The ζ -potential (derived from streaming potential measurements) of the negative crystals became positive in barium chloride solutions and the relation $d\zeta = k \cdot d \log c$ was found to hold. If the barium chloride was replaced by saturated barium sulphate the potential retained a positive value, which persisted in potassium chloride solution, but changed to a negative value when the potassium chloride was replaced by saturated barium sulphate.

⁹ Kruyt and Ruyssen, *Proc. Akad. Wetenschappen Amsterdam*, **37**, 624, 1934.

¹⁰ Ruyssen, *J. Physical Chem.*, **44**, 265, 1940.

CHAPTER VI

THE STABILITY OF COLLOIDAL SOLUTIONS

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Lyophobic and Lyophilic Systems. Colloidal solutions with liquid as the dispersion medium can be divided into two groups, *lyophobic* and *lyophilic* systems, according as the disperse phase has a low or high affinity for the dispersion medium. Typical examples of the former type are sols of the metals, sulphides and silver halides, while sols of gums, starches, proteins and soaps are instances of the latter group.

The presence of an electrical double layer surrounding the particles is essential, though not always sufficient for the stability of a lyophobic system. Lyophilic sols, on the other hand, show stability even at the isoelectric point. The work of Kruyt¹ provides strong evidence that solvation is the fundamental stabilising factor for lyophilic systems. The addition of substances, such as acetone or alcohol, which are able to dehydrate the particles, causes a hydrophilic sol to show a conversion from typical lyophilic to lyophobic properties.²

On account of its fundamental theoretical importance this chapter is devoted exclusively to the study of the stability of lyophobic systems.

Early Theories of Stability. In the early stages of colloid chemistry it was assumed that in a stable lyophobic sol, or suspension, agglomeration of the particles was prevented by the Coulomb repulsion between the particle charges. This idea was based on the experimental observation³ that any process, such

¹ H. R. Kruyt and H. G. Bungenberg de Jong, *Z. phys. Chem.*, **100**, 250, 1922,

² For a more complete account of the differences in the physical properties of lyophobic and lyophilic sols see for example, S. Glasstone, *Text-book of Physical Chemistry*, 2nd edn., Chap. XIV, Van Nostrand Co. and Macmillan & Co. 1947; A. E. Alexander and P. Johnson, *Colloid Science*, Vol. I, Chap. I, Oxford Press, 1949.

³ E. F. Burton, *Phil. Mag.*, **11**, 425; **12**, 472, 1906; F. Powis, *Z. phys. Chem.* **89**, 186, 1915.

as dialysis or the addition of electrolyte, which reduces the zeta-potential causes flocculation of the system. The concentrations of electrolyte required to flocculate three different sols are given in Table I.

TABLE I. FLOCCULATING CONCENTRATIONS OF ELECTROLYTE
IN MILLIMOLES LITRE⁻¹

Electrolyte	Fe ₂ O ₃ * + ve sol	As ₂ S ₃ * ve sol	AgI† ve sol
NaCl	9.25	51	—
KCl	9.0	49.5	—
KNO ₃	12.0	—	136
LiNO ₃	—	—	165
$\frac{1}{2}$ K ₂ SO ₄	—	65.5	—
MgCl ₂	—	0.72	—
Ca(NO ₃) ₂	—	—	2.38
Ba(NO ₃) ₂	—	—	2.20
K ₂ SO ₄	0.205	—	—
MgSO ₄	0.22	0.81	—
AlCl ₃	—	0.093	—
Al(NO ₃) ₃	—	0.095	0.067

* H. Freundlich, *Z. phys. Chem.*, **44**, 129, 151, 1903; **73**, 385, 1910.

† H. R. Kruyt and M. A. M. Klompé, *Kolloid Beihefte*, **54**, 484, 1942.

These values illustrate the well-known Schulze-Hardy rule, which states that the flocculating power of an electrolyte depends upon the valency of the ion which has a charge opposite to that of the colloid particle. The valency of the ion of the same sign is of little importance. For any given sol the flocculating concentrations of the univalent, divalent and trivalent ions are approximately in the ratio 100 : 1.6 : 0.14, or 1 : (1/2)⁶ : (1/3)⁶. This suggests that the flocculating concentrations are inversely proportional to the sixth power of the valency of the flocculating ion.

These facts gave rise to the general idea that the flocculation of a sol by an electrolyte is due to the adsorption of the oppositely charged ions with a consequent reduction of the particle charge. Although this may occur in certain special cases, it is impossible to reconcile this theory with more recent experiments⁴ which show that coagulation can occur in sols or suspensions in which

⁴ H. Freundlich and H. P. Zeh, *Z. phys. Chem.*, **114**, 65, 1925; H. R. Kruyt and P. C. van der Willigen, *ibid.*, **130**, 170, 1927.

the zeta-potential has been increased. Furthermore, it is also found⁵ that the amounts of different cations carried down in the precipitation of a negative colloid are not equivalent.

Development of the Modern Theories. Because of the obvious difficulties in the early theories, an attempt has been made in recent years to approach the problem of colloidal stability from a different point of view. Firstly it is necessary to consider, not the Coulomb repulsion between two similarly charged particles, but the much more complicated problem of the interaction between two particles each of which is surrounded by an electrical double layer. In its most rigorous form the theory has proved to be so difficult that the results obtained by various authors,⁶⁻¹¹ using different methods of approach, were not in agreement, even on the important question as to whether the double layer interaction leads to a repulsion or attraction between the particles of the sol. Largely due to the work of Verwey, these difficulties have now been removed,^{9, 12} and it is established that the effect of the double-layer interaction is always to cause a force of repulsion. In addition, we have also to take into account the mutual attractive forces between the particles due to London-van der Waals forces, which are discussed on page 145. The problem of the stability of the system can then be studied, as in Hamaker's¹³ early work, with the aid of potential energy diagrams.

Formation of the Electrical Double Layer and Potential Determining Ions. In a few instances, e.g. the mineral clays, acidic and basic dyestuffs, a stable sol is formed spontaneously on shaking up the finely divided substance in water. The stability

⁵ F. Powis, *Z. phys. Chem.* **89**, 91, 189, 1915; H. R. Kruyt and D. R. Briggs, *Proc. Akad. Sci. Amsterdam*, **32**, 384, 1929. See also Kruyt and Vogel, *Kolloid-Beihft*, **52**, 87, 1940.

⁶ I. Langmuir, *J. Chem. Phys.*, **6**, 893, 1938.

⁷ A. J. Corkhill and L. Rosenhead, *Proc. Roy. Soc.*, **172A**, 410, 1939.

⁸ S. Levine, *ibid.*, **170A**, 145, 165, 1939; S. Levine and G. P. Dube, *Trans. Faraday Soc.*, **36**, 215, 1940.

⁹ S. Levine, *ibid.*, **42**, 102, 128, 1946; **44**, 833, 1948.

¹⁰ B. Derjaguin, *ibid.*, **36**, 203, 1940.

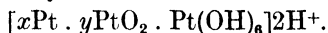
¹¹ E. J. W. Verwey, *ibid.*, **36**, 192, 1940.

¹² E. J. W. Verwey, *Philips Research Reports*, **1**, 33, 1945; E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier Pub. Co., 1948.

¹³ C. Hamaker, *Rec. trav. chim. Pay-Bas*, **55**, 1015, 1936; **56**, 3, 727, 1937.

is due to the presence of ionogenic groups on the particle surface. The electrical double layer of a sodium montmorillonite has the negatively charged surface of the crystallite as its inner layer and the hydrated Na^+ ions as the gegenions or counter ions of the diffuse layer.

In the preparation of stable metallic sols by the Bredig method it was at one time thought that the negative particle charge arises from the preferential adsorption of OH^- ions. However, for platinum sols Pennycuik¹⁴ has found evidence for the presence of platinum oxides and an acid $\text{H}_2\text{Pt}(\text{OH})_6$ on the particle surface. The dissociation of the latter gives rise to the charge, so that, according to this theory, the sol should be formulated



Whichever mechanism is assumed, it is still possible to regard the OH^- ions as the *potential determining ions* and the H^+ ions as the counter ions of the diffuse part of the double layer.

A stable negative sol of AgI is prepared by adding excess of potassium iodide to the dilute solution of a silver salt. The excess I^- ions are adsorbed on the particle surface, since according to the Fajans-Hahn law ions which can be incorporated into the crystal lattice are preferentially adsorbed. On adding a silver salt, e.g. AgNO_3 , to the negative sol the I^- ions are neutralised by the Ag^+ ions, and flocculation occurs due to the removal of the potential determining ions and destruction of the double layer. If sufficient AgNO_3 is added very rapidly to the system it may be converted to a stable positive sol by the adsorption of the excess Ag^+ ions without coagulation taking place.

Flocculation by the removal of the potential determining ions is the exception rather than the rule. The addition of indifferent electrolytes, i.e. electrolytes which do not alter the activity of the potential determining ions, reduces the potential barrier between the particles and brings about flocculation as indicated in Fig. 3. The flocculation values in Table I refer to such indifferent electrolytes.

The Total Surface or Double Layer Potential. When the particles in a sol are brought to the zero point of charge the equilibrium distribution of the potential determining ions is uniform

¹⁴ S. W. Pennycuik, *J. Amer. Chem. Soc.*, **52**, 4621, 1930 ; **61**, 2234, 1939.

throughout the solution. On increasing the concentration of the potential determining ions the equilibrium distribution is changed in the direction of more potential determining ions at the particle surface. It is just this non-uniform distribution of the ions which produces the double layer potential.

For systems, such as the negative AgI sols, in which the potential determining ions are indistinguishable from the ions in the crystal lattice an expression for the double layer potential can be found from thermodynamical considerations. Since the surface of the crystal always contains a very great number of I^- ions, the formation of the double layer does not appreciably change the *total number* of I^- ions at the surface. Consequently the surface potential (ψ_0) is determined solely by the activity (I') of the I^- ions at a point in the solution where the potential (ψ) is zero.¹⁵

ψ_0 is given by a Nernst equation $\psi_0 = \psi'_0 + \frac{kT}{\epsilon} \ln I'$ where ψ'_0 is a constant. If I'_0 is the activity at the zero point of charge when $\psi_0 = 0$, $\psi'_0 = -\frac{kT}{\epsilon} \ln I'_0$. Hence

$$\psi_0 = \frac{kT}{\epsilon} \ln \frac{I'}{I'_0} \quad . \quad . \quad . \quad . \quad (1)$$

ψ_0 , unlike the electrokinetic or ζ -potential, will not be affected by the addition of an indifferent electrolyte. For this reason, and also on account of the present uncertainty as to the exact relationship between ζ -potential and the total double layer potential, the existing theories of stability are developed in terms of ψ_0 only.

For a stable AgI sol the concentrations of I^- ions in the bulk of the solution is 10^{-5} N, while at the zero point of charge it is 10^{-10} N.¹⁶ It is therefore permissible to assume that the activity coefficients are unity, equation (1) then gives for this sol

$$\psi_0 = \frac{kT}{\epsilon} \ln 10^5 \sim -300 \text{ mV.}$$

The zeta-potential for a stable AgI sol is about -70 mV.¹⁷ The existence of potentials of this magnitude compels us in the theory

¹⁵ E. J. W. Verwey, *Chem. Revs.*, **16**, 363, 1935.

¹⁶ H. R. Kruyt and E. J. W. Verwey, *Z. phys. Chem.*, **167**, 149, 1933.

¹⁷ D. C. Henry, *Proc. Roy. Soc.*, **133A**, 106, 1931.

of stability to use the exact differential equation for a double layer derived from Poisson's equation on page 54.

$$\nabla^2 \psi = \frac{8\pi n z \epsilon}{D} \sinh \left(\frac{z e \psi}{kT} \right), \quad . \quad . \quad . \quad (2)$$

since the assumption, that $z e \psi / kT \ll 1$, which leads to the linear Debye-Hückel approximate equation is quite invalid. The solution of the exact equation (2) is restricted on account of mathematical difficulties to certain special cases. The model of two flat, parallel, double layers is the easiest to handle and is the only one considered here. It applies to the sols of iron oxide, tungstic acid and the mineral clays which have thin rectangular or disc-shaped particles. For the metallic and silver halide sols the model of spherical particles is a better approximation.¹⁸ For the sols of vanadium pentoxide and tobacco mosaic virus the theory for rod-shaped particles is required, this has not yet been developed.

The Distribution of Potential in a Flat Double Layer.

For a flat double layer ψ is a function of the normal co-ordinate only, hence we can write $\nabla^2 \psi = \frac{d^2 \psi}{dx^2}$. The equations are simplified by making the substitutions

$$y = \frac{z e \psi}{kT}, \quad v = \frac{z e \psi_0}{kT}, \quad \kappa^2 = \frac{8\pi n \epsilon^2 z^2}{D k T} = \frac{1}{\delta^2}$$

Equation (2) then becomes

$$\frac{d^2 y}{dx^2} = \kappa^2 \sinh y. \quad . \quad . \quad . \quad (3)$$

The solution of this equation is

$$y = 2 \ln \frac{1 + \gamma e^{-\kappa x}}{1 + \gamma e^{-\kappa v}} \quad . \quad . \quad . \quad (4a)$$

where

$$\gamma = \frac{e^{v/2} - 1}{e^{v/2} + 1}. \quad . \quad . \quad . \quad (4b)$$

It is easily verified that this solution satisfies the boundary conditions

$$\psi = \psi_0, \quad y = v, \quad \text{when } x = 0$$

$$\psi = 0, \quad \frac{dy}{dx} = 0, \quad \text{when } x = \infty.$$

¹⁸ E. J. W. Verwey and J. Th. G. Overbeek, *loc. cit.*, Part III.

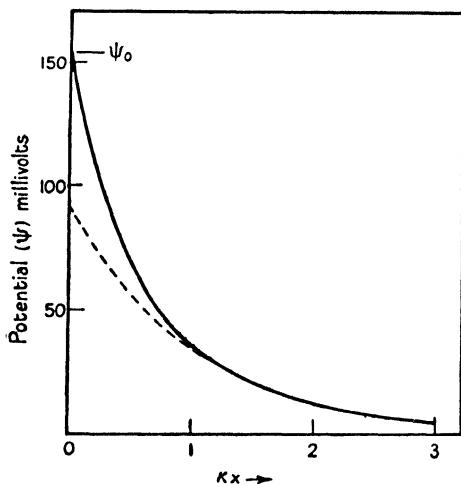
Since γ is always < 1 , it follows that for large distances such that $\kappa x > 1$, $\gamma e^{-\kappa x} \ll 1$ equation (4a) may then be simplified to

$$y = 2 \ln (1 + 2\gamma e^{-\kappa x}),$$

or

$$y = 4\gamma e^{-\kappa x} \quad (\kappa x > 1). \quad (5)$$

The potential distribution for a flat double layer calculated from



VI 1.—Potential distribution for flat double layer with $\psi_0 = 154$ mV.

————— calculated from exact equation (4a).
 according to approximate equation (5).

solved to satisfy the boundary conditions $\psi = \psi_0$ when $x = 0$

and $x = 2d$, also $\frac{d\psi}{dx} = 0$ when $x = d$. The solution involves an

elliptic integral which can only be solved numerically. However, when the interaction is not too great, i.e. when $\kappa d > 1$, it is sufficiently accurate to assume that the potential can be built up additively from the electric potential functions of two single double layers. In Fig. 2 the exact potential functions from Fig. 1 have been used to derive the potential distribution for two flat plates with $\psi_0 = 154$ mv. Since the potentials are additive it follows, from equation (5) for a single flat layer, that the potential ψ_a at

the exact equation (4a) is given in Fig. 1; the broken curve shows the potential derived from equation (5), it is evident that this latter equation is a very good approximation for distances down to $\kappa x = 1$, for all values of ψ_0 .

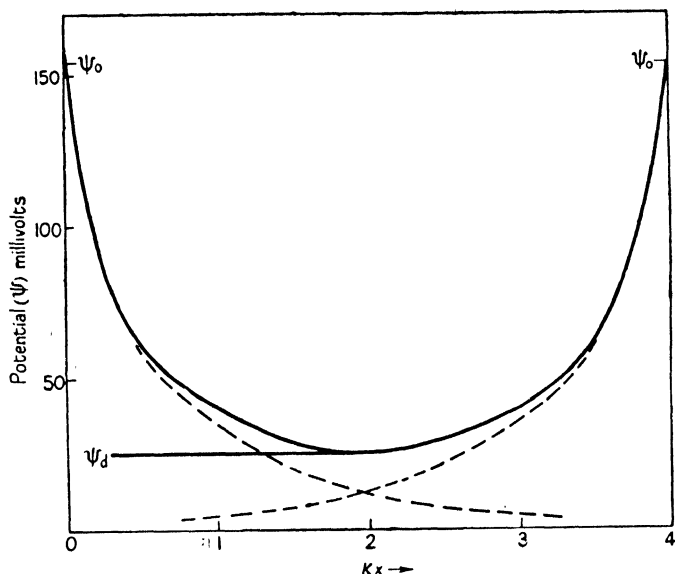
Potential Distribution for two Flat Double Layers. To derive an exact expression for the potential distribution for two flat plates separated by a distance $2d$, the exact equation (3) has to be

a point mid-way between the plates, where $x = d$, is given by the relation

$$u = 8\gamma e^{-\kappa d} \quad (6)$$

where $u = \frac{ze\psi d}{kT}$ and $\kappa d > 1$.

The Force of Repulsion between two Interacting Double Layers. The simplest way to find an expression for the force between two double layers is to follow an argument due to Lang-



VI 2.—Potential distribution between two flat double layers with $\psi_0 = 154$ mV.
..... potential distribution for one double layer.

muir¹⁹ and to consider the force of repulsion as arising from the osmotic pressure of the excess ions in the interparticle space where the double layers overlap.

If n_+ and n_- are the concentrations of the positive and negative ions at the plane $x = d$ midway between the plates where $\psi = \psi_d$, we have by Boltzmann's theorem $n_+ = ne^{-\frac{ze\psi_d}{kT}}$ and $n_- = ne^{\frac{ze\psi_d}{kT}}$. The osmotic pressure at a point in the mid-plane is then

$$kT(n_+ + n_-) = nkT(e^u + e^{-u}) = 2nkT \cosh u.$$

¹⁹ I. Langmuir, *J. Chem. Phys.*, **6**, 893, 1938.

The osmotic pressure at a point outside the field of the double layers where $\psi = u = 0$ is $2nkT$. The difference between these pressures is a measure of the force (p) acting on *unit area* of each plate. Hence

$$p = 2nkT (\cosh u - 1). \quad (7)$$

Since $\cosh u$ is always greater than unity the force is always repulsive.

The repulsive potential energy of the system can now be found by calculating the work done against this repulsive force as the plates are brought together from a very great distance.

Work done per unit area of the plates

$$\begin{aligned} &= -2 \int_{\infty}^d p \, dx \\ &= -2 \int_{\infty}^d 2nkT (\cosh u - 1) \, dx. \end{aligned} \quad (8)$$

In the most general case this integral cannot be evaluated on account of the complicated relation between u and x . The calculation has then to be made from free energy considerations.²⁰ However, when the interaction is not too great equation (6) can be combined with equation (8) to give the required result, which is valid for all distances such as at $\kappa d > 1$. Since u is then small ($\cosh u - 1$) can be replaced by $u^2/2$ and equation (8) yields for the repulsive potential energy per unit area of the plates

$$V_R = -2 \int_{\infty}^d nkT \cdot 64\gamma^2 e^{-2\kappa x} dx = \frac{64nkT}{\kappa} \gamma^2 e^{-2\kappa d} \quad (9a)$$

provided $\kappa d > 1$. Verwey and Overbeek²¹ show that a better approximation is given by the equation

$$V_R = \frac{64nkT}{\kappa} \cdot \gamma^2 \frac{e^{-2\kappa d}}{1 + e^{-2\kappa d}} \quad (9b)$$

when $\kappa d > 1$ the expressions (9a) and (9b) are identical. It is interesting to note that the double layer potential only enters into these expressions through the quantity γ defined by equation (4b).

For values of $v = \frac{ze\psi_0}{kT} > 8$, $\gamma \rightarrow 1$, and the repulsive potential

²⁰ E. J. W. Verwey and J. Th. G. Overbeek, *loc. cit.*; D. Derjaguin, *loc. cit.*

²¹ E. J. W. Verwey and J. Th. G. Overbeek, *loc. cit.*, p. 96.

becomes almost independent of ψ_0 , and is affected only by changes in the concentration of electrolyte which alter n and κ .

The Forces of Attraction between Colloidal Particles. The atoms of the inert gases are generally assumed to be spherically symmetrical and to have zero external field, the question therefore arises as to how the forces of cohesion, shown by their liquefaction, can occur. In an important paper published by London²² in 1930, it was shown that the spherical symmetry and zero external field are purely average effects. On account of the nuclear and electronic vibrations, such an atom may at any given instant show electrical asymmetry and hence a fluctuating dipole moment. This will induce a temporary dipole moment in surrounding atoms and a force of attraction will result. The interaction energy between two atoms was calculated by London to be

$$V = -\frac{3}{4}h\nu_0\alpha^2/r^6 \quad . \quad . \quad . \quad (10)$$

where h is Planck's constant, $\nu_0 =$ a characteristic frequency and $\alpha =$ the polarisability of the atom, r is the interatomic distance. This was the first satisfactory explanation of the universal attractive forces postulated by van der Waals.

A fundamental assumption in the quantum mechanical treatment is that these forces are additive, and hence in an assembly of atoms each atom attracts every other atom with a force which is, to a first approximation, independent of the presence of surrounding atoms. We can thus by a process of summation, or integration, use equation (10) to derive an expression for the attractive potential energy of two colloidal particles.

Rewriting equation (10) in the form $V = -\frac{\lambda}{r^6}$ where λ is a constant depending on the nature of the atom, we have for the force of attraction between two atoms

$$f = -\frac{\partial V}{\partial r} = \frac{6\lambda}{r^7} \quad . \quad . \quad . \quad (11)$$

The force of attraction between two atoms thus falls off very rapidly with increasing distance, it might therefore be expected that the London-van der Waals forces between two particles

²² F. London, *Z. Physik*, **63**, 245, 1930.

will be of rather short range. This, however, is not so, for when we calculate the attractive force between two assemblies of atoms it is found to vary inversely with a much lower power of the interparticle distance. For two flat plates Verwey and Overbeek²³ find

$$V_A = -\frac{A}{48\pi} \left\{ \frac{1}{d^2} + \frac{1}{(d+t)^2} - \frac{2}{(d+t/2)^2} \right\} \quad (12)$$

where $A = \pi^2 q^2 \lambda$, q = number of atoms in unit volume of the plates, $2d$ = interparticle distance and t = thickness of the plates. When $d \ll t$ this expression simplifies to

$$V_A = \frac{A}{48\pi d^2} \quad (13)$$

The constants λ , q and A will vary from substance to substance. For a number of atoms $\lambda \sim 5 \times 10^{-59}$ and for a large number of substances $q \sim 6 \times 10^{22}$ and hence $A \sim 10^{-12}$.

In colloid science we are not infrequently concerned with interparticle distances of the order of 1000 A.U., it must therefore be emphasised that these equations are only valid for distances below about 100 A.U. This is because in the London theory no account is taken of the fact that the electromagnetic disturbance set up by a fluctuating dipole takes a finite time to reach a distant atom. For large interatomic distances a more recent theory developed by Casimir and Polder²⁴ must be used, these authors show that for large distances equation (10) must be replaced by an expression of the form $V \propto 1/r^7$. The attractive force at great distances is less than that given by the original London theory.

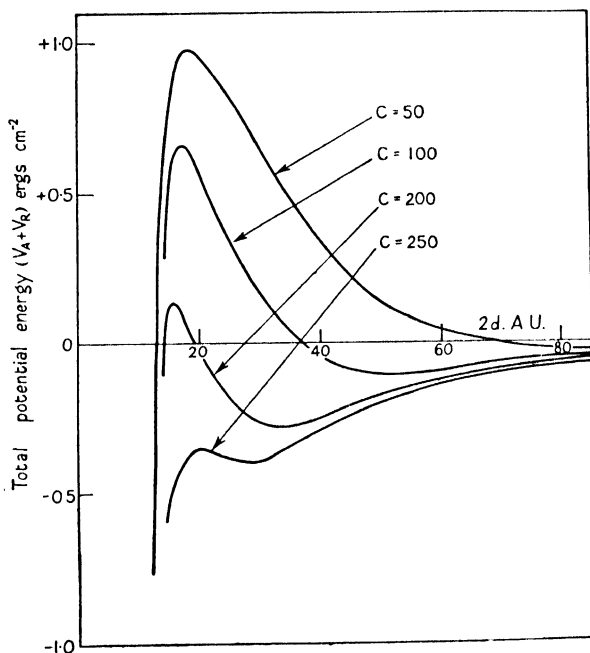
Total Potential Energy Curves and their Application to Colloid Stability. The equations (9b) and (13) for the repulsive and attractive potential energies of a system of two flat plates can now be combined to give the total potential-energy curve as a function of the interparticle distance. The resultant curves so obtained are shown in Figs. 3 and 4 for different concentrations of uni-univalent electrolyte and different double layer potentials.

For the calculation of V_R from equation (9b) the following data have been used, $n = c \times 6.03 \times 10^{17}$ where c is the electro-

²³ E. J. W. Verwey and Th. G. Overbeek, *loc. cit.*

²⁴ H. B. G. Casimir and D. Polder, *Phys. Rev.*, **73**, 360, 1948.

lyte concentration in millimoles litre⁻¹, $\kappa^2 = 8\pi n e^2 z^2 / DkT$, $D = 80$ and $T = 300^\circ \text{K}$. When greater accuracy is required the exact numerical solution for V_R given by Verwey and Overbeek²⁵ must be used, reference to their original curves shows that equation (9b) is a very good approximation.



VI 3.—Total potential energy curves for two parallel plates, showing effect of uni-univalent electrolyte on stability.

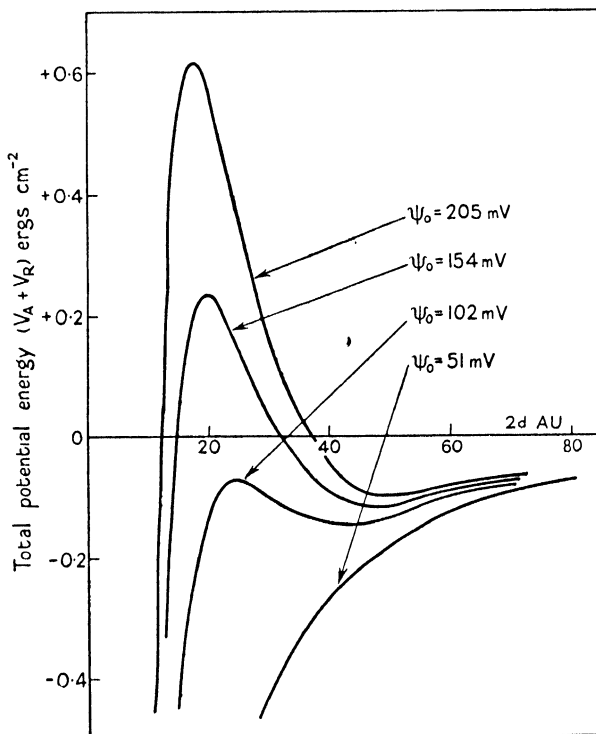
c = electrolyte concentration in millimoles litre⁻¹
 $\psi_0 = 205 \text{ mV}$. $A = 2 \times 10^{-12}$.

The values of the attractive potential have been calculated from equation (13) which holds when $d \ll t$, assuming $A = 2 \times 10^{-12}$.

At very small and very large interparticle distances the attractive potential always exceeds the repulsive potential. This is because the latter decreases exponentially from a finite value when $d = 0$, whereas the former decreases quadratically with increasing distance. In the intermediate range, where the

²⁵ H. Freundlich and H. Ishizaka, *Z. phys. Chem.*, **83**, 79; **85**, 398, 1913; J. Gann, *Kolloidchem. Beihefte*, **8**, 64, 1916.

interparticle distance is of the order of the double layer thickness ($\delta = 1/\kappa$) the repulsive potential may exceed the attractive potential giving rise to a pronounced potential maximum or potential barrier which opposes the close approach of the particles and confers stability on the system. The addition of electro-



VI 4.—Total potential energy curves for two parallel plates, showing effect of double layer potential on stability. Concentration of uni-univalent electrolyte = 100 millimoles litre⁻¹, $A = 2 \times 10^{-12}$.

lyte reduces the potential barrier, until finally the attraction prevails at all distances and flocculation will occur. Physically this can be understood as follows. The repulsive potential only becomes appreciable when the double layers are about to overlap. At low electrolyte concentrations δ is large, consequently when $d = \delta$, V_A is very small and the repulsive potential predominates. At large electrolyte concentrations δ is small, so that now when

$d = \delta$, V_A is very much greater and may exceed V_R at all distances.

It is clear from Figs. 3 and 4 that the quantity of electrolyte required for flocculation increases with the double layer potential. Verwey and Overbeek derive an interesting expression for the flocculating concentration of electrolyte by finding the condition that the total potential energy is never positive, i.e. the curve just fails to rise above the horizontal axis. This will occur at the point when $V_A + V_R = 0$ and $\frac{d(V_R + V_A)}{dd} = 0$. Since from equations (9a) and (13) we have $\frac{dV_A}{dd} = \frac{2}{d} \cdot V_A$ and $\frac{dV_R}{dd} = -2\kappa V_R$. These two conditions are satisfied when $\kappa d = 1$. The first condition now gives

$$\frac{A}{48\pi} \cdot \frac{1}{d^2} = \frac{64nkT}{\kappa} \cdot \gamma^2 \cdot e^{-2} \quad . \quad . \quad . \quad (14)$$

Since $\kappa^2 = 8\pi n\epsilon^2 z^2 / DkT$, equation (14) yields for the flocculating concentration, in ions cm.⁻³

$$n = \frac{107 D^3 k^5 T^5 \gamma^4}{A^2 (ze)^6} \quad . \quad . \quad . \quad (15)$$

The flocculating concentration of electrolyte is thus inversely proportional to the sixth power of the valency, in excellent agreement with the Schulze-Hardy rule. The numerical value of the flocculating concentration calculated from equation (15) depends upon the value chosen for A , the best agreement with the experimental values is found when A is about 2×10^{-12} , which is well within the limits set by the quantum-mechanical theory.

Kinetics of Coagulation. The quantitative study of the stability of a sol involves the measurement of the change in the number of particles over a period of time. In early investigations this was not determined directly but was derived from some physical property of the sol such as its viscosity or optical absorption coefficient.²⁵ The correct interpretation of such measurements is very difficult and it is now more usual to count the number of particles directly with the aid of an ultramicroscope.²⁶ The coagulation

²⁵ R. Zsigmondy, *Z. phys. Chem.*, **92**, 600, 1918; R. J. Hartmann, *Colloid Chemistry*, 2nd edn., Chap. XI, Pitman & Son, 1948.

is allowed to proceed for a known time, it is then arrested by the addition of a protective colloid, such as gelatin, and the number of particles counted.

Under the conditions represented by the lowest curves in Figs. 3 and 4 coagulation will take place with great rapidity. The theory was first given by von Smoluchowski,²⁷ who treated the problem as one of diffusion in which every collision leads, in the absence of any repulsive forces, to adhesion of the particles. Assuming the particles to be spherical of radius a , and taking into account the formation of secondary and more complex particles, von Smoluchowski was able to show that the total number of particles (Σn) present after time t seconds is given by the expression

$$\Sigma n = \frac{n_0}{1 + t/t_c} \quad . \quad . \quad . \quad (16)$$

where n_0 = initial number of particles in the monodispersed sol.

$t_c = 1/8\pi G a n_0$ and G is the diffusion constant.

t_c is called the time of coagulation, since it is the time in which the number of particles is halved and so makes an excellent measure of the rate of coagulation. Equation (16), which applies only to the case of rapid coagulation, has been fully confirmed by experiment.²⁸ By Einstein's theorem²⁹ $G = \frac{kT}{6\pi\eta a}$, where η is the viscosity of the dispersion medium, from which it follows that

$$t_c = \frac{3\eta}{4kT \cdot n_0} \quad . \quad . \quad . \quad (17)$$

For water as the dispersion medium at room temperature

$$t_c \sim 2 \times 10^{11}/n_0 \text{ seconds.}$$

For a 1 per cent. AgI sol with particles of radius 10^{-5} cm.

$$n_0 \sim 5 \times 10^{11},$$

hence the time of rapid coagulation will be about 0.5 second. As Kruyt has pointed out, the study of rapid coagulation is of little

²⁷ M. von Smoluchowski, *Phys. Z.*, **17**, 557, 585, 1916; *Z. phys. Chem.*, **92**, 129, 1917.

²⁸ H. R. Kruyt and A. E. van Arkel, *Rec. trav. chim. Pay-Bas*, **39**, 656, 1920; **40**, 169, 1921; A. Westgren and J. Reitstötter, *Z. phys. Chem.*, **92**, 750, 1918; *J. Phys. Chem.*, **26**, 537, 1922.

²⁹ A. Einstein, *Ann. Physik.*, **17**, 549, 1905; **19**, 371, 1906.

interest since it applies to a sol which has been deprived of its stable properties.

In the theory of slow coagulation, first developed by Fuchs,³⁰ the problem is regarded as one of diffusion in a field of force. The time of coagulation given by equation (17) is now increased by a factor

$$W = 2a \int_{2a}^{\infty} e^{V/kT} \cdot \frac{dR}{R^2} \quad . \quad . \quad . \quad (18)$$

where V is the total interaction energy of two spherical particles of radius a when their centres are separated by a distance R .

A sol is generally termed stable when it does not flocculate in a period of several days or weeks. This is only possible if $W \sim 10^9$. A crucial test of the modern theories of stability is therefore to determine if such values of W are physically possible. Verwey and Overbeek,³¹ using for V the expression $(V_A + V_R)$, have evaluated W for spherical particles by graphic integration. Their results, which are reproduced in Fig. 5, show that at low electrolyte concentrations W can easily attain the necessary value for high stability. The effect of particle size is, however, very critical. It is well known in flocculation experiments that the rate of flocculation frequently slows down until the process finally stops. This is easily understandable since if we start with a monodispersed sol of small particle diameter the gradual increase in size may be sufficient to produce a stable system. An electron microscope study of the particle size distribution in a stable sol for different values of the double layer potential and electrolyte concentration would be of particular interest.

Since the interaction energy (V) appears in the exponential term in equation (18) small changes in V produce very large changes in W . Verwey and Overbeek estimate very approximately that if W is to exceed 10^6 the height of the potential barrier $V_{max.}$ has to be about $15 kT$, whereas for W to exceed 10^{10} $V_{max.}$ has only to be increased to about $25 kT$. The corresponding values for flat plates have not been calculated, but it is interesting to consider the curves in Fig. 3, assuming that these approximate

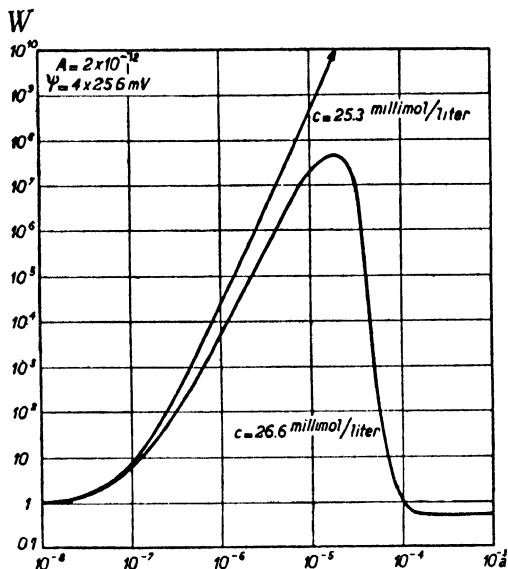
³⁰ N. Fuchs, *Z. physik.*, **89**, 736, 1934.

³¹ E. J. W. Verwey and J. Th. G. Overbeek, *loc. cit.*

criteria of stability apply there also. For flat plates of area 10^{-12} cm.² we have for the curve (a) in Fig. 3,

$$V_{\max.} \sim 10^{-12} \text{ ergs} \sim 25 kT,$$

since $kT = 4 \times 10^{-14}$ ergs. We therefore expect a high degree of stability. For the curve (b) $V_{\max.} \sim 0.6 \times 10^{-12}$ ergs $\sim 15 kT$, so that increasing the electrolyte concentration from 50 to 100 millimole litre⁻¹ has reduced the time of coagulation by a factor



VI 5.—Stability ratio as a function of the particle radius. Monovalent electrolyte. (Verwey and Overbeek.)

of about 10^5 . The size of the particles is again very critical since if we double the area, $V_{\max.}$ for curve (b) becomes $30 kT$, and we again have the condition for high stability.

Earlier Derjaguin³² gave as the criterion for the stability of spherical particles the condition $Da\psi_0^2 > 20 kT$. In the derivation of this expression the effect of the long range attractive forces is neglected and the linear Debye-Hückel approximation ($ze\psi_0 \ll kT$) is assumed. The most obvious objection to this condition is that it does not involve the electrolyte concentration.

³² B. Derjaguin, *loc. cit.*

The Minimum in the Total Potential Energy Curves for Large Interparticle Distances. We have so far neglected the influence of the shallow minimum which occurs in the potential curves at large distances when the London-van der Waals force exceeds the repulsive force. If the depth of this minimum is of the order of two or three times kT the particles will be held by long-range forces at definite distances apart. Outwardly the system will appear to be homogeneous, but under an ultramicroscope or polarising microscope it will show regions of higher concentration where the particles are oriented and form a kind of regular structure. Such phenomena are well known, as in the formation of tactoids in the tobacco mosaic virus sol.³³ This orientation and fixation of the particles by long-range forces may give rise to some forms of structural network which confers rigidity on the system. The gelation of many lyophobic sols is brought about by the addition of a small quantity of electrolyte,³⁴ which is insufficient for macroscopic flocculation. This is easily understood in the light of the curves in Fig. 3 in which the depth of the secondary minimum increases with the concentration of added electrolyte. Recent measurements³⁵ of the effect of the addition of electrolyte on the rigidity of bentonite gels, in which the colloidal clay particles are thin rectangular plates aggregated end-to-end, show that the rigidity is determined by the depth of this secondary minimum. Lyophobic gels frequently show the phenomenon of thixotropy, a reversible sol $\rightarrow$ gel transformation, which occurs on shaking. It is believed that the mechanical disturbance is sufficient to throw the particles out of the shallow minima and so produce a temporary breakdown of the structure of the gel.

Suspensions. A system is called a suspension when the particle dimensions exceed $1\ \mu$ and they become visible in the ordinary microscope. On account of their increased weight the particles in a suspension settle out in a matter of hours, while the particles in a colloidal solution may remain suspended for several weeks.

³³ J. D. Bernal and I. Fankuchen, *J. Gen. Physiology*, **25**, 111, 1941.

³⁴ H. R. Kruyt and J. Postma, *Rec. trav. chim. Pay-Bas*, **44**, 765, 1925; M. Aschenbrenner, *Z. phys. Chem.*, **127**, 415, 1927.

³⁵ M. B. M'Ewen and D. L. Mould, *Nature*, **166**, 437, 1950.

Apart from this, there is no fundamental distinction between a lyophobic sol or suspension.

The mechanical properties of the sediment formed from a suspension depend very markedly on the stability of the system. From a stable suspension the particles settle individually and, because of the repulsive forces between them, they are able to slide over one another and so take up the position of closest packing. The sediment adheres firmly to the bottom of the vessel and can only be redispersed with difficulty. Conversely, the sediment formed from an unstable suspension is an irregular, loosely packed, structure which is easily redispersed by shaking. This is because the ready adherence of the particles prevents the formation of a close packing. Such phenomena are of great technical importance in the ceramic industry.

It has long been known that the presence of calcium salts is essential for the promotion of an openwork structure in the soil, and hence for the drainage and aeration of crops. To obtain this loose structure the negatively charged colloidal clay particles must be kept in the flocculated state, this is achieved by the addition of gypsum, since a small concentration of the bivalent Ca^{++} ions is sufficient to maintain flocculation according to the Schulze-Hardy rule.

CHAPTER VII

OVERPOTENTIAL

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Introduction. In the thermodynamic treatment of the electrode potential (E_r) of, say, silver in silver nitrate the necessary assumption is made that the process occurs "reversibly". This implies that the electrode reaction takes place "infinitely slowly" and in practice such reversible potentials must therefore be measured under conditions such that no net current is passing through the circuit.

Suppose now the potential E of an electrode is measured whilst ions flow across the metal solution interface at a rate represented by the current density (c.d.), i . Then, without exception, E differs from E_r . We define

$$E - E_r = \eta \quad . \quad . \quad . \quad . \quad (1)$$

as the overpotential of the electrode process at the given c.d. For cathodic processes, η is negative and for anodic processes positive. In practice, it is generally referred to arbitrarily as a positive quantity, e.g. the overpotential associated with the deposition of hydrogen on a mercury cathode at a c.d. of 10^{-3} amp./sq. cm. in N/10 aqueous hydrochloric acid solution is about -1.04 volts and is often said to be 1.04 volts. In the equations deduced below, η will be allotted its correct sign.

There are three causes for the departure of the electrode potential from the reversible value on passage of a current :

(i) Positive ions in the immediate vicinity of the electrode-solution interface may become impoverished due to deposition and hence the cathode potential, dependent on the concentration of ions in the part of the solution with which the cathode is in immediate contact, is made less positive. (A converse mechanism occurs at

some current lines passing from cathode to anode or if a film (e.g. an oxide film) is present on the electrode surface and sets up an appreciable resistance to passage of current. The *ohmic overpotential*, η_r , is then given by IR where I is the current strength and R the resistance between the electrode and an equipotential surface in the capillary tip.*

In certain cases involving oxide films this ohmic overpotential may amount to a value of the order of 100 volts at medium c.d.s. Obviously, ohmic overpotential must also be eliminated before measurements of value on η_a can be made.

These three kinds of overpotential can be distinguished most satisfactorily by the manner in which they decay after cessation of the polarising current: η_c decays slowly and in a complex way; η_a decays exponentially and η_r instantaneously.

The activation overpotential of hydrogen presents the best known case of activation overpotential. It will sometimes be referred to below simply as "overpotential", η .

Sources of Discrepancies in Experimental Work. Two main difficulties have been encountered in measurements of hydrogen overpotential in the past, namely: (i) the *preparation of the surface* of solid electrodes in a reproducible, pure state, there having usually been an unknown quantity of oxide, or other impurity on the electrode surface; (ii) the existence in the solution of minute traces of capillary active *impurities and depolarisers* which vitiated measurements, particularly at low c.d. The very considerable discrepancies among the work of various authors † have been largely due to the lack of adequate methods of dealing with these factors.

* The terms¹ accepted here for these different kinds of overpotential appear more logical than the alternative and older terminology in which η_a is "over-voltage", η_c is "concentration polarisation" and η_r is "ohmic p.d.". The term "polarisation" can be retained as a general one referring to any departure of an electrode potential from its reversible value.

¹ Bowden and Agar, *Ann. Reports of the Chem. Soc.*, 90, 1938.

† Even among modern workers using Hg cathodes, there may be a discrepancy of 20 per cent. or more in the measured overpotential. Compare for example B  thune and Kimball² with the results of Jofa and Mikulin³ which are concordant with those of Bockris and Parsons.⁴

² B  thune and Kimball, *J. Chem. Phys.*, 13, 53, 1945.

³ Jofa and Mikulin, *J. Phys. Chem. Russ.*, 18, 137, 1944.

⁴ Bockris and Parsons, *Trans. Faraday Soc.*, 45, 916, 1949.

The first difficulty, which has caused a disproportionate quantity of work to have been concerned with Hg electrodes, has recently been overcome by Bockris and Conway⁵ who seal the solid cathodes after reduction in hydrogen into thin glass compartments containing hydrogen, these being broken open by a probe only after introduction into the oxygen-free atmosphere of the cell. To eliminate small trace impurities from solution *pre-electrolysis* has been successfully used, i.e. electrolysis on an auxiliary electrode for many hours, after which this electrode and its deposited impurities are removed from the solution (without introduction of oxygen).^{6, 7, 8}

Other causes of previous discrepancies, which cannot be gone into here⁹ concerned the use of a *commutator method*^{10, 11, 12} for measuring potentials of working electrodes, the current being switched off for a brief period whilst the cathode potential is recorded. Error was caused here owing to the decay of overpotential with time (but see^{8, 13}).

A modern cell⁸ for measurements of hydrogen overpotential on mercury cathodes is seen schematically in Fig. 2. As it has been shown that the presence of grease in the system may affect the behaviour,⁷ water-sealed joints and taps are used to prevent the access of oxygen to the cell.^{14, 15}

Methods of Investigation. There are five main ways of obtaining information on the mechanism of the reactions giving rise to hydrogen overpotential.

I. *Measurement of the overall rate of the reaction* $2\text{H}^+ + 2e \rightarrow \text{H}_2$ can be made as a function of the electrode potential whilst various external factors are altered one by one. Under most conditions

⁵ Bockris and Conway, *J. Sci. Instruments*, **25**, No. 8, 1948.

⁶ Aten and Zieren, *Rec. trav. Chim.*, **48**, 944, 1929.

⁷ Lewina and Sarinsky, *Acta Physicochim.*, **11**, 491, 1937.

⁸ Azzam, Bockris, Conway and Rosenberg, *Trans. Faraday Soc.*, **46**, 918, 1950.

⁹ Bockris, *Chem. Rev.*, **43**, 525, 1948.

¹⁰ Newbery, *J. Chem. Soc.*, **105**, 2422, 1914.

¹¹ Ferguson and Chen, *J. Physical Chem.*, **35**, 1156, 1932.

¹² Drucker, *Z. Elektrochem.*, **48**, 681, 1942.

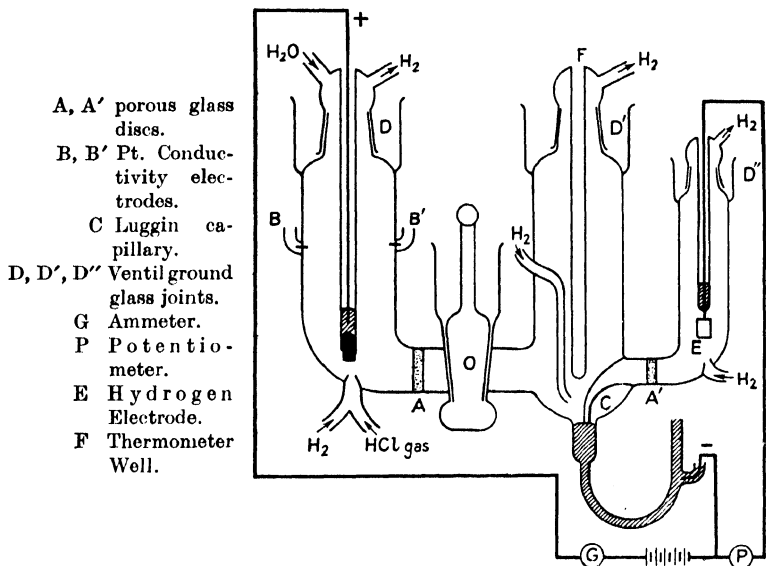
¹³ Hickling, *Trans. Faraday Soc.*, **33**, 1540, 1937.

¹⁴ Lewina and Silberfarb, *Acta Physicochim.*, **4**, 282, 1936.

¹⁵ See Ref. 8.

it is found that overpotential is proportional to $\log c.d.$ and it is the slope of this relation and the displacement of the latter by various factors which is of greatest interest. The following are the more important factors which may be varied.

(i) *Temperature.* As shown in a later section, knowledge of variation of current with temperature at constant overpotential enables the energy of activation of the slow process at the electrode



VII 2.—Apparatus for measuring overpotential.

to be calculated. This quantity is of direct use in assessing the probability of a given slow stage.¹⁶

(ii) *Concentration of hydrogen ions.* Variation of hydrogen ion concentration in solution gives direct information concerning the important question of whether hydrogen ions take part in the rate determining process, and related matters concerned with the structure of the double layer.⁷

(iii) *Concentration of neutral salts.* These latter affect the structure of the double layer at the cathode-solution interface.¹⁷ It follows that they also affect the relation between the concentration

¹⁶ Agar, *Faraday Soc. Discussion*, **1**, 81, 1947.

¹⁷ Stern, *Z. Elektrochem.*, **30**, 508, 1924.

of hydrogen ions in the bulk of the solution and that at the cathode-solution interface, and consequently that they may affect the velocity of the discharge.

(iv) *Solvent.* The solvent effect has become of obvious importance since the solvation energy of the proton and the mode of transfer of the proton from the solvent to the electrode became essential aspects of modern theories.¹⁸

(v) *Pressure.* Variation of this factor is particularly diagnostic of those theories according to which $i = Ae^{\alpha\eta F/RT}$ instead of the more usual form of the expression for the current, $i = Ae^{\alpha EF/RT}$, the overpotential and cathode potential being independent of pressure according to the first and second expression respectively.

II. *A.C. methods.* Determination of the capacity of the electrode-solution interface by A.C. of varying frequencies gives information concerning the complexity of the kinetics of the overall reaction.²⁰ If the behaviour is analogous to that of a model containing a condenser in parallel with a resistance, then there is only one slow stage at the electrode.²¹ In such a simple case, the capacity is independent of frequency over a wide range. If the observed capacity varies with frequency, it is composed not only of the capacity of the double layer, $C_{D.L.}$, but also of a component due to the accumulation of adsorbed hydrogen atoms on the electrode so that it is hence greater than $C_{D.L.}$. By the use of suitable experimental conditions it is also possible for electrodes of low overpotential with A.C. methods to measure the velocity of the process $H^+ + e \rightarrow H$ as distinct from that of the overall reaction $H^+ + e \rightarrow \frac{1}{2}H_2$.^{22, 23}

III. *Charge and discharge curves* (i.e. potential-quantity relation) during the cathodic formation of hydrogen and its anodic ionisation (*Oscillographic methods*). The course of the potential-quantity relation during the initial fraction of a second of passage of current differs according to the process occurring at any potential

¹⁸ Bockris and Parsons, *Trans. Faraday Soc.*, **44**, 860, 1948.

¹⁹ Hickling and Salt, *ibid.*, **36**, 1226, 1940.

²⁰ Agar, *Ann. Rep. Chem. Soc.*, **5**, 1, 1947.

²¹ Frumkin, Dolin and Ershler, *Acta Physicochim.*, **13**, 799, 1940.

²² Dolin and Ershler, *ibid.*, **13**, 747, 1940.

²³ Rosenthal, Dolin and Ershler, *ibid.*, **21**, 213, 1946.

on the electrode surface.^{24, 25} These relations can now be most conveniently observed by multiple trace oscillographic methods.²⁰

IV. *Decay on open circuit.* The type of overpotential-time relation obtained on cessation of the polarising current depends markedly upon the amount of atomic hydrogen adsorbed on the electrode surfaces and is highly diagnostic of this.²⁶

V. *Photochemical methods.* Although hitherto little used,²⁷ information on the influence of light on overpotential would seem to offer an excellent direct means of examining the direct acceleration of electronic processes at the cathode-solution interface⁹ and the resultant effect on overpotential.

Experimental Results. Bonhoeffer²⁹ showed that decrease of *hydrogen overpotential for various metals at a given c.d.* was parallel to the metal's power of catalysing the reaction $\text{H} + \text{H} \rightarrow \text{H}_2$. Bockris³⁰ pointed out that there is a close parallelism between hydrogen overpotential at a given current density and the *thermionic work function* (see Fig. 3).

There is a logarithmic relation between η and current density (see Fig. 4) over a range of c.d.s characteristic of the metal. Thus

$$\eta = a - b \log i \quad . \quad . \quad . \quad . \quad (3)$$

(a and b are constants and i is the current density). This equation was established empirically by Tafel²⁸ whose name it bears. At very low c.d.s, the overpotential becomes asymptotic to the $\eta/\log i$ axis.³¹⁻³⁵ At high c.d.s Azzam and Bockris³⁶ have extended the applicability of (3) up to c.d.s greater than

²⁴ Baars, *Sitzungsber. Ges. Beford. Naturwiss.*, Marburg, **63**, 213, 1928.

²⁵ Ershler, *Faraday Soc. Discussion*, **1**, 269, 1947.

²⁶ Armstrong and Butler, **29**, 427, 1933.

²⁷ Bowden, *Trans. Faraday Soc.*, **27**, 505, 1931; Hillson and Rideal, *Proc. Roy. Soc.*, **199**, 295, 1949.

²⁸ Tafel, *Z. physikal. Chem.*, **50A**, 641, 1905.

²⁹ Bonhoeffer, *ibid.*, **113**, 199, 1924.

³⁰ Bockris, *Trans. Faraday Soc.*, **43**, 417, 1947.

³¹ Wirtz, *Z. Elektrochem.*, **44**, 303, 1938.

³² Volmer and Wick, *Z. physikal. Chem.*, **172**, 429, 1935.

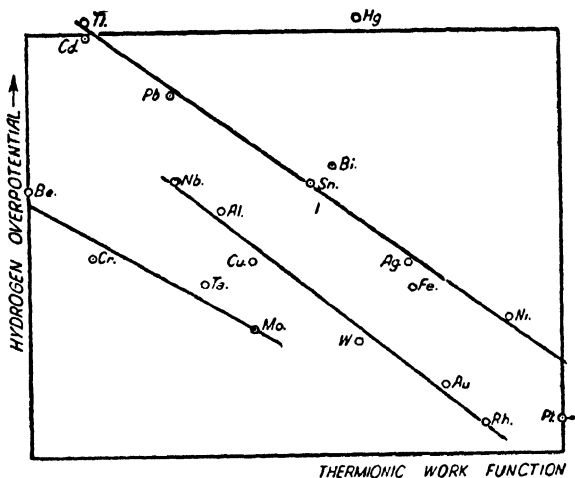
³³ Bowden and Grew, *Faraday Soc. Discussion*, **1**, 86, 1947.

³⁴ Legran and Lewina, *Acta Physicochim.*, **12**, 243, 1940; *J. Phys. Chem. Russ.*, **14**, 211, 1940.

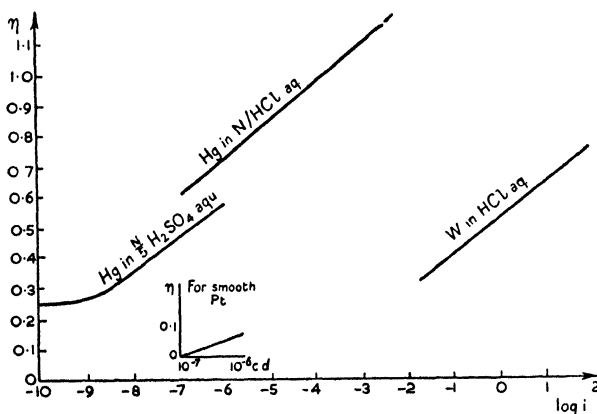
³⁵ Conway, *Thesis*, London, 1949.

³⁶ Azzam and Bockris, *Nature*, **165**, 403, 1950.

120 amps./sq. cm. In highly purified solution there is for a number of metals a range of c.d.s in which $b = 0.09 - 0.13$ at room temperatures. Extrapolation of the linear section of (3) gives



VII 3.



VII 4.

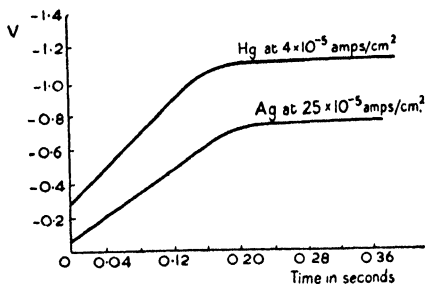
at $\eta = 0$, $i = i_0$, which is the current density at which the cathodic and anodic currents (see below) are equal, and provides a standard state at which the velocities of the reaction $2H^+ + 2e \rightarrow H_2$ on

various metals can be compared. Values of i_0 , together with those of the important but neglected heat of activation,¹⁸ are given in Table I.

Confusion was formerly caused by *variations of overpotential with time* which were due to impurities in the solution. There is a negligible variation (after the initial charging current has passed) on metals of high overpotential (Hg, Pb, etc.) in properly purified solutions but an appreciable (small) one on metals of low overpotential (Ni, etc.).

During the first few fractions of a second of polarisation, the electrode potential is found to be proportional to the quantity of electricity passed^{24, 40} (Fig. 5). During *decay*, the cathode potential on Hg is proportional to $\log t$ the slope of the relation being b , but on Pt a more complicated behaviour is observed.²⁸

Overpotential on Hg is independent of pH in dilute acid solutions from pH 4 to pH 1;^{7, 40} at higher H^+ ion concentrations, it decreases.^{44, 53} On Ag cathodes there is also an initial independence of pH in dilute solutions but the decrease with decreasing pH begins at a higher pH than with Hg.³⁵ More complicated effects are



V = potential against sat. calomel electrode.

VII 5.

³⁷ Kenyon, Diss., Cambridge, 1937.

³⁸ Agar and Llopis, *Anal. Fis. Quim.*, **43**, 427, 1947.

³⁹ Lukowzew, Lewina and Frumkin, *Acta Physicochim.*, **11**, 21, 1939.

⁴⁰ Bowden and Rideal, *Proc. Roy. Soc.*, **120A**, 59, 1928.

⁴¹ Bowden, *ibid.*, **126A**, 107, 1929.

⁴² Bowden and O'Connor, *ibid.*, **128A**, 318, 1930.

⁴³ Kaminsky, unpublished.

⁴⁴ Jofa and Stepanova, *J. Phys. Chem. Russ.*, **19**, 125, 1945.

⁴⁵ Knorr and Schwarz, *Z. physikal. Chem.*, **176**, 161, 1937.

⁴⁶ Erdey, Gruz and Wick, *ibid.*, **162A**, 53, 1932.

⁴⁷ Kabanov and Jofa, *Acta Physicochim.*, **10**, 616, 1939.

⁴⁸ Wirtz, *Z. physikal. Chem.*, **36B**, 435, 1937.

⁴⁹ Bockris and Wetterholm, unpublished.

⁵⁰ Bockris and Parsons, *Trans. Faraday Soc.*, **45**, 916, 1950.

⁵¹ Bockris and Conway, *ibid.*, **45**, 989, 1949.

⁵² Borrisowa and Proskurnin, *Acta Physicochim. U.R.S.S.*, **12**, 371, 1940.

⁵³ Bethune and Kimball, see ref. 2.

TABLE I.—HEAT OF ACTIVATION (ΔH^*) AND EXCHANGE CURRENT (i_0) FOR THE REACTION $2H^+ + 2e \rightarrow H_2$ AT VARIOUS CATHODE MATERIALS

I. Relatively reliable values

Electrode Material	Solution	α	i_0 amp. sq. cm.	ΔH^* kcal. grammol	Remarks	Ref.
Hg	0.20N H_2SO_4	0.52	$6 \cdot 10^{-12}$	18.0	25°	40
	0.25N H_2SO_4	0.50	$6.6 \cdot 10^{-13}$	20.7	20°	3
	1.0N H_2SO_4	0.50	$4.9 \cdot 10^{-13}$	—	20°	55
	0.2N D_2SO_4	0.52	$8 \cdot 10^{-13}$	20.9	25°	37
	0.1N HCl	0.49	$1.7 \cdot 10^{-12}$	—	22°	7
	0.1N HCl	0.48	$9 \cdot 10^{-13}$	—	20°	55
	0.1N HCl	0.50	$9 \cdot 10^{-13}$	21.1	20°	4
				± 0.3		
	1.0N HCl	0.49	$1.7 \cdot 10^{-12}$	21.7	20°	44*
				± 0.3		
	3N HCl	0.43	$8.0 \cdot 10^{-11}$	19.7	20°	44*
				± 0.4		
	5N HCl	0.46	$9.0 \cdot 10^{-11}$	19.7	20°	44*
				± 0.2		
	7N HCl	0.54	$2.7 \cdot 10^{-11}$	16.7	20°	44*
				± 0.6		
	10N HCl	0.61	$1.6 \cdot 10^{-11}$	17.5	20°	44*
				± 0.2		
	0.1N HCl in 36% methanolic solution	0.56	$5.1 \cdot 10^{-13}$	23.6	20°	4
				± 0.5		
Pb	0.1N HCl in 100% methanolic solution	0.56	10^{-11}	19.7	20°	4
				± 0.2		
	0.35N HCl in 100% methanolic solution	0.4	10^{-11}	—	—	33
		0.5				
	0.01-0.5N HCl in 100% methanolic solution	0.5	$2 \cdot 10^{-11}$	—	—	61
Pb	1.0N HCl	0.48	$2.0 \cdot 10^{-13}$	—	20° Surface scraped with knife—reduced by electrolytic evolution of H_2 before commencing experiment	47
Ga	0.2N H_2SO_4	0.5	$1.6 \cdot 10^{-7}$	15.2	87°, liquid state	40
Wood's alloy	0.2N H_2SO_4	0.4	$1 \cdot 10^{-8}$	16.4	87°, liquid state	40

Footnotes for Table I see p. 166.

TABLE I (cont.)

Electrode Material	Solution	α	i_0 amp. sq. cm.	$\frac{\Delta H^*}{\text{grammol.}}$	Remarks	Ref.
Ni	0.1N HCl	0.59	$2.0 \cdot 10^{-6}$	—	20°	39
	0.1N HCl	0.59	$1.2 \cdot 10^{-6}$	—	20° Electrode annealed H ₂ c. 400°	34
	0.1N HCl	0.59	$1.0 \cdot 10^{-6}$	—	20°	141
	0.1N HCl	0.59	$1.0 \cdot 10^{-6}$	6.9 ± 1.3	20° Electrode annealed H ₂ at c. 800° C. in contact hysil glass	85
Ag	NH ₄ Cl in liq. NH ₃	0.49	$7.3 \cdot 10^{-9}$	7.0	—50°	64*†
	0.001-0.01N HCl	0.47	$4 \cdot 10^{-7}$	—	20°	35
	0.1N HCl	0.49	$2.5 \cdot 10^{-6}$	—	20°	35
	1.0N HCl	0.46	$2.0 \cdot 10^{-4}$	—	Electrode annealed H ₂ at c. 700°; in contact hysil glass	35
Pt	5.0N HCl	0.49	$6.3 \cdot 10^{-6}$	—	20°	35
	7.0N HCl	0.53	$2 \cdot 10^{-7}$	—	20°	
	1.0N HCl	0.41	$1.6 \cdot 10^{-3}$	—	20° Extrapolated from values at c.d. > 1 amp.; over c.d. range 10^{-4} – 10^{-2} increases; electrode smooth acid etched and heated to 600° in H ₂ in contact with hysil glass	36

II. Very approximate values

Tl	1N HCl	0.7	10^{-16}	—	20° Surface scraped sharp knife	30
Bi	1N HCl	0.4	10^{-8}	—	20°	19
	1N HCl	0.6	10^{-7}	—	18° Surface scraped sharp knife	18
Nb	1N HCl	0.6	10^{-11}	—	20°	30
Be	1N HCl	0.5	10^{-9}	—	20° Dissolved at c.d. 10^{-3} amp./sq. cm.	30
Cu	1N HCl	0.5	10^{-8}	—	20° Surface annealed in H ₂ sealed to soda glass	30
W	5N HCl	0.6	10^{-6}	—	20° Surface annealed in H ₂ ; i_0 extrapolated measurements above 10^{-3} amp./sq. cm.; sealed to hysil glass	36
Au	1N HCl	0.7	10^{-5}	—	20° Plated	19
	1N HCl	1.3	10^{-6}	—	18° Plated	18

observed on Ni^{57, 85} and Pt.⁵⁸ *Salt additions* cause decrease of α , for Hg cathodes, though b is unaffected. On cathodes of lower overpotential the salt effects are different and more complicated.^{54, 55, 56}

In non-aqueous solutions^{18, 50, 59, 60, 61, 62}, there is a decrease of overpotential on Hg cathodes in N/10 methyl alcoholic HCl solutions compared with aqueous solutions of about 0.1 volt. The solvent effect depends markedly on the cathode material, particularly in mixed solvents.

Frumkin and Aladjalowa⁶⁶ examined the overpotential which "goes through" a Pd film and Bowden²⁷ found that hydrogen overpotential on Hg is reduced by *ultra-violet light*, the effect being dependent on the cathode potential (see also Hillson and Rideal²⁷).

General Relations for a Cathode Evolving Hydrogen.

(i) *Definitions of currents at cathode and anode.* Suppose $\vec{v}$ is the velocity of the reaction: $2\text{H}^+ + 2e \rightarrow \text{H}_2$;

Footnotes on Table I

(i) Note that knowing α and i_0 , the overpotential at any given c.d. can be calculated by means of the equation

$$\eta = 2.303 \frac{RT}{\alpha F} \log \frac{i_0}{i}$$

provided of course that α is constant.

(ii) Selection and division of the data in the above table is based upon a study of the relevant determinations. Particular importance was attached to the method of purifying the solution. Some of the values recorded in the similar table in (1) must now be discarded as they indicate that the electrode surface was poisoned.

* Calculated from this reference.

† Values in methanolic and ethanolic solutions are, however, little changed from those in water.⁵⁹

⁵⁴ Lewina and Sarinsky, *Acta Physicochim.*, **7**, 485, 1937.

⁵⁵ Jofa, Kabanov, Chistyakov and Kuchinski, *ibid.*, **10**, 317, 1939.

⁵⁶ Jofa, quoted by Frumkin, ref. 57.

⁵⁷ Jofa and Frumkin, *Acta Physicochim.*, **118**, 183, 1943.

⁵⁸ Dolin and Ershler, quoted by Frumkin, ref. 97.

⁵⁹ Bockris, *Faraday Soc. Discussion*, **1**, 95, 1947.

⁶⁰ Bockris and Ignatowitz, *Trans. Faraday Soc.*, **44**, 519, 1948.

⁶¹ Lewina and Silberfarb, *Acta Physicochim.*, **4**, 278, 1936.

⁶² Novoselski, *J. phys. Chem. Russ.*, **11**, 369, 1938.

⁶³ Eyring, Glasstone and Laidler, *J. Chem. Phys.*, **7**, 1053, 1939.

* Pleskov⁶⁴ also measured the overpotential in liquid ammonia solutions of NH_4Cl . The results were, however, largely vitiated by amalgam formation.

⁶⁴ Pleskov, *Acta Physicochim.*, **11**, 305, 1939.

⁶⁵ Parsons and Bockris, *Trans. Faraday Soc.*, 1951.

⁶⁶ Frumkin and Aladjalowa, *Acta Physicochim.*, **19**, 1, 1944.

and $\overleftarrow{v}$ that of its reverse. Then the *net cathodic current* will be

$$i_o = F(\overrightarrow{v} - \overleftarrow{v}) = \overrightarrow{i} - \overleftarrow{i} \quad . \quad . \quad . \quad (4)$$

where $\overrightarrow{i}$ and $\overleftarrow{i}$ are the rates of transfer of charge at the electrode in the two directions. At an electrode at which equilibrium is established, $i_o = 0$ and therefore

$$\overrightarrow{i} = \overleftarrow{i} = i_o \quad . \quad . \quad . \quad . \quad (5)$$

which may be called the *exchange current*.

(ii) *The Tafel Equation.* For the reaction $2\text{H}^+ + 2e \rightarrow \text{H}_2$, let it be assumed, for conditions under which $\overrightarrow{v} \gg \overleftarrow{v}$, (1) that the velocity of the rate determining stage is controlled by a process which can be undergone only by particles having more than some minimum (activation) energy and that such particles are Maxwellianly distributed; and (2) that the energy of activation of the reaction is affected by the electric field of the cathode by an amount proportional to some part ($E - X$) of the metal-solution p.d., E , where X may depend on the condition of the electrode surface, or the properties of the solution, etc.

Let the proportionality factor for this effect of the cathode field be α .

Hence,

$$i = Ae^{-\frac{U + \alpha(E - X)F}{RT}} \quad . \quad . \quad . \quad . \quad (6)$$

where U is the "thermal part" of the energy of activation of the reaction and A is a collision factor characteristic of the mechanism of the reaction; A may depend on the concentration of some entities in the solution near the electrode and/or on the electrode surface.

$$E = K + X - \frac{RT}{\alpha F} \ln i \quad . \quad . \quad . \quad . \quad (7)$$

where K is a constant. But $\eta = E - E_r$, where E_r is the potential of a reversible hydrogen electrode under the same conditions, except for flow of current, as those for the irreversible electrode.

Hence,

$$\eta = \left(K + X - \frac{RT}{F} \ln a_{\text{H}^+} \right) - \frac{RT}{\alpha F} \ln i \quad . \quad . \quad . \quad . \quad (8)$$

Or

$$\eta = a - b \log_{10} i \quad . \quad . \quad . \quad . \quad (9)$$

where a is a term dependent in the general case on $p\text{H}$;

and

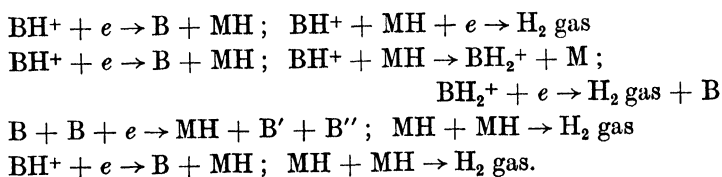
$$b = 2.303 \frac{RT}{\alpha F}.$$

Hence, assuming only a Maxwellian distribution of the particles governing the slow stage of the reaction⁶⁷ and an effect on the energy of activation proportional to some part of the cathode potential, hydrogen overpotential is found to be logarithmically related to current density. It is stressed that no particular mechanism of overpotential is assumed in this deduction.

(iii) *Specific theories of the slow stage in reactions at the cathode.* The main processes occurring at a cathode during the electrolytic evolution of hydrogen, involve (i) the transport of the solvated ion BH^+ to a position in the double layer at the electrode-solution interface, where it can be regarded as adsorbed; (ii) neutralisation of the proton, either by (a) electron transfer to the proton or (b) proton transfer to the electron-donating surface of the metal; (iii) desolvation of the proton; (iv) adsorption of hydrogen atoms produced in stage (ii) on the cathode surface; (v) desorption of the hydrogen atoms by (a) catalytic combination or (b) combination with a proton and an electron to form hydrogen molecules.

The above processes at the cathode can be divided into two parts: (I) the processes (ii), (iii) and (iv); and (II) the process (v). Processes (ii), (iii) and (iv) constitute the discharge of hydrogen ions, namely the production of adsorbed hydrogen atoms from solvated protons or solvent molecules; process (v) constitutes the combination of hydrogen atoms and/or ions to form molecules.

If the solvent molecule with which the hydrogen ion is solvated is represented by B and the cathode material by M, these reaction paths can be represented approximately as follows:



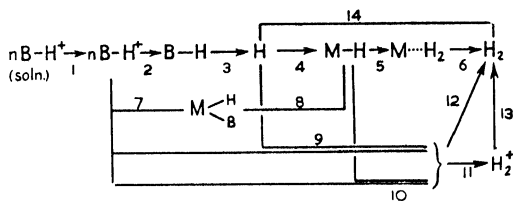
These reactions are depicted diagrammatically in Fig. 6. Various stages in these reaction paths have been assumed to be rate determining, which assumptions give rise to the various theories of

⁶⁷ Adam, *Physics and Chemistry of Surfaces*, 3rd ed., Oxford, 1941.

hydrogen overpotential. Those of modern interest are set out below :

Original authors	Postulated slow reaction	Name of mechanism
A: Main theories		
Smits ⁶⁸	$\text{BH}^+ + e \rightarrow \text{B} + \text{MH}$	Slow discharge
Horiuti ⁶⁹	$\text{BH}_2^+ + e \rightarrow \text{B} + \text{H}_2$	Molecular hydrogen ion
Eyring ⁶⁸	$\text{B} + \text{B} + e \rightarrow \text{MH} + \text{B}' + \text{B}''$	Prototropic transfer
Tafel ²⁸	$\text{MH} + \text{MH} \rightarrow \text{H}_2 + 2\text{M}$	Catalytic
Horiuti ⁷⁰	$\text{BH}^+ + \text{MH} + e \rightarrow \text{H}_2 \text{ gas} + \text{B} + \text{M}$	Electrochemical
B: Dual theories		
Kobosew ⁷¹	$\text{MH} + \text{MH} \rightarrow \text{H}_2 \text{ gas} + 2\text{M}$	Catalytic
	$\text{BH}^+ + \text{MH} + e \rightarrow \text{B} + \text{H}_2 \text{ gas} + \text{M}$	Electrochemical
Frumkin ⁷²	$\text{BH}^+ + e \rightarrow \text{B} + \text{MH}$	Slow discharge
	$\text{BH}^+ + \text{MH} + e \rightarrow \text{H}_2 \text{ gas} + \text{B} + \text{M}$	Electrochemical

For a review of older theories see ⁷³. The above equations are incomplete expressions of the theories and do not indicate the detailed mechanism of reaction.



VII 6.

1. Transport to electrode.
2. Neutralisation in the double layer.
3. Desolvation of the neutral complex.
4. Adsorption of the neutral atom.
5. Reaction of two adsorbed atoms.
6. Desorption of the hydrogen molecule.
7. Transfer of proton to adsorbed solvent molecule and neutralisation.
8. MHB reacts as MH.
9. Solvated proton or solvent molecule reacts with a free atom.
10. Reaction of a solvated proton or solvent molecule with an adsorbed H atom.
11. Formation of a hydrogen molecule ion.
12. Formation of a neutral molecule.
13. Neutralisation.
14. Direct combination.

⁶⁸ Smits, *Z. Elektrochem.*, **30**, 214, 1924.

⁶⁹ Hirota and Horiuti, *Bull. Chem. Soc. Japan*, **13**, 228, 1938.

⁷⁰ Horiuti, Okamoto and Hirota, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **29**, 223, 1936.

⁷¹ Kobosew and Nekrassow, *Z. Elektrochem.*, **30**, 529, 1930.

⁷² Frumkin, *J. Phys. Chem. Russ.*, **14**, 886, 1940.

⁷³ Bennet and Thompson, *J. Phys. Chem.*, **20**, 216, 1916.

It follows from the above that theories of hydrogen overpotential can be divided into two ill-defined groups, according to whether the rate determining process is the discharge of hydrogen ions or combination of entities on the electrode surface.

The principal modern contributions to the slow discharge theory can be divided into four sub-groups.

1. *General slow discharge theories* (Frumkin ^{57, 74, 75, 134}). In the work of this author, the discharge reaction $\text{BH}^+ + e \rightarrow \text{MH}$ is treated as a single process without detailed consideration of processes (ii)a, (ii)b, (iii) or (iv) of the above. Frumkin states ⁷⁴ that his version of the slow discharge theories does not distinguish between (ii)a or (ii)b.

This theory was first developed quantitatively by Volmer and Erdey-Gruz,⁸⁶ but these authors' version was incorrect, because it leads to the conclusion that in pure acid solution the overpotential changes by 0.058 volt for every tenfold change in the hydrogen-ion concentration. Frumkin ⁷⁴ avoided this difficulty by taking into account the difference in hydrogen-ion concentration in the bulk of the solution and that in the electrical double layer. On certain assumptions it can then be shown that change of pH has no effect on the overpotential.

2. *The (energy level) slow discharge theory* (Polanyi,⁷⁶ Butler ⁷⁷). The discharge reaction is considered without reference to a detailed mechanism but conditions for discharge are worked out on a potential energy diagram basis in terms of the properties of proton, solvent and metal.

3. *Molecular hydrogen ion* (Horiuti ⁶⁹). According to this mechanism, the rate controlling process is the neutralisation of the H_2^+ (or BH_2^+) ion formed by combination of BH^+ with MH .

4. *Prototropic transfer* (Eyring ⁶³). In this theory the rate determining step is the *transfer* of a proton from a *solvent molecule* in solution to a solvent molecule attached to the cathode surface. It is clear that this mechanism involves the discharge of hydrogen ions, as defined above, and is hence grouped under the heading "slow discharge".

⁷⁴ Frumkin, *Z. Physikal Chem.*, **164**, 121, 1933.

⁷⁵ Frumkin, *Acta Physicochim.*, **7**, 474, 1937.

⁷⁶ Horiuti and Polanyi, *ibid.*, **2**, 505, 1935.

⁷⁷ Butler, *Proc. Roy. Soc.*, **157A**, 423, 1936.

The combination theories are divisible into two groups, in each of which there are treatments which differ only in detail.

1. *Catalytic combination* (Tafel,⁷⁸ Kobosew,⁷¹ Horiuti,⁷⁸ Hickling⁷⁹). The rate determining step is the reaction between adsorbed hydrogen atoms.

2. *Electrochemical mechanism* (Horiuti,⁷⁰ Frumkin⁷⁵). The rate determining reaction is that between a solvated proton (BH^+), an adsorbed hydrogen atom and an electron.

The concept of dual theories originated with Kobosew and Nekrassow.⁷¹ A dual theory may be defined as one in which the rate of the overall reaction $2\text{BH}^+ + 2e \rightarrow \text{H}_2$ (gas) is controlled by two processes having specific rates of the same order and occurring simultaneously on the electrode surface.

In former times attention was concentrated on the two slow stages :



as the rival slow stages for a general theory of overpotential. It was first stressed by Butler,⁸⁰ however, that probably no single mechanism of overpotential is sufficient to explain the varying behaviour of different metals. This view has led recently to a more general formulation of the mechanism of hydrogen overpotential,⁸¹ in which equations for the rate of reaction are formulated so as to take into account all probable rate determining reactions at the cathode, assuming these to have a velocity of the same order (see Fig. 6). This is clearly the most general way to treat the electrode reactions.

The Heat of Activation of the Electrolytic Evolution of Hydrogen.

The temperature coefficient of the rate determining reaction at the electrode has been measured in two ways (cf. Agar¹⁶).

1. The overpotential η at a temperature T is measured against a reversible hydrogen electrode under the same conditions.

⁷⁸ Horiuti and Okomoto, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **28**, 231, 1936.

⁷⁹ Hickling and Salt, *Trans. Faraday Soc.*, **38**, 474, 1942.

⁸⁰ Butler, ref. 77.

⁸¹ Lukowzew, *J. Phys. Chem. Russ.*, **21**, 589, 1947.

2. The cathode potential E at any temperature T is measured against a standard half cell at a fixed temperature T_0 .

These two experimental methods lead to two different heats of activation, U_I and U_{II} , where,

$$\left(\frac{\partial}{\partial T} \ln i\right)_\eta = \frac{U_I}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\left(\frac{\partial}{\partial T} \ln i\right)_E = \frac{U_{II}}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Now

$$\frac{\partial \ln i}{\partial T} = \left(\frac{\partial}{\partial T} \ln i\right)_\eta + \left(\frac{\partial}{\partial \eta} \ln i\right)_T \frac{\partial \eta}{\partial T}, \quad . \quad . \quad (14)$$

so that

$$\left(\frac{\partial \eta}{\partial T}\right) = \frac{U_I/RT^2}{\left(\frac{\partial}{\partial \eta} \ln i\right)_T} \quad . \quad . \quad . \quad . \quad (15)$$

From the Tafel equation,

$$\left(\frac{\partial}{\partial \eta} \ln i\right)_T = -\frac{\alpha F}{RT} \quad . \quad . \quad . \quad . \quad (16)$$

$$\left(\frac{\partial \eta}{\partial T}\right)_i = \frac{U_I}{\alpha F T}, \quad . \quad . \quad . \quad . \quad (17)$$

and similarly,

$$\left(\frac{\partial E}{\partial T}\right)_i = \frac{U_{II}}{\alpha F T} \quad . \quad . \quad . \quad . \quad (18)$$

If E_0 is the potential between the reversible hydrogen electrode at T and the standard half cell at T_0 ,

$$\eta = E - E_r$$

and

$$\left(\frac{\partial \eta}{\partial T}\right)_i = \left(\frac{\partial E}{\partial T}\right)_i - \left(\frac{\partial E_r}{\partial T}\right) \quad . \quad . \quad . \quad (19)$$

Therefore,
$$U_I - U_{II} = \alpha F T \frac{\partial E_0}{\partial T}. \quad . \quad . \quad . \quad (20)$$

Now $\frac{\partial}{\partial T} E_0$ is the temperature coefficient of the hydrogen electrode together with the thermo-junction potential between the two solutions at different temperatures (see above). Neither of these quantities is known⁸² so that the relation between the two heats of

⁸² Gilbert, *Faraday Soc. Discussion*, 1, 320, 1947.

activation is uncertain. It follows that the true heat of activation is given by equation (12) above.

If α is constant with temperature the heat of activation at this reversible potential is related to that at an overpotential η by

$$[\Delta H^*]_I = U_I - \alpha \eta F \quad . \quad . \quad . \quad (21)$$

$$[\Delta H^*]_I = \alpha F \left(T \frac{\partial \eta}{\partial T} - \eta \right) \quad . \quad . \quad . \quad (22)$$

Usually there is a small variation of α with temperature and a mean of results over a certain temperature range is then calculated.^{83, 84, 85}

The Reaction Mechanism effective at a given Electrode.

Attempts have been made to distinguish between the various theories of hydrogen overpotential by invoking general qualitative criteria, such as the parallelism between catalytic power of various metals for the combination of hydrogen and the overpotential at a given c.d. on these metals; or the linear increase of overpotential with quantity of electricity passed which occurs with some cathode materials and which has been taken to indicate the validity of a simple slow discharge view. Nearly all the main theories are *qualitatively* capable of interpreting these general trends and consequently more exact and more comprehensive criteria are necessary for distinction between various possible slow reactions.

A single cathode material is therefore best studied by a number of methods and comparison of the observed phenomena with critical criteria such as those given below (Table II) enables mechanisms not applicable to the given cathode to be eliminated.

Catalytic (or Atomic Hydrogen) Theory. The catalytic mechanism has been treated in two fundamentally different ways. It is possible to assume the applicability of the classical thermodynamic relations between electrode potential and concentration of "electromotively" active material, and, by correlating the concentration of the latter with current, obtain a relation between η and c.d. Or, purely kinetic methods may be used with the assumption of some effect of the electrode potential on the reaction rate. These two methods can be termed respectively the "quasi thermodynamic" and "kinetic" catalytic theories.

⁸³ Parsons, *Thesis*, London, 1948.

⁸⁴ Jofa and Stepanova. See ref. 44.

⁸⁵ Potter, *Thesis*, London, 1950.

TABLE II. EXPERIMENTAL CRITERIA FOR THE MECHANISMS OF HYDROGEN OVERPOTENTIAL

Criterion	General Slow Discharge and Energy Level Slow Discharge	Molecular Hydrogen Ion	Prototropic Transfer	Catalytic	Electrochemical
α	$0 < \alpha < 1$	$0 < \alpha < 1$	$\frac{1}{2}$	$0 < \alpha < 2$	$0 < \alpha < 3/2$
λ^1	1	2	1	2	2
Limiting current ²	Absent	Absent	Absent	Present	Absent
pH effect on B^3	B constant for a given metal	B constant for a given metal	B constant for all metals	B varies	B constant for a given metal
pH effect on η	η const. in pure dil. acids. Decreases with decreasing pH if salts present and in conc. acid solutions	Similar to slow discharge	Const. in pure acid solutions; in presence of salts effects opposite to slow discharge prediction	Const. Possibly small (undetermined) change if M-H polar	Similar to slow discharge
Solvent effect, compared with aqueous solutions	Lowered in alcoholic solution and for high overpotential cathodes; little effect on low overpotential cathodes	Similar to slow discharge	Small increase in hydroxylic solvents; large effect in non-hydroxylic solvents	Depends on size and polarity of solvent molecule; and on adsorbing properties of electrode	Complex
Diffusion through films	Absent	Absent	Possible-improbable	Possible	Possible
Decrease of molec. H_2 pressure	E Unaffected	E Unaffected	η Unaffected	E Unaffected	E Unaffected
Variation of capacity with frequency	Unchanged	Varies	Varies	Varies	Varies

¹ This represents the expression $\frac{RT}{F i_0} \left(\frac{\partial i_0}{\partial \eta} \right)_{\eta=0}$ and can be shown to mean the number of charges per elementary process crossing the energy barrier at the electrode.

² *Limiting current.* This means the limiting current which would be expected to accompany some of the mechanisms postulated in Table II; it is unconnected with concentration overpotential.

Footnotes continued on p. 175.

Tafel²⁸ considered the slow combination between two hydrogen atoms on the electrode surface to govern their surface concentration. The atomic hydrogen was assumed to be electromotively active, i.e. the electrode potential became more negative with increasing concentration of adsorbed atomic hydrogen. An equation analogous to that of Nernst for the relation between reversible potential and ionic activity was assumed to apply, so that if n and n_r are the number of hydrogen atoms/sq. cm. on an electrode across which passes a current density i and on the reversible hydrogen electrode, respectively, then, neglecting the anodic current, it follows that:

$$E - E_r = \eta = \frac{RT}{F} \log_e \frac{1}{n}. \quad (23)$$

But $i = kn^2$, if the reaction $MH + MH \rightarrow H_2$ is of the second order.*

$$\text{Hence} \quad \eta = a - \frac{RT}{2F} \log_e i \quad (24)$$

where a is a constant.

The theory has an obvious interpretation of the relation between the electrode material and overpotential, namely that the overpotential is low for metals of good catalytic power and high for poor catalysts.

Two serious difficulties are thus encountered in Tafel's theory: (i) the b value of the Tafel equation, $(2.30)RT/2F$, is one found for few metals, (ii) there is no experimental foundation for applying the thermodynamic equation for electrode potentials to *adsorbed hydrogen*, although it is known to be valid with respect to gaseous molecular hydrogen at reversible electrodes. To avoid the first

* B. This represents an expression arising in the prototropic transfer theory of Eyring, Glasstone and Laidler, i.e.

$$B = C \frac{kT}{h} \frac{F}{N} \frac{\Delta S^*}{eR},$$

where C is the concentration of the entity involved in the rate determining process, and ΔS^* the entropy change in the formation of the activated complex in this reaction.

* The order of the reaction should be 2 or 1 according to whether the slow combination is $MH + MH \rightarrow H_2$ or $MH + H \rightarrow H_2$ respectively.

difficulty, it has been suggested^{79, 142} that the concentration of the hydrogen atoms outside the electrode surface should be connected to the concentration of those adsorbed on it by an adsorption isotherm. This gives $b = 2.30mRT/2F$ where m is about 1.6, so that a large range of experimentally observed values of b are satisfactorily interpreted. (If m be taken as 1.10, which is reasonable at an electrified interface,¹⁴⁴ $b = 0.03-0.30$ approximately, and these values cover those experimentally observed in pure and poisoned solutions.)

The use of equations which are fundamentally inapplicable to irreversible phenomena is avoided in the comprehensive statistical treatment of the catalytic mechanism by Okamoto and Horiuti,⁷⁸ from which quantitative calculations, which give results of the right order for nickel cathodes at very low c.d.s, have been made. Assuming that the number of chemisorbed hydrogen atoms on the electrode surface is small the result for b is that of Tafel, namely $RT/2F$. A limiting current corresponding to saturation of the surface with hydrogen atoms is predicted. If the interaction between the hydrogen atoms is taken into account, α becomes approximately 0.7 (but see ref. ⁸⁸).

The catalytic theory can be brought into agreement with the effect of the solvent⁶⁰ if it is assumed that molecules of solvent are adsorbed on the electrode surface,⁶³ and affect the velocity of the reaction thereon by their space consuming properties. Observations on the effect of water and alcohol vapour on thermionic emission⁸⁹ indicate reversible but not chemical adsorption on Pt; on Hg, water vapour is found not to be adsorbed at all⁹⁰ (but see ref. ⁹¹). This evidence from vapour phase experiments does not lessen the *a priori* probability that there is an *electrostatic* attachment of solvent dipoles to the electrode surface. Electrocapillary data offer no conclusive information on this point,^{92, 93} which seems likely to be decided in favour of solvent adsorption.⁹

⁸⁶ Volmer and Erdey-Grúz, see ref. 46.

⁸⁷ Glasstone, *Electrochemistry of Solutions*, 438, 1945.

⁸⁸ Frumkin, *Acta Physiochim.*, **12**, 481, 1940.

⁸⁹ Schaaf, *Z. physikal. Chem.*, **268**, 412, 1934.

⁹⁰ Salditt, *ibid.*, **155A**, 321, 1931.

⁹² See ref. 83.

⁹¹ Law, *Thesis*, London, 1951.

⁹³ Frumkin, see ref. 88.

Theory of Hydrogen Overpotential on Mercury in Acid Solution

(i) *Introduction.* For the systems mercury in acid solutions over a considerable concentration range, $\alpha = \frac{1}{2}$ at 25° C.^{54, 84}; no adsorbed hydrogen can be detected on the surface;^{94, 143} there is evidence against the presence of a limiting current.³⁶ B remains constant with change of concentration.⁴⁹ Overpotential is constant with pH variation in dilute solutions but decreases with pH if salts are present;⁵⁴ the overpotential is decreased in alcoholic solutions;⁵⁰ change of hydrogen pressure does not affect the cathode potential;⁵⁰ the build up of overpotential is linear with the quantity of electricity passed;^{24, 40, 95} the slope of the cathode-potential/ $\log . t$ relation after interruption of the polarising current is b .²⁶ The capacity is independent of frequency over a wide frequency range.⁵² Perusal of the table of criteria for the various theories shows that the behaviour is consistent with the general slow discharge theory. This conclusion is supported by electrocapillary and capacity measurements over a wide range of potentials.⁹⁶

The general slow discharge has been applied by Frumkin and his co-workers to the overpotential phenomena on Hg.^{57, 97} In a more ambitious theory due to Gurney⁹⁸ an attempt was made to express the discharge of hydrogen in terms of the energy levels of the proton solvated by the solvent and the electrons in the metal of the cathode. This theory was shown to lead to an energy of activation which was impossibly high,^{99, 100} owing to an incorrect energy of the hydration of the hydrogen ion assumed by Gurney and corrected later by Butler.⁷⁷ Gurney's theory also leads to an incorrect dependence of overpotential on the thermionic work function of the metals.⁹ (See also refs. 103, 104.)

⁹⁴ Fedotov, quoted by Frumkin, ref. 97.

⁹⁵ Barclay and Butler, *Trans. Faraday Soc.*, **36**, 128, 1940.

⁹⁶ Grahame, *Chem. Rev.*, **41**, 441, 1947.

⁹⁷ Frumkin, *Faraday Soc. Discussions*, **1**, 62, 1947.

⁹⁸ Gurney, *Proc. Roy. Soc.*, **134**, 137, 1932; Butler, *Electrocapillarity*, London, 147, 1940.

⁹⁹ Topley and Eyring, *Nature*, **133**, 292, 1934.

¹⁰⁰ Wagner, quoted by Wirtz, see ref. 31.

Let there be a large number of electronic energy levels in the metal which are filled with electrons up to the level of mean energy ϕ , where ϕ is the electronic work function of the metal. The energy required to remove an electron from the lowest energy level of a hydrogen atom is the ionisation potential, I . It is clear that the condition for a transfer of electrons from the metal to an adjacent hydrogen is $\phi < I$. In aqueous solution this condition for transfer must be replaced by a quantity including the solvation energy of the proton (L) and the repulsion energy R between neutral hydrogen atoms and water molecule. The condition for neutralisation is therefore

$$\phi < I - L - R. \quad . \quad . \quad . \quad (25)$$

Let the energy of interaction between the atoms of the metal surface and the hydrogen atoms be A , and the electrode be raised to a potential E with respect to the solution so that the electron energy levels of this metal will be depressed by an amount Ee . The condition for discharge therefore becomes

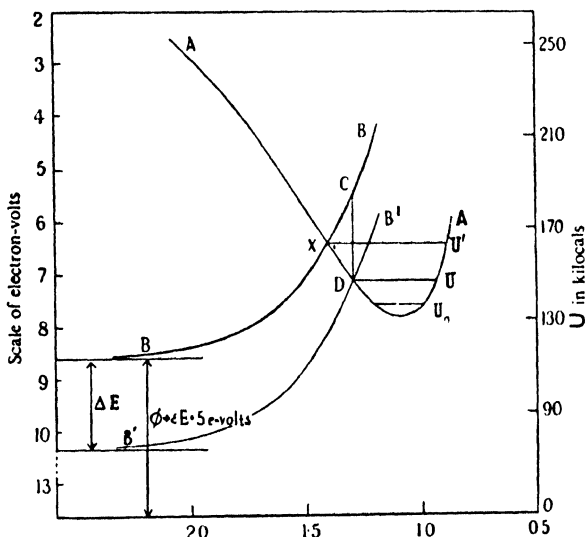
$$\phi + Ee + R - A < I - L. \quad . \quad . \quad (26)$$

In Fig. 7, let AA be the curve of $I - L$. Let BB be the curve of $U_1 + eE + R - A$, where U_1 is the energy of the electron level of the metal half occupied by electrons. Let B'B' be the corresponding curve of a lower level $U_1 - \Delta U_1$, whilst E is the same. The probability of finding an electron of this energy is $e^{-\frac{\Delta U_1}{kT}}$, if ΔU_1 is not too small. An electron in this level can neutralise an ion in the ionic level U_1 , which passes through the intersection point D. The probability of an ion having this energy is

$$e^{-\frac{U_0 - U}{kT}}. \quad . \quad . \quad . \quad (27)$$

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 falls 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 U_0 and the intersection point X, having energy U' .

Multiplying the probability of an ion having the energy U , by



VII 7.—Discharge of proton in H_3O^+ . (Butler, *Proc. Roy. Soc.*, vol. 157, 1936.)

the probability of an electron having the same energy, and integrating between U_0 and U we obtain

$$i = \int_{U_0}^U e^{\frac{(U_0 - U)}{kT}} e^{-\frac{\Delta U}{kT}} \text{const. } dU \quad . \quad . \quad (28)$$

$$\text{and} \quad \Delta U_1 = CD = \gamma(U' - U) \quad . \quad . \quad . \quad (29)$$

where γ may be taken as a constant. Hence,

$$i = \int_{U_0}^U e^{(U_0 - U)/kT} e^{-\gamma(U' - U)/kT} \text{const. } dU \quad . \quad (30)$$

and we obtain

$$\log i = \text{const.} + (U_0 - U')/kT. \quad . \quad . \quad (31)$$

From this it follows that

$$-\frac{d}{dE} \log i = \frac{1}{kT} \frac{dU'}{dE} = \frac{e}{\gamma kT} \quad . \quad . \quad (32)$$

which is the experimental relation if $\gamma = 2$.

Butler divided metals into two groups with respect to their overpotentials, namely those for which no adsorption of H atoms takes place, and those for which adsorption occurs, as in Ni and Pt. By this means it is possible to give a theory of the reversible hydrogen electrode and to show that for a nickel cathode a reasonable estimate of the energy of activation (7-27 kilocal.) may be made.

The essential value of the Gurney-Butler treatment given above lies in the fact that it enables some measure of the energy of activation of proton discharge to be made in terms of the molecular properties of the substances taking part in this reaction. The value of the constant α is left undecided according to Butler's treatment, though shown to be of the right order. The rate equation for the reaction is not formulated, so that no calculation of the " a " factor of the Tafel equation is possible. The structure of the double layer is also ignored so that no treatment of the pH effect on overpotential is possible. Further, the adsorption energy of hydrogen atoms on the metal surface is only taken into account for metals of low overpotential, whereas the parallelism between overpotential and the work function of the metal makes it probable that it should be an important term for most metals.

Recently Parsons and Bockris⁶⁵ have used potential energy diagrams in a somewhat different way to that of the above theory. A calculation of the free energy of activation of the proton discharge reaction is made and then this value used in the theory of absolute reaction rates applied to the discharge reaction. The theory results in a quantitative calculation of the hydrogen overpotential on Hg in acid solutions. It is shown that, within the limits of the accuracy of the calculation, the calculated values of a and b are in agreement with the experimental ones. The essential steps in this theory can be described as follows.

(ii) *Calculation of energy along reaction co-ordinate.* If the initial state of the electrode reaction is taken as the partially desolvated hydroxonium ion adsorbed on the Hg surface and the final state as the hydrogen atom adsorbed on the electrode surface together with the water molecule from which the transition has

taken place, then the energy of the initial and final states can be shown to be respectively :

$$I - \phi - L + L'$$

and

$$R - A$$

where it is assumed that there is zero metal-solution p.d. at the electrode-solution interface. Here I is the ionisation energy of hydrogen ; ϕ the thermionic work function of the metal¹⁰¹ ; L the solvation energy of the proton ; and L' is the energy of transfer of an ion from the bulk to the electrode, involving the energy of desolvation together with the interactions with the image forces at the electrode. R is the interaction energy between a hydrogen atom and a water molecule and A the energy of adsorption of hydrogen atoms on the metal.

The curves drawn in Fig. 8 represent the potential energy of the initial and final states of the reaction as a function of distance of the proton from the electrode ; and the energy difference between the equilibrium positions of the initial state and the point of intersection between the energy-distance curves of the initial*and final state gives, therefore, the heat of activation for the process. (This assumes the identity of potential energy and heat content, which involves no important error at 25° C.) The position of the curve of the initial state is established by considering the equilibrium between hydrogen ions in solution and hydrogen gas, thus yielding a value for L of about 260 kilocal.¹⁰⁶ The value thus calculated for the heat of activation is then combined with the calculated entropy of activation to give the free energy of activation for the reaction.

(iii) *Formulation of the rate equation.* The rate constant of any chemical reaction occurring with a free energy of activation ΔG^*

¹⁰¹ Bockris, *Nature*, **159**, 539, 1947.

¹⁰² Bockris and Parsons, see ref. 4.

¹⁰³ Hulbert and Hirschfelder, *J. Chem. Physics*, **9**, 61, 1941.

¹⁰⁴ Essin and Kosheurev, *Acta Physicochim.*, **13**, 169, 1941.

¹⁰⁵ Grahame, *Chem. Rev.*, **41**, 441, 1947.

¹⁰⁶ Bernal and Fowler, *J. Chem. Phys.*, **1**, 515, 1933.

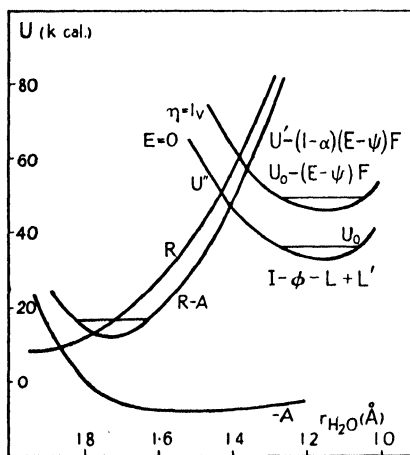
is given by the theory of absolute reaction rates (Eyring, Glasstone and Laidler ¹⁰⁷) by

$$K' = \tau \frac{kT}{h} e^{-\frac{\Delta G^*}{kT}} \quad (33)$$

where τ is a transmission coefficient and kT and h have their usual significance. In the deposition reaction ΔG^* may be obtained as described above and τ may be taken as unity.^{108, 109} Consequently the rate of discharge of protons at zero applied p.d. is

$$i = F(a_{H^+})_{v_1} \frac{kT}{h} e^{-\frac{\Delta G^*}{kT}} \quad (34)$$

where $(a_{H^+})_{v_1}$ is the surface activity of hydrogen ions in the double layer at zero electrode solution p.d.



VII 8.

If the electrode is raised to a potential E with respect to the solution the protons in the double layer are raised to a potential ψ_1 thus increasing the energy of the system by $\psi_1 F$ and the energy levels of the electrons in the metal are lowered, i.e. the work function is increased, by EF . Hence the net result is to lower the potential energy curve of the initial state by $(E - \psi_1)F$, i.e. U_0 becomes $U_0 - (E - \psi_1)F$.

If α is an expression for the relative slopes of the curves for the initial and final states then the intersection of the two curves is lowered by the fraction $(1 - \alpha)$, i.e., U' becomes $U' - (1 - \alpha)(E - \psi_1)F$.

¹⁰⁷ Eyring, Glasstone and Laidler, *J. Chem. Phys.*, **7**, 1053, 1939.

¹⁰⁸ Hirschfelder and Wigner, *ibid.*, **7**, 516, 1939.

¹⁰⁹ Eyring and Wynne-Jones, *ibid.*, **3**, 492, 1935.

¹¹⁰ Stern, *Z. Electrochemie*, **30**, 508, 1924.

Hence, if $\vec{i} \gg \overleftarrow{i}$ then,

$$i = F(a_{H^+})_{\psi_1} \frac{kT}{h} e^{-\frac{(U' - (1-\alpha)(E - \psi_1)F - (U_0 - (E - \psi_1)F))}{kT}} e^{\frac{\Delta S^*}{R}} \quad (35)$$

The surface activity $(a_{H^+})_{\psi_1}$ is related to the surface activity $(a_{H^+})_0$ in the absence of a double layer by

$$(a_{H^+})_{\psi_1} = (a_{H^+})_0 e^{-\psi_1 F/kT} \quad (36)$$

Hence,

$$E = -\frac{RT}{\alpha F} \ln i + \frac{RT}{\alpha F} \ln \left(\frac{FkT}{h} \right) + \frac{RT}{\alpha F} \ln (a_{H^+})_0 + \frac{\Delta G^*}{\alpha F} + \frac{(\alpha-1)}{\alpha} \psi_1 \quad (37)$$

$(a_{H^+})_0$ which is expressed in g. mol. cm.⁻², may be related to the more usual bulk concentration $(a_{H^+})_B$, by the relation

$$(a_{H^+})_B = \chi \cdot (a_{H^+})_0 \quad (38)$$

where χ may be defined as the thickness of the region containing only ions which are at a potential ψ_1 with respect to the solution.^{104, 105, 110} Thus it is numerically about twice the thickness of the double layer.

Subtracting the reversible potential of hydrogen and utilising the equation

$$\psi = \psi_0 + \frac{RT}{F} \ln (a_{H^+})_B \quad (39)$$

it follows that :

$$\begin{aligned} \eta = & -\frac{RT}{\alpha F} \ln i + \frac{RT}{\alpha F} \ln \left(\frac{FkT}{h} \right) \\ & + \frac{\Delta G^*}{\alpha F} + \frac{\alpha-1}{\alpha} \psi_0 - (E_r)_0 - \frac{RT}{\alpha F} \ln \chi. \end{aligned} \quad (40)$$

(iv) *The absolute calculation of overpotential.* The value of α obtained by calculation is 0.5 — 0.6 and this may be compared with the experimental value for Hg cathodes in aqueous solution, which is 0.5.^{33, 111, 4}

The calculated activation energy of the process can also be compared with the experimental value. Experimentally the measured quantity $RT^2 \frac{d}{dT} \ln i_0$ is the heat of activation of the

¹¹¹ Jofa, quoted by Frumkin, ref. 134.

reaction at the reversible potential since the activated state has the same volume as the initial state. The mean numerical value for the activation heat in these solutions is 19 kcal./g. ion⁴ at the electro-capillary maximum although over a range of 50° there is an increase in the measured quantity with temperature greater than the probable experimental error. The value of ΔH^* can be calculated directly from the curves of Fig. 8 and yields the value 14 kilocal.

The numerical results cited lead to the conclusion that the most probable rate determining step in the hydrogen evolution reaction for a mercury cathode is a proton transfer from a solvent sheath in the double layer to an adsorption position on the metal surface.

Mercury in Alkaline Solution.—Evidence on the mechanism of hydrogen overpotential of Hg in alkaline solution is less extensive.^{37, 38} Experiments by Bockris and Watson¹¹² on the salt effect and concentration effects have shown, however, that the rate determining reaction is that between an alkali metal atom and a water molecule.

Theory of Hydrogen Overpotential on Other Metals. Systematic experimental evidence under appropriate conditions concerning hydrogen overpotential on other metals is available only on smooth platinum.

The value of b at low c.d.s is about 0.03¹¹⁸ ($\alpha = 2$). The anodic charging curves obtained on closing the circuit²⁵ are not linear; formation of adsorbed layers of hydrogen has been established by means of these charging curves and from the results of measurements on the decay of overpotential and the capacity of the electrode changes with frequency.¹¹⁹ The effect of pH and salts is

¹¹² Bockris and Watson, *J. Chimie et Physique*, 1951.

¹¹³ Gatty and Spooner, *The Potential Behaviour of Dissolving Metals*, Oxford, 1938, Appendix III.

¹¹⁴ Herasymenko and Slendyk, *Z. physikal Chem.*, **149**, 123, 1930.

¹¹⁵ Bowden, *Trans. Faraday Soc.*, **31**, 505, 1933.

¹¹⁶ Jofa *et al.*, *Acta Physicochim.*, **12**, 231, 1940.

¹¹⁷ Jofa *et al.*, *J. Phys. Chem. Russ.*, **14**, 58, 1940.

¹¹⁸ Hammett, *Trans. Faraday Soc.*, **29**, 770, 1933.

¹¹⁹ Ershler, *Faraday Soc. Discussion*, **1**, 269, 1947.

complicated and differs markedly from the corresponding phenomena on Hg.¹²⁰ Investigation of the kinetics of the removal and formation of adsorbed hydrogen have been studied and it has been shown that in the region of the reversible potential the rate of the slow discharge process $H^+ + e \rightarrow H_{Ads}$ is 10-20 times greater than the rate of the overall reaction $2H^+ + 2e \rightarrow H_2$.

This evidence indicates that the slow neutralisation, hydrogen molecule ion, electrochemical and prototropic transfer processes are not applicable mechanisms for the hydrogen overpotential on platinum, and it is probable that in this case a slow combination mechanism is the rate controlling one. The possibility of such a mechanism is made more likely by the recently established transfer of overpotential through a thin foil of Pd, thus directly manifesting the hitherto only assumed electromotive activity of H atoms.⁶⁶ On Ni¹²¹ and on Ag electrodes,³⁵ evidence on pH and salt effects is also against a slow discharge mechanism.

Present State of Theory of Hydrogen Overpotential.

It appears to be established that upon metals of a high overpotential, such as Hg, Pb, etc., the mechanism in aqueous acid solution consists in the slow discharge of protons onto adsorption sites on the cathode surface. On metals of very low overpotential, such as platinum, the rate determining reaction appears to be the combination of hydrogen atoms, at least at low c.d.'s. On metals of intermediate overpotential, the strong adsorption of hydrogen atoms upon the metal surface, together with the fact that the value of b upon such metals is about 0.1, indicates the probability of the electrochemical mechanism. However, this cannot yet be regarded as established; knowledge of the value of λ would be of particular importance here.

Activation Overpotential of Oxygen.

(i) *Some experimental facts.* Early experiments on Pt¹²⁴ appeared to show marked similarities between hydrogen and

¹²⁰ Dolin and Ershler, quoted by Frumkin, ref. 97.

¹²¹ Lukowsew and Lewina, *J. Phys. Chem. Russ.*, **21**, 599, 1947.

¹²² Butler and Armstrong, *J. Chem. Soc.*, 743, 1934.

¹²³ Review: Klemenc, *Z. physikal Chem.*, **185**, 1, 1939.

¹²⁴ Bowden, *Proc. Roy. Soc.*, **126A**, 107, 1929.

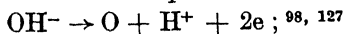
oxygen overpotential but this has not yet been confirmed by further work.^{125, 126} The coefficient α of the Tafel equation for Pt in H_2SO_4 is about 0.4-0.5.^{124, 127, 128} Bowden found that light *reduces* the oxygen overpotential on Pt as it does with hydrogen overpotential.

In aqueous acetic acid and aqueous dioxan solutions * containing H_2SO_4 , Bockris found that the oxygen overpotential on Pt is increased regularly with increasing concentration of non-aqueous component.¹²⁸

Measurements of oxygen overpotential at medium and high current densities by Hickling and Hill¹²⁹ on a variety of metals in alkaline solutions show few systematic trends, illustrating the complexity of the phenomena.

Butler,^{130, 131} Hickling,^{129, 132, 133} and their co-workers have carried out a detailed examination of the state of the surface of anodes during the electrodeposition of oxygen and this is discussed in a later chapter.

(ii) *Theory of oxygen overpotential.* Similar possibilities exist for oxygen overpotential as for hydrogen overpotential. The slow reactions which have been considered are: (i) combination of two oxygen atoms which are loosely held on a surface containing strongly held adsorbed oxygen; ¹³⁵ (ii) slow discharge of the "hydroxyl radical": this can be regarded as a hydration product of the oxygen ion, so that the equation can be written:



(iii) prototropic transfer from water molecules adsorbed on the surface of an electrode to those in solution.⁶³

¹²⁵ Cassel and Krumbein, *Z. physikal. Chem.*, **171**, 70, 1935.

¹²⁶ Garrison, *T. Amer. Electrochem. Soc.*, **65**, 273, 1934.

¹²⁷ Roiter and Jampolskaya, *Acta Physicochim.*, **7**, 247, 1937.

¹²⁸ Bockris, *Faraday Soc. Discussion*, **1**, 229, 1947.

¹²⁹ Hickling and Hill, *ibid.*, 236.

¹³⁰ Butler and Drever, *Trans. Faraday Soc.*, **32**, 427, 1936.

¹³¹ Pearson and Butler, *ibid.*, **34**, 1163, 1938.

¹³² Hickling, *ibid.*, **41**, 333, 1945.

¹³³ Hickling, *ibid.*, **42**, 518, 1946.

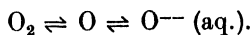
¹³⁴ Frumkin, *Acta Physicochim.*, **18**, 23, 1943.

¹³⁵ Foerster, *Z. physikal. Chem.*, **169**, 236, 1909.

* Experiments in anhydrous solution are impractical because of the difficulty of finding solvent which yields a sufficiently conducting solution and is not attacked by evolved oxygen.

The slow discharge mechanism has been worked out in some detail ;⁹⁸ at present there is as yet too little evidence to give great weight to any of these views. Mechanism (ii) seems improbable in view of the effect of addition of non-aqueous components to the solution which should have a lowering effect.¹²⁸ Particularly on those metals such as Cu, Fe, etc., which first dissolve before becoming passive and evolving oxygen, the course of the reaction is bound to be extremely complicated and not accounted for adequately by any single slow stage referred to above.

(iii) *Adsorption of oxygen and the reversible oxygen electrode.** The researches of Langmuir¹³⁶ on gas adsorption on metal filaments have 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 Villars¹³⁷ 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. 9. 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 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. A reversible oxygen electrode would depend on the realisation of the two equilibria



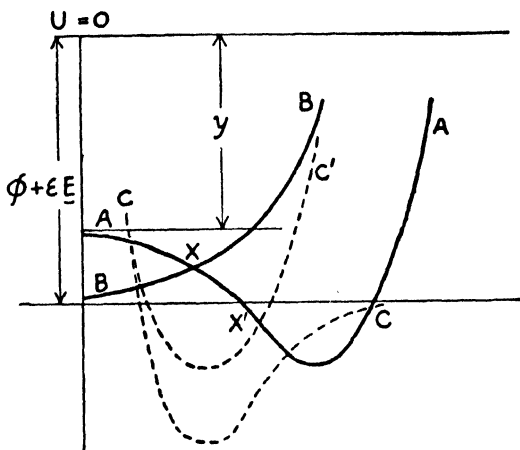
It is, however, well known that the reversible oxygen electrode cannot be realised. This might be due to the failure of either of these equilibria, but it will be shown below that the deposition of oxygen from the solution and the ionisation of oxygen adsorbed

* This section is essentially that given by J. A. V. Butler, *Electrocapillarity*, London, 1940, p. 148.

¹³⁶ Langmuir, *J. Amer. Chem. Soc.*, **37**, 1139, 1915.

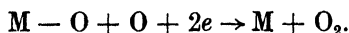
¹³⁷ Langmuir and Villars, *ibid.*, **53**, 486, 1931.

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.



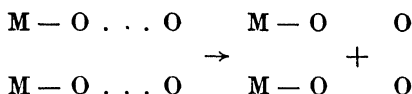
VII 9.—Conditions of discharge of oxygen ions and deposition of oxygen.

When the rate of deposition of oxygen on the electrode by an anodic current exceeds the rate of desorption, the electrode will quickly become 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.:



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.,



Activation Overpotential of Other Electrode Processes.*

The deposition of chlorine and bromine ions is associated with small overpotentials¹³⁸ and the difficulty in these cases is to separate the activation overpotential from the concentration overpotential as they may be of the same order. The current-voltage relation is linear in the neighbourhood of the reversible potential and logarithmic at higher c.d. when the Tafel relation tends to become valid, although for the cathodic dissolution the equation best representing the results is

$$\eta = a - b \log i - ci.$$

The electrodeposition of the azide ion from an aqueous solution of NaN_3 has been recently examined on platinum electrodes and requires the very high overpotential of about 4 volts at measurable c.d.s.¹³⁹ The value of α is about 1 and it increases with rise of temperature. No mechanisms analogous to those hitherto suggested for hydrogen overpotential seem to be capable of giving an adequate explanation of the results.

It should be clear that overpotential is the rule rather than the exception in electrodeposition and the detailed examination of that developed by substances other than hydrogen and oxygen would be of greatest value to the general theory of the kinetics of electrode reactions.

* For a discussion of the overpotential involved in the deposition of metals, see next chapter.

¹³⁸ Chang and Wick, *Z. physikal. Chem.*, **172**, 448, 1935.

¹³⁹ Stout, *Trans. Faraday Soc.*, **41**, 69, 1945.

¹⁴⁰ Hickling and Salt, *ibid.*, **36**, 1226, 1940.

¹⁴¹ Kolotyrkin and Frumkin, *Compt. rend. Acad. Sci., U.R.S.S.*, **73**, 446, 1941.

¹⁴² Bockris, *Thesis*, London, 1945

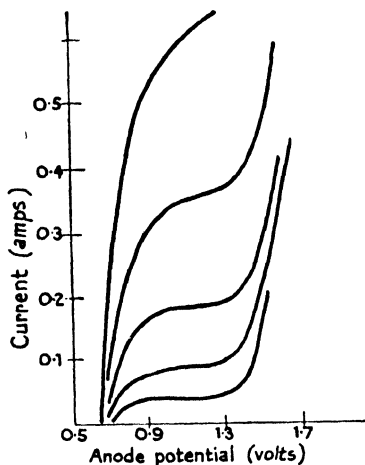
CHAPTER VIII

CONCENTRATION POLARISATION AND THE DEPOSITION OF METALS

J. A. V. BUTLER

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 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.



VIII 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

Nernst³ 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 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/nF . Hence the transition current i_0 is

$$\frac{i_0}{nF} = \frac{Dc_0}{\delta}.$$

¹ Wilson and Youtz, *J. Ind. and Eng. Chem.*, **15**, 603, 1923; Goldschmidt, *Z. f. Elektrochem.*, **7**, 257, 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. ($Dc_0/\delta = \text{mols./cm.}^2 \times \text{secs.}$).

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

$$\frac{Dc_0}{\delta} + \frac{\alpha i_0}{z\mathbf{F}}, \text{ which is equal to } i_0/u\mathbf{F}$$

and therefore,

$$\frac{i_0}{n\mathbf{F}} \left(1 - \frac{n\alpha}{z} \right) = \frac{Dc_0}{\delta}.$$

When the ion is completely discharged at the electrode $n = z$.⁵

Wilson and Youtz¹ 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 ,

$$i_0 = \mathbf{F} \cdot Dc_0/\delta = 10^5 \cdot 10^{-5} c_0/0.05 = 20c_0 \text{ amps.,}$$

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 cathodic reduction of solutions of quinhydrone. The potential

⁵ For theory of limiting currents at dropping mercury electrode and polarograph, see MacGillivray and Rideal, *Rec. trav. chim.*, **56**, 1013, 1937; MacGillivray, *ibid.*, **57**, 33, 1938; see also Lingane and Kolthoff, *J. Amer. Chem. Soc.*, **61**, 825, 976, 1045, 1939.

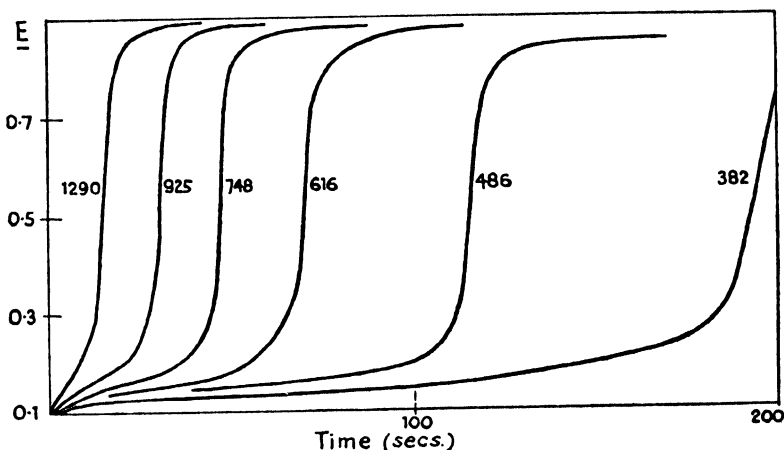
⁶ Nernst and Merriam, *loc. cit.*; cf. Eucken, *Z. Elektrochem.*, **38**, 341, 1932. For photographic demonstration of diffusion layer, see Antweiler, *ibid.*, **43**, 596, 1937; **44**, 719, 831, 1938.

⁷ Brunner, *Z. physikal. Chem.*, **47**, 56, 1904.

⁸ Butler and Armstrong, *Proc. Roy. Soc.*, **139A**, 406, 1933.

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



VIII 2.—Variation of cathode potential with time in cathodic reduction of 0.05 per cent. quinhydrone solution. Numbers are currents in amps. $\times 10^{-6}$, for electrode of 4.3 cm.² (Armstrong and Butler.)

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.

Sand,⁹ following Weber,¹⁰ applied Fick's diffusion equation,

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2},$$

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.,

$$D\left(\frac{dc}{dx}\right)_{x=0} = \frac{i}{nF}.$$

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

$$c_s = c - k \frac{i}{nF} \sqrt{\frac{t}{D}}.$$

If the transition time, $t = \tau$, is identified with the time in which c_s 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:

$$\frac{D(c_s - c_0)}{\delta} = \frac{i}{nF}(1 - \xi),$$

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

$$\frac{c_s}{c_0} = 1 - \frac{i}{i_0},$$

where $i_0 = nFDc_0/\delta$ is the rate of diffusion when $c_1 = 0$.

Similarly, for the case in which the concentration of the depolariser is greater at the electrode than in the solution we have

$$\frac{c_s}{c_0} = 1 + \frac{i}{i_0}.$$

¹¹ *J. Physical. Chem.*, **24**, 816, 1910.

Agar and Bowden¹² have used these equations to determine the displacement of the potential during the passage of current, writing

$$\Delta V = \frac{RT}{nF} \log \left(\frac{c_e}{c_0} \right).$$

For small values of αt this can be reduced to

$$\begin{aligned} c_e - c_0 &= \frac{i}{nF} \cdot \frac{\delta}{D} \cdot \frac{4}{\pi^{1/2}} \sqrt{\alpha t} \text{ (approx.)} \\ &= 1.129 \frac{i}{nF} \sqrt{\frac{t}{D}}, \end{aligned}$$

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
$$\Delta V = \frac{RT}{nF} \log \left(1 \pm \frac{i}{i_0} \right).$$

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
$$\Delta V = \frac{RT}{nF} \log \frac{c_e}{c_0} = \frac{RT}{nF} \log \left\{ 1 - (1 - \xi) \frac{i}{i_0} \right\}.$$

¹² *Proc. Roy. Soc.*, **169A**, 206, 1938.

* For larger values of αt , Rosebrugh and Miller gave the approximation

$$c_e - c_0 = \frac{i}{nF} \cdot \frac{\delta}{D} \left\{ 1 - \frac{8}{\pi^2} e^{-\alpha t} \right\},$$

i.e. $c_e = 0$ when
$$- \frac{c_0 n F D}{i \delta} = 1 - \frac{8}{\pi^2} e^{-\alpha t},$$

or writing $-i_0 = c_0 n F D / \delta$ 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 $i = i_0$.

† A similar expression is given by Gardam, *Faraday Soc. Discussion*, **1**, 182, 1948; see also Hoar and Agar, *ibid.*, p. 162.

Agar and Bowden also show that the resistance of the diffusion layer gives rise to an ohmic potential drop which is normally 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.

A more thorough discussion of the problem has been given by Levich,^{12a} using modern hydrodynamical concepts, and following the lines along which similar heat transfer problems have been treated. Dimensional methods have also been used by Agar.^{12b} For a rotating disc electrode Levich finds that the conventional Nernst diffusion layer thickness is given by

$$\delta = 1.62 \left(\frac{D}{V} \right)^{\frac{1}{2}} \left(\frac{\nu}{\omega} \right)^{\frac{1}{2}} \text{ cm.}$$

where D is the diffusion coefficient, ν the kinematic viscosity and ω the angular velocity.

In Sand's experiments¹³ on the deposition of metals, and Karnoglanoff's¹⁴ 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 Armstrong⁸ found that for the reduction of methylene blue and quinone solutions and the oxidation of hydroquinone solutions, the transition time τ 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

^{12a} *Acta Physicochim.*, **17**, 257, 1942; **19**, 117, 133, 1944; *Faraday Soc. Discussion*, **1**, 37, 1948.

^{12b} *Ibid.*, p. 26.

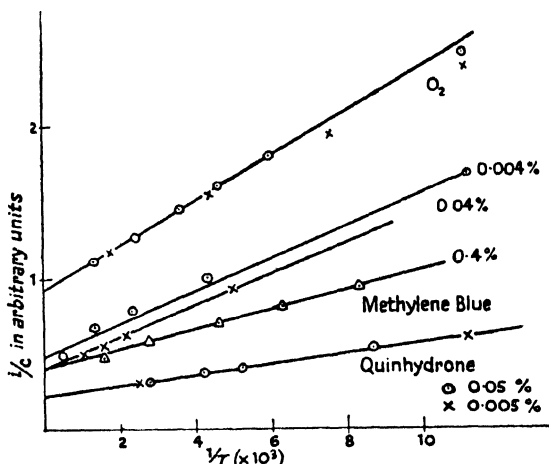
¹³ Sand and Cottrell, *Z. physikal. Chem.*, **42**, 385, 1903.

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 nitrobenzene¹⁶ and the anodic solution of gold in hydrochloric acid.¹⁷ Both i_0 and α are approximately proportional to the concentration.

Butler and Armstrong¹⁸ suggested the following explanation of this relation. Suppose that initially there is an amount q_0 of the depolariser (measured as the quantity of electricity required to reduce



VIII 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.

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

$$q_t = q_0 - it + f(c, t).$$

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

$$f(c, t) = \alpha' + \beta t,$$

¹⁵ *Proc. Roy. Soc.*, **143A**, 89, 1933.

¹⁶ *Trans. Faraday Soc.*, **32**, 989, 1936.

¹⁷ *Ibid.*, **30**, 1173, 1934.

¹⁸ *Loc. cit.*, ref. 8.

where α' is the amount of diffusion in the initial stages and β the ultimate constant rate of diffusion. Therefore

$$q_t = q_0 + \alpha' - (i - \beta)t.$$

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_0 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 Blanc¹⁹ 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 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

Lakhani²¹ 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,

¹⁹ Abh. Bunsen-Ges., 1910, No. 3.

²⁰ Cf. Glasstone, *J. Chem. Soc.*, 250, 1924.

²¹ *Thesis*, Edinburgh.

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 Blanc²⁴ thought the first step to be the dehydration of the ion, which might be a slow process giving rise to an overvoltage. Hughes²⁵ 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 Clark²⁸ 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. Volmer²⁹ 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. Brandes³⁰ 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

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; see also discussion on Structure of Metal Coatings, *Trans. Faraday Soc.*, **31**, 1043 *seq.*, 1935.

²⁴ *Loc. cit.*; *Trans. Faraday Soc.*, **9**, 251, 1914.

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.

and the transport of ions over the surface is the determining factor then as shown by Brandes,³⁶ the relation should be $i \propto V(\delta)$.

The experiments mentioned caused the authors to decide in favour of case 2(b). Erdey-Grúz³⁷ 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 zinc³⁸ and copper³⁹ 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 direction decreased, and the result is (see p. 189) 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

³⁶ *Loc. cit.*, ref. 30.

³⁷ *Z. physikal. Chem.*, **172**, 157, 1935.

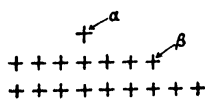
³⁸ Essen and Levin, *J. Gen. Chem. Russ.*, **6**, 1539, 1936.

³⁹ Essin, Antropov and Levin, *Acta Physicochimica, U.R.S.S.*, **6**, 447, 1937; *J. Gen. Chem. Russ.*, **7**, 2719, 1937.

⁴⁰ Butler, *Trans. Faraday Soc.*, **28**, 379, 1932.

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.

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).



VIII 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 Volmer⁴¹ 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 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 Evstropov⁴³ made similar observations and Essin, Antropov and Levin⁴⁴ 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 pheno-

⁴¹ *Z. physikal. Chem.*, **157**, 182, 1931.

⁴² *Ibid.*, **162**, 63, 1932.

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.

menon is not well understood. Kohlschutter⁴⁵ 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 Glasstone⁴⁶ 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 zinc⁴⁷ and cadmium⁴⁸ 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 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 Sofeysky,⁵² who conclude that the polarisation observed is probably due to the hindered diffusion of the metal into the mercury.

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; see also J. Heyrovský, *Faraday Soc. Discussions*, **1**, 212, 1947.

⁵¹ Matheson and Nichols, *Trans. Amer. Elect. Soc.*, **73**, 193, 1938; see also J. E. B. Randles, *Faraday Soc. Discussions*, **1**, 11, 1947.

⁵² *Acta Physicochimica*, **6**, 447, 1937. For discharge of NH_4^+ ions, see Loschkarev and Essin, *J. Gen. Chem. Russ.*, **8**, 510, 1938.

CHAPTER IX

THE BEHAVIOUR OF OXYGEN AND HYDROGEN AT ELECTRODES

J. A. V. BUTLER

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*.

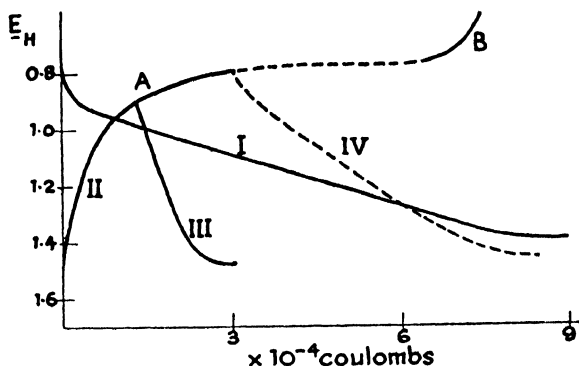
Butler and Armstrong studied the behaviour of platinum electrodes under similar circumstances in greater detail.² The main features observed are shown in Fig. 1. The potential of a platinum electrode in an aqueous solution containing oxygen is usually $+0.8$ to $+0.9$ volt, with reference to a hydrogen 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

¹ *Proc. Roy. Soc.*, **125A**, 446, 1299.

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.

value is 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 $E_h = +0.7$ volt (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



IX 1.—Behaviour of a 1 cm.² platinum electrode in dilute H₂SO₄; current, 3.1×10^{-6} amps. (Armstrong, Himsworth and Butler.)

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 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 1.2×10^{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. 188) 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 suggested¹ that this stage marks the reduction of a layer of *oxide* formed at the surface of the platinum. Armstrong, Himsworth and Butler² 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 $E_h = +0.5$, 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

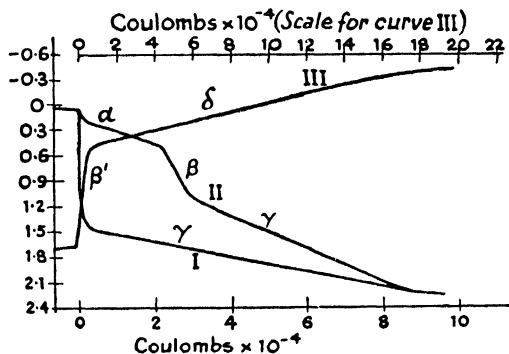
⁴ *J. Chem. Soc.*, 743, 1934.

⁵ Beans and Hammett, *J. Amer. Chem. Soc.*, **47**, 1215, 1925; Hammett, *ibid.*, **46**, 7, 1924.

⁶ *Trans. Faraday Soc.*, **34**, 1163, 1938. These results have been confirmed by Hickling, *ibid.*, **41**, 333, 1945. He considers that the oxygen deposited forms a unimolecular layer of platinous oxide.

4.8×10^{-4} coulombs/cm.², and stage γ 10.2×10^{-4} coulombs/cm.² The process γ is evidently the deposition of a monatomic layer of adsorbed oxygen as previously observed (p. 205), 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 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



IX 2.—Typical anodic and cathodic oscillograms in sulphuric acid. (Pearson and Butler, *Trans. Faraday Soc.*, 1938.)

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.

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 Wick⁷ 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 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 Butler⁹ 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, found¹⁰ 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.

When active platinum electrodes are anodically polarised with small currents in solution 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 $E_h = +0.4$ to 0.5 ; (2) the return occurs from near the potential at which the deposition of adsorbed oxygen begins, i.e. *ca.* 1.0 volt. Fig. 3 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,

⁷ *Z. physikal. Chem.*, **172A**, 429, 1935.

⁸ *Acta Physicochimica*, **8**, 565, 1938.

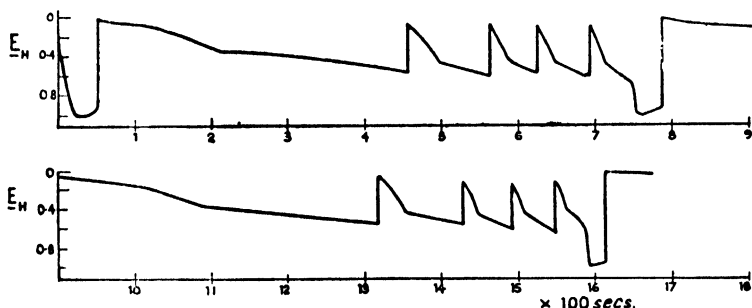
⁹ *Loc. cit.*, ref. 4.

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; *Faraday Soc. Discussions*, **1**, 122, 1948.

until the hydrogen near the electrode has been used up. The potential then falls gradually to $E_h = 0.4$, 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.

Slygin and Frumkin¹² have made extensive experiments on the



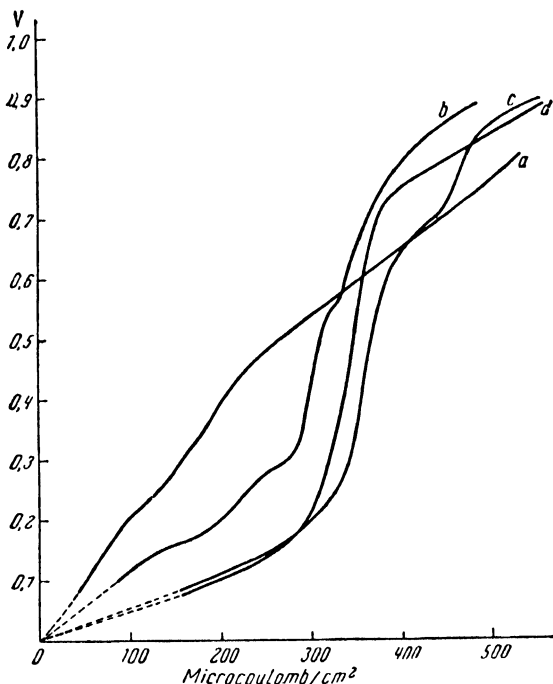
IX 3.—Periodic oscillations of potential of platinum electrode on anodic polarisation in a solution containing hydrogen. (Armstrong and Butler.)

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 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. 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.

¹² *Acta Physicochimica, U.R.S.S.*, **3**, 791, 1935; **4**, 911, 1936; **5**, 819, 1936.

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, IX 4.—Charging curves. (a) In $\text{Na}_2\text{SO}_4 + 0.02n \text{ NaOH}$; is 1.2×10^{15} (b) In $\text{Na}_2\text{SO}_4 + 0.02n \text{ H}_2\text{SO}_4$; (c) In HCl; (d) In KBr + $0.02n \text{ HCl}$. (Erschler, Deborin and Frumkin.) 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

$$Q = (A_0 - A)F - (E_0 - E).$$

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.

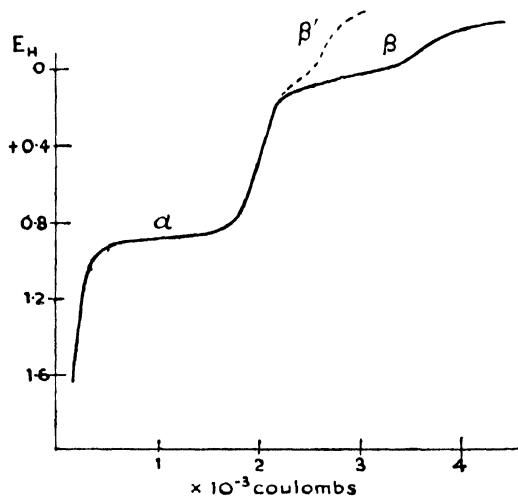
In later papers of this series¹³ bright platinum electrodes have been studied. Erschler obtained charging curves, similar to those of platinised electrodes, but rather less reversible, at electrodes which were in contact with extremely small quantities of solution, from which all the oxygen could be 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 volt, is present on the electrode. When platinum is heated in oxygen at 900° for 10 secs., an atomic layer (1.3×10^{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 group¹⁴ 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 de-

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. Further papers in *Acta Physicochimica*, **11**, 45, 1939; **13**, 347, 747, 1940; **21**, 213, 1946; *Faraday Soc. Discussions*, **1**, 269, 1948.

¹⁴ Butler and Drever, *ibid.*, **32**, 427, 1936.

scribed 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



IX 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.

(e.g. Fig. 5). This marks the reduction of the "oxide", and the amount of oxide present after the anodic treatment can be measured by the length 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

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.

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.

With new electrodes the formation of the oxide occurs very slowly. The following table shows the amounts of oxide formed (as measured by the cathodic coulombs required to reduce it) at palladium electrodes in successive experiments :

OXIDATION OF PALLADIUM IN N/5 NaOH WITH 8.5×10^{-3} AMPS.

<i>Anodic coulombs</i>	<i>Cathodic coulombs</i>	<i>Anodic coulombs</i>	<i>Cathodic coulombs</i>
(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

* With 28×10^{-6} amps.

It can be seen that when a comparatively large amount of oxide has been formed by long anodic treatment and reduced, it is reformed 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

* 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 Buryànek¹⁷ found that after drying over sulphuric acid its composition was close to $\text{Au}(\text{OH})_3$, 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.

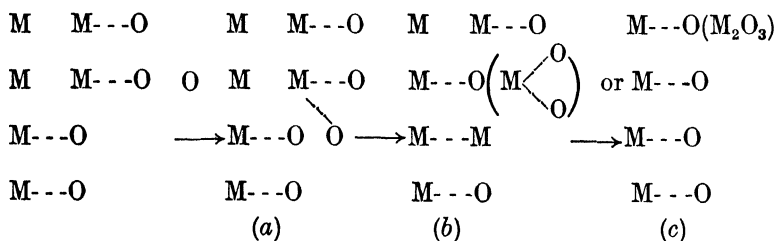
¹⁶ *Loc. cit.*, ref. 2.

¹⁷ *Chem. Listy.*, **16**, 189, 299, 329, 1922; Jirsa and Tellinck, *Z. Elektrochem.*, **30**, 286, 1924.

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.

Hickling^{17a} has also studied the anodic behaviour of gold in sulphuric acid and in alkaline solutions. He concludes that in both cases the fundamental process is the formation of a uni-molecular layer of auric oxide.

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 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.



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).

^{17a} *Trans. Faraday Soc.*, **42**, 518, 1946.

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.

Hickling and Taylor or Spice^{17b} have also studied the anodic polarisation of copper, nickel and silver. In alkaline solution they conclude that oxygen deposited at the nickel electrode in the form of a layer of nickelic oxide rather greater than one molecule in thickness; which slowly thickens on prolonged anodic treatment. With copper cuprous oxide is first formed, but is almost at once oxidised to cupric oxide. With silver in alkali, they suggest that the primary process is the formation of Ag_2O in a film, which may be rather more than one molecule thick. This is followed by the formation of a higher silver oxide, which on standing decomposes to Ag_2O_2 . It is evident that the behaviour of these metals in alkali is very similar to that of gold and the platinum group metals described above.

The Anodic Passivity of Metals. Passivity was independently discovered by Bergmann¹⁸ and by Keir¹⁹ about 1790, who

^{17b} *Trans. Faraday Soc.*, **44**, 262, 1948; **43**, 762, 1947; *Disc. Faraday Soc.*, **1**, 277, 1948.

¹⁸ *De diversa phlogisti quant. in metallis (Opuscula phys. et chem.)*.

¹⁹ *Phil. Trans.*, **80**, 374, 1790.

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 Wetzlar²⁰ in 1827 and in 1836 Schönbein²¹ 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 opinion²² 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 Hittorf²³ 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 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 change, which has been pictured variously as a change of valency,²⁵ of electron density,²⁶ of internal equilibrium between possible ionic states.²⁷

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.

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.

(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 this³¹ 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 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. Evans³⁴ 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

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).

³⁴ *J. Chem. Soc.*, 1020, 1927.

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 Burnham³⁸ 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 Meunier⁴⁰ 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. 216).

The important question is not, however, whether such films exist, but how they came to be formed, on metals which in the active state readily pass into solution. It has been found that 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

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.*, **128A**, 657, 1930; Boas and Rupp, *Ann. Physik*, **13**, 1, 1932; Rupp, *Kolloid Z.*, **69**, 375, 1934; Iitaka, Miyake and Iimori, *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.

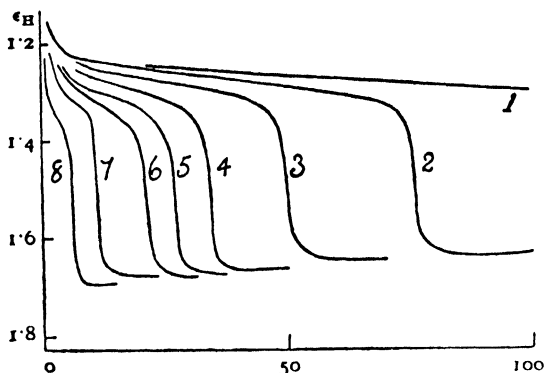
³⁸ *J. Physical Chem.*, **21**, 107, 1917; cf. Bancroft and Porter, *ibid.*, **40**, 37, 1936; Lepin, *Acta Physicochimica, U.R.S.S.*, **8**, 659, 1938.

³⁹ *Z. anorg. Chem.*, **107**, 103, 1919.

⁴⁰ *Bull. Soc. Chem. Belg.*, **36**, 435, 1927.
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.

sufficient to cause passivation, the transition only occurs after a certain time⁴² which is shorter the greater the current (Fig. 6).

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



IX 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.

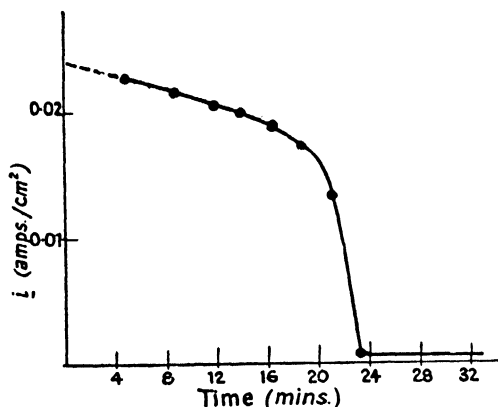
product of the electrolysis, such as a metallic salt or a basic salt formed by hydrolysis, until the solution becomes supersaturated and a solid thereupon crystallises on the electrode surface. This covers up a portion of the surface and so increases the current density on the remainder, and in time 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

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.

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.

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).



IX 7.—Passivation at a shielded electrode of iron in $2n$ H_2SO_4 . (W. J. Müller.)

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

$$t = C - A \left\{ \frac{i}{i_0 - i} + \frac{2.3}{i_0} \log \frac{i_0 - i}{i_0 - i_R} \right\},$$

where i_0 = initial current, i_R = residual current, and C and A are constants defined by

$$C = \frac{s\delta A}{F(1 - \mu)i_0}; \quad A = \frac{s\delta^2}{\chi F(1 - \mu)w_0},$$

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 $\log \tau$ is plotted against $\log i_0$, the slope being 2 in many cases, i.e. the results can be represented by

$$\tau = B i_0^{-n},$$

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 collaborators⁴⁴ under very different experimental conditions, viz. with violent agitation produced by causing a stream of the solution from a centrifugal pump to impinge on the surface

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.

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. 196), 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 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

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.

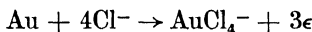
the chloride-ion concentration. It is equivalent to the amount of chloride in 2×10^{-4} cms. of solution.

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

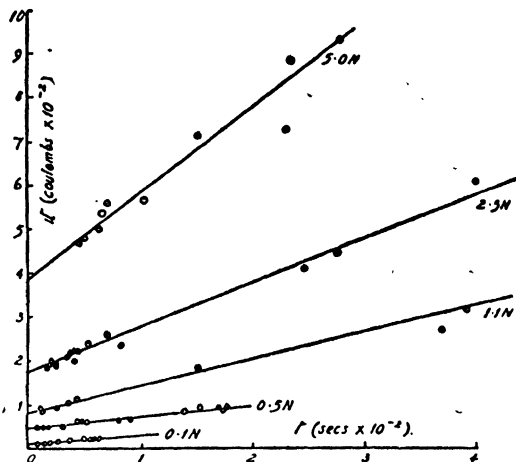
consider the process of setting up the diffusion layer in greater detail than previously (p. 197). The exact calculation by Fick's equation of concentration changes near an electrode when ions are removed at a high constant rate presents great difficulties, for the boundary condition

used by Sand and others (p. 193) 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

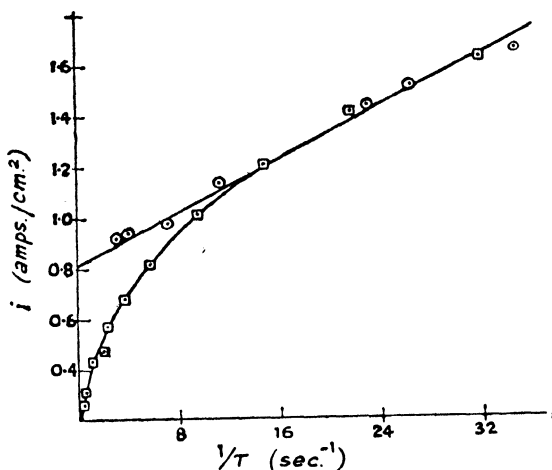


at the rate $4i/3F$ equivts./sec., while they are brought up by ionic transport at the rate $n_a i/F$, where n_a is the anionic transport number. The net rate of depletion of chloride ions at the electrode can thus be taken roundly as i/F equivts./sec. and the total amount of the ions used up in the whole passivation process is it/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/F . We therefore need to consider for how long ions can reach the electrode at this rate.



IX 8.—Plots of $i\tau$ against τ for passivation process. (Pearson and Butler, *Trans. Faraday Soc.*, 1938.)

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



IX 9.—Effect of stirring on the passivation times of gold in HCl.
(Shutt and Walton.)

side of the diffusion layer to the other, we see that the condition under which ions can arrive at a rate approximating to i/F is $D\Delta c/\Delta x = i/F$. Taking D as 2×10^{-5} and 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/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 0.05*N*, HCl

	<i>Unstirred solutions</i>	<i>Violent stirring</i>
i_0	3.6×10^{-3}	80×10^{-3}
α	34×10^{-3}	0.6×10^{-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.

Shutt and Stirrup showed⁴⁸ 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 Shutt⁴⁹ have also found that the anodic behaviour

⁴⁸ *Trans. Faraday Soc.*, **26**, 635, 1930.

⁴⁹ *Ibid.*, **34**, 1455, 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. See Ryan and Heinrich, *Trans. Amer. Electrochem. Soc.*, **77**, 121, 1939.

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.

CHAPTER X

MEMBRANE POTENTIALS AND ELECTRICAL PROPERTIES OF LIVING CELLS

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“ You cannot determine a process from a potential.”—H. GASSER.¹

IN order to discuss the electrical properties of living cells and tissues it is necessary to know something of the physico-chemical structure of the system, since the electrical events within and around the cell are but one facet of the physical and chemical history of the cell. The ionic composition of the cell and its environment, the distribution of charges across the membrane and the chemical reactions which maintain the system are of particular interest. The first part of this chapter is devoted, therefore, to a brief description of the physical-chemistry and electro-chemistry of cell systems.

Structure and Composition of the Plasma Membrane. The living cell is the elementary unit of which plant and animal tissues are composed. It is a highly organised collection of chemical material in aqueous solution separated by a specialised boundary layer from the aqueous inter-cellular fluid.* This boundary layer of the cytoplasm is the *cell membrane* or *plasma membrane*. It is an essential part of the cell and injury to it usually proves fatal to the cell. It is a barrier across which all exchanges between cell and environment must take place. It prevents dispersal of certain cell constituents into the interstitial fluid and the indiscriminate invasion of the cell by material from the environment. It is readily permeable by certain ions, e.g. H^+ , K^+ , OH^- and Cl^- , and impermeable by others, e.g. Na^+ and SO_4^- , and by protein and colloid components. It is the site of the electrostatic and chemical forces which give rise to the potential difference between the inside and the outside of the cell.

¹ Gasser, *Cold Spring Harbor Symposia Quant. Biol.*, **1**, 138, 1933.

* The cell environment or milieu intérieur of Claude Bernard.

The plasma membranes of a great many different kinds of cell, such as nerve and muscle fibres, erythrocytes, plant cells and ova, e.g. trout eggs, have a common structural plan, as revealed by permeability and surface tension studies and by electrical measurements.

Most cell membranes show a high permeability to lipid-soluble substances and a low permeability to substances not lipid soluble. This suggests that the membrane contains a continuous distribution of lipid molecules. The transverse electrical resistance of such a membrane would be high in comparison with that of intra- or inter-cellular fluids. Electrical conductivity studies on cells and cell suspensions are consistent with this hypothesis, giving resistances of the order of thousands of ohms per sq. cm. of plasma membrane surface. The electrical capacitance of cell membranes is of the order of $1 \mu\text{F}$ per sq. cm. for a wide range of plant and animal tissues.^{2, 3}

Measurements of surface tension in living cells, inaccurate though they possibly are, suggest a very low value of the order of 0.1 to 1.0 dyne cm^{-1} . Such a low surface tension could be obtained with a lipid membrane film only if a highly surface-active material such as protein is adsorbed at the aqueous boundary of the film. Any lipid material in contact with a protein solution, even of a concentration as small as 10^{-7} , will adsorb the protein over all its surface, thereby having the surface tension of the oil/water interface greatly reduced. Thus if the plasma membrane contains a layer of lipid molecules it must also contain protein adsorbed at the oil/water interfaces, since the inter- and intra-cellular fluids of plants and animals contain protein.⁴ Typical results of cell surface tension measurements are given in Table I.

These similarities suggest very strongly a close resemblance between the structure of different membranes. The fact that the resistance and capacitance are largely unaltered with injury, death or ionic permeability changes suggests that the bulk of the membrane volume is occupied by what Cole has described as

² Cole, *Cold Spring Harbor Symposia Quant. Biol.*, **8**, 110, 1940.

³ Floyd, *Science Progress*, **36**, 214, 1948.

⁴ Davson and Danielli, *The Permeability of Natural Membranes*, C.U.P., 1943.

TABLE I. THE SURFACE TENSION OF TYPICAL CELLS

Cell	Surface Tension dyne cm. ⁻¹	Authority
<i>Amoeba dubia</i>	1.3	} Full references in Danielli. ⁶
<i>Arbacia punctulata</i> : egg . . .	0.08-0.2	
<i>Busicon caniculatum</i> : egg . . .	0.5	
<i>Rana</i> : leucocyte	1.3	

" . . . a massive, inert and durable framework. . . ." Resistance and capacitance measurements suggest upper and lower limits for the membrane thickness, as will be shown later, of the order of 1μ and $1m\mu$ respectively.

Two other independent methods of study, viz. birefringence measurements with polarised light (Schmidt *et al.*) and the total extraction of lipid with lipid solvents (Gorter and Grendel) place an upper limit of a few molecules on the thickness of the erythrocyte membrane.⁶

Thus the plasma membrane is generally agreed to consist of layers of orientated molecules or micelles of a lipo-protein complex probably not more than a few molecules thick (i.e. up to 100 Å.U.).

Various arrangements of lipid and protein molecules are possible to form the plasma membrane, and the simplest discussed by Danielli^{5, 6} is shown in Fig. 1. The lipid component consists of a continuous film of molecules with the two surface layers (one each side of the film) having the polar groups in the oil/water interfaces. The primary layer of protein molecules is adsorbed at the interface and consists of denatured (possibly reversibly denatured) polypeptide chains, lying in the interface. Single chains may be several hundred Ångstrom units long^{6, 7} and cross-linked to similar chains, thus holding the membrane together and giving elasticity to it.

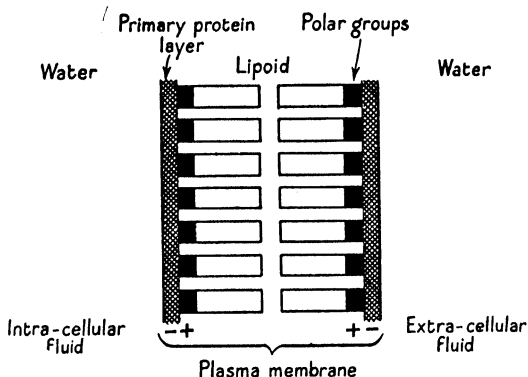
The protein material, and possibly also the lipid, is distributed over the cell surface in a repeated pattern. If the pattern is not

⁵ Danielli, *J. cell. comp. Physiol.*, **7**, 393, 1936.

⁶ Danielli, Ch. III in *Cytology and Cell Physiology*, ed. by G. Bourne, Oxford, 1942.

⁷ Astbury, *The Forms of Biological Molecules in Essays on Growth and Form*, Oxford, 1945.

strictly regular there may be patches of the membrane which are abnormally permeable, but only a small fraction of the total membrane area is likely to be involved. These patches are not accidents of development or growth but specially differentiated zones, likened by Danielli⁶ to the active patches of a catalyst. Such abnormal permeability, involving only a small fraction of the total surface has been observed in erythrocytes.



X 1.—Arrangement of lipo-protein material to show possible structure of plasma membrane (after Danielli, see refs. 4, 5 and 6).

It is sometimes convenient to regard the membrane as a more or less dense passive network through the pores of which small enough molecules or ions may pass under favourable conditions of charge and concentration gradient, the size of the pores in the network probably varying from place to place. This view of the cell membrane as a passive molecular sieve, although outmoded for most cells, is the accepted explanation for the sulphur alga *Beggiatoa mirabilis*.^{8, 9}

The cell membrane as defined above is not the same as the structure which can be seen under the microscope in stained sections of dead tissue, or even in living tissue as viewed by polarised light or with the phase contrast microscope. The "membrane" of the histologists may indeed have as its "core" the plasma membrane defined here, but its thickness is much greater than the

⁸ Ruhland and Hoffman, *Planta*, **1**, 1, 1925.

⁹ Schonfelder, *ibid.*, **12**, 414, 1930.

100 Å.U. which is the probable upper limit of thickness of plasma membranes. With the electron microscope, it is possible to see, in dead cellular material, the remnants of the plasma membrane, i.e. such parts of it as remain unchanged when the cell dies. Unfortunately, it is not yet possible to examine living material in the electron microscope.

The plasma membrane constitutes a relatively non-conducting layer of material separating two highly conducting media, viz. the intra- and inter-cellular fluids. Thus is formed a condenser, which, because of the small thickness of the dielectric in comparison with the dimensions of the surfaces, can be regarded as a parallel plate condenser without appreciable error. The capacitance per sq. cm. of surface area of such a two-plate condenser is :

$$C = 8.8 (k/d) \quad . \quad . \quad . \quad . \quad (1)$$

where C = capacitance in $\mu\text{F. cm.}^{-2}$ of plate area, k = dielectric constant, and d = thickness of the dielectric in Å.U.

C is of the order of $1 \mu\text{F. cm.}^{-2}$ hence d is of the order of $10k$ Å.U. Nothing much is known about the value of k for the plasma membrane, but it is certainly greater than 1 and unlikely to be greater than 10^3 , thus setting the limits 1μ and $1 \text{ m}\mu$ on the thickness of the lipid film. For a lipid layer composed of an oil like olive oil, k will be approximately 3, giving $d = 26$ Å.U., and a transverse resistance of the order of several thousands of ohms, which agrees well with membrane resistance measurements.

Fricke¹⁰ has shown by impedance measurements of cell suspensions that the thickness of the erythrocyte membrane is of the order of 50 Å.U., and a similar value has been obtained by Fricke and Curtis for leucocytes and for yeast cells.¹¹

For small cells the space taken up in the cell by a plasma membrane of thickness 50 Å.U. is an appreciable part of the total volume of the cell, as shown by Table II. It is thus improbable that virus cells possess a plasma membrane of the type under discussion. The permeability properties of small cells may be directly related to the structural and chemical properties of the whole cell.

¹⁰ Fricke, *J. Gen. Physiol*, **9**, 137, 1925.

¹¹ Fricke and Curtis, *ibid.*, **18**, 821, 1935.

TABLE II.—PERCENTAGE OF CELL VOLUME OCCUPIED BY PLASMA MEMBRANE 50 Å.U. THICK

Cell	Cell Diameter	Percentage of Cell Volume
Nerve axon . . .	{ 10 μ	0.2
	1 μ	2
Bacterium . . .	{ 2 μ	1
	250 $m\mu$	12
Bacteriophage . . .	50 $m\mu$	50
Poliomyelitis virus . . .	10 $m\mu$	100

Osmotic and Ionic Equilibria. The equilibrium between cell and environment is not the static equilibrium of classical thermodynamical theory. Metabolic exchanges are continuous, and energy is constantly being supplied to the system. As Krogh¹² has pointed out “. . . the large differences in concentration of individual ions between the interior of living cells and the fluids surrounding them, . . . are normally, and perhaps always, brought about and also maintained by some special activity on the part of the cell, while diffusion processes are all the time tending to reduce them . . .”. When maintained, these differences are the result of steady states, which differ in principle from equilibria by the need for energy to maintain them.

As used in this chapter, the term “membrane permeability” means the “property of allowing the transit of solvent or solute ions or molecules across the cell boundary layer”. The process of permeation may be entirely “passive” as when it occurs by osmosis or diffusion, or it may be “active” as when it occurs against a concentration gradient and associated with positive metabolic work.*

Most living cells are in osmotic equilibrium with their environment, in consequence of the free permeability of the plasma membrane by water: moreover, on account of its low tensile strength, the membrane cannot withstand more than a small osmotic pressure

¹² Krogh, *Proc. Roy. Soc. B*, **133**, 140, 1946.

* But see Höber (1945), *Physical Chemistry of Cells and Tissues*, Churchill, section 8, introduction (pp. 525-529), for a full discussion of passive and active transfer.

difference, except plant cells surrounded by a rigid cellulose wall, which can withstand a considerable *increase* of intra-cellular pressure.

Osmotic exchanges across the cell boundary suggest that the Boyle-van't Hoff law $PV = \text{const.}$ is sufficiently closely obeyed if account is taken of the volume occupied by the osmotically inactive components inside the cell. Thus if V' is the reduced volume, corrected for the volume of the inert components, the osmotic observations fit the equation $PV' = \text{const.}$,¹³ provided the selective permeability of the plasma membrane is not modified under the experimental conditions.

In a membrane system containing a mixture of electrolytes, if one ion, usually a colloid or protein ion, is unable to diffuse through the membrane, the resulting distribution of ions on the two sides of the membrane is known as a Donnan equilibrium.¹⁴ There is, in general, an unequal distribution of the diffusible ions between the two sides of the membrane. For two electrolytes with monovalent ions and a common anion, the ionic concentrations are given by :

$$x^2 = y(y + z). \quad . \quad . \quad . \quad . \quad (2)$$

Where x, y = activities of the diffusible ions,

z = activity of the indiffusible ion.

The ratio x/y is termed the Donnan ratio and usually designated by λ .

As a result of the unequal ionic concentrations, differences of osmotic pressure and electrical potential exist between the two electrolyte concentrations bounded by the membrane. The potential difference, as given by the Nernst equation, is :

$$V = 58 \log_{10} x/y \text{ mV. at } 18^\circ \text{ C.} \quad . \quad . \quad . \quad (3)$$

i.e. $V = 58 \log_{10} \lambda \text{ mV. at } 18^\circ \text{ C.} \quad . \quad . \quad . \quad (3a)$

From thermodynamic considerations, when equilibrium has been reached between the two phases, the potential difference between identical electrodes in contact with the two solutions must be zero. Hence the membrane must possess a potential equal in

¹³ Lucké and McCutcheon, *Physiol. Rev.*, **12**, 68, 1932.

¹⁴ Donnan, *Z. Electrochem.*, **17**, 572, 1911.

magnitude to that given by equation (3) but opposite in sign.¹⁵ The Donnan distribution has been observed in living cells, particularly erythrocytes, but more recent investigations do not confirm this.

The semi-permeability of the plasma membrane has already been referred to briefly. Unfortunately, despite the fact that a vast amount of data on permeability has been collected, there is inadequate quantitative information on which to base calculations. Most cells are so small that it is impossible to collect enough cytoplasm for micro-chemical analysis. The available data are obtained from the chemical and physical analysis of the contents of certain large cells such as the giant plant cells of *Valonia* and *Nitella* and the giant axons of the squid, and from experiments involving osmotic and ionic exchanges between cell and environment when the environmental fluid has been modified.

For plant cells, the criterion used to indicate permeability is a reversible change in cell size on immersion in a hypertonic test medium. The cell behaves like an osmometer. On transfer to the new environment, water transport occurs first, and the cell shrinks: the protoplast* of the cell becomes detached from the rigid cellulose wall, and can be seen microscopically. If ionic transport occurs, the osmotic balance progressively readjusts itself to suit the ionic distribution, and, finally, the plasmolysis is reversed, i.e. de-plasmolysis occurs. The rate of de-plasmolysis is taken as an index of the penetration rate of the ion. For animal cells, e.g. muscle fibres, change in weight has been widely used as an index of transport, together with histological estimation of the volume of the inter- and intra-cellular spaces. The methods are used for the study of both electrolyte and non-electrolyte substances. Some substances, e.g. certain monohydric alcohols, enter so quickly that plasmolysis cannot be observed.

¹⁵ Greenberg in Ch. XIV of *The Chemistry of the Amino Acids and Proteins*, ed. by C. L. A. Schmidt. Thomas.

* The rigid cellulose wall which envelopes the plant cell is readily permeable by water and crystalloids. The protoplast consists of the semi-fluid boundary layer of the cytoplasm, built up on the plasma membrane. It has the qualitative permeability properties of the plasma membrane, but, being thicker, is observable microscopically.

As far as non-electrolytes are concerned, the factors which determine permeability of plant and animal cells are lipid solubility and molecular volume. Substances which are lipid soluble can pass through the plasma membrane, irrespective of their molecular volume, at rates which are roughly proportional to their lipid solubilities. Collander¹⁸ concludes, for the plant cell *Chara*, that certain lipid-soluble substances of small molecular volume penetrate quicker than would be expected from their lipid solubility, which suggests that the lipid film of the plasma membrane may be porous. Certain non-lipid soluble substances of small molecular volume, e.g. urea, can also pass through the membrane of *Chara*, other plant cells and erythrocytes, and presumably do so through these pores. Danielli, however, points out⁴ that Collander bases his conclusions, on qualitative arguments only, by plotting permeability ($P = \text{mol./cm.}^2/\text{hour/mol./litre}$) against oil/water partition coefficients. According to Danielli's calculations (Appendix A, *loc. cit.*) the plot should be of $PM^{\frac{1}{2}}$, for rapidly penetrating molecules, and of $PM^{\frac{1}{2}}e^{2500x/RT}$, for slowly penetrating molecules, against partition coefficients, where M is the mass of the penetrating molecule and x is the number of non-polar groups per molecule. This criticism of Danielli's, does not, however, explain how the practically lipid insoluble substances of small molecular volume, like urea, penetrate the plasma membrane. It still leaves open the possibility of a lipid pore factor.

The evidence regarding permeability by electrolytes is conflicting, particularly in respect of potassium and sodium ions, and will be discussed here in some detail since it bears directly on the problem of the origin of the resting potential of the membrane.

The electrolyte content of cells varies with the species, and Tables IIIA and IIIB show the wide range of concentrations found in certain plant cells, erythrocytes, nerve and muscle cells.

In Table IV are given, for some of these cells, the values of the ratio *internal concentration/external concentration* for sodium, potassium and chlorine ions. The potassium and chlorine ion ratios are particularly important as many workers attribute the

¹⁸ Collander, *Trans. Faraday Soc.*, **33**, 985, 1937.

membrane potential to them, i.e. explain it as a concentration potential or a Nernst boundary potential.

TABLE IIIA. IONIC CONTENT OF CELLS (mM. per kg.)

	Na	K	Ca	Mg	Cl	SO ₄
<i>Plant cells *</i>						
Valonia macrophysa . .	90	500	1.7	—	597	—
Valonia ventricosa . .	35	576	—	—	608	—
Halicystis Osterhoutii . .	557	6	8	17	603	—
Nitella clavata	10	54	10	18	91	8
Chara ceratophylla . .	142	88	5	16	225	4
<i>Erythrocytes †</i>						
Man	{ — 27 36	110 135 125	— 0 —	— 3 —	— 74 —	— — —
Rat	12	100	—	—	—	—
Guinea pig	15	105	—	—	—	—
Cat	104	6	—	—	—	—
Dog	107	9	—	—	—	—

* After Osterhout, *Bot. Rev.*, **2**, 283, 1936.

† After Kerr, *J. Biol. Chem.*, **117**, 227, 1937; J. P. Peters, "Body Water", Thomas (quoted from Fulton in *Howell's Textbook of Physiology*, 1935, 15th edn.); and Krogh.¹²

TABLE IIIB. IONIC CONTENT OF CELLS (mM. per kg. intra-cellular water)

Nerve Axon and Muscle Cells *	K	Cl	Remarks
Loligo forbesi: axon . .	279	109	Webb and Young, 1940
Loligo pealii: axon . .	310	130	Bear and Schmitt, 1939
Libinius: axon	158	—	{ Fenn <i>et al.</i> , 1934, per kg. whole nerve, not axoplasm
Homarus: axon	203	—	
Maia: axon	230	—	Cowan, 1934; corrected Young, 1936
Rana: axon	176	—	Fenn <i>et al.</i> , 1934, corrected
Equides: splenic n. . .	125	—	Alcock and Lynch, 1911
Loligo: muscle	250	—	Bialaszewicz and Kupfer, 1936, corrected
Loligo: muscle	160	—	Manery, 1939, corrected

* Quoted from Webb and Young, *J. Physiol.*, **98**, 299, 1940, *q.v.* for full references.

TABLE IV. RATIOS OF SOME INTERNAL TO EXTERNAL IONIC CONCENTRATIONS

	Na	K	Cl	Remarks
<i>Plant cells</i>				
Valonia macrophysa	0.18	41.6	1.03	} Osterhout, <i>Bot. Rev.</i> , 2 , 283, 1936
Valonia ventricosa .	0.07	48.0	1.05	
Halicystis Osterhoutii	1.12	0.53	1.04	
Nitella clavata .	46.1	1065	100.5	
Chara ceratophylla .	2.4	63	3.1	
<i>Animal cells</i> *				
Loligo forbesi: axon	—	29	0.2	Webb and Young, 1940
Loligo pealii: axon .	—	26	0.26	Bear and Schmitt, 1939
Maia: axon . .	—	20	—	Cowan, 1934, corrected Webb and Young, 1940
Rana: axon . .	—	65	—	Fenn <i>et al.</i> , 1934; Erlanger and Gasser, 1937

* Quoted from Webb, and Young, *J. Physiol.*, **98**, 299, 1940, *q.v.* for full references.

Ionic Permeability of Plant Cells. Plant cells are usually highly resistant to invasion by inorganic neutral salts. Ions such as Li^+ and SCN^- when added to the sea-water environment of *Valonia* do not penetrate into the sap of the cells even after some days.¹⁷ Similarly Li^+ ions penetrate slowly into *Chara* cells and do not reach equilibrium concentration even after 1-2 weeks' exposure to the test medium.¹⁸ Certain salts, e.g. of K and Na, modify the condition of the plasma membrane. *Nitella* cells absorb NO_3^- ions from a sodium nitrate solution, but in the presence of calcium nitrate this does not occur. Alkali ions increase permeability (as measured by plasmolysis) in the order: $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ and anions in the order: $\text{Br}^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^-$.¹⁹

Ionic Permeability of Muscle and Nerve Fibres. For present purposes, muscle and nerve fibres can be regarded as cylinders of great length and small diameter, although many muscle fibres are somewhat conical. Muscle fibre diameters lie between 50 and 200 μ , and nerve fibre diameters between 1 and 1000 μ , but more usually between 1 and 50 μ —only certain giant

¹⁷ Cooper, Dorcas, and Osterhout, *J. Gen. Physiol.*, **12**, 427, 1929.

¹⁸ Collander, *Protoplasma*, **33**, 215, 1939.

¹⁹ Osterhout, *J. Gen. Physiol.*, **4**, 275, 1922.

fibres having diameters greater than 50μ . Muscles consist of hundreds or thousands of muscle fibres, laid more or less parallel. There are interstices between the fibres, containing blood vessels or occupied by a tissue fluid derived from the blood and having practically the same ionic composition. The extra-cellular space occupies in all about 13 per cent. of the fresh weight of the muscle.

Hill and Kupalov²⁰ determined the vapour pressure of blood in osmotic equilibrium with frog muscle and found it equal to that of 0.726 per cent. NaCl solution (g. per 100 g. water), i.e. a concentration of 248 mM. Their figures for millimolal and equivalent concentrations of single cations and anions are given in Table V. The sum of cation and anion millimolal concentrations is 239, the discrepancy between that total and 248, for equivalent NaCl, being made up by creatine. The anion deficit (58 m.equiv.) must be assumed to be made up by protein within the muscle fibres (see p. 243).

TABLE V. MILLIMOLAL AND EQUIVALENT CONCENTRATIONS OF CATIONS AND ANIONS FOR FROG MUSCLE

Cations			Anions		
Species	mM.	m. equiv.	Species	mM.	m. equiv.
K ⁺	109	109	Cl ⁻	19	19
Na ⁺	31	31	HCO ₃ ⁻	7	7
Ca ⁺⁺	7	14	Lactate ⁻	3	3
Mg ⁺⁺	14	28	Inorganic phosphate	14	26
			Organic phosphate	35	69
Total	161	182	Total	78	124

The osmotic pressure observed can be explained only if all the soluble constituents are in solution in the "free" or "unbound" water of the muscle. Less than 4 per cent. of muscle water is "bound", the total water content for frog muscle being 800 g. per Kg. of muscle. Thus all the potassium is in free solution and

²⁰ Hill and Kupalov, *Proc. Roy. Soc. B*, **106**, 445, 1930.

not masked in any way at all by formation of a complex with any other molecule. In this connection, Meyer²¹ has pointed out that the electron shell of potassium is almost the same as that of argon and similarly stable. Only free potassium ions can exist.

Against this, however, is the evidence from tracer experiments with K^{42} in the rabbit, according to which 60 per cent. of the potassium of skeletal muscle is bound in some way, i.e. non-exchangeable.*²² A restricted K^{42} exchange has also been recorded for heart muscle.²⁴

Conway²⁵ has suggested that ionic permeability of frog muscle fibres is dependent on ion size and not on charge; the plasma membrane is thus freely permeable by potassium and chloride ions, as well as by all smaller ions, but impermeable by sodium ions. Ion size refers to the hydrated ion, and Conway attributes sodium impermeability, as against potassium permeability, to the relatively greater hydration of sodium. Boyle and Conway²⁶ give hydrated ion sizes, determined from ionic mobility data, in the order $Na^+ > K^+ > Cl^-$. Lorente de Nó²⁷ states, however, that the reverse is the true order, viz. : $Cl^- > K^+ > Na^+$, and he questions the validity of applying Stokes' equations to ionic movements in an electrostatic field, which was the method used by Boyle and Conway to calculate ion size. If Lorente de Nó is correct, then, in order to explain the sodium impermeability, or apparent impermeability, of the plasma membrane an additional hypothesis is necessary. Krogh¹² considers the apparent sodium impermeability as due to an active transport, directed outwards, the sodium ions entering the muscle fibres at least as fast as the potassium ions. Conway²⁸ calculated the rate of energy consumption,

²¹ Meyer, *Trans. Faraday Soc.*, **33**, 1056, 1937.

* But Fenn *et al.*²³ found a more complete exchange of K^{42} , and suggest the presence of Na^{24} in the K^{42} employed by Hevesy and Hahn.

²² Hevesy and Hahn, *K. danske vidensk. Selsk. Biol. Medd.*, **16**, 1, 1941.

²³ Fenn, Noonan, Mullins and Haeger, *Amer. J. Physiol.*, **135**, 93, 149, 1941.

²⁴ Krogh, Lindberg and Schmidt-Nielsen, *Acta Physiol. Scand.*, **7**, 221, 1944.

²⁵ Conway, *Biol. Rev. Camb. Phil. Soc.*, **20**, 56, 1945.

²⁶ Boyle and Conway, *J. Physiol.*, **100**, 1, 1941.

²⁷ Lorente de Nó, *A Study of Nerve Physiology* in Ch. 1., Vol. 131, 1947. Studies from the Rockefeller Institute.

²⁸ Conway, *Nature*, **157**, 715, 1946.

necessary for sodium extrusion on the basis of Krogh's assumption (that sodium and potassium enter the cell at the same rate), and found it about twice as much as the rate of metabolism in resting muscle. Hence he concludes that sodium ions cannot permeate the muscle fibre plasma membrane, or, at most, do so in very small amounts. He also suggests that an active process of dehydration of the sodium ion could provide a mechanism for slow extrusion. Poisoning of the metabolic processes with cyanide does not interfere with the sodium impermeability.

The changes in ionic composition, brought about in the muscles of the normal animal by work, or exposure to a low-potassium test medium, are reversible. Recovery involves uptake of potassium and elimination of sodium, both against the concentration gradient. This necessitates an active process, but it is not necessary for both exchanges to be active. Non-medullated nerve is similar to muscle.^{29, 30} The permeability properties of both are summarised in Table VI. Sodium penetration occurs with muscle and nerve when the external potassium concentration falls below 10 m. equiv.p. l.

TABLE VI. PERMEABILITY PROPERTIES OF MUSCLE AND NERVE

	Permeable		Impermeable	
Cation	K ⁺ NH ₄ ⁺	H ⁺	Na ⁺ Mg ⁺⁺	Ca ⁺⁺
Anion	Cl ⁻ HCO ₃ ⁻	OH ⁻ NO ₃ ⁻	CH ₃ COO ⁻ HPO ₄ ⁻	SO ₄ ⁻

The Intra-cellular Organic Anions. The potassium within nerve and muscle cells, and perhaps in all cells, is held by the electrostatic attraction of the indiffusible anions. As noted earlier, all the potassium in frog muscle is required to make up the osmotic pressure, and, in any event, the potassium ion cannot be masked. It is shown by Table V, that there is, in frog muscle, an anion

²⁹ Shanes, *J. cell comp. Physiol.*, **27**, 115, 1946.

³⁰ Steinbach, *ibid.*, **17**, 57, 1941.

deficit of 58 m. equiv. but no osmotic deficit.²⁰ In the giant nerve axons of the squid, however, there is an anion deficit of some 400 m.equiv. and an osmotic deficit of 300-700 mM.^{31, 32} The anions concerned are those which hold the potassium, and are probably proteins, esters of organic acids and phosphoric acid.* Taurine, betaine and dicarboxylic amino acids have been suggested as providing the necessary anions.³² It is difficult to account for the non-exchangeability of 60 per cent. of muscle potassium shown by the K^{42} experiments, and no anion or K-complex is known which would lead to this behaviour.

Electrodes and Electrode Fluids for Potential Measurements. In order to measure potentials or other electrical properties of biological systems it is necessary to use some form of fluid electrode so as to make suitable electrical contact with the system, but it will be evident from the foregoing discussion that great care must be taken to ensure that the fluid medium does not alter the membrane properties in some unknown or undesirable manner. For instance, potassium chloride solutions abolish the resting potential of the plasma membrane of nerve, block impulse transmission through the treated part and may cause swelling, due to water transport into the fibre. A potassium chloride electrode would only be used, therefore, when it was the deliberate intention to produce these effects. For other purposes, electrodes containing a fluid in osmotic and ionic equilibrium with the axon would be used, e.g. the appropriate "Ringer" fluid.† It is usual to employ silver-silver chloride or mercury-calomel electrodes in contact with a suitable saline phase. For many purposes these can be regarded as non-polarisable.

Passive Membrane with Pores. When two solutions of the same monovalent electrolyte, but of different concentrations ‡ c_1 and c_2 are separated by a sieve-like membrane of large pore size,

³¹ Bear and Schmitt, *J. cell. comp. Physiol.*, **14**, 205, 1939.

³² Webb and Young, *J. Physiol.*, **98**, 299, 1940.

* The inorganic phosphate anions are diffusible.

† The composition of fluids in osmotic and ionic equilibrium with the tissues and body fluids of various animals is given by Pantin.³³

³³ Pantin, *Notes on Microscopical Technique for Zoologists*, Cambridge, 1946.

‡ Strictly activities.

the potential difference between the two solutions is the liquid-liquid junction potential given by :

$$E = 58 \frac{u - v}{u + v} \log_{10} \frac{c_1}{c_2} \text{ mV. at } 18^\circ \text{ C.} \quad (4)$$

where u , v are cation, anion mobilities. If the pore size is reduced sufficiently the ionic mobilities are reduced. Usually, the mobility of one ion species is diminished more than the other. Hence the ratio $\frac{u - v}{u + v}$ increases in value numerically. In the limit, with further decrease of pore size, cation or anion impermeability occurs, and the potential reaches its maximum numerical value given by :

$$E = 58 \log_{10} \frac{c_1}{c_2} \text{ mV. at } 18^\circ \text{ C.} \quad (5)$$

With an artificial membrane such as parchment, a relative slowing of the anion occurs, and Table VII shows the diffusion potentials obtained with various solutions, of concentrations 0.1 and 0.01 M., in direct contact (liquid-liquid junction potential) and with a parchment membrane interposed.³⁴

TABLE VII. DIFFUSION POTENTIALS BETWEEN 0.1 M. AND 0.01 M. SOLUTIONS (THE SIGN SHOWS THE POTENTIAL OF THE MORE DILUTE SOLUTION) (after Michaelis)

Salt	Liquid-Liquid jn P.D. (mV.)	P.D. with Parchment Membrane (mV.)
KCl	0	+10
LiCl	-15	- 4
K ₂ SO ₄	+15	+27.5
NaOH	-32	-14

Thus, two solutions of potassium chloride, of concentration ratio $\frac{c_1}{c_2} = 10$, when separated by a natural or artificial membrane, would have a potential difference between them of any value from - 58 mV. to + 58 mV., at 18° C., according to the nature and extent of the effect exerted by the membrane on ionic mobilities.

³⁴ Höber, *Physiol. Rev.*, **16**, 52, 1936.

If the membrane is uniformly charged, this fact will be reflected in altered ionic mobilities.*

If two solutions of the same concentration of different electrolytes having a common anion are in contact, the potential difference measurable between them is given by :

$$E = 58 \log_{10} \frac{u_1 + v}{u_2 + v} \text{ mV. at } 18^\circ \text{ C.} \quad . \quad . \quad (6)$$

where u_1 and u_2 are the cation mobilities and v is the common anion mobility. If a membrane is interposed between the solutions, the potential difference is increased in magnitude, as shown by Table VIII, due to changes in relative cation mobilities within the membrane.³⁴ The ratio of the mobility of hydrogen and lithium ions within the membrane, as calculated from the data of Table VIII, is approximately 1000.

TABLE VIII. CHEMICAL POTENTIALS BETWEEN 0.1 M. SOLUTIONS (THE SIGN SHOWS THE POTENTIAL OF THE KCl SOLUTION) (after Michaelis)

Salts	Liquid-liquid ju P.D. (mV.)	P.D. with Dried Collodion Membrane (mV.)
KCl: HCl	+27.3	+93
KCl: RbCl	+ 0.58	+ 8
KCl: KCl	0	0
KCl: NaCl	- 4.47	-48
KCl: LiCl	- 6.96	-74

The events within the membrane have so far been ignored in this simplified account. When two solutions are separated by a membrane, there are formed three phases, viz. the two bulk phases and the membrane phase, and two-phase boundaries. What happens at the phase boundaries will depend on the membrane permeabilities and the sort of system considered. Teorell³⁵ has developed an expression for the total potential difference with

* A charged membrane is one that contains fixed ions of one sign associated with water-soluble ions of opposite sign. The sign of the charge on the membrane is the sign of the bound ions, which may be either adsorbed on the surface of the pores or chemically combined with the substance of the membrane. The effect of membrane charge is to alter ionic mobilities, and so to modify the potential difference across the membrane. For a full discussion see Dean, *Chemical Reviews*, **41**, 503, 1947.

³⁵ Teorell, *Proc. Soc. Exp. Biol. Med.*, **33**, 282, 1935.

Calculations from equation (7a) for $x = 1$, $c_1 = 100$ and $u/v=0.63$ give the results shown in Table IX. It will be seen that as the concentration c_2 of solution 2 is progressively varied, the total potential difference reaches a minimum value and then reverses in sign. This behaviour is analogous to what has been found with frog skin by various workers, e.g. Dean and Gatty.

TABLE IX. POTENTIAL (mV.) ACCORDING TO EQUATION (7a) BETWEEN TWO SOLUTIONS OF NaCl ($c_1 = 100$; $c_2 = \text{VARIABLE}$) SEPARATED BY MEMBRANE FOR WHICH $x = 1$ AND $u/v = 0.63$ (after Teorell)

NaCl conc. c_2	Donnan P.D. $\phi_1 + \phi_2$	Henderson P.D. π	Total P.D. $\phi_1 + \phi_2 + \pi$
100	0	0	0
10	1.2	-13.2	-12.0
5	2.2	-17.4	-15.2
1	12.2	-26.4	-14.2
0.5	22.2	-29.4	- 7.2
0.1	58.0	-31.6	+26.4

On account of the complexity of cell-systems, these models are not very accurate representations of natural membranes. They are based always on the assumption of a classical thermodynamic equilibrium state being reached and maintained, whereas, as already pointed out, cell-systems are energy consuming and in dynamic equilibrium—i.e. a steady state—and their membrane properties are dependent on oxidative processes. The Donnan equilibrium condition is not applicable to such systems. Further, practically nothing is known about ionic mobilities through membranes, or of ionic concentrations within them. The study of these simple models is of great heuristic value, however, in the present state of knowledge of the subject.

Multi-cellular and Syncytial Membranes.* The permeability properties of the plasma membrane of cells are also exhibited by other membranes found in plant and animal tissues. As Krogh

* The term syncytium is given to a group of cells in close connection with one another so that the lines of separation between them are faint or indiscernible, and they appear to be continuous with each other. Sometimes the cells of a syncytium appear to be connected by bridges of cellular substance passing across the interstitial space.

has stated: "All membranes made up of exudation products from cells, as, for example, the cellulose walls of plant cells, the chorion of many eggs, the chitin of arthropods, etc., are only passively permeable, but the same appears to be true of a number of membranes made up of living cells or syncytia which are . . . flat and very thin. While non-living membranes in organisms show properties essentially like those of artificial membranes and practically constant, the properties of the living membranes may depend upon a number of conditions affecting their vitality, as, for example, oxygen lack . . .".

There are many examples of such membranes in the animal body, e.g. the capillary endothelium, the glomerular syncytium, the cells lining the kidney tubules, the skin and the gastro-intestinal mucosa; but only the skin and the gastric mucosa have been widely studied by electrical methods. In plants, the skin of fruits is an example of this type of membrane.

The Membrane Potential of Plant Cells. If two identical non-polarisable electrodes, e.g. a pair of silver-silver chloride-saline electrodes, are placed in direct contact with the intact external surface of a large plant cell, such as *Nitella*, the potential difference observed will usually be small or zero, but sometimes is quite large, e.g. 30 mV. That is to say, the outer surface of these cells is often iso-electric or nearly so, but sometimes shows considerable variations.³⁶ These large plant cells consist of the rigid, permeable cellulose wall, enclosing a thin (10μ) protoplasmic layer which in turn surrounds a large vacuole containing sap. If the cell protoplasmic surface is injured by cutting or crushing, a potential difference develops between the site of injury and an intact region of the same cell. With cell sap used to make contact with the intact region and identical electrodes as before, the following are typical results of injury potential measurements:

<i>Valonia macrophysa</i>	. — 65 mV.
<i>Halicystis Osterhoutii</i>	. + 50 mV.
<i>Halicystis ovalis</i>	. . + 60 mV.
<i>Nitella clavata</i>	. . — 15 mV.
(The sign is that of the injured region.)	

³⁶ Osterhout and Hill, *J. Gen. Physiol.*, **18**, 499, 1934-5.

The injury to the cell gives more or less direct access to the sap within, so that the electrode on the injured region is, in effect, inside the cell, and the potential difference measured is due to the asymmetry of the membrane. The site of the injury potential is the intact membrane underneath the reference electrode, and the so-called injury potential is in fact the membrane potential of the resting cell.*

With capillary electrodes introduced into the giant plant cell, direct measurements of the membrane potential have been made, including observations with the cell sap replaced by various fluids. In *Halicystis*, with sap present (pH 5.6) on both sides, the potential is about 70 mV.: with sea water at pH 8.1, the potential is some — 30 mV. Large effects are produced by potassium but not by sodium, and the outer surface of the membrane is very sensitive to the potassium ion but not the inner. The injury potential is readily changed in sign and magnitude by alteration of the external environment. For example, the injury potential of *Nitella* with sap on the outside is — 15 mV., but in pond-water (the natural environment) it is + 100 mV. This difference is attributed to the high potassium content of the cell relative to pond-water. (See Table IIIA.) Anoxia also reduces the potential. Osterhout found a potential difference of 85 mV. between a region of *Nitella* in contact with 0.01 M. potassium chloride and one in contact with 0.01 M. sodium chloride: also some 54 mV. between two regions in contact with 0.01 M. and 0.0001 M. potassium chloride.³⁷

Attempts to determine ionic mobilities in the cell surface layer have been made on the assumption that the potential difference across the membrane is due to diffusion potentials.³⁸

Substitution in equation (4), with the mobility of $Cl^- = 1$, gives:—

* The term "membrane polarisation" is often used to denote the resting potential of the membrane, i.e. the potential difference measured across the membrane under resting conditions, after due allowance has been made for liquid-liquid junction potentials between the saline of the electrodes and the intra- and extra-cellular fluids. Reduction of the membrane potential, e.g. by injury, is often termed "depolarisation".

³⁷ Osterhout, *Trans. Faraday Soc.*, **33**, 997, 1937.

³⁸ Damon, *J. Gen. Physiol.*, **16**, 375, 1932-3.

	Mobility K^+	Mobility Na^+	Mobility Ratio K^+/Na^+
Valonia . .	20	0.2	100
Nitella . .	85.5	2.2	39

Treatment of *Nitella* with distilled water changes the relative mobilities from $K^+ > Na^+$ to $Na^+ > K^+$. Treatment of *Valonia* with guaiacol changes the relative mobilities from $K^+ > Cl^- > Na^+$ to $Na^+ > Cl^- > K^+$: before treatment $u_{K^+}/v_{Cl^-} = 20$ and $u_{Na^+}/v_{Cl^-} = 0.2$, but after treatment these ratios become 0.36 and 4.5, respectively.³⁷ These treatments do not injure the cells, and it must be assumed that the composition or structure of the membrane is modified.

The injury potential in multi-cellular plants, like the injury potential of muscle and nerve, is always such that the injured region is negative with respect to the intact region. Injury potentials may be as large as -120 mV., and usually some -40 to -70 mV.

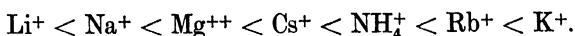
The Membrane Potential of Muscle and Nerve Fibres. The intact external surface of a muscle or nerve, in the resting state is iso-electric or nearly so. That is to say, the outer surfaces of the cells composing the muscle or nerve are at the same potential. If the fibres underneath one electrode are damaged, or the tissue is cut across, and an electrode applied to the cut surface, a potential difference of some 30 or 40 mV. is found between the injured and intact regions, the injured region being negative. This is the injury potential, first reported in 1841 for muscle³⁹ and in 1843 for nerve.⁴⁰ It is now known that the injury permits a more or less direct connection with the interior of the cells of the tissue, and that the site of the injury potential is the intact membrane beneath the reference electrode; the potential is the polarisation potential of the resting membrane. A muscle or nerve comprises a bundle of cells—the muscle or nerve fibres—lying more or less parallel to one another. Injury to the fibres permits direct electrical

³⁹ Matteucci, *Compt. rend. Acad. sci.*, **13**, 540, 1841.

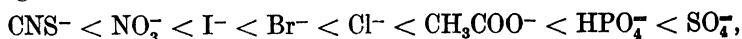
⁴⁰ Du Bois Reymond, *Ann. Physik. u. Chem.*, **58**, 1, 1843.

connection to the intra-cellular fluid of each damaged fibre. The injury potential is thus the resultant of the parallel connection, in the electrical sense, of the injury potentials of all the injured fibres, partly short-circuited, however, by the presence of saline from the electrodes and by the normal interstitial fluid.

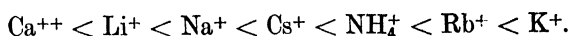
Studies of the effect of different fluids, in contact with the fibres underneath the reference electrode, confirm that the injury potential originates in the intact membrane. This provides a method for observing the effects of different substances on the membrane potential. For frog muscle, Höber ⁴¹ showed that cations were arranged in the following order of effectiveness on the injury potential:—



Anions also were found to influence the potential, but to a less degree, in the order:—



For frog nerve (medullated) Netter ⁴² found the injury potential (i.e. the membrane polarisation) independent of the species or valency of the anion and dependent on the cation in the order:—



For the non-medullated nerve of the crab, Cowan (Fig. 3) found an approximately linear relation between the injury potential and the logarithm of the potassium chloride concentration in contact with the fibres.⁴³ According to Lorente de Nó, the relation is different for medullated frog nerve, e.g. sciatic, and the time course of the effect is very slow.²⁷

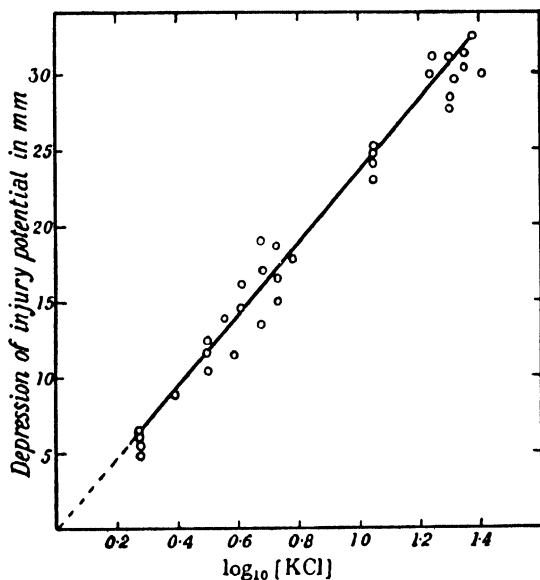
With single nerve or muscle fibres many of the observations on the injury potential have been repeated and confirmed. The exterior surface of the single fibre is approximately iso-electric, and the injured region is negative with respect to the uninjured region. With a micro-electrode inserted into a single fibre, the potential difference across the membrane has been observed directly in squid, crab and lobster axons and frog muscle. The injury potential measured with external electrodes is always found to be less than

⁴¹ Höber, *Pflüger's Arch.*, **106**, 599, 1905.

⁴² Netter, *ibid.*, **218**, 310, 1927.

⁴³ Cowan, *Proc. Roy. Soc. B*, **115**, 216, 1934.

the directly measured membrane potential, due to the short-circuiting effect of the interstitial fluid on the injury potential, as already mentioned. For single giant axons of the squid, crab and lobster, cutting, crushing or injury by chloroform depolarises the membrane, i.e. reduces the membrane potential.⁴⁴ In the squid, the directly measured resting membrane potential is about 50 mV.



X 3.—Approximately linear relation between the injury potential and the logarithm of the potassium chloride concentration in the fluid surrounding nerve fibres of the crab. The potential is plotted in terms of the galvanometer reading in mm. The potassium concentrations are expressed as multiples of that in sea-water (38.8 mgm. per 100 gm). (After Cowan, see ref. 43.)

(inside negative) and this is reversed to 15 mV. (outside negative) by the action of isotonic potassium chloride solution.⁴⁵ In frog muscle fibres, the resting potential is about 87 mV. (inside negative).

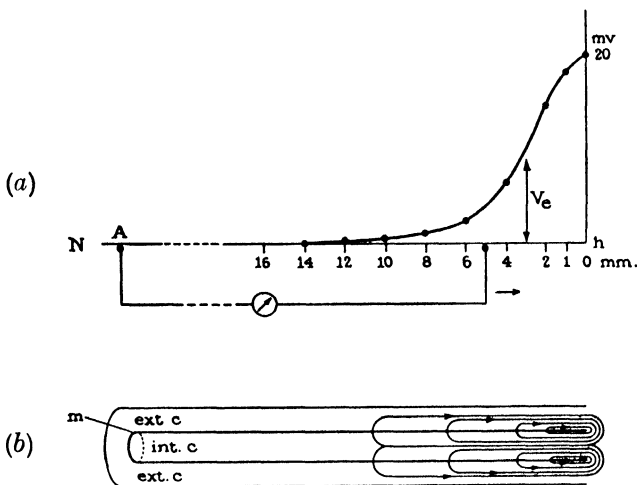
Resting and Injury Potentials in Nerve: Further Analysis.

When a nerve is injured, e.g. by crushing, the injury potential can be recorded not only directly over the site of injury but from points of the nerve adjacent to the injury. If one electrode is fixed at a distance of a few centimetres from the site of injury and

⁴⁴ Hodgkin and Huxley, *J. Physiol.*, **104**, 176, 1945.

⁴⁵ Curtis and Cole, *J. cell. comp. Physiol.*, **19**, 135, 1942.

the second (nearer the injury) is moved along the nerve towards the injured region, the longitudinal distribution of the injury potential can be determined. Fig. 4a shows the spatial distribution of the injury potential of the sciatic nerve of the bullfrog.



X 4.—(a) and (b). (a) The nerve N is injured at point h , and the injury potential, V_e , is measured with respect to a remote reference point A . The spatial distribution of V_e along the nerve is shown. (b) Diagram to show the flow of current at the site of injury of the nerve; m = nerve fibre membrane, ext. c. and int. c. = external and internal conducting media, respectively. The arrows show the direction of flow of the positive ions. (After Lorente de N6, see ref. 27.)

Except for the first millimetre or so in the immediate neighbourhood of the site of injury, the distribution is exponential:

$$V = V_0 e^{-x/\lambda} \quad . \quad . \quad . \quad (8)$$

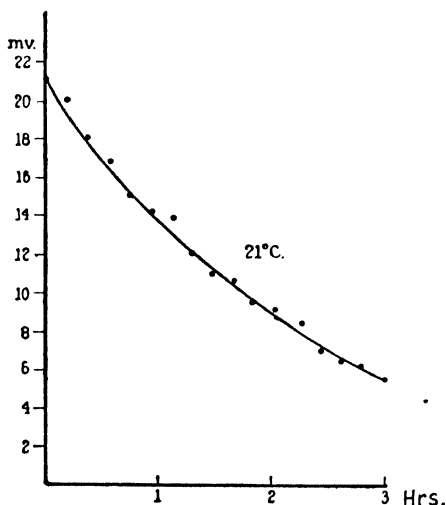
where V = the potential difference between the point at distance x from the injury and the remote reference point.

V_0 = the value of V at $x = 0$.

λ = the space constant (sometimes called the attenuation constant or characteristic length).

The space constant is the distance along the nerve in which the potential falls to $1/e$ of its initial value. The value of λ for frog sciatic nerve is about 3 mm. The distribution of injury potential is explained on the assumption that there is a continuous

flow of current (positive ions) in the interstitial fluid from the uninjured part of the nerve towards the negative injured region, in order to restore electric equilibrium. There is, of course, a corresponding flow of negative ions in the reverse direction, and within the axons the current flows to complete the circuit. It is the resting potential across the uninjured portion of the nerve which maintains this current. The lines of current flow are illustrated diagrammatically in Fig. 4b; the total longitudinal current



X 5.—Plot of the injury potential against time after the injury. (After Lorente de N6, see ref. 27.)

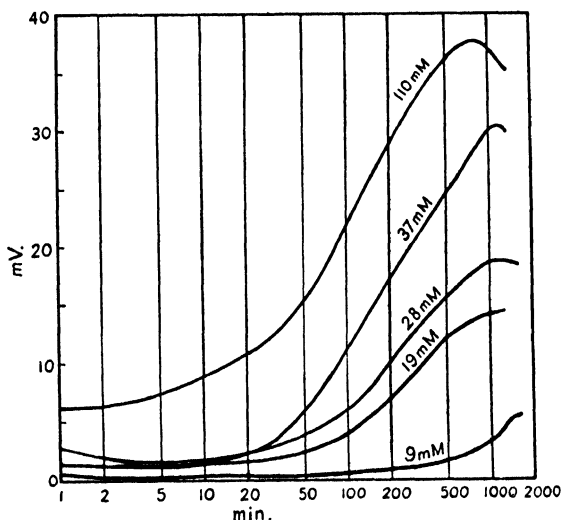
is equal to the total transverse membrane current. The transverse membrane current density is highest immediately adjacent to the injury ($x \simeq 0$) and diminishes as x increases. After several hours the injury potential decreases practically to zero, as shown in Fig. 5. This is the initial stage of nerve repair, after injury, in the intact animal.

Potassium chloride, applied to nerve, produces a lowering of the potential at the site of application.

In this respect its action can be likened to injury produced mechanically. A concentration as small as 9 mM. added to the Ringer fluid (K^+ ions being exchanged for Na^+ ions in equivalent amounts) is effective. Fig. 6 shows the temporal course of depolarisation of frog sciatic nerve produced by various concentrations of potassium chloride from 9 mM. to 110 mM. The potassium chloride penetrates rapidly to the nerve axons through the connective tissue sheath and the interstitial spaces, as shown by the conduction block which occurs in a few minutes (e.g. 15 min. for a 110 mM. solution). Thus the much longer times taken for a steady state of depolarisation to occur

are not due to slow penetration of the K^+ ion but to its slow action in producing depolarisation.

This does not agree closely with what is to be expected from the Bernstein hypothesis about the origin of the resting potential of nerve: that (1) the fibre is impermeable to anions and Na^+ ions, and (2) the potential is a concentration potential, proportional to the logarithm of the ratio *Internal K^+ concentration/External K^+ concentration*. On this hypothesis, the effect of a change in the

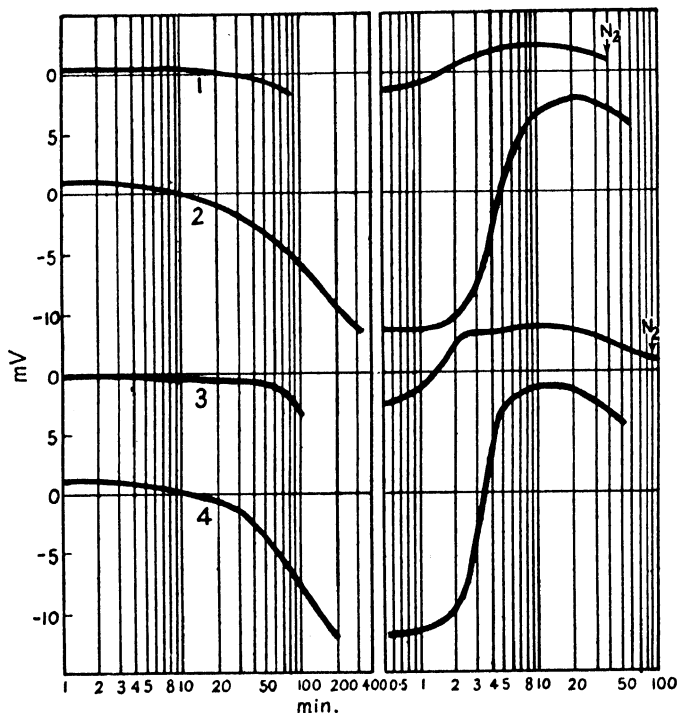


X 6.—Temporal course of potential change (depolarisation) produced by the application of potassium chloride to frog sciatic nerve. The potential was measured with respect to an intact segment of the nerve, and the millimolar concentrations were as shown on the various curves. (After Lorente de N6, see ref. 27.)

external K^+ ion concentration should be maximal soon after penetration of the ion has occurred. Further, if the external K^+ ion concentration is lowered, e.g. to zero, the membrane potential does not increase indefinitely, but for frog nerve reaches a maximum of about 60 mV.

If a nerve is placed on electrodes, containing Ringer solution, so that the stretch of nerve under one electrode is rendered anoxic (e.g. nitrogen replaces all the air normally present), then depolarisation of the anoxic part of the nerve occurs. The extent is not

as great as with potassium chloride but the time course is shorter (Fig. 7). On re-admission of oxygen, the nerve becomes repolarised very rapidly (5-10 min.) and the potential may overswing. If the cycle is repeated, the depolarisation is much greater but the



X 7.—Curve 1: depolarisation effect of anoxia on frog sciatic nerve. After 100 min. oxygen was re-admitted to the chamber and repolarisation occurred (right-hand portion of curve) with some overswing. At N_2 nerve was rendered anoxic again. Curve 2: Repetition of the cycle on the same nerve giving greater depolarisation and rapid repolarisation, on re-admission of oxygen, with more marked overswing. Curves 3 and 4: The same on another, similar preparation. (After Lorente de Nó, see ref. 27.)

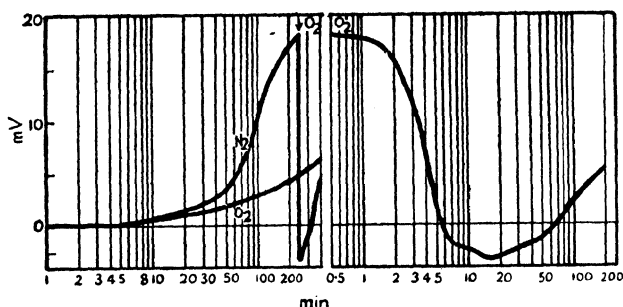
time course is unaltered: on re-admission of oxygen, the same rapid repolarisation occurs usually with some overswing.

Combination of the effects of the K^+ ion and of anoxia, shows that complete repolarisation of the potassium treated nerve can occur in the continued presence of the potassium (Fig. 8).

These experiments of Lorente de Nó suggest ²⁷ that the oxidative processes of the membrane are more important in the determination

of membrane potential than is the potassium ratio. If this is so the Bernstein hypothesis should be abandoned, but there is as yet no alternative to replace it.* In general terms, Lorente de N6²⁷ has proposed the following two hypotheses:

- (1) "Oxidative metabolism creates the E.M.F. of the membrane."
- (2) "The resting membrane potential has the value at which the electrostatic forces balance the non-Coulomb forces created by oxidative metabolism."



X 8.—Polarisation changes produced in frog sciatic nerve by combination of anoxia and potassium treatment. One of a pair of nerves was kept in oxygen and the other rendered anoxic. The nerves were both treated with 16.5 mM. potassium chloride. Depolarisation is shown by the upward trend of the curves. On re-admission of oxygen to the anoxic segment, very rapid repolarisation occurred with overswing. The repolarisation phase is redrawn on the right-hand portion of the figure on an expanded time scale. (After Lorente de N6, see ref. 27.)

He goes on to say, "The membrane itself must be considered as a system in chemical equilibrium and the membrane potential must be regarded as one of the components of the system which is comparable with any of the chemical species that participate in the equilibrium reactions, because changes in the equilibrium point will result not only from changes in the concentration of chemical components but also from changes in the membrane potential. Thus, for example, the fact that an increase of the membrane potential brought about by an applied current restores the polarisability of the membrane as well as the excitability of the nerve fibre could hardly be explained in any other way than by

* Compare Chap. XI, p. 298 *et seq.*

the assumption that the increase of the membrane potential brought about by the current displaces the equilibrium point of a chemical system in the same manner as oxidation of certain chemical species by respiration.

“In view of the relative independence of the membrane potential of the composition of the external medium and even of the internal concentration of potassium, it seems probable that the establishment of the double layer is mainly referable to the oxidation-reduction systems of the chain of oxidative enzymes and substrates, and it seems reasonable to believe that ordinary ions such as K^+ and Na^+ can play a specific rôle only in so far as they directly or indirectly participate in enzymatic reactions.”

Effects of Current Flow through Cells and Tissues.

When a potential is applied to a biological system so as to cause a flow of current through the cells and tissues, certain changes occur in the ion concentrations at the phase boundaries of the system. In general, the ionic mobilities and transfer numbers of the various ion species are different in the different phases of the system. When the field is switched on and current flows, the additional force acting on the ions, i.e. the electric force of the applied field, produces a redistribution of ions in the vicinity of the phase boundaries. The concentration of a given ion species will increase on one side of a boundary and decrease on the other. The new distribution is a steady state distribution maintained by the current flow; it appears in the external circuit as a counter-E.M.F., opposing the current flow, and usually approaches the steady value asymptotically. If the effect of current flow on the lipo-protein complex of the membrane is to cause it to acquire a charge (e.g. as happens with colloid ampholytes at a pH away from the iso-electric point), there will be relative retardation of anions or cations passing through the membrane (according to the sign of the charge) with production thereby of a counter-E.M.F. The counter-E.M.F.s produced by current flow are properly named polarisation E.M.F.s, and the phenomenon is similar in every way to polarisation in electrode systems—i.e. over-voltage. When the current is switched off, the system returns to its initial state.

It has long been known that the transverse conductance of membranes separating different solutions is not the same for the two directions of current flow. This asymmetry is usually termed the rectifier effect, and has been demonstrated with both artificial and natural membranes. Suppose a collodion membrane is prepared with pores large enough to allow anions and cations to pass through; let it separate a neutral solution of potassium phosphate from a sodium chloride solution. If a current is passed from the potassium phosphate side to the sodium chloride side of the system, the resistance is less than when the current is reversed. That is to say, the membrane is more easily penetrated by K^+ and Cl^- ions than by Na^+ and HPO_4^- ions.

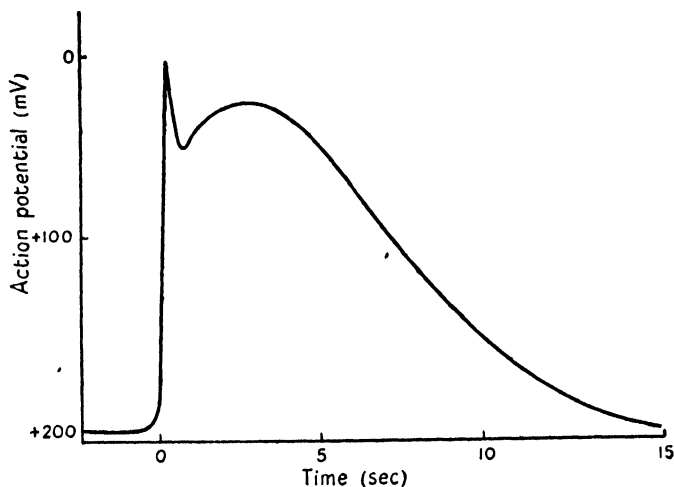
A model nerve axon can be made up with such a collodion membrane in the form of a cylinder packed with and surrounded by gauze or cotton wool, soaked in these two salines. If, by means of externally applied electrodes, a continuous current is passed through such a model so as to flow partly inside the "axon" and partly outside, then the spread of current at the anode is found to be greater than at the cathode and the anodic polarisation is greater than the cathodic polarisation. Since the same total current is flowing at anode and cathode, it follows that the current density at the anode is less than at the cathode. This behaviour is found in nerve axon.

The ratio of the conductance in one direction to the conductance in the reverse direction is a measure of the efficiency of a rectifier element. The plasma membrane of the squid giant axon has a ratio better than 100/1, which is of the order found with a good metal rectifier.

If the current flow is of sufficient intensity and of sufficiently rapid onset or decay, certain plant and animal cells respond by initiation of a propagated potential wave—the action potential. Cells which respond thus to adequate stimulation are giant plant cells, nerve fibres and muscle fibres. The excitability properties of nerve and muscle fibres are discussed in the next chapter.

The Action Potential of Giant Plant Cells. When giant plant cells are stimulated by an adequate electrical stimulus (usually 100-200 mV. applied to the cell is sufficient) the action

potential wave of negativity is initiated and spreads over the cell surface. In *Nitella* ⁴⁶ the wave lasts a few seconds and full recovery to the initial resting state takes about 15 sec.; the velocity of propagation is 2 to 20 cm. sec.⁻¹. The action potential can be suitably recorded with one electrode in contact with the intact surface of the cell and a second electrode on a region injured by potassium chloride or chloroform. The onset of the wave is rapid and corresponds to the "spike" potential of nerve and muscle (see Chap. VIII). The diagram in Fig. 9 shows the typical time



X 9.—The action potential of the giant plant cell, *Nitella*, recorded with respect to an electrode in contact with a part of the cell wall injured by potassium chloride (after Osterhout, see ref. 47).

course of the wave. The resting potential of 200 mV., which is the injury potential due to the action of potassium chloride or chloroform at one of the electrodes, is decreased to zero rapidly and returned slowly to its original value. That is to say, the resting potential across the cell membrane is temporarily destroyed as the wave of action passes over the cell surface. Measurements of the transverse resistance of the membrane show that a large decrease occurs when the action potential wave passes under the measuring electrode, e.g. from 10^5 ohm. cm.⁻² to 5×10^2

⁴⁶ Blinks, Harris and Osterhout, *Proc. Soc. Exp. Biol. and Med.*, **26**, 836, 1928-9.

ohm. cm.⁻². There is simultaneously a 15 per cent. decrease in membrane capacitance. Thus the action potential wave is a phase of structural breakdown of the plasma membrane: the resting potential across it is destroyed and its permeability is very greatly increased, temporarily. This is believed to be associated with transfer of potassium ions from inside the cell through the cell membrane.⁴⁷

Resistance and Capacitance Measurements. When direct current is used for measuring resistance of cells and tissues certain precautions must be observed. Current must not flow for more than a few seconds or even milliseconds in order to minimise polarisation effects, and with excitable tissues the current strength must be less than that required to evoke an action potential. Collateral current paths must be avoided or reduced to a minimum which can be neglected or allowance made for it. A Wheatstone bridge circuit is to be preferred to current and voltage measurement in a simple circuit. In general, with direct current measurements, the quotient *voltage/current* is not a constant for different current values. Cells and tissues do not obey Ohm's Law, but the inter- and intra-cellular fluids must do so to about the same extent as weak solutions of electrolytes do, but this is difficult to demonstrate because of membrane and polarisation effects.

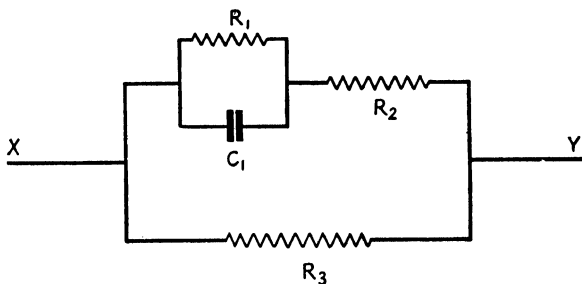
When alternating current measurements are made with a Kohlrausch bridge circuit or similar arrangement, polarisation effects are usually greatly reduced or zero. The membrane capacitance becomes a relatively less important factor in the impedance as the frequency is increased. The simplest representation of the cell membrane in terms of electrical circuit elements is as a leaky condenser, i.e. a capacitance C_1 in parallel with a resistance R_1 (Fig. 10). In series with this is the resistance of the intra-cellular fluid, represented by R_2 in the figure. R_3 is the resistance of the external conducting medium which surrounds the cell and shunts it electrically and hence is in parallel with the cell element. This arrangement represents a single cell with electrodes X, Y on the exterior of the cell or a suspension of cells with electrodes X, Y

⁴⁷ Osterhout, *Physiol. Rev.*, **16**, 216, 1936.

placed in the external medium. The impedance of the equivalent network of Fig. 10 is given by the following expression :—

$$Z = \frac{(R_1 + R_2)R_3 + jR_1R_2R_3C_1\omega}{(R_1 + R_2 + R_3) + jR_1(R_2 + R_3)C_1\omega} \quad (9)$$

As the frequency is increased, it is clear that, in the limit, the impedance reduces to $R_2R_3/(R_2 + R_3)$. The lowered value of the impedance at high frequencies reflects the high conductivity of the interior of the cell as compared with the membrane. That is to say, when a tissue is placed in an alternating field, as the frequency is increased, more of the energy of the field is absorbed by the cell and relatively less by the interstitial fluid. Electrical



X 10.—Resistance-capacitance network to represent the behaviour of a single cell or a suspension of cells in an electric circuit.

analogues of biological systems can be elaborated almost indefinitely, particularly when the equivalent circuit is very complex. In view of the many alternative circuits available, analysis of a biological system in this way is of limited value.

Transverse resistivity of the membrane and membrane capacity for various types of cells have been computed from D.C. and A.C. measurements, on the assumption that the system is sufficiently accurately represented by a network similar to that of Fig. 10. Resistivity figures vary considerably from one experiment to the next, and a wide range of values has been recorded by the same workers when different methods have been used. For the squid giant axon which is some 0.5 mm. diameter, D.C. measurements have given values from 400 to 1100 ohm cm.⁻²; A.C. measurements yielded values less than 200 ohm cm.⁻²; a D.C. pulse method, with internal electrode, gave very low values with an average

of only 23 ohm cm.⁻²; calculations from other A.C. measurements have given a value of 350 ohm cm.⁻². A value of 300 ohm cm.⁻² is probably the best average figure. For the lobster axon of 75 μ . diameter, values of 600 to 7000 ohm cm.⁻² have been recorded.⁴⁸

Typical membrane capacity figures are given in Table X.

TABLE X. CAPACITY OF PLASMA MEMBRANE OF DIFFERENT CELLS

Cell	Capacity (μ F. cm. ⁻²)
Hipponoë eggs . .	0.87
Asterias eggs . .	1.1
Arbacia eggs . .	0.73
Salmo eggs . . .	0.57
Erythrocyte . .	{ 0.81 0.95
Loligo axon . . .	1.1
Carcinus axon . .	1.1
Homarus axon . .	1.33
Nitella	0.94
Yeast	0.6
Sartorius m. . . .	c. 1

Full references are given in ², ³, ⁴⁴.

A great many electrical conductivity measurements have been made with cell suspensions such as erythrocytes and ova in various saline media. Maxwell⁴⁹ developed the following expression for the resistance of a uniform suspension of homogeneous spheres randomly distributed in a uniform field :

$$\frac{1 - r_1/r}{2 + r_1/r} = \rho \cdot \frac{1 - r_1/r_2}{2 + r_1/r_2} \quad . \quad . \quad . \quad (10)$$

i.e.
$$r = r_1 \frac{(1 - \rho)r_1 + (2 + \rho)r_2}{(1 + 2\rho)r_1 + 2(1 - \rho)r_2} \quad . \quad . \quad (10a)$$

where r , r_1 , r_2 = specific resistances of the whole suspension, medium and spheres.

ρ = volume concentration of the spheres: if the volume of the spheres is x and that of the containing medium is y , then $\rho = x/(x + y)$.

⁴⁸ Hodgkin and Rushton, *Proc. Roy. Soc. B*, **133**, 444, 1946.

⁴⁹ Maxwell, *Treatise on Electricity and Magnetism*, Clarendon Press, Oxford, 1873, Art. 314.

This equation is not directly applicable to most living cells since they are not usually spherical in shape nor homogeneous in composition. Moreover no difference in conductivity between membrane and cell interior is allowed for, nor is the membrane capacitance represented. For conducting spheres surrounded by a thin, poorly conducting layer, Maxwell's expression for the equivalent resistance, r_2' of a two-phase sphere (*loc. cit.*, Art. 313) gives:—

$$r_2' = r_2 + z_3/a \quad . \quad . \quad . \quad (11)$$

where z_3 = membrane impedance per unit area of membrane

a = radius of sphere.

Substitution of the value of r_2 from equation (11) for r_2 in equation (10a) and replacement of r by z , the impedance of the suspension, gives

$$z = r_1 \frac{(1 - \rho)r_1 + (2 + \rho)(r_2 + z_3/a)}{(1 + 2\rho)r_1 + 2(1 - \rho)(r_2 + z_3/a)} \quad . \quad . \quad (12)$$

By an analysis based on these equations, Cole⁵⁰ has shown that in certain eggs (Hipponoë and Arbacia) fertilisation increases the apparent membrane capacity. In others it is unaltered. At high frequencies (1-16 kc./s.) a divergence was found, in both fertilised and unfertilised eggs, from the simple equivalent network of Fig. 10. He attributes this to a hitherto unidentified structure. Rothschild⁵¹ employed Maxwell's equations in his studies of trout eggs, and found no significant capacity change of the cell membrane after fertilisation—0.57 $\mu\text{F. cm.}^{-2}$ before and 0.58 $\mu\text{F. cm.}^{-2}$ after, at 1 kc./s. Spontaneous rhythmical impedance changes were observed, almost entirely capacitative, of the order of 5-10 per cent., when measured at a frequency of 1 kc./s., with a period of 1-3 min.

Skin Potentials and E.M.F.s. The skin of animals such as the frog or man is a complex aggregate of cells arranged in a thin sheet consisting of several layers of cells of various types, all in different stages of growth and development. Skin cells are, in general, constantly being shed at the outer surface and replaced by new cells growing from the innermost layer—the germinal layer. Thus a piece of skin is a very complicated heterogeneous

⁵⁰ Cole, *J. Gen. Physiol.*, **12**, 29, 1928.

⁵¹ Lord Rothschild, *J. Exp. Biol.*, **23**, 77, 267, and **24**, 390, 1946-7.

system and it is not surprising that although many measurements of skin potential and resistance have been made, agreement about the interpretation of the results has not been possible so far. Many complex experiments involving current flow across the skin have also been described.

In general, with intact or isolated skin from animals, a potential difference can be recorded between any two parts of the skin. In the frog the potential difference across the isolated skin, with Ringer solution on each side, amounts to some 40 mV, with the outside negative. Replacement of the Na^+ ion on the outside by K^+ ion reduces the potential to zero. This is similar to the effect of the potassium ion on the cell membrane in simpler systems, e.g. in the nerve fibre. Concomitantly the transverse resistance of the frog skin is diminished. Anoxia and oxidative poisons, e.g. KCN and CO, also reduce the potential. Bromoacetate which interferes with carbohydrate breakdown, and inhibits lactate production, has no effect on the potential. The potential falls only when the skin stores of lactate are used up; it can be restored by addition of lactate. Narcotics which depress metabolism also decrease the potential. In these, and in other ways, the complex heterogeneous sheet of cells resembles the cell membrane, thus justifying the comment of Krogh (see p. 247).

There is great variability in the behaviour of frog skin, and hence adequate statistical control of measurements is necessary: this precaution has not usually been observed. On account of the complex, multi-cellular nature of the skin, the results obtained cannot be used to test directly whether concentration potentials or liquid-liquid junction potentials occur in their simple form, as has been done with artificial membranes. Possibly the behaviour of the piece of skin could be explained, statistically, in terms of the responses of the plasma membranes of the individual cells of which the skin is constituted, together with the short-circuiting effects of the interstitial fluid, if only enough were known about the reactions and behaviour of each individual cell or group of similar cells.^{52, 53}

⁵² Dean and Gatty, *Trans. Faraday Soc.*, **33**, 1040, 1937.

⁵³ Höber, *Physical Chemistry of Cells and Tissues*, Churchill, 1945.

In man the skin of the palms of the hand and of the soles of the feet differs considerably from the skin elsewhere on the body. The potential is nearly always most negative in these areas, and, measured with respect to a reference electrode on the arm, often amounts to some -50 mV., but may be as low as -5 or -10 mV. The potential varies continuously—slowly and to a less extent at low skin temperatures, e.g. 15°C ., rapidly and more widely at higher temperatures, e.g. 25°C . The mean potential is relatively unaffected by skin temperature.

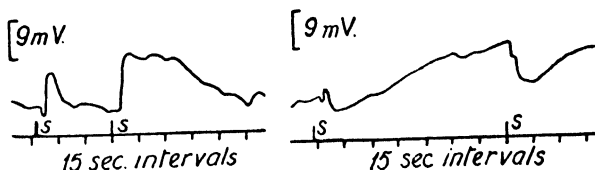
The effect of different concentrations of sodium and potassium chloride solutions on the resting potentials is shown in Table XI. The salines were the liquid phase, in direct contact with the skin, of silver-silver chloride electrodes, the potentials being measured with a D.C. amplifier system having a high input impedance and grid current less than $10^{-3}\mu\text{A}$.

TABLE XI. TYPICAL SKIN POTENTIALS IN MAN WITH DIFFERENT STRENGTHS OF SALINE AT THE TWO ELECTRODES (sign is that of palmar electrode: reference electrode on dorsum of fore-arm)

Electrolyte	Concn. gm. %	Potential mV.
NaCl	0.09	-1
	0.9	-10
	9.0	-18
NaCl	0.09	-5
	0.9	-16
	9.0	-26
KCl	0.09	$+5$
	0.9	-5
	9.0	-15

Changes in potential can be evoked by suitable stimulation of the subject, e.g. by a single maximal deep breath, in and out. The amplitude and time course of these changes are not correlated with skin temperature. These "potential responses" to stimulation are of a very variable character and may be negative or positive with respect to the resting level and consist of a single wave or of several waves, negative and positive, in succession. Typical

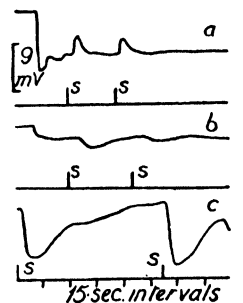
responses are shown in Fig. 11. These responses arise from the skin of the palmar surface of the hand, and it is generally thought



X 11.—Typical potential responses, recorded from the palmar surface of the finger; stimulus (*s*)—a single maximal deep breath. Same subject, 45 min. interval between the two records. (Floyd and Keele, see ref. 54.)

that the phenomenon is due to sweat gland activity, although concomitant vascular changes (i.e. changes in blood vessel calibre) may contribute to the recorded potential.

The character of the potential response is markedly affected by the flow of current through the skin. The records in Fig. 11 were taken with a current flow through the skin of less than $10^{-3} \mu\text{A.}$ which produces negligible polarisation effects. Fig. 12 illustrates the effect of currents as small as $0.05 \mu\text{A.}$ and $0.2 \mu\text{A.}$, with electrodes of area 39 sq. mm. With larger currents, maintained constant throughout the experiment by a saturated triode valve circuit, the response increases in size. The increase is linear with currents up to $10 \mu\text{A.}$ and falls off in the range $10\text{--}100 \mu\text{A.}$ With current flowing the response to stimulation is always in the same direction, i.e. a decrease in the E.M.F. produced by the current flow. The size of the response is inversely proportional to the area of the electrode on the palmar surface of the hand, and hence directly proportional to the current density. The time course of the response is dependent on the skin temperature, being much longer (4–6 min.) at 15°C. and usually less than 1 min.



X 12.—The effect of current flow through the skin on the potential responses. (*a*) Potential responses: stimulus (*s*) a single maximal deep breath; (*b*) Responses with a mean current flow of $0.05 \mu\text{A.}$ Note reversal of direction of the response; (*c*) Responses with constant current flow of $0.2 \mu\text{A.}$ Responses are in same direction as in (*b*) but of greater amplitude. (Floyd and Keele, see ref. 54.)

at 30° C., but the magnitude is unaffected by skin temperature changes.^{54, 55}

Potentials of the Stomach. A great interest has been taken in the ability of the stomach to produce electrical potentials because of the possibility of correlating electrical activity with the chemical action of HCl production. The potentials can be measured in the intact animal with an electrode at the end of a stomach tube, and the method has been used clinically, in man.⁵⁶ A great deal of work has also been done on isolated stomach wall, which continues to function for many hours after removal. Attempts to show that the maintained potential of the stomach wall is responsible for a current flow related to the secretion of HCl have been unsuccessful however.⁵⁷ Although a current density of 1 mA. cm.⁻² can be obtained from the stomach, the maximum energy output obtained (some 40 μ W. cm.⁻²) is only one-sixth of that required for HCl production (13 μ gm. cm.⁻²/min.). The problem is complicated by the difficulty of measuring or calculating the shunting effect of extracellular fluids and material, within the stomach wall. The subject has recently been reviewed at length by Eva Crane.⁵⁸

Note added in proof. Recent work (notably Keynes and Lewis, *J. Physiol.*, **113**, 73 and Creese, *J. Physiol.*, **114**), has shown conclusively that all the intracellular potassium of nerve and muscle is free to exchange with K⁴² and is not bound²² (see p. 241). Similarly, studies with Na²⁴ are showing that nerve and muscle fibres are permeable to sodium and that an extrusion mechanism is continuously at work, but the energy consumed by the process is much less than calculated by Conway²⁸ (see p. 241).

⁵⁴ Floyd and Keele, *Trans. Faraday Soc.*, **33**, 1046, 1937.

⁵⁵ Floyd and Keele, *J. Physiol.*, **86**, 2P, 1936.

⁵⁶ Goodman, *Surg. Gynec. and Obst.*, **75**, 583, 1942.

⁵⁷ Rehm and Hokin, *Amer. J. Physiol.*, **154**, 148, 1948.

⁵⁸ Eva Crane, "Bioelectric Potentials, their Maintenance and Function" in *Progress in Biophysics*, **1**, 1950, Butterworth.

CHAPTER XI

ELECTRICAL PROPERTIES OF NERVE AND MUSCLE

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“To record shape has been far easier than to understand it.”

—C. S. SHERRINGTON.¹

THE earliest electro-physiologist, Luigi Galvani, in 1786 * used a frog nerve muscle preparation in his experiments on electric discharges. He observed that the muscles of the leg contracted whenever the foot of the frog, hung from a copper hook through the spine, came in contact with an iron wire. We now know that the preparation was being used as a galvanometer, detecting the contact potential of two dissimilar metals, copper and iron. Galvani's interpretation of his early experiments was that animal tissues produced electricity, which discharged through the conducting path provided by the metal wires. Volta rejected this interpretation and later, about 1800, showed that the contact potential of two dissimilar metals was responsible for evoking the muscular contraction in Galvani's experiment, i.e. that the preparation responded to electrical stimulation. Galvani subsequently made many other important observations, although the significance of them was not appreciated at the time.

The Nerve Muscle Preparation: Excitability. The preparation which has been most commonly used to study the excitability properties of nerve and muscle is the *sciatic nerve-gastrocnemius muscle* of the frog, which is usually isolated from the animal and set up in a special chamber providing a suitable environment for the duration of the experiment. The sciatic nerve contains many thousands of nerve fibres, of which several hundreds terminate in the gastrocnemius muscle (one of the muscles of the calf of the leg). Mechanical, thermal, chemical and electrical

¹ Sherrington, *Man on his Nature*, p. 133, Cambridge, 1940.

* There were earlier attempts to link up electrical phenomena and body tissues, but these consisted mostly of the use of the Leyden jar or frictional electricity machines to stimulate tissues, particularly muscle, and had elements of magic or quackery about them.

stimuli applied to the preparation (either to the nerve or muscle) can cause the muscle to twitch if the stimulus is strong enough, e.g. a heated glass rod or a crystal of sodium citrate placed on the nerve. This property of responding to adequate stimulation is referred to as *excitability*. When the muscle responds, following stimulation of the nerve, it is said to be stimulated indirectly, i.e. through its motor nerve. There is no *direct* evidence, in such a simple experiment, for the excitability of the nerve, but it is obviously necessary to postulate the excitability property for nerve if the distinctness of nerve and muscle tissue is accepted, e.g. on histological (i.e. structural) evidence. Clearly, also, there must be some sort of transmission phenomenon between nerve and muscle, by which the excitation process is passed on to the muscle, thereby causing the muscle twitch.

When muscle is stimulated directly, e.g. by applying electrodes to it and passing a suitable current, the muscle twitches. This experiment is not, as it might appear, evidence for the direct excitability of muscle, because the muscle contains the nerve endings of its motor nerve. It is necessary to exclude the possibility that these endings are excitable and more sensitive than the muscle fibres, and hence that the twitch is occurring in a manner closely similar to that of indirect stimulation of the muscle, just described. This can be shown by use of the drug curari which blocks transmission of excitation from nerve to muscle. Thus the twitch which occurs in a curarised preparation, on direct stimulation of the muscle, is evidence for the intrinsic excitability of muscle. In the doses used for such curarisation, the drug curari has no direct, intrinsic effect on muscle.

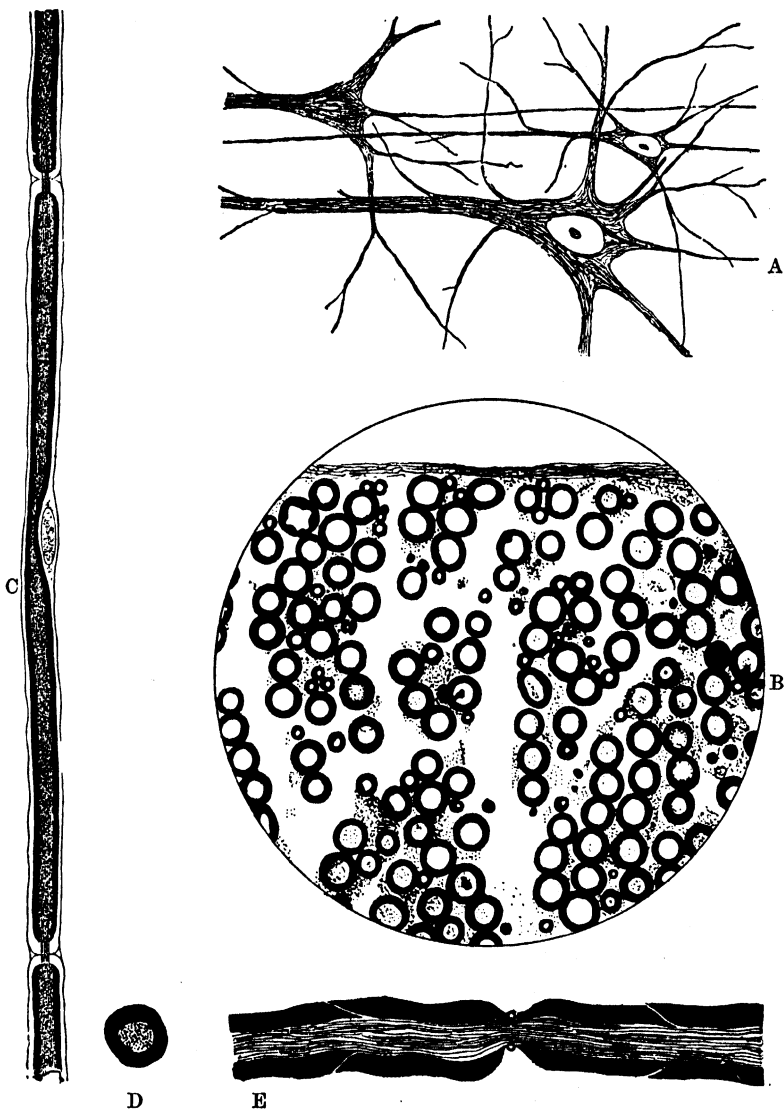
The existence of excitation in a nerve is only demonstrable indirectly, e.g. by ultimate effects such as the contraction of muscle or secretion of glands innervated by it, or by electrical recording from the nerve. Nerve fibres when excited do not show any changes detectable by mechanical or optical methods,* whereas

* Recent studies by D. K. Hill, *vide J. Physiol.*, **111**, 304, show both translucency and mechanical changes in nerve accompanying the transmission of impulses, but the magnitude of the changes is small—1 part in 10^3 for 10,000 impulses, as diameter increase, attributed to osmotic pressure increase consequent upon sodium and potassium exchanges.

muscle fibres shorten, or will do so if free from constraint, and the contraction is accompanied by changes in optical properties, e.g. in translucence and birefringence. In the past many of the electrical properties of nerve have been inferred from experiments with the nerve-muscle preparation, the muscle twitch (minimal or maximal, according to the particular experiment) being used simply as an index of nerve excitation. Modern methods of direct electrical recording from single nerve fibres have made possible the direct test of these hypotheses and their elaboration.

When a resting nerve fibre is excited by an adequate stimulus, a potential wave is created at the site of stimulation, and is propagated along the fibre without decrement and with a constant velocity whose magnitude depends largely on the fibre diameter. This propagated wave is the *action potential* or *nerve impulse*. Relative to a resting part of the fibre, the active region is negative, as it is in the giant plant cell (see Chapter X), hence the action potential is sometimes referred to as a wave of negativity. The present chapter is concerned mainly with a description of the processes involved in the initiation and propagation of the action potential, and it will be shown that the stimulus induces a transient change in the state of the plasma membrane of the nerve fibre. That is to say, the event is a surface phenomenon; or, at least, it occurs at a complex interface. A similar event occurs in muscle fibres when they are excited, but the process is complicated by the concomitant mechanical changes.

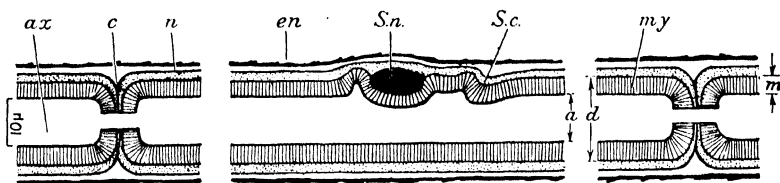
The Structure of Nerve. A necessary preliminary to the discussion of nerve action is a brief description of the main structural features of nerve. The complete nerve cell or *neurone* is an irregular-shaped cell with at least one long process—the nerve fibre or *axon*. The irregular cell is usually termed the *soma*: it is from 1 to 30 or 40 μ . across and varies enormously in its detailed form according to the species of animal and the part of the nervous system in which it occurs. The axon or *axis cylinder* is usually from 1 to 20 μ . in diameter and may be a metre or more in length. Excitation and impulse conduction are usually studied in nerve axon, although the excitation process always invades the soma at some stage and often starts there, e.g. in the transmission of



XI 1.—A : Three irregular nerve cells or soma with many branched dendrites the largest of which is the nerve fibre or axon ; B : Cross section of sciatic nerve of the cat showing different sizes of the axons composing the nerve. The axon sheaths are black, the inner, white areas are the axis cylinders ; C : Longitudinal section of medullated nerve fibre. Two constrictions or nodes of Ranvier are seen, and a Schwann cell nucleus lies between them external to the black sheath of the axon ; D : Cross section of a single medullated nerve fibre seen in B ; E : Enlarged view of node of Ranvier region of axon seen in C. (After Schafer's *Essentials of Histology*, Ed. Carleton. Longmans.)

nerve impulses from one neurone to another in the central nervous system of most animals. The soma is not, however, as readily accessible for direct experimental study as the axon, hence much less is known about the excitability of its plasma membrane. The shapes and some structural details of typical nerve cells are shown in Fig. 1.

The inside of the nerve fibre, i.e. the *axoplasm*, is probably fluid although there is some evidence for a jelly-like consistency. It is fairly certain that the contents of the axon are arranged in a systematic and orderly fashion, e.g. the coalescence of rodlets

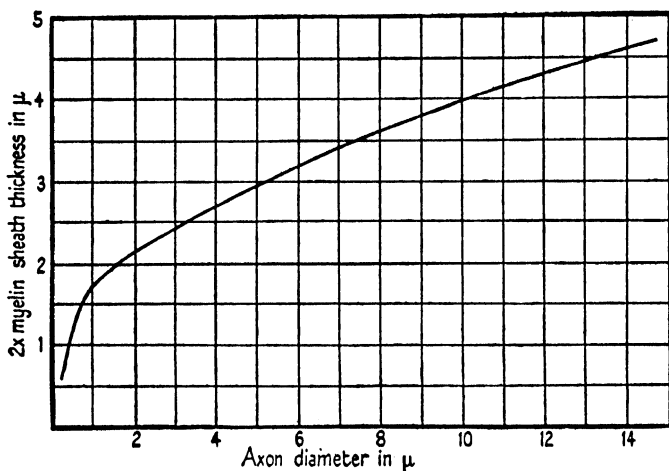


XI 2.—Diagram to show the detailed structure of a nerve axon : *ax*, axis cylinder containing axoplasm and constricted at the nodes of Ranvier ; *my*, myelin ; *S.c.*, Schwann cell enveloping the myelin ; *S.n.*, nucleus of the Schwann cell ; *n*, neurilemma which surrounds the Schwann cell and axon, also constricted at the nodes ; *en*, endoneurial tube, the outermost covering of the fibre. At the nodes a disc-like structure is found at *c*. The internal diameter of the axon is *a*, the external diameter *d*. Hence $2m = d - a$, where *m* is the myelin thickness. (After Young, "History of the Shape of a Nerve-Fibre" in *Essays on Growth and Form*, Oxford, 1945.)

to form the fibrils seen histologically. The surface of the axoplasm is most probably a boundary layer of the same sort as the plasma membrane of other types of cells, as discussed in Chapter X. In vertebrates, in addition to the axon membrane, the presence of which cannot be demonstrated by microscopic techniques, all but the very small nerve fibres are surrounded by a fatty substance, myelin, which can be shown up by suitable histochemical methods, e.g. silver staining.* The myelin is interrupted regularly by constrictions called nodes of Ranvier (Fig. 2). The stretch of nerve between two consecutive nodes of Ranvier is termed a segment of Ranvier, and each segment is surrounded by a thin independent cell structure called a Schwann cell forming a transparent web-

* It has been suggested that all fibres are myelinated, but that the thickness of the myelin surrounding the smallest fibres is below microscopic resolution.

like sheath. The internodal distance is about 1 mm. but in fishes has been reported up to 7 mm. Outside this is another sheath, the neurilemma, which extends over each segment and shows regular constrictions at the nodes. Outside the whole fibre is a tougher sheath or tube, the endoneurial tube, which surrounds the fibre and does not constrict at the nodes. These sheaths are thought to be freely permeable by water and electrolytes, so that the interstitial fluid, for example, has free access to the axon, and all



XI 3.—Curve relating thickness of myelin, m , and axon diameter, a , in peroneal nerve of rabbit (see Fig 2). (After Young, see Fig. 2.)

metabolic exchanges take place across the axon membrane unimpeded by the sheaths.

The myelin thickness increases with axon diameter as shown in Fig. 3, for the axons of the peroneal nerve of the rabbit. The thickness of the myelin probably influences the nerve impulse conduction velocity: the thicker the myelin and the richer its lipid content, the greater is the velocity for a given axon diameter. In animals such as the crab and the squid, large nerve fibres are found without a myelin sheath and without a node of Ranvier structure.

Electrical Stimulation. Of all the different methods of exciting nerve and muscle, electrical methods are the methods of choice, because they give the maximum precision and reproducibility.

bility. The stimuli can be graded accurately in duration and intensity, and can be applied many times to the tissues without harmful effect, whereas with other stimuli it is difficult to obtain excitation without injury. The electrical stimulus can be obtained in many different ways of which the following are the most usual :

- (1) The direct current from a battery or accumulator.
- (2) The pulse from the secondary circuit of an induction coil, with D.C. pulses applied to the primary circuit.
- (3) The discharge from a condenser.
- (4) The pulses from an electronic generator, e.g. a flip-flop or multi-vibrator circuit.

The stimulus obtained from all of these sources is some form of pulse. The duration, amplitude and wave-shape of the pulse depend on the particular generator used and on the circuit conditions. When these factors are known the nerve response can be measured, and related to them, as, for example, in the determination of the strength-duration curve, i.e. the curve relating the strength and duration of stimulus pulse, of known and constant wave-shape, which will just excite the nerve.

The Strength-duration Curve. Within certain limits, the longer the duration of the stimulus pulse applied to a nerve fibre, the smaller the amplitude of pulse required just to excite the fibre. If the pulse strength is increased above that required just to excite, no further effect on the fibre is obtained. The minimum pulse strength of (theoretically) infinite duration which just excites is called the rheobase. In practice, a pulse duration of some 10 millisec. is usually adequate to determine the rheobase. There is a minimal duration of pulse which will excite, whatever its strength. This duration was called the *excitation time* by Lucas. The *strength-duration curve* is often used to describe the excitability of a tissue, and to distinguish between two tissues of different excitability. Interpolation on the curve will give the duration of the pulse of twice rheobasic strength which just excites. Lapicque termed this the *chronaxie* of the tissue.

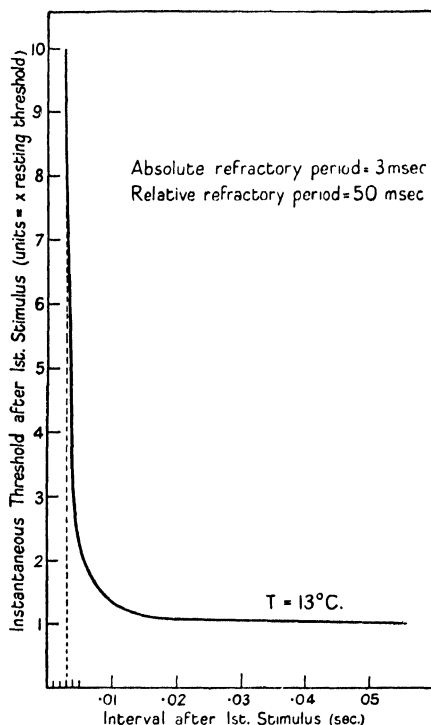
For the determination of the strength-duration curve, a condenser discharge is often used : the "duration" of the exponentially decrementing pulse is measured by the time constant of the

That is to say, for excitation by short duration stimuli, a fixed quantity of electricity is required. This can also be deduced from Hill's two-factor theory of nerve excitation which treats the nerve fibre as a leaky condenser.²

Alternatively, the hyperbolic shape of the strength-duration curve, for short durations of the stimulus, can be deduced from the constant quantity relation.

Threshold of Excitation: Refractoriness. The strength of the stimulus which is sufficient just to excite a nerve fibre determines the *threshold of excitation* for the fibre. The threshold fluctuates spontaneously and randomly to the extent of a few per cent.,* hence it is defined statistically as that strength of the stimulus which, applied repeatedly, excites the fibre 50 per cent. of occasions. This is the *resting threshold* of the fibre. Immediately after excitation, the fibre is quite inexcitable

for a millisecond or two (*absolute refractory period*). During the absolute refractory period no stimulus will excite, of whatever strength. Recovery of excitability occurs with rapid onset, and is usually complete in from 5 to 20 millisecon. (*relative refractory*



XI 5.—Curve showing absolute refractoriness of frog sciatic nerve for 3 msec. after application of stimulus, and relative refractoriness for further 50 msec. by which time the instantaneous threshold has returned to the resting value.

(After Adrian, *J. Physiol.*, **54**, 1, 1920.)

² Hill, *Proc. Roy. Soc. B*, **119**, 305, 1936.

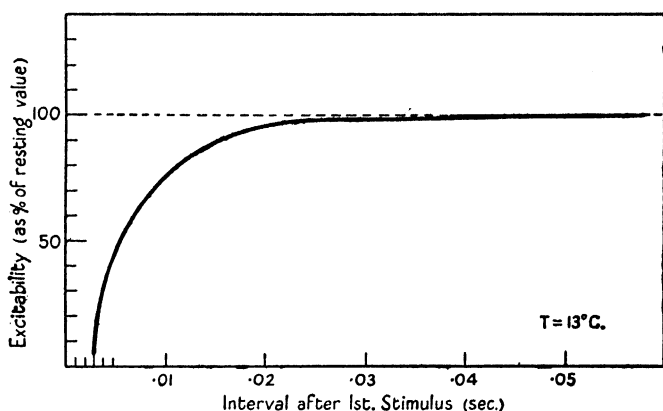
* Blair and Erlanger reported a 10 per cent. spontaneous fluctuation in frog nerve³ but Hodgkin found only $\frac{1}{2}$ per cent. variation in crab nerve.⁴

³ Blair and Erlanger, *Amer. J. Physiol.*, **114**, 309, 1936.

⁴ Hodgkin, *Proc. Roy. Soc., B*, **126**, 87, 1938.

period). During recovery, in order to excite the fibre, a stimulus strength above the resting threshold is required. Fig. 5 is a plot of the instantaneous threshold values immediately following the application of a first stimulus. For 3 millisecc. after the first stimulus, the preparation was absolutely inexcitable. For the ensuing 50 millisecc., stimuli greater than the resting threshold were required to excite.

The excitability of nerve is usually expressed, as a percentage, by the reciprocal of the relative strength (in threshold units) of a stimulus which will just excite. Thus if, at a certain moment



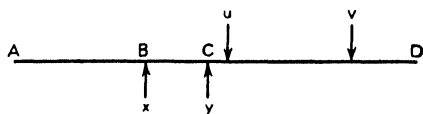
XI 6.—The data of Fig. 5 converted to excitability figures (see Text). (After Adrian, *J. Physiol.*, **54**, 1, 1920.)

during the relative refractory period, a stimulus $5 \times$ resting threshold is required just to excite, the excitability at that moment is $1/5$ th, expressed as a percentage, i.e. 20 per cent. The plot of excitability against time after the application of the first stimulus shows the time course of recovery of excitability. Fig. 6 presents the data of Fig. 5 in this form.

As the action potential spreads along the fibre it leaves behind it a stretch of absolutely refractory axon which is completely inexcitable and cannot be invaded by another excitation wave. Recovery to the original resting state follows the same course as at the locus of stimulation. This can be demonstrated by application of two stimuli in rapid succession to one end of a length of

frog nerve, so that two nerve impulses are evoked, separated in time by a few millise., and recorded at the other end of the nerve. A part of the nerve between the stimulating and recording points is now cooled, and it is found that the second nerve impulse fails to reach the recording electrodes. The recovery process, behind the first action potential wave, is slowed down by cooling so that the second impulse travels into the wave of absolute refractoriness behind the first impulse, and dies out. As will be explained later, the action potential is self-propagating but the axon in front of it must be excitable for this to occur. Absolute refractoriness lasting up to 50 millise. has been observed in cooled nerve.⁵

Electrotonus. When a potential is applied to a piece of wire or a thread soaked in saline, all the current flows in the segment lying between the electrodes. There is no spread of current to the extrapolar regions. Thus, in the diagram of Fig. 7, AD is the wire or thread,



and electrodes x, y are applied at points B, C dividing the conductor into three regions: AB and CD are the extrapolar regions and BC the interpolar region. u, v are recording electrodes u being near to y and v being a remote reference electrode on the same extrapolar segment. When a potential is applied to the electrodes x, y all the current flows in the segment BC and no potential difference is recorded between u and v , i.e. there is no extrapolar current spread.

Nerve differs from an ordinary conductor in this respect. If AD is a nerve, and a potential, too small to excite, is applied across x and y , then the current spreads into the extrapolar regions AB and CD, and a potential difference can be recorded between u and v . The extrapolar spread is usually called *electrotonus*, but it would be better to use the term *extrapolar potential*. It occupies a few

XI 7.—Diagram to show extrapolar and interpolar regions of conductor AD: electrodes, x, y applied at points B, C divide the conductor into three regions—AB (extrapolar), BC (interpolar) and CD (extrapolar). The second pair of electrodes u, v are recording electrodes, placed, in the diagram, to record from the extrapolar segment CD when current flows in the segment BC via electrodes x, y .

⁵ Hodgkin, *J. Physiol.*, **90**, 183, 211, 1937.

millimetres of the nerve and decrements rapidly so that it is barely perceptible at a distance of 10-15 mm. from the electrodes *x*, *y*. The electrotonus in the vicinity of the anode is called *anelectrotonus*, and of the cathode, *catelectrotonus*. The extrapolar spread is due solely to the capacitative property of the plasma membrane of the axon. If the membrane capacitance were zero, i.e. if the transverse membrane conductance were of the same order as the conductance of the interstitial fluid or the axoplasm, there would be no extrapolar spread (see also p. 282).

The sub-threshold current flow via electrodes *x*, *y* produces opposite effects at anode and cathode, tending to enhance or diminish the resting potential across the axon membrane. Anodal polarisation increases the membrane potential, and the potential rises outside the fibre in the vicinity of the anode. Cathodal polarisation diminishes the membrane potential, and the potential falls in the vicinity of the cathode. As explained in Chapter X (footnote, p. 249) the resting membrane potential is often referred to (although incorrectly) as the membrane "polarisation". The action at the cathode due to current flow is thus often termed "depolarisation" of the membrane.

If the current strength is adjusted to threshold value or above, then, when the circuit is made, a propagated action potential is evoked, which originates only at the cathode. When the circuit is broken, and the current ceases to flow, the collapse of anodal polarisation is equivalent to the cathodal polarisation created at the make of the circuit, and excitation may then occur at the anode. While the constant current is maintained some nerves remain passive, e.g. most frog and mammalian fibres: others respond repetitively, e.g. crab fibres,⁶ earthworm giant fibres,⁷ and occasionally frog sciatic fibres.⁸ Prolonged repetitive response to a maintained constant current is regarded by some workers as evidence for "good physiological condition" of non-myelinated fibres.⁶

When the sub-threshold stimulus current is flowing the extra-

⁶ Hodgkin and Huxley, *J. Physiol.*, **106**, 341, 1947 and Hodgkin, *ibid.*, **107**, 165, 1948.

⁷ Amassian and Floyd, *Nature*, **157**, 412, 1946.

⁸ Erlanger and Blair, *Amer. J. Physiol.*, **114**, 328, 1935.

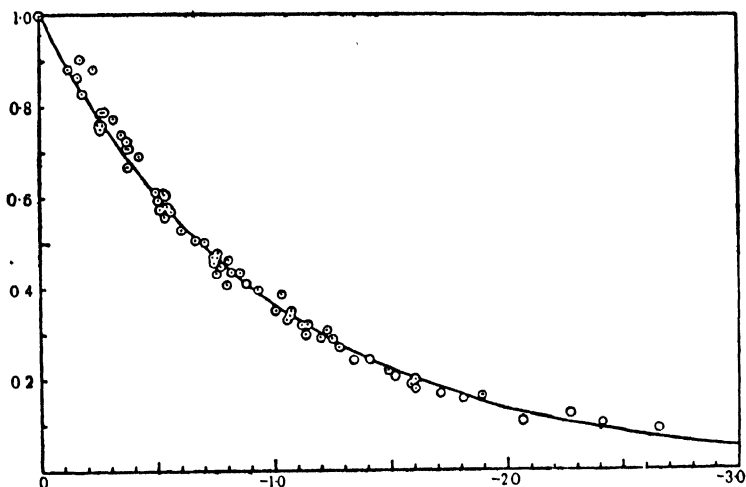
polar potential spreads spatially along the axon according to an exponential relation :

$$v = v_{x=0} e^{-x/\lambda} \quad . \quad . \quad . \quad (5)$$

where v = extrapolar potential at distance x from the stimulating electrode

and λ = the space constant of the nerve.

That is to say, the extrapolar potential falls to $1/e$ of its value in a distance λ along the axon. Values of 0.5 to 3.0 mm. have been



XI 8.—The spatial distribution of extrapolar potential in the neighbourhood of the cathode, from a number of experiments with 60-80 μ diam. single nerve axons of the common lobster (*Homarus vulgaris*). Ordinate: $v/v_{x=0}$ Abscissa: x/λ . The full line is the theoretical distribution. (After Hodgkin and Rushton, see ref. 9.)

reported for λ .^{4, 5, 9, 10} This is identical with the spread of injury potential, discussed in Chapter X, and the space constant is the same. It will be recalled that the spread of the injury potential is due to the local current flow, in the vicinity of the cut surface of the nerve. The injury current has a similar effect on the fibre as the current at a stimulating cathode.

Fig. 8 shows the plot of $v/v_{x=0}$ at the cathode against x/λ for a number of experiments with 60-80 μ . diameter single nerve axons

⁹ Hodgkin and Rushton, *Proc. Roy. Soc. B*, **133**, 444, 1946.

¹⁰ Cole and Curtis, *J. Gen. Physiol.*, **22**, 37, 1938.

of the common lobster (*Homarus vulgaris*), after Hodgkin and Rushton.⁹ The full line is the theoretical curve of equation (5), and the deviations of the observations from it are small. The theoretical distribution of equation (5) is not an *ad hoc* postulate but a consequence of hypotheses about the behaviour of a nerve fibre as a core-conductor, i.e. a cable-like structure (see p. 303).

At the make (or break) of the current circuit, with sub-threshold stimuli, the extrapolar potential is not established immediately but attains its maximum (or minimum) in a few milliseconds. The shape of the curves is such as might be expected from a capacitative structure, the process involved being passive charge or discharge of the membrane capacity. This simple type of response is obtained at the anode for all stimuli strengths but at the cathode only when the applied current is less than about $0.5 \times$ threshold. For stronger cathodal stimuli the response is more complex and is discussed fully on page 284 *et seq.*

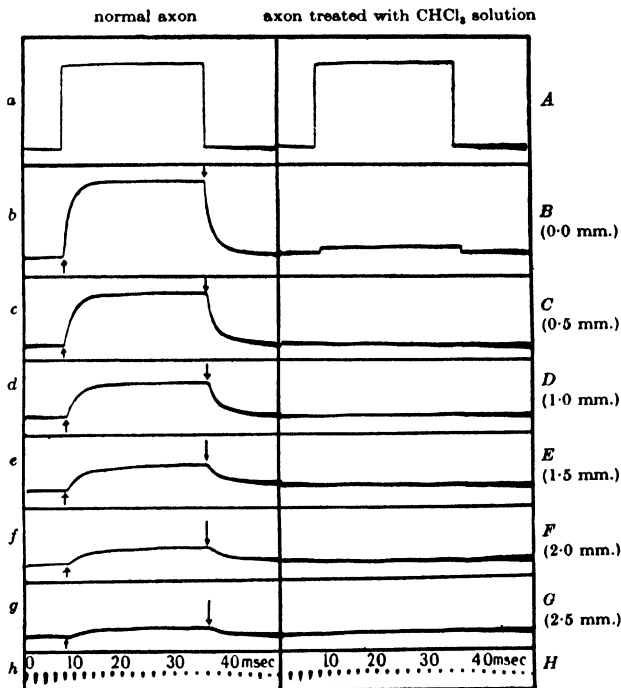
Extrapolar Potential and Membrane Capacitance. If the axon membrane is damaged by the application of a lipoid solvent such as chloroform, the nerve loses its excitability and the capacity of the axon membrane becomes zero. Fig. 9 shows both the spatial spread and the time course of the extrapolar potential of a normal axon (*a-g*) and of a chloroform treated axon (*A-G*) of the common lobster. Records *a* and *A* of the E.M.F. across a 61.7 k. ohm resistance in series with the axon, show that the sub-threshold current was the same for the two series of readings. Records *b* to *g* show the extrapolar spread and the time course at distances up to 2.5 mm. from the cathode. Records *B* to *G*, for the same distances, show that there is no extrapolar spread in the treated axon (apart from a small potential in *B* probably due to finite thickness of the nerve fibre). That is to say, the extrapolar spread is due solely to the accumulation or dissipation of charge at the axon membrane.⁹

According to the equations of cable theory for nerve axon, developed by Hodgkin and Rushton,⁹ the "make" curve should be anti-symmetrical with the "break" curve. The experimental results of Fig. 9 deviate somewhat from this ideal. To a first approximation, the time course of the extrapolar potential is

exponential with time constant τ whose value is from 1 to 3 milli-sec.^{4, 5} Thus :

at "make"
$$v = v_{t=\infty}(1 - e^{-t/\tau}) \quad . \quad . \quad . \quad (6)$$

and at "break"
$$v = v_{t=0} e^{-t/\tau} \quad . \quad . \quad . \quad (6a)$$



XI 9.—Oscillograms to show the time course of the extrapolar potential, at different distances from the cathode (given by the figures in brackets), obtained with (left) a normal axon (a — g), and (right) a chloroform treated axon (A — G), of the lobster, *Homarus vulgaris*. Explanation in text. (After Hodgkin and Rushton, see ref. 9).

Combination of the equations for space and time decrement gives :

at "make"
$$V = V_{x=0} e^{-X}(1 - e^{-T}) \quad . \quad . \quad . \quad (7)$$

and at "break"
$$V = V_{x=0} e^{-(X+T)} \quad . \quad . \quad . \quad (7a)$$

where $X = x/\lambda$ and $T = t/\tau$.

The more precise expressions for the spatial spread and temporal course of the extrapolar potential, developed by Hodgkin and Rushton in this country⁹ and by Davis and Lorente de Nó in

America¹¹ are complicated and involve the probability integral function "*erf x*". The basic assumptions which lead to these results are very important, however, and are discussed on page 303.

Summation of the Local Excitatory Disturbance. If a short duration (e.g. 10-20 μ sec.) sub-threshold cathodal stimulus is applied to a nerve fibre, the extrapolar potential evoked by the stimulus outlasts the pulse, as might be expected from what has just been said about the build-up and decline at make and break of the circuit. If a second cathodal stimulus is applied to the fibre a millisecond or so after the first, the threshold of the fibre is found to be lowered. The effect of the second stimulus is superposed on the trace of the first. This summation property of the local excitatory response of nerve axon can be demonstrated in two ways. First by direct electrical recording from nerve,¹² and second by study of the excitability of a nerve muscle preparation at different times after the application of a sub-threshold "conditioning" shock. A second or "testing" shock is applied and its strength adjusted so that it just excites the preparation. The strength of "testing" shock required at different times after the application of the "conditioning" shock gives a measure of the instantaneous threshold of the fibre, and it is possible in this way to plot the time course of the extrapolar potential.^{13, 14}

Fig. 10 shows the time course of the local excitatory disturbance as obtained by Katz¹⁴ with the sciatic-gastrocnemius preparation of the Hungarian frog *Rana esculenta*. The conditioning shocks used were of strengths 0.95, 0.5 and $-1.0 \times$ threshold (the minus sign indicating an anodal stimulus, which cannot excite and leaves behind it an extrapolar potential of sign opposite to that of the cathodal stimuli). The two lower curves in Fig. 10 labelled B and C, are similar in shape and represent the temporal exponential decay of the extrapolar potential in accordance with equation (6a).

The uppermost curve, labelled A, obtained with a cathodal shock greater than $0.5 \times$ threshold, is of quite different shape.

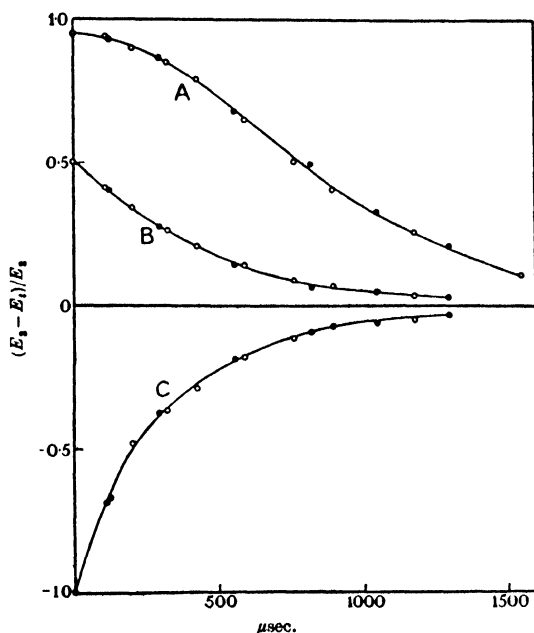
¹¹ Davis and Lorente de N6, "A Study of Nerve Physiology", in Ch. IX, Vol. 131, *Studies from the Rockefeller Institute for Medical Research*, New York, 1947.

¹² Erlanger and Blair, *Amer. J. Physiol.*, **99**, 108, 1931.

¹³ Gildermeister, *Pflug. Arch. ges. Physiol.*, **124**, 447, 1908.

¹⁴ Katz, *Proc. Roy. Soc. B*, **124**, 244, 1937.

The "hump" represents a local response, additional to that evoked by weaker shocks and adding its effect to the exponentially decaying potential. As will be shown presently, this local response is the embryo action potential: when it is of sufficient amplitude and involves a minimum critical extent of the nerve, it develops into the propagated action potential.



XI 10.—Time course of local excitatory disturbance in frog nerve obtained with three different conditioning shocks: A, B, C = 0.95, 0.5, $-1.0 \times$ threshold. (After Katz, see ref. 14.)

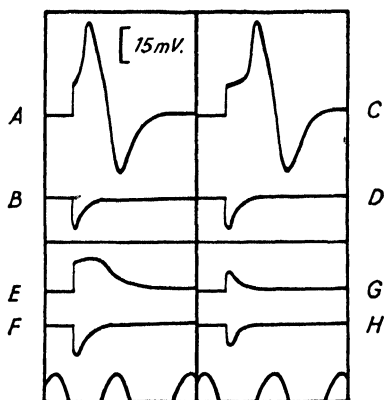
Initiation of the Propagated Action Potential. The growth of the local excitatory response and the initiation of the propagated action potential have been studied by direct electrical recording from single nerve fibres^{4, 16} and from whole nerves, mostly the sciatic nerve of the frog.^{15, 17} As already stated, the temporal course of the extrapolar potential is approximately

¹⁵ Katz, *J. Physiol.*, **106**, 66, 1947.

¹⁶ Pumphrey, Schmitt and Young, *ibid.*, **98**, 47, 1940.

¹⁷ Lorente de N6, "A Study of Nerve Physiology", Chs. XII and XVI in Vol. 132 of *Studies from the Rockefeller Institute for Medical Research*, New York, 1947.

exponential for all anodal stimuli and for cathodal stimuli less than $0.5 \times$ threshold. That is to say, for stimuli up to $0.5 \times$ threshold the anodal and cathodal responses are symmetrical. As the cathodal stimulus is increased above $0.5 \times$ threshold, the local response deviates more and more from the exponential pattern, and, at threshold the large propagated action potential is elicited.



XI 11.—Potential changes at stimulating electrodes produced by stimuli of various strengths, as follows: A, $1.05 \times$ threshold strength; B, -1.05 ; C, 1.00 ; D, -1.00 ; E, 1.00 ; F, -1.00 ; G, 0.61 ; H, -0.61 . The negative sign indicates anodal stimulus. Time, 1 msec. The difference between C and E was due to fluctuation in excitability. Single nerve fibre of crab. (After Hodgkin, see ref. 4.)

Fig. 11 shows the potential changes recorded from a crab single nerve fibre at the stimulating electrode with shocks of various strengths. Records G and H are practically symmetrical, but E and F are obviously different. In E the "hump" and the prolongation of the response are characteristic of the cathodal local response for shocks near to threshold.

If the anodal local response, with sign changed, is subtracted from the corresponding cathodal local response (obtained by reversing the leads from the stimulator), the resulting curve is the temporal distribution of the excess of

cathodal response over the exponentially decaying anodal response. This has been done in Fig. 12 for the two responses E and F of Fig. 11. The inset gives the time course of the *local action potential* as Hodgkin termed this difference.⁴ When this is done for stimuli of different strengths (Fig. 13), a family of curves is obtained, showing the development of the local action potential at the cathode (inset, Fig. 13). Obviously, for cathodal stimuli less than $0.5 \times$ threshold, the local action potential is zero, since the anodal and cathodal responses are symmetrical. Above this value, the local action potential grows rapidly until it bursts over into the propagated spike potential at threshold.

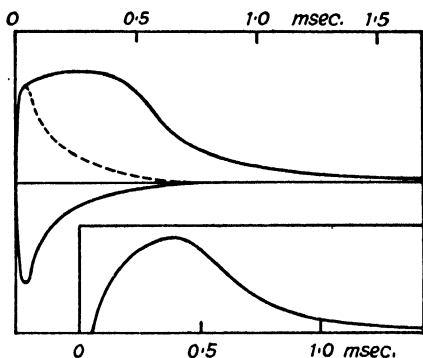
The rapid growth of the local action potential is strikingly displayed in Fig. 14 where the amplitude of the local response, at 0.29 millisecon. after application of the stimulus pulse, is plotted against the strength of the stimulus in threshold units. The value at 0.29 millisecon. was chosen because in these experiments that was the time constant of the exponentially decaying electrotonic potential. The curve of Fig. 14 emphasises, therefore, the totally different time course of the local action potential from that of the exponentially decrementing charge and discharge process of the membrane.

In partially refractory fibres, the local action potential is reduced in size or may not develop at all. Thus a cathodal shock of just sub-threshold strength, when applied to a fibre 2.5 millisecon. after a test shock (i.e. within the relative refractory period) evokes only the exponentially decrementing electrotonus. Similarly, in the supernormal phase, which follows the propagated action potential and refractory period, a local action potential can be evoked by shocks which are too weak to elicit the response in a resting fibre.

The differences found by Hodgkin between the local action potential and the electrotonic potential can be summarised as in the table on page 288.

Thus it is practically certain that the local action potential is a separate physical process, quite distinct from the process of charge and discharge of the axon membrane which gives rise to the electrotonic potential.

Similar results have been obtained with single giant axons of the squid.¹⁶ Both the crab and the squid axons are unmyelinated. In frog nerve, which is myelinated, Katz¹⁴ studied changes in



XI 12.—Cathodal and anodal potentials from E and F, Fig 11. The difference between them gives the local action potential (inset). (After Hodgkin, see ref. 4.)

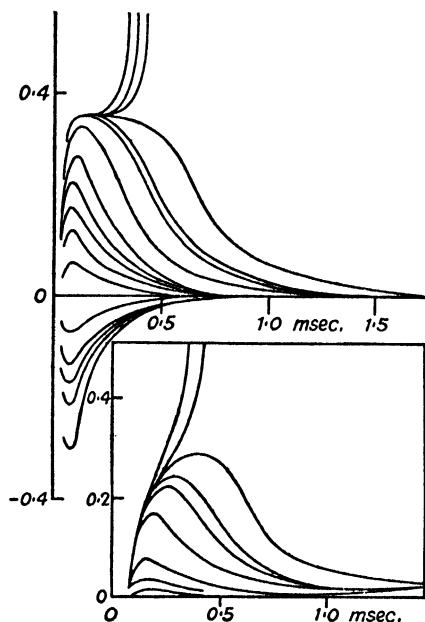
Local Action Potential

- (1) Size increases at increasing rate with stimulus.
- (2a) Increases for some 500 μ sec. after stimulus and then decays, not exponentially.
- (2b) Total duration, and time to attain maximum, increase with stimulus strength.
- (3a) Reduced or abolished in refractory period.
- (3b) Enhanced in supernormal period.
- (4) Spatial spread not exponential; decline to two-thirds in 0.5 mm.

Electrotonic Potential

- (1) Size $\propto$ stimulus strength.
- (2a) Approx. exponential temporal decay, $\tau \approx 300 \mu$ sec.
- (2b) Time constant of temporal decay is constant.
- (3a and b) Practically no change during refractory and supernormal periods.
- (4) Spatial spread exponential, $\lambda \approx 0.5$ mm.; decline to one-third in 0.5 mm.

excitability with the sciatic-gastrocnemius preparation. His curves (one of which is reproduced in Fig. 10) resemble very closely



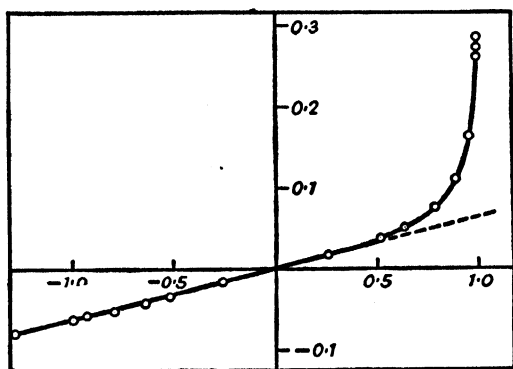
XI 13.—Family of curves like E and F, Fig. 11, for different strengths of stimuli as follows: 1.00 (upper 6 curves); 0.96; 0.85; 0.71; 0.57; 0.43; 0.21; — 0.21; — 0.43; — 0.57; — 0.71; — 1.00. The ordinate scale gives the potential as a fraction of the propagated spike potential (about 40 mV.). The differences between corresponding cathodal and anodal responses yield a family of curves for the local action potential (inset): stimulus strengths for these are 1.00 (upper 5 curves); 0.96; 0.85; 0.71; 0.57. (After Hodgkin, see ref. 4.)

those for the directly recorded potential changes illustrated in Figs. 11 to 14. He subsequently confirmed his results by direct measurement from the nerve.¹⁵

The Propagated Action Potential. The local action potential is a non-propagated wave of negativity which develops at the cathode when the stimulus lies in the range 0.5 to $1.0 \times$ threshold.

At threshold, the response bursts over into the spike potential,

and the local response becomes a propagated wave of negativity, the action potential. With crab axon a varying latency of initiation is found of some 0.5 to 1.5 millisecc. For a given axon, the propagated action potential travels without decrement at a constant velocity, typical for the axon concerned. The duration of the action potential is the time taken for the wave to pass a fixed point of



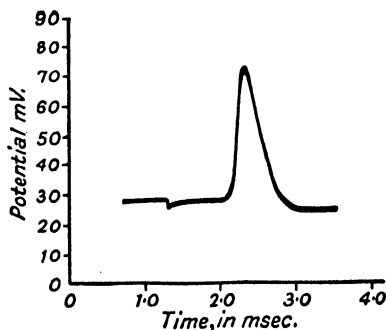
XI 14.—Relation between potential at 0.29 msec. after stimulation (ordinate) and strength of stimulus (abscissa). (After Hodgkin, see ref. 4).

the axon, and is of the order of a millisecond, so that the wavelength is given by :

$$\text{Wavelength} = \text{duration} \times \text{velocity}. \quad (8)$$

The wavelength varies from a millimetre or so up to about 100 mm. for mammalian fibres of high conduction velocity (100 m. sec.⁻¹).

XI 15.—Monophasic action potential in a 490 μ nerve fibre of the squid. The duration is approximately 0.7 msec. The small initial downward deflection is the stimulus artefact occurring 1 msec. before the action potential. (After Schmitt and Schmitt, *J. Physiol.*, **98**, 26, 1940.)



The time course of a typical action potential wave, as it passes a given point of the axon, is shown in Fig. 15. By a conversion of

the abscissa scale, through multiplication by the conduction velocity, the same curve becomes the spatial distribution of the wave along the axon.

The wave of Fig. 15 is usually referred to as the monophasic action potential. It is obtained by a single lead recording, the reference electrode being placed on a region of the nerve which has been injured so that it cannot be invaded by the action potential. The monophasic (monopolar lead) wave is thus the time course of the propagated wave of negativity. If the two recording electrodes are placed near together at the surface of the intact axon, so that their distance apart is small in comparison with the wavelength, the temporal course of the recorded potential is, approximately, the first derivative with respect to time of the monophasic action potential. This is a diphasic wave and it is shown in Fig. 16 in correct time relation to the monophasic wave. In practice, the electrodes are seldom on the axon membrane surface but at a finite distance from it, e.g. 0.5 or 1.0 mm. Thus they record the potential difference in the field surrounding the axon. This gives a triphasic wave (Fig. 16) which resembles the second derivative of the monophasic wave.¹⁷

The velocity of conduction increases with the diameter of the fibre and with the amount of myelin surrounding the fibre. Within a single species (the rabbit) Gasser¹⁸ found a linear relation between conduction velocity and diameter, in fibres of size 1 to 20 μ . with conduction velocities of 6 to 120 m. sec.⁻¹. Other evidence suggests that the velocity is proportional approximately to the square root of fibre diameter. The squid giant axons of 1 mm. diameter which are unmyelinated, only conduct at 25 m. sec.⁻¹, whereas the heavily myelinated giant fibres of the earthworm, of diameter 50 to 100 μ ., conduct at about the same velocity.*

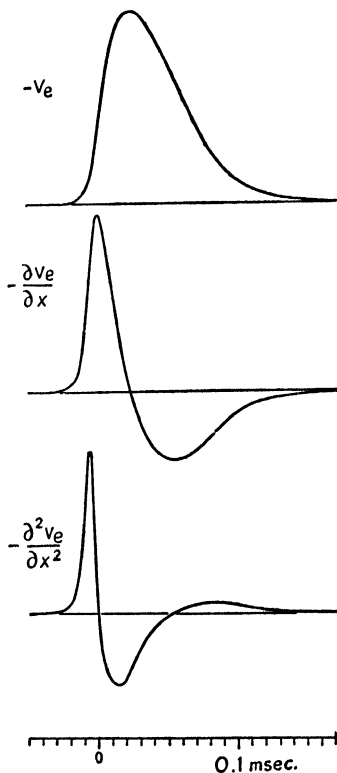
The Mechanism of Propagation. The transmission of nerve impulses can be blocked in nerve fibres by cooling, pressure, drugs or by anelectrotonus. When an impulse dies out in a block, a

¹⁸ Gasser, *Ohio J. Sci.*, **41**, 145, 1941.

* The conduction velocity of earthworm giant fibres is possibly greater than this because of transmission delays at the intersegmental septa demonstrated by Stough, *J. Comp. Neurol.*, **40**, 409, 1926.

transient, non-propagated potential change can be recorded from the stretch of normal axon immediately distal to the block. Using cold and pressure blocks of 3 to 5 mm., in frog sciatic nerves, Hodgkin ⁵ showed this *extrinsic potential* to be similar to catelectrotonus in both spatial and temporal distributions (Fig. 17). The

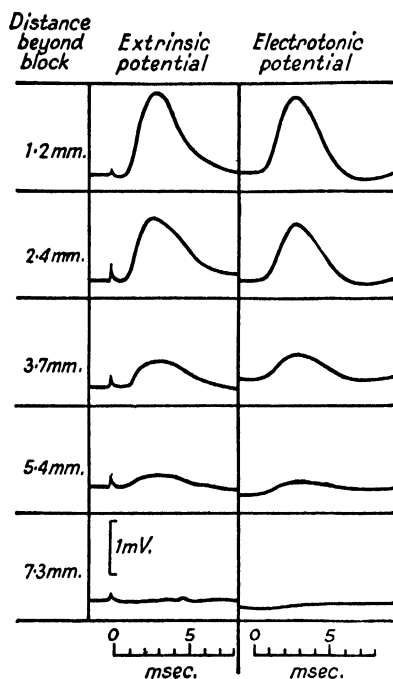
XI 16.—Uppermost curve: monophasic action potential ($-V_e$). Middle curve: first derivative of the monophasic potential ($-\frac{\partial V_e}{\partial x}$), or the corresponding time derivative with suitable abscissa transform. Lowest curve: second derivative of $-V_e$ ($-\frac{\partial^2 V_e}{\partial x^2}$, or corresponding time derivative). $\frac{\partial^2 V_e}{\partial x^2}$ is directly proportional to the transverse membrane current of the fibre. The time scale relates to α fibres of the frog's sciatic nerve. (After Lorente de Nó, see ref. 17.)



extrinsic potential is also closely similar, in both time course and spatial spread, to the excitability changes which occur simultaneously in the distal portion of the nerve, when an impulse dies out in the block. The excitability distal to the block may be increased by as much as 90 per cent.; and, if the length of nerve blocked is too short, some impulses will “jump” across the block.

The similarity of spatial and temporal characteristics of catelectrotonus, extrinsic potential and excitability suggests a common

causal mechanism. The obvious cause is the local current flow set up by the local potential changes at the membrane. The nerve axon is, in effect, a core conductor immersed in a volume of conducting medium—the tissue fluid and saline surrounding it. The



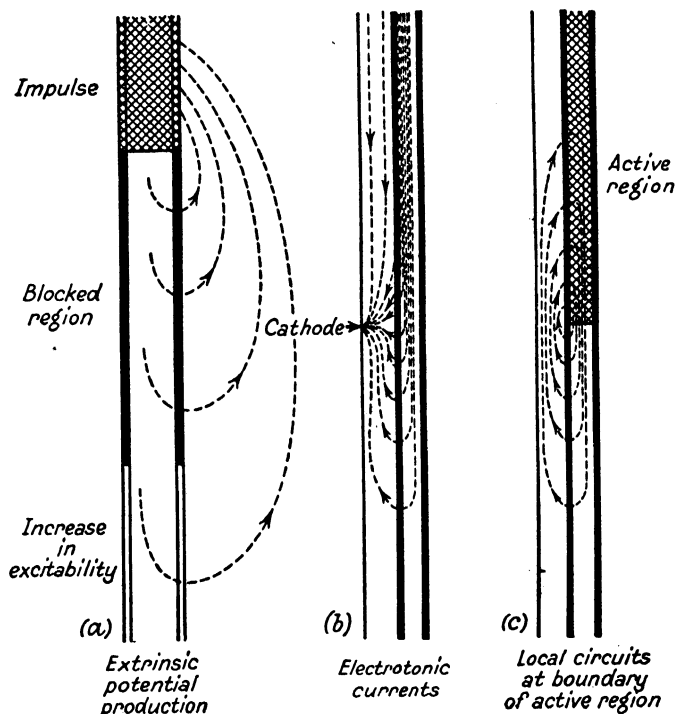
XI 17.—Extrinsic potential and applied catelectrotonic potential at various distances beyond a 3.5 mm. cold block. Frog sciatic nerve. Amplification and time scale are same throughout. (After Hodgkin, see ref. 5.)

potential changes at the surface of the axon give rise to ionic current flow in the volume conductor surrounding the axon, and electrodes placed in it will record the potential differences in the field. When the impulse dies out in the blocked nerve, the wave of negativity is arrested but not immediately extinguished. While it persists it acts as a current “sink” (of decreasing magnitude) and the nerve in the neighbourhood of the block is surrounded by a local current field, like an eddy current, shown in plane section diagrammatically in Fig. 18. The lines of flow of the current around the axon form a toroidal shell, with the current flowing one way outside the fibre and the opposite way inside. The shape of

the field is determined partly at least by the difference in conductivity between the axon membrane and the intra- and inter-cellular fluids.

The figure shows also, for comparison, the current fields at a stimulating cathode (extrapolar field) and at the wave front of a propagated action potential. The increase of excitability distal to the block is due to the local spread of current beyond the block.

This affects the normal axon in the manner of a sub-threshold stimulus. In a similar way, the local current (termed the *action current*), flowing ahead of the propagated action potential wave, stimulates the as-yet-uninvaded stretch of nerve. That is to say, the action potential wave is self-propagating. This hypothesis of

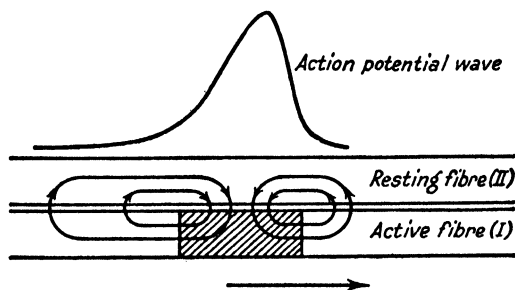


XI 18.—To show similarity between mechanisms of (a) extrinsic potential, (b) cathodal depolarisation, (c) normal impulse propagation. The broken lines represent the direction of flow of positive ions. (After Hodgkin, see ref. 5.)

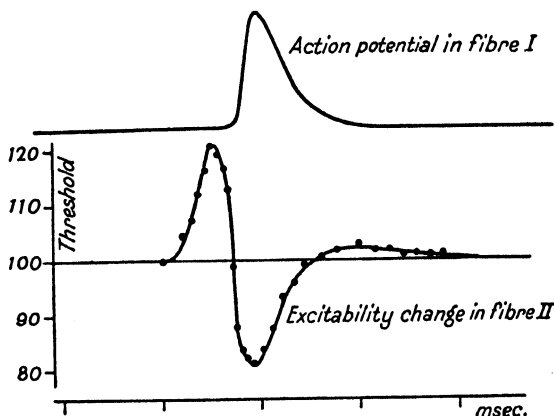
electrical transmission of the nerve impulse by local current flow appears to be adequate to explain propagation without any additional special assumption.

Just as an active stretch of axon influences the adjacent resting stretch of the same axon, lying in the current field of the active region, so activity in one axon modifies the excitability of adjacent axons. The current field of the first axon penetrates the second axon and produces transient changes in excitability of the order

of 20 per cent. at maximum in crab nerve.¹⁹ Each action potential wave in fibre I produces a triple effect in fibre II, which becomes less excitable at first, then passes through a more excitable phase and finally through a period of slightly reduced excitability. These



XI 19.—Diagram of action current (due to action potential in fibre I) penetrating fibre II. The spatial distribution of the action potential in fibre I is shown in the upper part of the diagram. The arrow shows direction of propagation. (After Katz and Schmitt, see ref. 19.)



XI 20.—Excitability changes in fibre II (Fig. 19) during the transmission of an impulse in fibre I, the time course of which is shown in the upper part of the figure. (After Katz and Schmitt, see ref. 19.)

three phases correspond to the directions and intensities of the current field of fibre I. The direction of the field reverses twice, as shown diagrammatically in Fig. 19. These changes in excitability are shown, in Fig. 20, in correct time relation to the action potential in fibre I. The excitability changes are always

¹⁹ Katz and Schmitt, *J. Physiol.*, **97**, 471, 1939.

sub-threshold : they are never sufficient to initiate an action potential in fibre II.

When action potentials are set up simultaneously in both fibres, the mutual interaction which results produces complex changes in conduction rates in the two fibres. The mechanism of this effect on conduction velocity is unknown.

The Field surrounding an Active Nerve. The current and potential field surrounding an active nerve have been recorded by Lorente de Nó. The nerve was placed on a sheet of blotting paper 30×20 cm., soaked with Ringer solution, and both nerve and conducting medium placed on a block of insulating material. The impulses were initiated in a segment of nerve insulated by mineral oil. A test electrode recorded the potential due to the spread of the action current in the plane of the blotting paper.

As can be seen from Fig. 21, the current flows outward from the nerve in the two end segments of the nerve and towards the nerve in the central segment, occupied by the action potential wave. The field is thus divided into three zones by two zero iso-potential lines. The sign of each zone is indicated in the figure. Approximately, the active segment of the nerve behaves as a current sink and the other segments as current sources. The behaviour of the nerve when completely surrounded by a volume conductor is closely similar to that recorded for the plane conductor. These experimental findings accord well with theoretical studies based on a theorem of Helmholtz.¹⁷

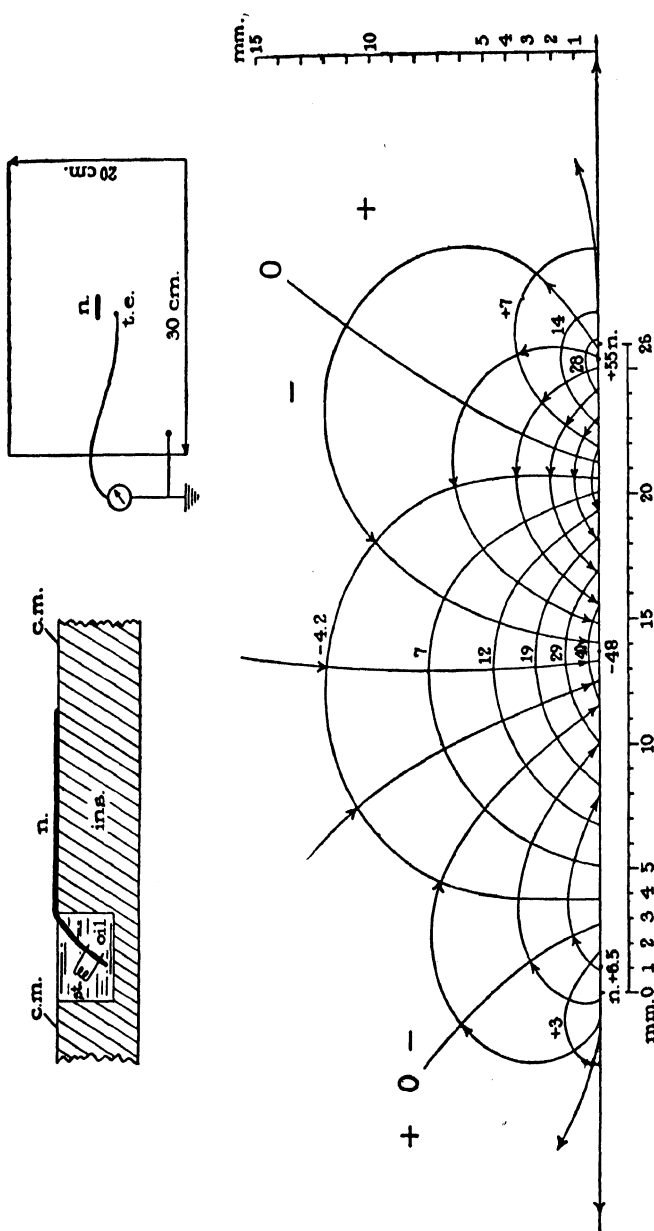
The Action Potential Wave. It had always been assumed until about 1940 that the action potential wave was a wave of depolarisation of the axon membrane^{20, 21} resulting from a reversible breakdown of axon structure which reduced the resting potential across the membrane to zero. The wave of negativity was explained as due to the temporary access from the external medium to the axoplasm, permitting a transient measurement of the membrane potential, like a transient and reversible injury potential. Recent studies^{22, 23} with single giant axons of the

²⁰ Bernstein, *Electrobiologie Braunschweig*, Vieweg, 1912.

²¹ Lillie, *Protoplasmic Action and Nervous Action*, Chicago, University Press, 1923.

²² Curtis and Cole, *J. cell. comp. Physiol.*, **19**, 135, 1942.

²³ Hodgkin and Huxley, *J. Physiol.*, **104**, 176, 1945.



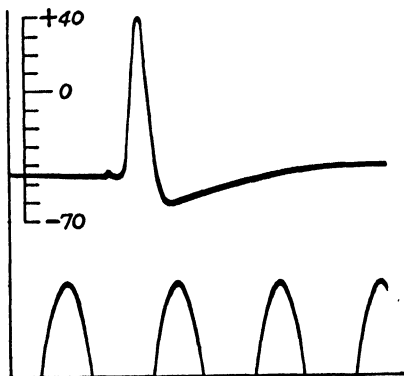
XI 21.—Current field surrounding active nerve. The orthogonal set of iso-potentials is also shown. Top left shows the nerve, n , with its end in oil for stimulation without spread of stimulus artefact. Top right shows the plan of the experimental arrangement with the nerve in the centre of the plane conducting medium. $t.e.$ is the test electrode for recording the potential in the field. The nerve is of length 26 mm. stretching from n to n . The active region of the nerve occupies about 18 mm., from 3 mm. to 21 mm. on the scale at the bottom of the figure, and propagation is from left to right. (After Lorente de Nó, see ref. 17.)

squid, *Loligo forbesi*, into which it has been possible to insert micro-electrodes, have shown that the membrane potential is in fact reversed in sign and magnitude when a propagated action potential wave occurs. This is illustrated in Fig. 22 which shows the potential of the micro-electrode, inside the axon, relative to the external medium. The resting membrane potential is about 45 millivolts, inside negative. The action potential wave overshoots the zero mark to the extent of some 40 millivolts. That is to say there is almost complete transient reversal of membrane potential. The classical and revised concepts of the wave of activity are shown diagrammatically in Fig. 23.

Hodgkin and Huxley²³ discuss four possible explanations to account for the reversal of membrane potential during activity:

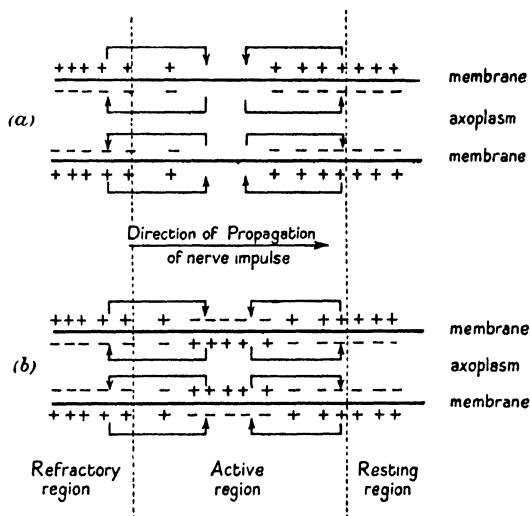
(1) *Transient selective permeability of the active membrane to anions, present in the axoplasm in high concentration and in the external medium in low concentration.* It is unlikely that the concentration or mobility of any anion would be sufficient to dominate the components of the potential due to K^+ and Cl^- ions.

(2) *Changes in the orientation of molecular dipoles at the membrane surface.* A transient wave of negativity would arise with a membrane consisting of a bimolecular lipo-protein complex, of the type discussed in Chapter X, if re-orientation of the inner layer of dipoles occurred during the excitation process. The order of the events recorded is compatible with this assumption, but it is difficult to express the ideas rigorously.



XI 22.—Action potential of single giant nerve fibre of the squid, recorded with a micro-electrode inside the fibre. The potential is that of the micro-electrode measured with respect to an electrode in contact with the external medium (sea water). The small wave is the stimulus artefact. Time tracing: 500 c.p.s. (After Hodgkin and Huxley, see ref. 23.)

(3) *Apparent inductance of the membrane.* An inductive element in nerve membrane reactance was postulated by Cole and Baker in 1941 in order to account for their observations on the squid giant axon.^{24, 25} The inductance is localised to the surface membrane and is approximately of value 0.2 H. It is in series with the membrane rectifier-element resistance and in parallel with the membrane capacitance, as shown in the equivalent



XI 23.—Diagram to show (a) classical and (b) revised concepts of membrane polarisation changes during the passage of a wave of activity along a nerve axon. (After Hodgkin and Huxley, see ref. 23.)

circuit of Fig. 24a. In Fig. 24b is shown a similar arrangement proposed by Hodgkin and Huxley to explain the transient reversal of potential recorded by them. In Fig. 24b the closure of switch S for a certain time represents excitation of the axon. Closure of S for 1 to 3 millisecc. produces an overshoot of potential of the duration and magnitude required.

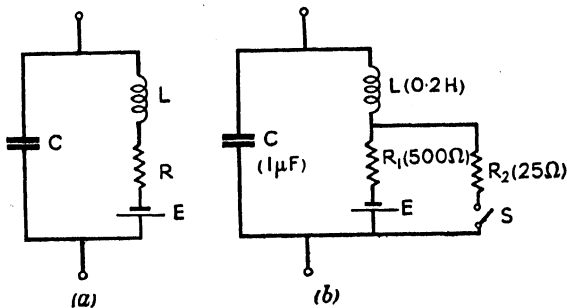
(4) *A series capacitance hypothesis.* The resting membrane potential is assumed to be in series with a capacitance instead of in parallel with it, which is the more usual assumption.

More recently Hodgkin and Katz²⁶ have proposed yet another

²⁴ Cole and Baker, *J. Gen. Physiol.*, **24**, 771, 1941.

²⁵ Cole, *ibid.*, **25**, 29, 1941. ²⁶ Hodgkin and Katz, *J. Physiol.*, **108**, 37, 1949.

hypothesis, which requires a large transient increase in the permeability of the membrane to sodium, so that the permeability to potassium is now negligible in comparison. A reversed membrane potential of some 60 mV. can be obtained in such a system if the concentration ratio $\text{Na}_{\text{external}}/\text{Na}_{\text{internal}}$ is of the order of 10. It follows that the size of the action potential will be greatly dependent on the concentration of sodium in the external fluid, and there should be no reversal of the potential if the external sodium concentration is made equal to the internal concentration.



XI 24.—Equivalent circuits to represent the electrical behaviour of nerve axon during excitation. (See refs. 23, 24 and 25.)

Similarly, increase of the sodium of the external fluid should increase the magnitude of the potential reversal. Their experimental results, obtained with the giant axon of the squid, are consistent with the quantitative formulation of the hypothesis based on a relatively simple equation developed by Goldman.²⁷ He assumed (1) that the voltage gradient through the thin, high resistance membrane, separating different concentrations of potassium, chloride and sodium, is constant, (2) that the ions move under the action of diffusion and electric forces, and (3) that the concentrations of the ions at the membrane boundaries are directly proportional to the concentrations in the aqueous solutions. These assumptions lead to the following expression for the membrane potential:

$$E = 58 \log_{10} \left[\frac{P_K K_i + P_{Na} Na_i + P_{Cl} Cl_o}{P_K K_o + P_{Na} Na_o + P_{Cl} Cl_i} \right] \text{ mV. at } 18^\circ \text{ C.} \quad (9)$$

²⁷ Goldman, *J. Gen. Physiol.*, **27** 37, 1943.

where K_i , Na_i and Cl_i are the activities inside the axon and K_o , Na_o and Cl_o the activities outside. P_K , P_{Na} and P_{Cl} are the permeability coefficients for the ions indicated by the suffix. The values of the permeability coefficients are dependent on the mobilities and solubilities, thus :

$$P_K = \frac{RT}{Fa} u_K b_K \quad . \quad . \quad . \quad (9a)$$

with similar expressions for Na^+ and Cl^- ions, where a is the membrane thickness, u the ionic mobility within the membrane and b the partition coefficient between membrane and aqueous solution. This equation does not take account of any chemical combination of the ions which might occur during the action potential wave, and is restricted in its scope to the three sorts of ions considered. The internal concentrations used for numerical evaluation are :

$$K_i = 345 \text{ mM.}; \quad Na_i = 72 \text{ mM.}; \quad Cl_i = 61 \text{ mM.}$$

If the membrane permeabilities P_K , P_{Na} , P_{Cl} are assumed to change from a ratio of 1.0 : 0.04 : 0.45 in the resting condition (resting potential 59 mV.) to a ratio 1.0 : 20 : 0.45 in the active condition, this expression gives an action potential of 97 mV., which is 9 mV. greater than observed experimentally. This difference can be accounted for by current flow through the membrane, since the formulation takes no account of this. The theoretical resting potential of 59 mV. is 11 mV. greater than the measured value 48 mV., and the difference is accounted for by a liquid-liquid junction potential between sea-water and axoplasm.

Fig. 25 shows the change in amplitude of the observed action potential with various external sodium concentrations, the sodium deficit in the weaker sodium solutions being made up by dextrose.

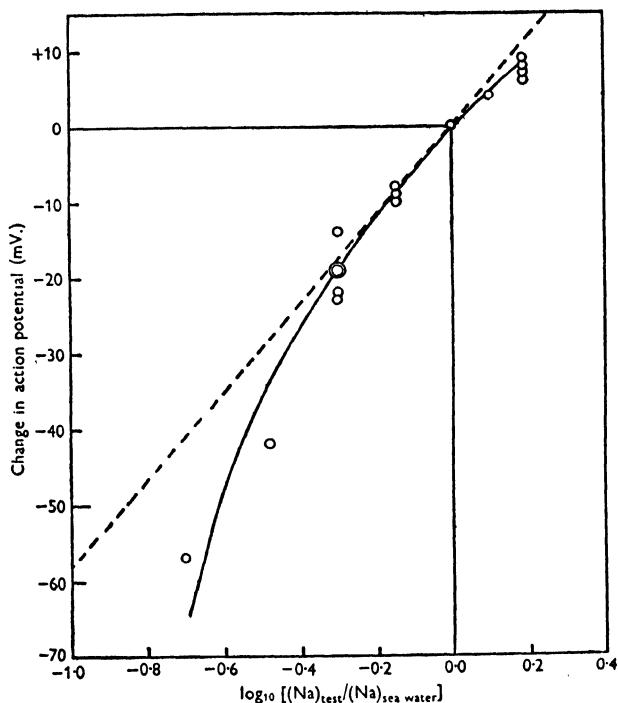
Potassium Leakage from an Active Nerve Fibre. It has been shown both by electrical studies^{28, 29, 30} and by use of the K^{42} radioactive isotope of potassium³¹ that, during the passage of an action potential along a crab nerve axon, potassium leaks out of the fibre and is reabsorbed during the recovery phase. The quantity of potassium flux, per nerve impulse, through 1 sq. cm. of membrane, was found by the electrical method, to be 1.73×10^{-12}

²⁸ Hodgkin, *J. Physiol.*, **106**, 305, 1947.

²⁹ Hodgkin, *ibid.*, **106**, 319, 1947.

³⁰ Hodgkin and Huxley, *ibid.*, **106**, 341, 1947. ³¹ Keynes, *ibid.*, **107**, 35P, 1948.

moles, and the rate of reabsorption was 3×10^{-10} mol. cm.⁻² sec.⁻¹ when the external potassium was three times the normal value.³⁰ The membrane capacitance of crab axons (*Carcinus maenas*) is approximately $1.35 \mu\text{F. cm.}^{-2}$ and the resting potential across the membrane is 61 mV., hence the charge on the resting membrane is



X1 25.—Change in amplitude of action potential (measured from a micro-electrode inside giant nerve fibre of the squid to an external electrode) caused by alteration of external sodium concentration. The broken line has a slope of 58 mV. (After Hodgkin and Katz, see ref. 26.)

8.2×10^{-8} coulomb cm.⁻². Since 1 faraday $\equiv 9.65 \times 10^4$ coulomb, this charge is equivalent to an excess of 8.5×10^{-13} mol. cm.⁻² of monovalent cation outside the membrane and a similar deficit within. The calculated potassium leakage, based on electrical measurements, of 1.73×10^{-12} mol. cm.⁻² is equivalent to a charge of 16.75×10^{-8} coulomb, or about twice the calculated resting membrane charge. As there would probably be an actual loss of potassium ions with the passage of each impulse (including exchange

with sodium ions, which enter the fibre), it is reasonable to find that the potassium ions lost carry a charge greater than that of the resting membrane.

The absolute magnitude of potassium leakage per impulse is small, and the amount relative to the *total* potassium content of the axoplasm is of the order of 10^{-5} per impulse. The quantity 1.73×10^{-12} mol. cm.⁻² is equivalent approximately to 1 ion per $10^4 \text{ \AA}^2$ of membrane area: such an area of membrane would contain nearly 500 fatty molecules, if $20.5 \text{ \AA}^2$ is taken as the area per molecule.³²

Direct measurement on the crab axon by a Geiger counter technique with K^{42} gave 2.1×10^{-12} mol. cm.⁻² per impulse, which is in good agreement with the figure obtained by the electrical conductivity method just discussed.

Resting and Action Potentials of Muscle Fibres. The resting and action potentials of muscle fibres have also been studied by the micro-electrode technique. Unfortunately, giant muscle cells are unknown and hence these studies have had to be made by the insertion of very fine micro-electrodes into muscle fibres only some 70μ . in diameter.³³ Graham and Gerard found, for frog sartorius muscle fibres, an uncorrected average resting potential of 62 mV., recorded directly across the membrane, with a correction of 10 mV. for boundary potentials, giving a corrected figure of 72 mV. (65 fibres in 20 muscles). Ling and Gerard³⁴ with an improved technique and in a more extensive study, found the membrane potential to be 98 mV. at $20-22^\circ \text{C}$. when 3 *M* KCl was used to eliminate the liquid junction potential. Hodgkin and Nastuk³⁵ in a more complete study found a resting potential of some 87 mV. (inside negative) and a reversal of the potential to 28 mV. (inside positive) with the passage of the action potential wave, giving an amplitude of $87 + 28 \text{ mV.} = 115 \text{ mV.}$ for the action potential wave at 19°C . As with nerve axon, the reversal of potential disappears if the external sodium concentration is reduced, and the action potential itself is abolished in a sodium free

³² Adam, "The Physics and Chemistry of Surfaces", 3rd edn., Oxford Univ. Press, 1941. ³³ Judith Graham and Gerard, *J. cell. comp. Physiol.*, **28**, 99, 1946.

³⁴ Ling and Gerard, *J. cell. comp. Physiol.*, **34**, 383, 1949.

³⁵ Hodgkin and Nastuk, *J. Physiol.*, **108**, 42P, 1949.

external medium. There is a nearly linear relation between the amplitude of the action potential and the logarithm of the Na^+ ion concentration outside the fibre, over the concentration range 20 to 120 mM.; the slope of the line is approximately 60 mV. The resting potential is practically unchanged over the same range.

The hypothesis of transient sodium permeability, put forward by Hodgkin, Huxley and Katz in order to explain the action potential wave, is essentially a modification of the Bernstein hypothesis (Chap. X, p. 255), which is based on an acceptance of the Nernst principle that the potential measured (the action potential in this instance) is proportional to the logarithm of the ionic concentration ratio across the membrane. The equation of Goldman is derived from an extension of the principle to non-equilibrium systems, and reduces to the Nernst equation for a simple semi-permeable membrane. It includes also the resting potential of the membrane.

It will be recalled (Chap. X, p. 257) that Lorente de N6 rejects the Bernstein hypothesis for the explanation of the resting potential of nerve. It is not possible at present to reconcile fully the two viewpoints. The main objection to the evidence quoted by Lorente de N6 is that it was obtained in experiments on whole nerves and not on single fibres. Until these experiments have been repeated on single giant fibres such as those of the squid, further discussion is useless.

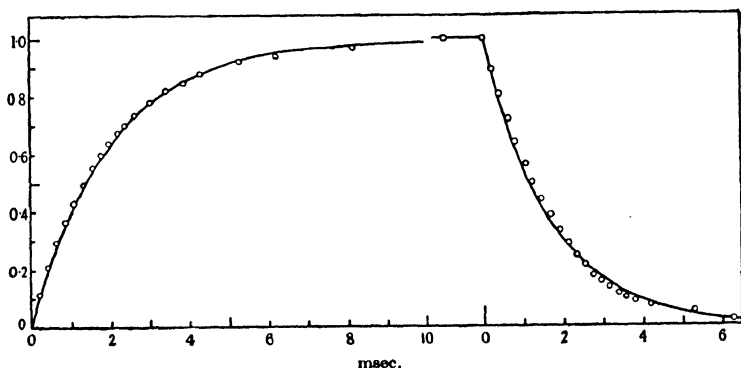
Theories of Nerve Excitation: Equations of Cable Theory. A precise mathematical theory of nerve excitation has not yet been developed. Only the response to sub-threshold stimulation has been analysed.^{9, 11} All theories must be based, however, on certain assumptions about the structure of nerve, and the usual assumption is that the nerve fibre is rather like a cable surrounded by a fluid conducting medium such as sea-water, viz. that it is a cylindrical conductor immersed in a volume conductor but separated from it by a thin layer of insulating material, with low transverse conductance, permitting a large capacitance per unit area. Since about 1900, many workers have used the equations of cable theory to describe the behaviour of an ideal "nerve" with this cable-like property.

Subject to certain simplifying assumptions about the potential

distribution along the nerve, the purity of the ohmic and capacitance components and the infinitesimal size of the electrodes, it can be shown that the quantitative behaviour of the fibre is described by a differential equation of the general form :

$$\frac{\partial^2 U}{\partial X^2} = \frac{\partial U}{\partial T} + F(X, T) \quad . \quad . \quad . \quad (10)$$

The solution of this equation yields expressions for the spatial and temporal distributions along the axon. For $F(X, T) = 0$, the approximate forms of these have already been discussed (p. 282). The fit of the experimental observations to the theoretical curve



XI 26.—The time course of the total charge on the membrane, in the extrapolar region, at make and break of the current. The total charge was computed by graphical integration from the extrapolar potential records. The full lines are the plots of the exponential equations (11a) and (11b), with time constants $\tau = 2.02$ and 1.65 msec. respectively. (After Hodgkin and Rushton, see ref. 9.)

is not so good for the temporal distribution (Fig. 9) as for the spatial distribution (Fig. 8). If, however, the total membrane charge is computed by graphical interpretation from the potential records, the observations fit the theoretical curves extremely well for both make and break of the square wave stimulus pulse, as shown in Fig. 26. The theoretical equations of the make and break curves are of the form :

$$\text{make :} \quad \xi = \alpha(1 - e^{-t/\tau}) \quad . \quad . \quad . \quad (11a)$$

$$\text{break :} \quad \xi = \alpha e^{-t/\tau} \quad . \quad . \quad . \quad (11b)$$

Unfortunately the determination of the total membrane charge is too laborious for routine experimental use. For further development of the theory reference should be made to the original papers.

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