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A STUDY OF CELLS WITH LIQUID–LIQUID JUNCTIONS

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The object of this research was to investigate both theoretically and experimentally the electromotive force of cells with liquid–liquid junctions, especially the effect of the nature of the junction on the value, stability and reproducibility of the measured electromotive force, and finally to show that both stability and reproducibility are experimentally realizable under just the conditions to be expected from theoretical considerations.

Theoretical Considerations.—As we are primarily interested in the conditions for the stability and reproducibility of the cells rather than with the absolute values of the e. m. f., we shall here make the simplifying and inaccurate assumption that the ions obey the laws of ideal dilute solutions. Any deviations from the truth of this assumption will be referred to as "salt effects"; these may greatly affect the absolute values of the e. m. f., but not its reproducibility nor to any great extent its stability; a discussion of "salt effects" will be given elsewhere.[1] It will also be sufficient for all the points which we wish to emphasize if we consider solutions containing only univalent ions; the more general case of solutions containing ions of different valency makes the formulas somewhat more involved without introducing any new physical complications.

Let c_i denote the concentration, μ_i the chemical potential, z_i the valency, taking account of its sign, u_i the mobility and t_i the transport number of ions of type i. It is then a well-known thermodynamic result that the liquid–liquid junction potential $d\phi$ due to diffusion between a solution with concentrations c_i and another with slightly different concentrations $c_i + dc_i$ is given by the formula

$$-\epsilon d\phi = \Sigma_i z_i t_i \, d\mu_i \tag{1}$$

where $-\epsilon$ is the charge of an electron and z_i is $+1$ or -1 according as the ion i is positively or negatively charged. The assumption that the ions obey the laws of ideal dilute solutions implies the relation

$$\mu_i = RT \log_e c_i + \mu_i^\circ \tag{2}$$

where R is the gas constant, T the absolute temperature and μ_i° depends on the temperature and the solvent but not the concentration. Substituting (2) in (1) we get

$$-\epsilon d\phi = RT\, \Sigma_i z_i t_i \frac{dc_i}{c_i} \tag{3}$$

but by the definition of transport number

$$t_i = \frac{u_i c_i}{\Sigma_j u_j c_j} \tag{4}$$

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[1] Guggenheim, *J. Phys. Chem.*, **36**, in press.

whence

$$-\epsilon d\phi = RT \frac{\Sigma_i z_i u_i \, dc_i}{\Sigma_i u_i c_i} \tag{5}$$

Since the transport of ions on the passage of current from a solution of concentrations c_i to another with concentrations $c_i + dc_i$ is reversible, the applicability of thermodynamics to the problem can hardly be questioned, and Equation 5 may safely be regarded as strictly valid for univalent ions obeying the laws of ideal dilute solutions. If however there are finite differences between the concentrations of the two solutions in contact, the transfer of at least some of the ions on the passage of current may be irreversible; for example, if the first solution contains a finite quantity of ions of a type not present at all in the second solution, then the passage of a minute current in the one direction will carry some ions of this type into the second solution, but a reversal of the current will not return them. To apply thermodynamics to junctions with finite differences in the concentration we have to assume a transition layer of intermediate composition varying continuously from that of the first solution at the one end to that of the second at the other. If at any time we know the concentrations at all points of the transition layer we can obtain the whole liquid–liquid junction potential ϕ by integration of (5)

$$-\epsilon\phi = RT \int_{\mathrm{I}}^{\mathrm{II}} \frac{\Sigma_i z_i u_i \, dc_i}{\Sigma_i u_i c_i} \tag{6}$$

where I denotes the first solution and II the second. In the simple case of a concentration cell where Solutions I and II contain only one uni-univalent salt, the same in both, the integrand in (6) is a perfect differential and so the integral can be evaluated directly. Using the suffixes + and − to refer to the cations and anions respectively, setting

$$c_+ = c_- = c \qquad z_+ = +1 \qquad z_- = -1 \tag{7}$$

and regarding the mobilities as independent of the concentrations, we get

$$-\epsilon\phi = RT \frac{u_+ - u_-}{u_+ + u_-} \log_e \frac{c^{\mathrm{II}}}{c^{\mathrm{I}}} \tag{8}$$

But in the general case of more than two species of ions the integrand in (6) is not a perfect differential and so the integration cannot be performed without further knowledge of the variation of the concentrations along the transition layer. In other words, in the case of more than two ionic species the junction potential will depend on the nature of the junction.

The type of junction most easily treated mathematically is that which we will call the "continuous mixture layer." Its nature is defined as follows: the composition at any point of the transition layer is a linear combination of the compositions of the extreme liquids I and II; or, in other words, the solution at any point of the transition layer may be regarded as a mixture in certain proportions of the two extreme solutions, I and II. For these conditions (6) can be integrated directly if one treats the mobilities as independent of the concentrations. The result is

$$-\epsilon\phi = RT\,\frac{\Sigma_i z_i u_i(c_i^{II} - c_i^{I})}{\Sigma_i u_i(c_i^{II} - c_i^{I})}\log_e\frac{\Sigma_i u_i c_i^{II}}{\Sigma_i u_i c_i^{I}} \tag{9}$$

a formula which we owe to Henderson,[1a] but neither his experiments nor those of subsequent writers were designed in such a way as to fulfil the conditions corresponding to the assumptions underlying this particular integrated form of the general differential equation, (6). Experiments to be described below show that when these conditions are observed, reproducible values are obtained for the e. m. f. measured. In the particular case where the solutions I and II have equal specific conductivities

$$\Sigma_i u_i c_i^{I} = \Sigma_i u_i c_i^{II} = S \tag{9a}$$

and Equation 9 becomes indeterminate. In this case we have

$$-\epsilon\phi = RT\int_0^1 \frac{\Sigma_i z_i u_i(c_i^{II} - c_i^{I})\mathrm{d}\lambda}{S} = RT\,\frac{\Sigma_i z_i u_i(c_i^{II} - c_i^{I})}{S} \tag{9b}$$

A second type of junction which allows (6) to be integrated explicitly is what we shall call the "constrained diffusion junction." It may be described as follows: the composition of the liquid is artificially maintained constant and the same as that of Solution I at all points to the left of a certain fixed plane A; similarly, the composition to the right of another parallel plane B is maintained the same as that of Solution II; subject to these constraints the ions diffuse freely between A and B until a steady state is reached, after which the junction potential should remain constant. The solution corresponding to these contraints shows that the difference of potential ϕ between A and B is independent of the distance A B and is determined by the transcendental equation

$$\frac{\Sigma_+ u_i c_i^{II}\, e^{\epsilon\phi/RT} - \Sigma_+ u_i c_i^{I}}{\Sigma_- u_i c_i^{II} - \Sigma_- u_i c_i^{I}\, e^{\epsilon\phi/RT}} = \frac{\log_e \frac{\Sigma_i c_i^{II}}{\Sigma_i c_i^{I}} - \frac{\epsilon\phi}{RT}}{\log_e \frac{\Sigma_i c_i^{II}}{\Sigma_i c_i^{I}} + \frac{\epsilon\phi}{RT}} \times \frac{\Sigma_i c_i^{II}\, e^{\epsilon\phi/RT} - \Sigma_i c_i^{I}}{\Sigma_i c_i^{II} - \Sigma_i c_i^{I}\, e^{\epsilon\phi/RT}} \tag{10}$$

where Σ_i, Σ_+, Σ_-, denote, respectively, summation over all ions, over all positive ions and over all negative ions. This formula for solutions containing only ions of the same numerical valency was given by Planck.[2] The corresponding more general formula for ions of several different valencies was obtained by Pleijel.[3]

As was only to be expected this solution is in general different from that of Henderson, because under the conditions of constrained diffusion a steady state is reached in which the solution at each point cannot be

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[1a] Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

[2] Planck, *Wied. Ann.*, **39**, 161 (1890); **40**, 561 (1890).

[3] Pleijel, *Z. physik. Chem.*, **72**, 1 (1910).

regarded as a mixture of the two extreme liquids. The values given by the formulas of Henderson and of Planck for various junctions have been compared by Cumming and Gilchrist.[4] For the junction hydrochloric acid of concentration c (Solution I) against potassium chloride of concentration kc (Solution II), the difference is zero when $k = 1$. For $k < 1$ the continuous mixture layer gives the higher potential difference while the opposite is the case when $k > 1$. As long as the concentration of the potassium chloride is greater than that of the hydrochloric acid, the difference between the potentials given by the two formulas is never more than 1.5 millivolts; the difference is maximum in the neighborhood of $k = 5$. Both formulas give a flat minimum in the neighborhood of $k = 10^3$. The position of the minimum depends very much on the exact value assumed for the transport numbers of K^+ and Cl^- in potassium chloride.

The physical conditions corresponding to the Planck formula have not generally been understood.[5] There is no restriction as to the "sharpness" of the boundary, the potential being in fact independent of the length of the transition layer provided there is a steady state in which the length of the layer is artificially maintained constant. It was suggested by Bjerrum[6] that these conditions might be obtained if the junction were within a membrane kept washed on the two sides with the two outer solutions, but apparently this has never been tried previous to the author's attempts to be described in a later section. The only other evidence the author has been able to find of Planck's formula being correctly interpreted is in an unpublished fragment of Gibbs.[1]

A third definite type of junction is that which may be described as the "free diffusion junction"; the conditions defining it are that the transition layer should be initially short compared with the distance between the two electrodes, an absolutely sharp boundary being of course impossible, and that unconstrained diffusion should be allowed to take place. Under these conditions the length of the transition layer is always increasing, but, if there is cylindrical symmetry, that is, if the gradients of the concentrations and of the electrical potential are throughout parallel to a fixed straight line, it appears that the potential difference between the ends is independent of the time, at least after a sufficient time has elapsed for the effect of the initial deviations from "sharpness" to have died out. This type of junction has been discussed by Taylor.[8] The fundamental equations cannot be integrated explicitly with these boundary conditions.

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[4] Cumming and Gilchrist, *Proc. Faraday Soc.*, **9**, 174 (1913).

[5] Cumming and Gilchrist, *ibid.*, **9**, 174 (1913); Büchi, *Z. Elektrochem.*, **30**, 443 (1924); Planck, *Sitzb. Preuss. Acad. Wiss.*, **34**, 285 (1927).

[6] Bjerrum, *Z. Elektrochem.*, **17**, 58 (1911).

[7] Gibbs, "Collected Works," Vol. I, p. 431.

[8] Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

Taylor has therefore tried to obtain an approximate solution.[9] In order to follow Taylor it is best to consider first the free diffusion of a non-electrolyte obeying the laws of ideal dilute solutions. We shall suppose that there is cylindrical symmetry, all gradients being parallel to the x-axis. Let c denote the concentration and μ the chemical potential of the solute; let u denote the mobility of a solute molecule and V its velocity; let t be the time, T the absolute temperature and R the gas constant. Then the equation of continuity is

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x}(cV) \tag{11}$$

and the equation of motion

$$V = -u\frac{\partial \mu}{\partial x} = -u\frac{RT}{c}\frac{\partial c}{\partial x} \tag{12}$$

Substituting from (11) into (12) we obtain the general differential equation for the diffusion of an ideal solute

$$\frac{\partial c}{\partial t} = RTu\frac{\partial^2 c}{\partial x^2} = \kappa\frac{\partial^2 c}{\partial x^2} \tag{13}$$

where $\kappa = RTu$ is the "diffusion coefficient."

For the case of "free diffusion" between two solutions of concentrations $c_0 + \Delta$ and $c_0 - \Delta$, the boundary conditions are

For all t $c = c_0 + \Delta$ for $x = +\infty$ $c = c_0 - \Delta$ for $x = -\infty$
For $t = 0$ $c = c_0 + \Delta + f(x)$ for $x > 0$ $c = c_0 - \Delta + f(x)$ for $x < 0$

where $f(x) = 0$ except for $-l < x < +l$ in which interval $f(x)$ is indefinite and may even be discontinuous provided it remains finite. $f(x)$ is a measure of the uncontrollable initial deviations from "sharpness." The exact solution of (13) is

$$c = c_0 + \Delta\frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{\kappa t}}} e^{-\xi^2}\,\mathrm{d}\xi + \frac{1}{2\sqrt{\pi\kappa t}}\int_{-l}^{+l} f(\xi)\, e^{-(\xi - x)^2/4\kappa t}\,\mathrm{d}\xi \tag{14}$$

From the form of the last term it may be shown that the influence of the initial deviations from sharpness will be halved in a time not greater than l^2/κ and will have completely died out when t is several times as great as l^2/κ. After this initial period, c is a function of $x/\sqrt{t}$; hence if at any time, t_1, we plot c against x, this same curve will also represent c as a function of x for any subsequent time t_2 provided only we alter the scale of x in the ratio $\sqrt{t_2/t_1}$. This solution should give a general idea of the nature of the solution for the corresponding case of electrolytes, which we shall consider next.

For ions of type i we have the equation of motion

$$V_i = u_i\left[-\frac{\partial \mu_i}{\partial x} - z_i\epsilon\frac{\partial \psi}{\partial x}\right] \tag{15}$$

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[9] Since the present paper was first submitted for publication in June, 1929, the author has been in correspondence with Dr. Taylor and his criticism of Dr. Taylor's treatment is modified in consequence.

where ψ is the electric potential at the plane x, so that in place of (21) we get the general differential equation for ionic diffusion

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x}\left[u_i c_i \frac{\partial \mu_i}{\partial x} + u_i c_i z_i \epsilon \frac{\partial \psi}{\partial x}\right] \tag{16}$$

If we multiply by z_i, sum over all i and use the condition of electrical neutrality

$$\Sigma_i z_i c_i = 0 \tag{17}$$

we get

$$-\epsilon \frac{\partial \psi}{\partial x} = \frac{\Sigma_i z_i u_i c_i \frac{\partial \mu_i}{\partial x}}{\Sigma_i u_i c_i} = RT \frac{\Sigma_i z_i u_i \frac{\partial c_i}{\partial x}}{\Sigma_i u_i c_i} \tag{18}$$

This equation derived from dynamic considerations is equivalent to (5), which was obtained thermodynamically. Substituting from (18) into (16)

$$\frac{\partial c_i}{\partial t} = RTu_i \frac{\partial^2 c_i}{\partial x^2} - \frac{\partial}{\partial x}\left[u_i c_i z_i\, RT \frac{\Sigma_j z_j u_j \frac{\partial c_j}{\partial x}}{\Sigma_j u_j c_j}\right] \tag{19}$$

There are as many equations of this form as there are types of ions.

For the case of "free diffusion" the boundary conditions are

for all t $c_i = c_i^\circ + \Delta_i$ for $x = +\infty$ $c_i = c_i^\circ - \Delta_i$ for $x = -\infty$
where $2c_i^\circ = c_i^{I} + c_i^{II}$ and $2\Delta_i = c_i^{II} - c_i^{I}$

There are also the boundary conditions for $t = 0$, but the effect of these, as in the case of a non-electrolyte, will fall to one-half in a time of the order l^2/RTu_i, where l is the length of the initial transition layer whose nature will be accidental and irreproducible; when the time is great compared with l^2/RTu_i the effect of the initial deviations from sharpness will be negligible. The diffusion coefficient $\kappa_i = RTu_i$ is for univalent ions generally of the order 1 cm.²/day, so that if the initial irregular transition layer has a length 0.5 mm., its effect will be halved in about four minutes and will be negligible in thirty to forty minutes. After this transient period the solution will be the same as if the initial boundary had been infinitely sharp; but from the form of Equation 19 and the boundary conditions it is clear that the solution must take the form that c_i is a function of x, t the various c_j°, Δ_j and the various $\kappa_j = RTu_j$, but all the c_j°, Δ_j have the same dimensions as c_i, while the κ_j have the same dimensions as x^2/t; therefore, the solution will, as in the case of a non-electrolyte, be of such form that c_i is a function of x^2/t or of $y = x/2\sqrt{t}$. Taylor comes to this conclusion by a similar argument. His reasoning is, however, somewhat obscured chiefly by a misprint of t/x^2 instead of x^2/t and to a less extent by his appearing to ignore the dimensions of energy which cancel out owing to the peculiar units used by him. We thus have

$$\frac{\partial^2 c_i}{\partial x^2} = \frac{d^2 c_i}{dy^2} \times \frac{1}{4t} \qquad \frac{\partial c_i}{\partial t} = -\frac{dc_i}{dy} \times \frac{y}{2t} \tag{20}$$

Substitution in (26) gives

$$-2y\frac{\mathrm{d}c_i}{\mathrm{d}y} = \kappa_i\frac{\mathrm{d}^2c_i}{\mathrm{d}y^2} - \frac{\mathrm{d}}{\mathrm{d}y}\left[\kappa_ic_iz_i\,\frac{\Sigma_+\kappa_j\,\frac{\mathrm{d}c_j}{\mathrm{d}y} - \Sigma_-\kappa_j\,\frac{\mathrm{d}c_j}{\mathrm{d}y}}{\Sigma_j\kappa_jc_j}\right] \tag{21}$$

where we have written the diffusion coefficient κ_i in place of RTu_i. If all the ions had the same mobility and so the same diffusion coefficient κ, (21) would reduce to

$$-2y\frac{\partial c_i}{\partial y} = \kappa\frac{\partial^2 c_i}{\partial y^2} \tag{22}$$

with the solution

$$c_i = c_i(y) = c_i{}^\circ + \Delta_i\frac{2}{\sqrt{\pi}}\int_0^{y/\sqrt{\kappa}} e^{-\xi^2}\,\mathrm{d}\xi \tag{23}$$

equivalent to (14) without the transient term. Taylor next asserts that when the mobilities are not all equal, the solution of (21) can take the form

$$c_i = c_i(y) = N_i + \sum_{n=0}^{\infty} A_n^i\int_0^{y/\sqrt{\gamma_i}} e^{-\xi^2}\,\xi^n\,\mathrm{d}\xi \tag{24}$$

where the N_i, A_n^i and γ_i are constants. Actually it can be shown that any continuous monotonic function of y which tends to a finite limit when y tends to $+\infty$ or $-\infty$ can be expressed in the form of the right-hand side of (24); moreover, the value of γ_i in such an expansion is quite arbitrary. Whether the form given by (24) is of any value depends therefore on whether the series converges rapidly, and this will depend on the value chosen for γ_i. The convergence would generally be very slow if one simply set $\gamma_i = \kappa_i$. If one could find a particular value of γ_i to make the series in (24) converge rapidly for all values of y, it might possibly be sufficient to retain only the first term of the series; (24) would then take the form (23) with γ_i in the place of κ_i. Taylor indeed suggests this form as an approximate solution and shows how to choose γ_i so as to give the most rapid possible convergence of the series and so the best possible fit for small values of y. With such a value of γ_i a slowly convergent series may be required to give a reasonably good fit over the whole range of y and the first term might well give a bad fit for larger values of y. In Taylor's opinion this can never be so bad as to more than counteract the exact fit at $y = 0$ and $y = \pm\infty$. This he has, however, not proved and is in the author's opinion a rather dangerous assumption, especially in cases where the diffusion potential given by the "free diffusion junction" differs widely from that of the "continuous mixture layer." In junctions of the type concentrated acid against dilute neutral salt this may well be the case, but such junctions are rarely used in practice. Taylor actually applies his computation only to the case of hydrochloric acid against potassium chloride of the same concentration, where the difference between the two types of junction is only 0.3 to 0.4 mv. Taylor points out a check on his approximation by comparison of the computed cation and anion concentrations at various planes in the transition layer. Theoretically these should, of course, be equal. Even if they were found so in his check this would not be sufficient proof that his approximation gave the true distribution. Actually one finds that at those parts of the transition layer where the fit is not automatically good, the differences between the computed cation and anion concentrations differ by from 37 to 56% of the deviation of composition from that of a mixture of the electrode solutions. It is difficult to estimate the inaccuracy of the approximation, but in view of the above figures the present author thinks it may be a not inappreciable fraction of the correction term to the "continuous mixture" value. It is easy to show that for a single uni-univalent salt the diffusion equation can be integrated exactly, the solution being of precisely the same form as for a non-electrolyte, the effective diffusion coefficient being the harmonic mean of those of the two ions, that is to say that we have to set in Equation 14

$$\frac{1}{\kappa} = \frac{1}{2}\left(\frac{1}{\kappa_+} + \frac{1}{\kappa_-}\right) \tag{25}$$

The author, therefore, suggests as an approximate solution of the diffusion equation for several electrolytes with a common anion that each salt (but not each ion) be assumed to diffuse independently of the others. This solution, in contrast to Taylor's, will at least satisfy the condition of electrical neutrality and has, moreover, the advantage of considerably greater simplicity. Which solution will in a given case be the more accurate it is difficult to judge. For the particular junction considered by Taylor the difference between the two solutions is inappreciable. It is most unfortunate that the mathematical treatment of the "free diffusion junction" should be so intractable, even when all salt effects are neglected, the more so as experiment shows that of the three junctions discussed it is the simplest to produce, the most stable and quite as reproducible as the better of the other two discussed above.

A fourth type of junction must also be discussed briefly, not because of its simple nature, but because, unlike the other three types so far discussed, it corresponds exactly to conditions that have been used in practice; the type of junction referred to is that known as the "flowing junction." In this junction the two solutions stream toward each other and after meeting flow away in parallel streams. The characteristic feature of this type of junction is the extreme thinness of the transition layer. The flowing junction was used first by Lamb and Larson[10] and shortly after by MacInnes and Yeh.[11] In both cases excellent reproducibility is reported. The former authors do not discuss theoretically the nature of the transi-

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[10] Lamb and Larson, This Journal, **42**, 229 (1920).

[11] MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

tion layer; the latter believe it to be the same as that which we have discussed above under the name "continuous mixture layer." This assumption seems surprising because the thinner the layer the greater is the importance of diffusion as compared with mixing, but this particular type of junction is characterized by the thinness of the transition layer. An alternative possibility is that it rather resembles the junction described above under the name "constrained diffusion" except for the complete absence of cylindrical symmetry. There will certainly be a steady state which will depend very little on the rate of flow provided it is sufficiently great and yet not so great as to produce turbulence; on the other hand, it may well depend on the curvature of the stream lines and so on the exact shape of the apparatus used. There is also the possibility that neither mixing nor diffusion can be neglected, although in this case one would expect changing the rate of flow to have a detectable effect, which has not been observed. Scatchard,[12] who has also used the flowing junction with success, writes[13] "I have always regarded our flowing junctions as 'continuous mixture boundaries' because it seems to me that the time is too short for diffusion to become noticeable but I know no way of demonstrating their nature." It should be possible to check this if one knew the thickness of the transition layer, the rate of flow and the diffusion coefficients. Although the "flowing junction" has in certain cases given greater reproducibility than any other type of junction previously tried, its interest from a theoretical point of view must be considerably diminished by the uncertainty of the factors which determine the steady state. If the steady state observed is independent of the shape of the apparatus, it seems likely that the junction must "*a posteriori*" be of the "continuous mixture" type. If, on the other hand, the steady state observed depends on the curvature of the stream lines, its theoretical consideration will be too complicated to be worth attempting.

Previous Measurements of Cells with Liquid–Liquid Junctions.—The numerous researches involving the use of cells with liquid–liquid junctions fall into two classes: those in which the junction potential was made as small as possible (usually by making one of the two liquids a concentrated solution of potassium chloride) and neglected, and those in which the junction potential was appreciable and was one of the factors of primary interest. We need discuss previous work of the latter class only. Almost all investigators mention that the e. m. f. observed is not constant, but may change several millivolts through "aging"; such effects are reported for example by Weyl,[14] and by Lewis and Rupert.[15]

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[12] Scatchard, THIS JOURNAL, **47**, 696 (1925).

[13] Private communication to the author.

[14] Weyl, "Dissertation," Karlsruhe, **1905**.

[15] Lewis and Rupert, THIS JOURNAL, **33**, 299 (1911).

This is explained by Bjerrum[16] on the assumption that there is initially a transition layer of the "continuous mixture" type, which owing to its thinness is unstable and is soon disturbed by diffusion effects. Chanos[17] found that a symmetrical cell with two liquid–liquid junctions could give e. m. f. values up to 6 mv. if one of the junctions was stirred. Cumming and Gilchrist[18] also report one cell in which the e. m. f. rose 11 mv. in the first ten minutes and a further 10 mv. in twenty-four hours; they also report an e. m. f. as high as 15 mv. in a cell symmetrical except as regards the age of the two junctions. These authors made an extended study of the reproducibility and stability of junctions formed in various ways, but their discussion shows a lack of understanding of the essential characteristics of a junction that determines its reproducibility. For example, they associate the Planck formula with a "sharp" boundary; actually the initial transition layer is almost certainly formed by mixing and the most immediate consequence of "sharpness" is instability. They also associate the Henderson formula with a transition layer in which the two extreme solutions A and B have been mechanically mixed by stirring; this procedure merely transforms the indefinite type of junction between A and B into two junctions of equally indefinite type, one between A and C, the other between C and B, where C denotes the solution obtained by stirring A and B together.

In certain cases fair reproducibility in the initial values of the e. m. f. has been obtained, as for example by Lewis and Sargent[19] and by Lewis, Brighton and Sebastian,[20] but in every case the liquid–liquid junctions were between two solutions of the same concentration of two uni-univalent salts with one ion in common. All the measurements by the flowing junction method of Lamb and Larson[10] and those of MacInnes and Yeh[11] were also on cells of this type. From this brief review of the literature there appears no evidence of reproducibility and stability ever having been obtained in a cell containing a junction between two solutions of different electrolytes at different concentrations, unless one of these was a concentrated solution of potassium chloride.

Experimental Technique

All the cells measured were of the type

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid 0.1\ N\ \mathrm{HCl} \mid c\ \mathrm{KCl} \mid 0.1\ N\ \mathrm{KCl} \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

where the concentration c of the potassium chloride bridge was varied from 0.1 to 3.5 N. In choosing this type of cell there were several points considered to be in its favor. First, the e. m. f. measured is due entirely

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[16] Bjerrum, *Z. Elektrochem.*, **17**, 58 (1911).

[17] Chanos, *Ann. de l'Univ. Lyon*, **1**, 18 (1906).

[18] Cumming and Gilchrist, *Trans. Faraday Soc.*, **9**, 174 (1913).

[19] Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909).

[20] Lewis, Brighton and Sebastian, *ibid.*, **39**, 2253 (1917).

to the liquid junction and to salt effects, the electrode potentials canceling. Second, the diffusion potentials were as great as or greater than those ever encountered in ordinary practice unless more concentrated solutions of a strong acid be used. Third, when the bridge solution was 3.5 *N* potassium chloride the junctions were exactly of the type usually encountered in *P*H measurements. Finally, in some of the measurements, the technique used required that the whole system should be closed; this precluded the use of a hydrogen electrode. On the other hand, the cells had the definite disadvantage that the calomel electrode in acid solution is appreciably affected by oxidation.[21] No very great importance is therefore attached to the absolute values of the e. m. f. measured, owing to uncertainty in the electrodes. On the other hand, the relative values obtained are believed to be reliable on the following grounds. During the period of preliminary measurements, March to July 1928, numerous electrodes were prepared and any two electrodes, which should be identical, never differed by more than 0.4 mv. and only rarely by more than 0.2 mv. None of the measurements made during this early period are reported here as it is uncertain to what extent lack of reproducibility may have been due merely to unskilled technique. All the measurements reported were made between September, 1928 and February, 1929 inclusive. The same calomel–potassium chloride half element was used in all the measurements; three calomel–hydrochloric acid half elements were used; all four half elements were prepared on August 28, 1928. The three calomel–hydrochloric acid elements were compared with one another at intervals; they were also compared with a fourth similar half element prepared on November 10, 1928. The greatest difference ever observed between any two of the three half elements used was 0.20 mv., whereas the greatest difference ever found between one of these and the fourth one was 0.33 mv. We shall see that these fluctuations due to the electrodes are of the same order of magnitude as those in the measured e. m. f.'s of the cells with junctions of a reproducible type; it has therefore seemed most reasonable to apply no correction for the differences between the three calomel–hydrochloric acid electrodes used. That the hydrochloric acid electrodes did not change appreciably relatively to the potassium chloride electrode during the five months in which the measurements were made is shown by the reproducibility of the e. m. f. measured at different times with the same type of junction. The author considers that the measurements justify belief in a reproducibility of about 0.2 mv. when the junction is made in a suitable way.

The half element vessels used were a slight modification of that designed by Lewis, Brighton and Sebastian.[20] As may be seen from Fig. 1, the significant addition is the stopcock, A, which can be connected to a

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[21] Randall and Young, THIS JOURNAL, 50, 989 (1928).

reservoir so that liquid may be sucked up the side-tube B. The extra stopcock in the circuit between E and B has been dispensed with. At C there is a junction by means of a piece of rubber tubing; this makes it possible to clean the side-tube and stopcock A without disturbing the electrode. D is merely a trap for air bubbles and is probably unnecessary

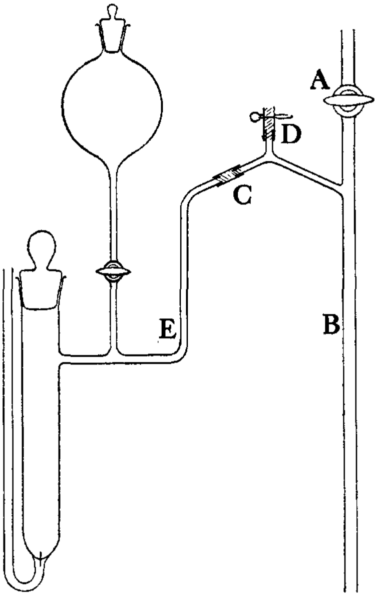

Fig. 1.

All measurements were made with the electrode vessels in a water thermostat at 18°, in which the temperature fluctuations were not more than 0.01°. The liquid–liquid junctions were either in this same water thermostat or in an air thermostat at 18 ± 0.3°, according to the type of junction. Furthermore, the temperature of the whole room was automatically regulated so that the air around the thermostats was generally very near 18° and never deviated by more than 1°.

The measurements were made with a potentiometer constructed by Wolff and a mirror galvanometer made by Siemens and Halske. A Weston normal cell was used as standard. The thermostat and all the electrical apparatus were virtually in an earthed "cage." The electrical equipment could easily measure to an accuracy of 0.01 mv., but in general readings were made correct to 0.1 mv. or 0.05 mv. only.

The cells measured contained in general two liquid–liquid junctions, one between potassium chloride solutions of concentrations 0.1 N and c, the other between potassium chloride of concentration c and 0.1 N hydrochloric acid. According to theory the potential difference across the former should be independent of the method of forming the junction and easily reproducible. This was to some extent confirmed by measuring the symmetrical cells

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid 0.1\ N\ \mathrm{KCl} \mid c\ \mathrm{KCl} \mid 0.1\ N\ \mathrm{KCl} \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

The junctions were made by simply dipping the side tubes of the two electrode vessels into a U-tube containing potassium chloride at concentration c. Generally a small e. m. f. less than 0.2 mv. was observed and this was found to be independent of the concentration c of the bridge potassium chloride and unaffected by stirring with an accuracy of 0.01 mv. On the strength of this no special pains were taken in making the junction between the two potassium chloride solutions, as the reproducibility of the e. m. f. is determined by the nature of the other junction.

"Continuous Mixture Junction."—This junction, unlike the "constrained diffusion" and "free diffusion" junctions, is theoretically unstable and will be disturbed by diffusion. The instability can be minimized by making the mixture layer long, since the time required for diffusion to annihilate deviations from the steady state conditions is proportional to the square of the distance through which these deviations are initially present. Bjerrum[16] in 1911 stated that the time required was proportional to the first power of this distance, but he now[22] agrees that this was an error. As already emphasized, the "continuous mixture" junction cannot be made merely by stirring, as this procedure may do no more than replace one junction by two of equally indefinite type. The method adopted is shown diagrammatically in Fig. 2. B is the side-tube of the electrode vessel; from C to D is a rubber connection. Initially the cocks A and E are open and the system is filled with 0.1 *N* hydrochloric acid from F to G, the quantity of solution in the beaker H being only a few cc. The mechanical stirrer I is started. Into the beaker H is slowly poured about 10 cc. of a mixture of say 95% 0.1 *N* hydrochloric acid and 5% of *c* potassium chloride containing one drop of methyl orange solution. Then successive 10-cc. portions are added of mixtures 0.1 *N* hydrochloric acid and *c* potassium chloride, the proportion of the latter increasing steadily until eventually pure *c* potassium chloride was being added. By the time the beaker was full the concentration of hydrochloric acid in it was quite negligible compared with that of the potassium chloride. The diameter of Tube K was so chosen that when the beaker was full liquid had been sucked nearly up to L. This could be seen clearly owing to the drop of indicator added. In the case of the more concentrated potassium chloride solutions there was no difficulty whatever in preparing a mixture layer in this way, but with 0.1 *N* potassium chloride there was a tendency for the liquid added to the beaker to stream up into the tube B, if the temperatures of the solutions used were a fraction of a degree above 18°. The 0.1 *N* potassium chloride solution when not in use was, therefore, kept in the air thermostat. The mixture layer having been prepared in this way, the procedure taking rather less than ten minutes, the stirrer was stopped, the stopcocks A and E were closed, rubber tubing disconnected at C and the electrode vessel placed in the water thermostat with the side-tube B dipping into a U-tube containing a potassium chloride solution of concentration *c*, into the other end of which dipped the calomel–potassium chloride electrode vessel. The U-tube was also in the water thermostat so that all parts of the circuit, where there were concentration gradients, as well as both electrodes, were in the water thermostat. The e. m. f. of the cell was then observed at intervals extending over several hours. In Table I are given the results of four typical sets of measurements; the first three were made with three different calomel–hydrochloric acid electrodes, while the fourth was made on a different day with the same electrode as the first. The times are measured from the returning of the electrode vessel to the water thermostat after the preparation of the mixture layer.

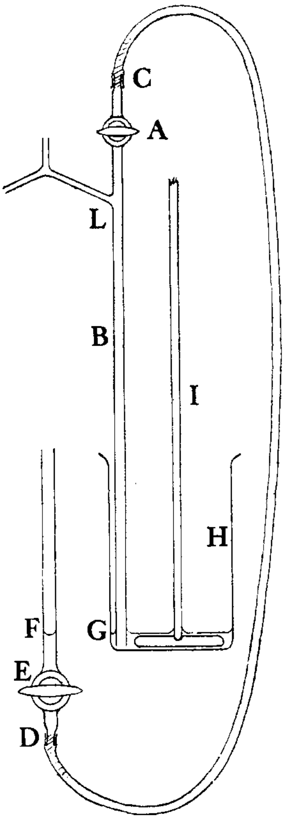

Fig. 2.

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[22] Private communication.

TABLE I

"CONTINUOUS MIXTURE" JUNCTION. BRIDGE SOLUTION 1 N POTASSIUM CHLORIDE

Electrode 1		Electrode 2		Electrode 3		Electrode 1	
Time, min.	E. m. f., mv.	Time, min.	E. m. f., mv.	Time, min.	E. m. f., mv.	Time, min.	E. m. f., mv.
0	7.9	0	7.7	0	7.7	0	7.7
13	8.25	14	8.3	24	8.2	10	8.0
27	8.4	38	8.5	50	8.35	21	8.1
51	8.45	64	8.55	96	8.45	35	8.2
77	8.5	110	8.65			59	8.25
123	8.6						
311	8.75	298	9.2	284	8.6		

For each concentration of the bridge solution at least nine such sets of measurements were made, generally three sets with each of the three electrodes. It was found that the e. m. f. rose generally about a half millivolt in the first ten minutes, but after that only about a quarter millivolt in the next two hours. If we neglect the readings in the first ten minutes and give equal weight to all readings in the next two or three hours, the

TABLE II

EXPERIMENTAL OBSERVATIONS

Concn. of bridge KCl	Mean E. m. f., mv.	R. M. S. dev. in mv.	No. of measurements	Date
	A. "Continuous Mixture Layer"			
0.1	27.4	0.11	39	......
0.2	20.9	.16	31	......
0.5	13.05	.24	33	......
1.0	8.3	.09	20	Early Sept., 1928
1.0	8.3	.11	12	Late Oct., 1928
1.0	8.3	.24	33	Jan., 1929[a]
1.75	4.9	.14	32	......
2.5	3.1	.19	35	......
3.5	1.55	.11	34	......
	B. "Free Diffusion Junction"			
0.1	27.0	0.24	23	Nov., 1928
0.2	19.95	.11	22	Nov., 1928
0.5	12.55	.18	23	Nov., 1928
1.0	8.9	.17	30	Oct., 1928
1.0	8.4	.18	26	Dec., 1928
1.0	8.4	.28	15	Feb., 1929
1.75	5.15	.14	26	Nov., 1928
2.5	3.4	.21[b]	31	Dec., 1928
3.5	1.1	.15	17	Nov., 1928

[a] The measurements given in detail in Table I are taken from this set; from the value of the R. M. S. deviation it can be seen that the set chosen for illustration is one of the least favorable as regards reproducibility.

[b] One reading after the lapse of ten minutes has been neglected in a case where obviously the steady state was far from reached. Its inclusion would increase the R. M. S. deviation to 0.24 mv.

results given in Table IIA are obtained. The first column gives the concentration of the bridge potassium chloride solution, the second the mean value of the measured e. m. f. in millivolts, the third the root mean square deviation of the individual readings from the mean and the fourth the number of readings made after the first ten minutes. From the dates given in the last column it is clear that there has been no serious change in the electrodes over the whole period during which these measurements were made. These results show that the junction prepared in this way is reproducible with a probable error of less than 0.2 mv. It is noteworthy that the order of magnitude of this uncertainty is independent of the absolute value of the total measured e. m. f.

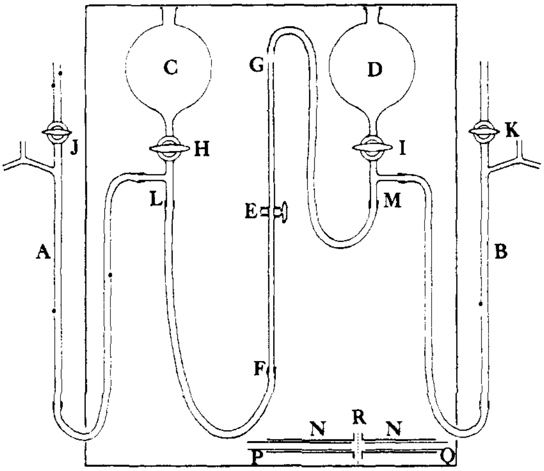

Fig. 3.

"Free Diffusion Junction."—The method of preparing a junction of this type is very simple and is shown diagrammatically in Fig. 3. A and B are, respectively, the side tubes of the calomel potassium chloride and calomel hydrochloric acid half element cells. C and D are reservoirs filled, respectively, with potassium chloride of concentration c and with 0.1 N hydrochloric acid. The cock E has the same bore (2-mm. diameter) as the tube FG. A rectangle surrounds that part of the apparatus which was within the air thermostat, the electrodes being in the water thermostat. Suppose all cocks initially closed; then on opening E and the reservoir cock on the calomel–potassium chloride electrode vessel (see Fig. 1) 0.1 N potassium chloride will flow from J to G; the cock on the electrode vessel is then closed and the cock H opened; potassium chloride of concentration c then flows from H to G, displacing the 0.1 N potassium chloride; we then have a junction between the two potassium chloride solutions at the T-piece just below the cock H. The cock E is closed, after which the tube from E to G is thoroughly rinsed and then filled with 0.1 N hydrochloric acid by means of a capillary pipet. The whole of the apparatus to the right of G being filled with 0.1 N hydrochloric acid, the cock I is opened and while solution is trickling out of the rubber tubing at G, this is connected to the upper end of the tube FG. By opening and closing again the cocks J and K, one can make sure that the pressure difference across the cock E is not more than a few mm. of water. After an interval of about twenty minutes for temperature equilibrium to be obtained, the thermostat stirrers are stopped to avoid vibration and the cock E carefully opened. A "free diffusion junction" is thus formed at the upper end of the cock E. The thermostat stirrers were restarted generally after about half an hour, the transition layer by that time being presumably long enough not to be seriously disturbed by slight vibration. It was found that the time taken for the e. m. f. to reach a steady value varied from a few minutes to about three-quarters of an hour; this corresponds to initial accidental deviations from sharpness extending over a length of the order of 0.5 mm. Once the steady value was reached, it did not vary more than a few tenths of a millivolt over a period of twenty-four or even forty-eight hours. Examples of four sets of measurements are given in Table III. The times are measured from the opening of the stopcock E. The reproducibility is even better than in the case of the continuous mixture junction and the stability much greater, as it should be according to theory.

TABLE III

"FREE DIFFUSION JUNCTION." BRIDGE SOLUTION $N/2$ POTASSIUM CHLORIDE

Time, min.	E. m. f., mv.	Time	E. m. f., mv.	Time, min.	E. m. f., mv.	Time	E. m. f., mv.
21	12.45	18 min.	12.35	10	12.75	14 min.	12.5
56	12.5	33 min.	12.35	20	12.9	29 min.	12.55
57	[a]	95 min.	12.55	37	12.9	30 min.	[a]
89	12.45	18 hrs.	12.75	39	[a]	53 min.	12.3
108	12.5			62	12.45	73 min.	12.35
				105	12.55	3.5 hrs.	12.7
						4.5 hrs.	12.75
						45 hrs.	12.8

[a] Denotes the time when the thermostat stirrers were restarted. In the second experiment they were never stopped.

A summary of all measurements made is given in Table IIB. For the sake of consistency all readings taken after more than a quarter of an hour are included, though in a few cases the steady state had not been quite reached in this time. The first column gives the concentration c of the bridge potassium chloride, the second the mean of all readings taken after more than a quarter of an hour, the third gives the root mean square deviation of the individual readings from the mean, the fourth the number of individual readings and the last the date when the set of measurements was made. It will be seen that the probable error in the liquid–liquid junction e. m. f. is again no more than 0.2 mv. and its order of magnitude is independent of the absolute value of the whole measured e. m. f. Cells with 1 N potassium chloride as bridge were measured in October, 1928, December, 1928, February, 1929; the last two sets of measurements are in good agreement, but the first gives an e. m. f. 0.5 mv. higher. This discrepancy has not been explained, but it is to be noted that the measurements in October, 1928 were the first of their kind.[23]

[23] There is now reason to suspect a deficiency in the air-thermostat. In later measurements in collaboration with Miss Unmack the erratic fluctuations have been reduced to 0.1 mv. by improving the control of the temperature of the junction.

In Figure 4 the value of the e. m. f. has been plotted against the concentration of the bridge potassium chloride, the latter on a logarithmic scale to reduce the curvature and so facilitate interpolation. The "continuous mixture layer" points fall on a smooth curve; so do the "free diffusion" points, if for 1 *N* potassium chloride the October, 1928 value be rejected and the two later sets of measurements taken as correct. The maximum difference between the two types of junctions is just under 1 mv. for 0.2 *N* potassium chloride; for concentrations of potassium chloride above 1 *N* it is probably less than the experimental uncertainty.

It is worth noticing that in the case of 0.1 *N* potassium chloride the value for the "free diffusion" junction is less than that for the "continuous mixture" layer by 0.4 mv. as compared with 0.33 mv. computed by Taylor. While we attribute less certainty to our absolute values than to the relative values, it is, however, satisfactory to find how well they too agree with values computed by Taylor, taking account of salt effects by a semi-empirical intrapolation formula. For the case of 0.1 *N* potassium chloride Taylor computes the values 27.9 mv. for the "continuous mixture" layer and 27.6 mv. for the "free diffusion" junction at 25°. The observed value of Lewis, Brighton and Sebastian,[20] 27.8 mv., lies between these, while that of MacInnes and Yeh,[11] using the flowing junction, 26.8 mv., deviates by a whole millivolt. The corresponding computed values for 18° are 27.2 mv. (C. M.) and 26.9 mv. (F. D.) in excellent agreement with our observed values 27.4 mv. (C. M.) and 27.0 mv. (F. D.).[24]

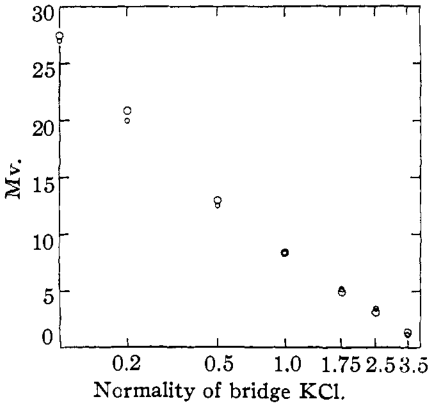

Fig. 4.—O, Continuous mixture layer; o, free diffusion.

A few measurements were made on the "free diffusion junction" by a different technique involving the use of agar-agar. Into a U-tube of height 22 cm. and bore 5 mm. in diameter was poured a hot solution of 1 *N* potassium chloride containing 3% agar-agar until the tube was approximately half full; the solution was left to congeal on cooling. The upper halves of the two limbs of the U-tube were then filled, respectively, with 0.1 *N* potassium chloride and 0.1 *N* hydrochloric acid. The two limbs were then connected to the two electrode vessels by rubber tubing filled with the respective solutions. The U-tube was immersed in the water thermostat and measurements were made. Table IV contains all the measurements. It will be seen that within ten minutes the e. m. f. reaches the value 8.9 mv. and then does not increase by more than half a millivolt in a

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[24] This agreement is now believed to be fortuitous. The absolute value of the e. m. f. of this cell will be discussed in a forthcoming publication by Miss Unmack and the present author.

whole week; this type of junction is the most stable used and the reproducibility is also as good as that of any other type. The mean value, 9.1 mv., of the e. m. f. is 0.7 mv. higher than that of the corresponding junction measured by the former method. The difference may well be due to the effect of the agar-agar on the mobility of the ions, in particular the hydrogen ion.

Table IV

"Free Diffusion Junction" with Agar-Agar

Bridge solution 1 *N* KCl + 3% agar-agar

Time	E. m. f., mv.	Time, min.	E. m. f., mv.	Time	E. m. f., mv.	Time	E. m. f., mv.
0 min.	8.45	2	8.25	2 min.	8.0	2 min.	8.3
2 min.	8.65	9	8.7	34 min.	8.9	20 min.	8.9
11 min.	8.9	29	8.95	52 min.	8.95	100 min.	9.05
41 min.	9.1	35	9.1	75 min.	9.0	7 hrs.	9.1
81 min.	9.15	129	9.1	103 min.	9.05	24 hrs.	9.2
106 min.	9.2			126 min.	9.05	2 days	9.2
20 hrs.	9.35			215 min.	9.1	3 days	9.25
				285 min.	9.1	4 days	9.3
				2 days	9.2	5 days	9.35
						7 days	9.4

Mean 9.1. "R. M. S." deviation, 0.14.

"Constrained Diffusion Junction."—It was suggested by Bjerrum (in 1911)[16] that this type of junction might be realized if the transition layer were within a membrane kept washed on the two sides by the two extreme solutions. The apparatus used is similar to that used for the "free diffusion junction" except for the middle portion between G and F and is shown in Fig. 3. R is a collodion membrane, on each side of which is a rubber washer; the two outer tubes N are held together by rubber bands round small hooks; the inner horizontal tubes P, Q are, respectively, connected by rubber tubing to the T pieces L and M and take the place of the vertical tube FG. The cocks H, I are open and by means of screw clamps the rate of flow of the solutions from C, D into the two surfaces of the membrane is regulated.

It was found that the e. m. f. measured with this apparatus was rather sensitive to changes in the rate of flow, but much more to appreciable differences in the rates on the two sides than to the absolute rates. By using as membrane one obtained from Göttingen (denoted as "Membranfilter Fein") and making the rates as nearly as possible equal on the two sides and from about one drop per second to one drop per ten seconds, values were obtained for the e. m. f. fluctuating over a range of about 1 mv. A rough computation by means of Helmholtz' formula as corrected by Perrin,[25] shows that the effect of a possible electrokinetic potential must be quite negligible. The fluctuations observed were presumably due to the transition layer's sometimes being in motion, so that the boundary conditions corresponding to Planck's formula were not accurately fulfilled. All these measurements are summarized in Table V. The first entry gives the number of times the rates of flow were adjusted, the second the total number of readings made, the third the mean e. m. f. and the

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[25] Perrin, *J. chim. phys.*, **2**, 611 (1904).

fourth the root mean square deviation of the individual readings from the mean. It will be seen that this method is two to three times less accurate than the two types of junctions previously described. The mean value obtained for the e. m. f. is only 0.2 mv. higher than that given by either of the other two types of junction. The value calculated by Planck's formula, neglecting salt effects, was 0.8 mv. higher than the value for the "continuous mixture" junction; the remaining 0.6 mv. discrepancy may be partly due to salt effects and partly experimental error.

TABLE V

"CONSTRAINED DIFFUSION JUNCTION" BY MEANS OF MEMBRANE

Bridge solution 1 N KCl

Number of cells	18	Mean e. m. f. in mv	8.5
Number of readings	45	"R. M. S." deviation	0.42

"Sharp" Junctions of Indefinite Type.—Apart from the experimental realization of junctions of the "continuous mixture," "free diffusion" and "constrained diffusion" types, a few measurements were made on "sharp" junctions of the indefinite type in general use. The instability and irreproducibility reported by other investigators were completely confirmed in the case of a junction between two different electrolytes at different concentrations. In Table VIA are given some typical measurements of the cell

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid 0.1\ N\ \mathrm{HCl} \mid 1\ N\ \mathrm{KCl} \mid 0.1\ N\ \mathrm{KCl} \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

in which the junctions were made simply by dipping the side tubes of the electrode vessels into a U-tube containing the bridge solution. Table VIB gives some similar examples in which the side-tubes were plugged

TABLE VI

JUNCTIONS OF INDEFINITE TYPE

Bridge solution 1 N KCl

Time	E. m. f., mv.	Time	E. m. f., mv.	Time	E. m. f., mv.	Time	E. m. f., mv.	Time	E. m. f., mv.
A. Side-tubes dipped into bridge solution									
8 min.	10.3	8 min.	6.4	8 min.	9.2	0 min.	8.4	0 min.	8.95
35 min.	11.4	35 min.	7.3	35 min.	11.35	? min.	9.2	? min.	9.9
76 min.	11.8	76 min.	8.1	76 min.	12.4	28 min.	10.4	28 min.	12.2
128 min.	11.9	128 min.	8.5	128 min.	12.95	73 min.	11.0	73 min.	13.1
5 hrs.	11.95	5 hrs.	9.2	5 hrs.	13.0				
21 hrs.	11.65	21 hrs.	10.2	21 hrs.	11.3				
B. Junction with cotton plugs									
0 min.	10.2	0 min.	11.8	0 min.	12.2	0 min.	11.3	0 min.	10.8
5 min.	11.95	5 min.	13.4	5 min.	12.65	17 min.	12.7	17 min.	12.9
36 min.	12.8	36 min.	13.35	36 min.	14.0	51 min.	12.75	51 min.	12.55
61 min.	12.85	61 min.	13.2	61 min.	14.1	75 min.	12.7	75 min.	12.35
123 min.	12.8	123 min.	12.85	123 min.	14.15	115 min.	12.65	115 min.	11.6
C. Junction drawn up into side-tube									
0 min.	9.0	0 min.	8.5	8 min.	8.5	3 min.	8.65	0 min.	8.85
3 min.	8.8	7 min.	8.6	41 min.	8.55	36 min.	8.65	6 min.	9.2
21 min.	8.8	32 min.	8.85	130 min.	8.6	125 min.	8.7	24 min.	9.45
83 min.	8.8	60 min.	8.9	20 hrs.	8.85	20 hrs.	9.9	86 min.	9.7
139 min.	8.85							142 min.	9.8

with cotton wool before immersion in the U-tube. The times are measured from the moment of immersion of the side-tubes into the U-tube containing the 1 N potassium chloride. A glance at these tables is sufficient to show that there are irregular fluctuations of the order of several millivolts. The "sharp" junctions made in this way do not correspond to any definite conditions for a steady state and so would not be expected to give good reproducibility. It is nevertheless striking that the fluctuations in the "sharp" junction are so much greater than the greatest differences between the three reproducible types of junction studied. In fact the values obtained for the e. m. f. with the "continuous mixture" and "free diffusion" junctions rarely differed by more than 0.5 mv. and in the particular case of 1 N potassium chloride as bridge they were practically identical. This seems to show that for this particular junction the difference between "free diffusion" layer and the "continuous mixture layer" is insignificant. If the only cause of indefiniteness in the "sharp" junction was the variability in the relative importance of the parts played by diffusion and by mixture in the formation of the transition layer, it would be difficult to explain why the fluctuations with the "sharp" junction should be more than a tenth of what they actually are. There is, however, a characteristic difference between, on the one hand, the three reproducible types of junction discussed from a theoretical point of view and on the other the ordinary "sharp" junction; in the former it is assumed that there is cylindrical symmetry, that is to say, that all concentration gradients are along one and the same direction, while this is far from the case in the latter, where the junction is at the tip of the side-tube of the electrode vessel. The equipotential surfaces in the latter will be highly curved and will depend not only on the exact size and shape of the tip of the side-tube, but also on its position relative to the walls of the U-tube into which it dips; the conditions are altogether too complex for theoretical discussion. It would thus appear that cylindrical symmetry is the most important requisite for reproducibility. To test this suggestion some measurements were made in which the junction was drawn up into the side-tube of the electrode vessel. The transition layer would thus be indefinite as regards the relative parts played by mixture and diffusion, but would approach cylindrical symmetry, though the symmetry might not be complete because the solution when being drawn up the side-tube would probably stream faster in the center than along the walls of the tube. A large number of measurements were made with the junction made in this way and it was found that in most cases a reproducibility of a few tenths of a millivolt was obtained, but once in a while much larger deviations of over a millivolt might occur. Table VIC illustrates one set of nine experiments; the four not recorded were quite similar to the first three in the table; the fourth in the table is also in good agreement for a few hours, but by the next day it has lost its stability; the fifth is typical of the occasional exception. This method of making a junction has been previously used in this Laboratory by Bjerrum and Unmack[26] with very similar results. It is no doubt a great improvement on the usual method and the reproducibility is quite good, if sufficient measurements are made to make the "exceptions" insignificant. The cause of the occasional exception is presumably in the setting up of streams or vortices when the solution is being drawn up into the side tube; these might completely destroy the cylindrical symmetry of the transition layer.

Since the completion of the rest of the present research, the author has been making measurements with hydrogen electrodes in collaboration with Miss Unmack. We made a few experiments in which cylindrical symmetry was deliberately avoided, as, for example, by making the two solutions meet at the junction of two tubes of different bore. The resulting e. m. f.'s were erratic to the extent of several millivolts, even though one of the solutions was 3.5 *N* potassium chloride.

Conclusion

Owing to considerations of salt effects discussed elsewhere[27] the absolute values of the e. m. f. measured are of little interest as they give no simple information of thermodynamic interest. It was partly for this reason that no great pains were taken over the preparation of the electrodes beyond having three calomel–hydrochloric acid electrodes that agreed amongst themselves. It has been shown that cells with liquid junction give reproducibility comparable with that of cells without liquid junction, but only when the transition layer is of such a type that reproducibility can be expected from theoretical considerations. Perhaps the most interesting quantitative result of the measurements is that as long as there was cylindrical symmetry the free diffusion junction gave values for the e. m. f. differing generally by only a few tenths of a millivolt from that given by the continuous mixture layer. This would probably no longer be the case for a junction between concentrated hydrochloric acid and dilute potassium chloride, but for the commonest type of junction, 3.5 *N* potassium chloride against a much more dilute solution, it seems not unlikely that the difference will be small. Hence in computations of the liquid junction potential, salt effects being neglected, it may be allowable to use the formula corresponding to a "continuous mixture layer" even if the actual junction is of the "free diffusion" type.

In a recent paper of great interest MacLogan[28] gives the results of a purely experimental study of the cell.

[26] Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab Math.-fys. Medd.* [1] **9**, (1929).

[27] Guggenheim, *J. Phys. Chem.*, **36**, in press.

[28] MacLogan, *Biochem. J.*, **23**, 309 (1929).

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid 0.1\ N\ \mathrm{HCl} \mid \text{sat. } \mathrm{KCl} \mid 0.1\ N\ \mathrm{KCl} \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

He finds in complete agreement with our own results that the important condition for both reproducibility and stability is that the junction should be within a tube and not at its tip.

The author would like to express here his gratitude to Professor Bjerrum for his invaluable advice and encouragement, as well as his friendly criticism; he is also indebted to the Rask-Ørsted Foundation for the award of a grant.

Summary

1. The diffusion potential between two ideal dilute solutions of different electrolytes or mixtures of electrolytes depends on the nature of the transition layer between the two end solutions.

2. The "continuous mixture" layer should give a reproducible potential difference, corresponding to Henderson's formula, but it is theoretically unstable. The instability can be minimized by making the transition layer sufficiently long. This has been realized experimentally and an e. m. f. obtained reproducible and constant to within 0.2 mv. over several hours.

3. The "constrained diffusion" junction with cylindrical symmetry represents a steady state with a transition layer of unchanging length. The potential difference is given by Planck's formula and is independent of this length. It is difficult to realize experimentally, a reproducibility of only 0.4 mv. having been obtained.

4. In the "free diffusion" junction with cylindrical symmmetry the transition layer increases in length proportionally to the square root of the time, but the potential difference should not change. It is easy to realize experimentally and an e. m. f. has been obtained reproducible and constant to within 0.2 mv. over at least twenty-four hours. Unfortunately there is no formula giving the potential difference explicitly, the general validity of Taylor's approximate treatment being questionable.

5. The "sharp" junction is theoretically indefinite. Experiment confirms this by giving e. m. f. values fluctuating over several millivolts when there is not cylindrical symmetry.

6. The "flowing junction" is either a special case of the "continuous mixture layer" or else represents a steady state determined by the shape of the apparatus used and so too complicated for theoretical discussion. It is generally assumed to be the former.

7. In the cell

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid 0.1\ N\ \mathrm{HCl} \mid c\ \mathrm{KCl} \mid 0.1\ N\ \mathrm{KCl} \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

where c varies from 0.1 to 3.5, as long as the transition layer has cylindrical symmetry, the e. m. f. obtained never differs by more than a few tenths of a millivolt from that given by the "continuous mixture" junction.

On the other hand, irregular fluctuations of several millivolts are obtained when the junction is at the end of a thin tube dipping into a wider one.

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PREPARATION OF NEGATIVE COLLOIDAL FERRIC OXIDE BY HYDROLYSIS OF PRUSSIAN BLUE

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Hydrolysis of a solution of ferric chloride yields a positive ferric oxide sol. In order to account for the character of the electrical charge on this sol, Powis[1] offers the following explanation. While both ferric ions and chloride ions are adsorbed by the colloidal particle, the former are preferentially adsorbed, and since they are relatively more positive than the chloride ions are negative, the micelle acquires a positive charge. The same author points out the fact that, in general, colloidal suspensions of the hydroxides of multivalent metals are positive. This is because they are prepared by dialysis or hydrolysis of one of their salts having a univalent anion.

Frequent mention is made in the literature of negative colloidal ferric oxide.[2] The general methods of preparation have consisted, in the main, of operations in one or in two steps. In the latter case a positive sol is prepared and then recharged by allowing it to come into contact with a solution containing some negative ion which is sufficiently adsorbed to give to the micelle a negative charge. The other mode of operation, while essentially the same, is different in that the positive form is not isolated but is recharged in the same system in which hydrolysis is performed. Thus Powis[1] prepared negative ferric oxide by allowing a dilute solution of ferric chloride to flow into an excess of sodium hydroxide solution.

Von Kohei Hakozaki[2] has shown that positive colloidal iron oxide can be recharged negatively by the addition of potassium ferrocyanide. The tetravalent ferrocyanide ions are not only highly negative but they also have a large volume and are probably only slightly hydrated. The last two factors enable these ions to be strongly adsorbed and the first likewise contributes to make them very effective in reversing the charge on a positive iron oxide sol. From these facts it was suggested to us that if hy-

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[1] Powis, *J. Chem. Soc.*, **107**, 818 (1915).

[2] Fischer, *Biochem. Z.*, **27**, 223 (1910); Dhar and Sen, *J. Phys. Chem.*, **27**, 376 (1923); Dhar, Sen and Gosh, *ibid.*, **28**, 457 (1924); Kruyt and van der Spek, *Kolloid-Z.*, **22**, 81 (1918); **25**, 17 (1919); von Kohei Hakozaki, *ibid.*, **39**, 319 (1926).