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A STUDY OF HYDROGEN AND CALOMEL ELECTRODES.

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We shall collect in this paper the main results of investigations which have been in progress for many years, and which have dealt with the potential of the hydrogen electrode in different concentrations of hydrochloric acid and of potassium hydroxide; with the dissociation constant of water; with the potential of calomel and silver chloride electrodes in solutions of potassium chloride and of hydrochloric acid; with the problem of establishing definite and reproducible potentials at the boundaries between solutions; and with improvements in the experimental procedure used in such investigations.

These results have not hitherto been published, except that some of the preliminary data were included in the paper "The Free Energy of Oxygen, Hydrogen and the Oxides of Hydrogen" by Lewis and Randall.[1] In order to avoid repetition reference will be made to that paper (L. and R.). One of the data there given for the hydrogen potential in dilute acid was later found to be erroneous, for some reason which has not been explained, and this was made the subject of an entirely new investigation.

The apparatus which we have used has, in large part, been described at meetings of the American Chemical Society, and has been used by

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[1] Lewis and Randall, THIS JOURNAL, 36, 1969 (1914).

other investigators. We shall describe briefly, therefore, only those details which experience has shown to be necessary or highly convenient for exact measurements of electromotive force.

Experimental Methods.

Thermostat and Potentiometer.—On account of the electrical conductivity of films of moisture on glass apparatus, water thermostats are not well adapted to the most precise measurements of electromotive force. A petroleum oil of high boiling point, known under the trade name of petrolatum oil, has proved itself well adapted for use as a thermostat fluid. It is, however, much more viscous than water and more energetic stirring is necessary in order to maintain constancy of temperature. The use of oil eliminates electric leaks within the thermostat, but, unless precautions are taken, stray currents from external sources may cause serious error in potentiometer readings. An extraordinarily successful system for the prevention of external leaks has been described by White.[1] This system consists of a metallic shield, all portions of which are connected with one another by heavy copper wires, thus furnishing an equipotential base for the whole apparatus. If the thermostat is of metal it is made a part of this shield, and if not it is placed upon one of the metallic sheets which constitute the shield. The potentiometer, the electric key, the galvanometer, and all supports for the conducting wires rest upon similar sheets of metal. Since the electric current was used for heating and regulating the thermostat a pedal was contrived by which all external connection with the thermostat could be cut off at the moment of making measurements, but this device was rarely, if ever, needed with a good equipotential shield.

The potentiometer which we have used was of a simple and inexpensive type which requires a little more time for reading than the standard potentiometers, but which possesses the advantage that it may be immediately tested at any time, under the conditions of actual use, for any change in the resistance coils. It consists (Fig. 1) of two decade resistance boxes, B B, of 9999 ohms each, in series with the working battery W B and an external resistance, R_1, R_2, which may be readily adjusted to give a current of exactly 0.0001 ampere. The total resistance in the two boxes is kept at 9999 ohms, and the terminals of one box lead through the galvanometer G to the cell X under investigation. When the plugs in the two boxes are adjusted to zero deflection of the galvanometer, the e. m. f. to be determined is read directly from the box, each ohm corresponding to 0.0001 volt. By means of a commutator the measured cell may be connected to the terminals of the other box, thus checking the potentiometer.

Since the standard cell at 25° gives 1.0181 volts, and the resistance of the box is 9999 ohms, a portion of the external resistance R_1 is made into

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[1] White, THIS JOURNAL, **36**, 2011 (1914).

a coil of exactly 182 ohms, the current in the potentiometer is adjusted by throwing a switch which places in circuit this coil, the resistance boxes, the standard cell SC and the galvanometer, and by varying the external resistance until zero deflection is obtained.

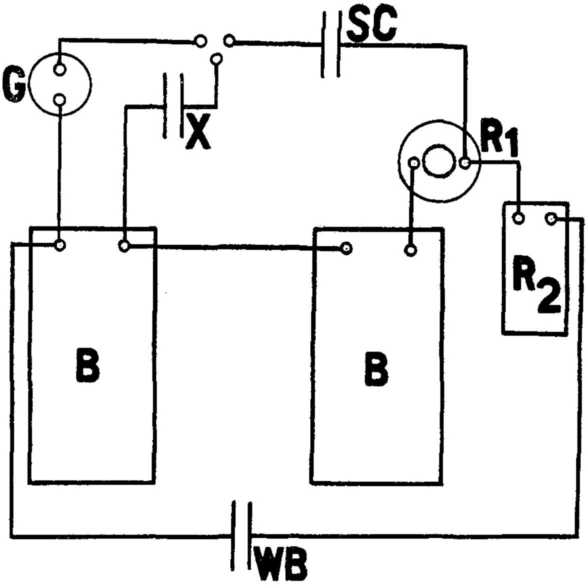

Fig. 1.

Standard and Working Cells.—At least two standard cadmium cells of 1.0181 volts were always kept in the thermostat and these were checked against each other and against fresh cells which were made up from time to time. As a working battery a large cell of the Hulett[1] type containing unsaturated $CdSO_4$ solution proved extremely satisfactory.

Preparation of Materials.—All the solutions used were made from doubly distilled water. The hydrochloric acid solutions were made by dissolving HCl gas. The solutions of KOH were made from potassium amalgam produced by electrolysis of pure aqueous potassium carbonate. Certain of the best grades of commercial KCl are pure enough to be used directly in calomel electrodes. Others contain an unknown impurity which has a surprisingly large effect upon the e. m. f. and which can only be eliminated by several recrystallizations.

The calomel was usually prepared by treating dilute mercurous nitrate with dilute KCl or HCl, although several other methods were tried at various times. It was washed and freed from the finer particles by several decantations. It was then allowed to stand for several days under the solutions in which it was to be used, the liquid being renewed from time to time. A glass tube, about one end of which a piece of hardened filter paper is tied by silk thread, and the other end of which is attached to a suction pump, furnishes a satisfactory method of draining away the solution. All the mercury used was washed with diluted HNO_3 and doubly distilled in a current of air at low pressure by the Hulett method.

The Hydrogen Generator.—The production of an uninterrupted current

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[1] Hulett, *Phys. Rev.*, **27**, 33 (1908).

of pure hydrogen over a long period, and in amounts which can be readily controlled, is needed in many branches of scientific work. We have devised for this purpose the electrolytic cell shown in Fig. 2. A large U-tube, A, containing enough sand in the bend to prevent conduction of dissolved gases from one limb to the other through convection, is nearly filled with concentrated caustic solution of pure grade and this solution is electrolyzed between the anode F and the cathode G, both of platinum. The oxygen produced at the anode escapes through the open tube H while the hydrogen produced at G passes through the tube B filled with cotton wool, to remove every trace of spray, then through P_2O_5 in tube C and finally through the tube D containing a platinum wire held taut by a platinum spring. This wire is maintained by a current at a bright red heat in

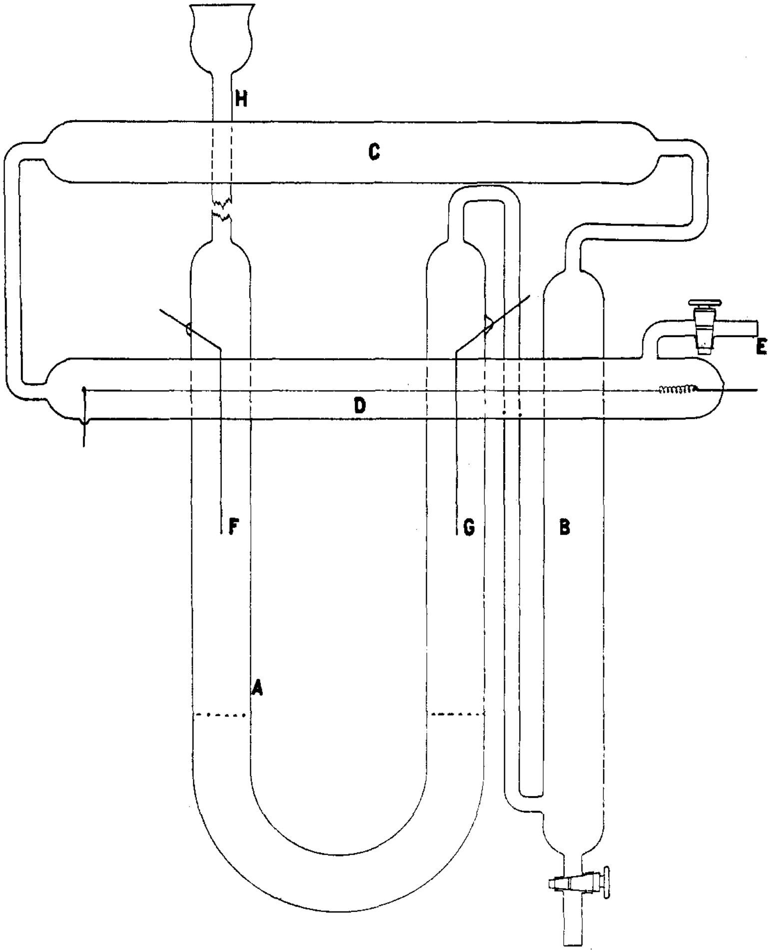

Fig. 2.

order to remove any trace of oxygen which may have passed by diffusion into the cathode chamber. The pure hydrogen emerges at E where it may, if desired, be sent through another tube of P_2O_5 to eliminate moisture. The solution is maintained in tube H at a height sufficient to balance the hydrostatic pressure in the apparatus to which the hydrogen is led. The stream of hydrogen is regulated by a rheostat which determines the electrolyzing current. This generator will operate for many months without requiring attention, and furnishes hydrogen of a high degree of purity. Indeed for all ordinary purposes the amount of oxygen which diffuses through the sand is so small that the tube containing the hot platinum wire may be dispensed with.

The Iridium Electrodes.—Finely divided iridium is unquestionably the best catalyzer known for the electrode reaction in which gaseous hydrogen is converted into hydrogen ion. A very small electrode covered with this material and saturated with hydrogen gives extremely reproducible potentials. Electrodes of gold covered with finely divided iridium, which were first used in this investigation and have since been used by others, are the most satisfactory. The coating of iridium, which very readily peels off from a platinum surface, clings tenaciously to the softer metal. Gold has the further advantage that it does not, like platinum, absorb gases in large amount, and therefore these electrodes come very quickly to equilibrium. A thin plate (1.5 cm. square) of gold or of platinum, welded to a platinum wire and covered with a coherent film of gold, is made the cathode in a 5% solution of iridium chloride. The best results were obtained with a very small current running for from 12 to 24 hours. The electrode should then be steel-gray in color and is ready for use. Too large a current gives a deposit which appears more like platinum black and which is easily rubbed off. An electrode properly prepared is good for months of continual service, although the life seems to be shorter in alkaline than in acid solutions.

The Hydrogen Electrode.—Figure 3 illustrates the hydrogen electrode as it has been used almost without modification throughout this whole investigation. Hydrogen from the generator described above enters at A, and is washed in the bubbler B with the same solution that is contained in the electrode vessel. This efficient bubbling apparatus saturates the gas with water vapor, so that the current of hydrogen may run for a long period of time without changing the composition of the solution in the main vessel. The gas rises from the tip C, saturating and stirring the whole liquid from G to F, and leaves the apparatus through the small trap E, which also contains a small amount of the same solution. The platinum wire attached to the electrode D is sealed by lead glass into the ground glass stopper M. L is a joint made by fusing together the end of the platinum wire and the connecting wire of copper. The surface of the solution stands at the height F so that the iridium electrode is about one-half immersed. The apparatus from F through G, H, I to J is filled with the solution. With the form of construction shown it is an easy matter to fill the tube without leaving any bubbles of air. The reservoir K filled with the same solution serves to rinse out the tube I, J from time to time. The whole apparatus may be mounted upon a transite board or, for the sake of greater mobility, may be held in a clamp, the several parts being rigidly attached to one another to avoid accidental breakage. The whole is immersed in the thermostat about to the point L.

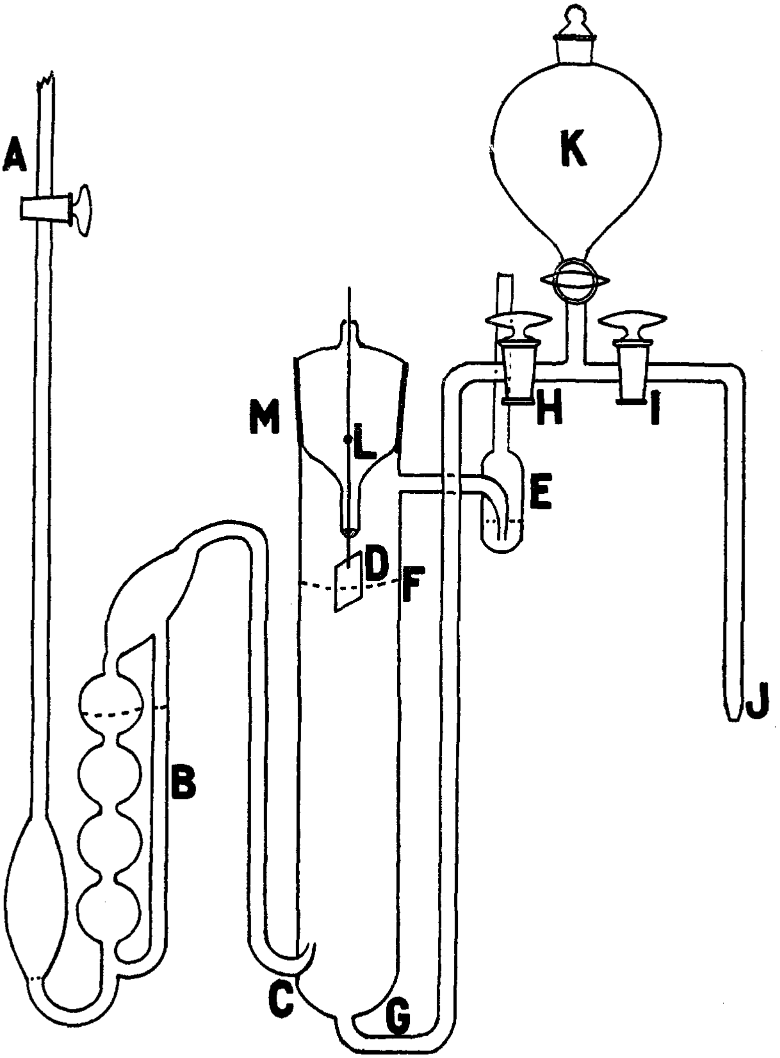

Fig. 3.

The tube J dips into an open tube through which communication is made to other electrode vessels. This connecting tube may be filled with the same solution as is contained in the hydrogen electrode vessel or with any other solution which is desired. All measurements in acids were made with one of the stopcocks H, I closed. These stopcocks are not greased and there is a film of acid in the closed stopcock which suffices to carry the current during measurement. In order to make sure that no liquid potential is accidentally established, the second stopcock may be closed up and the first opened. No difference of potential in acid solution has ever been observed during this procedure (but this is not true for solutions of salts and alkalies). If it is desired that both stopcocks be open, the same liquid that is in the electrode vessel is placed in the connecting tube at J and the stopcocks H and I are opened after the current of hydrogen has been cut off by the stopcock A, and the opening of the trap E has been closed.

If hydrogen enters the cell at the rate of one or two bubbles per minute several hours are required for the saturation of the solution and for the removal of air. After this time the potential is absolutely independent of the rate of flow of hydrogen and the generator may be entirely cut off for many hours without any change.

Calomel and Silver Chloride Electrodes.—All calomel and silver chloride electrodes were referred to the normal calomel electrode, which is not only extremely reproducible, but also may be used for months without change in potential. Calomel freed from the finer particles, and well washed as described above, is shaken for several hours with a small amount of mercury and molal KCl (for this purpose 1 mol per liter of solution). The solution is drawn off and the process repeated several times. The vessel used for the normal calomel electrode is shown in Fig. 4, one-third actual size. The vessel being thoroughly clean and dry, mercury is introduced to the level C and covered with about 5 mm. of the paste of calomel and mercury. The whole vessel is then filled with the solution used

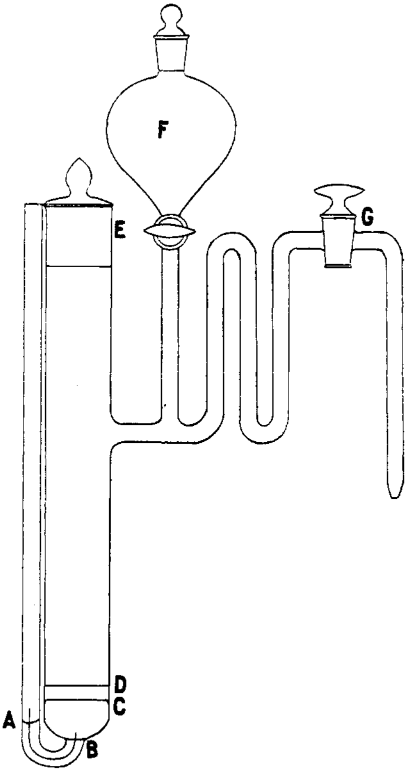

Fig. 4.

in the last shaking with calomel. The glass stopper E is inserted and the joint paraffined. It is very important that the platinum tip B should never be wet by the solution during the process of filling. The other end A of the platinum lead may be connected with a copper wire by a drop of mercury, or, better, by fusion as shown in the case of the hydrogen electrode. The reservoir F containing the same solution is used for replenishing the liquid in the connecting tube. In order further to avoid change of composition within the vessel, the stopcock G is closed, except when readings are taken.

Other calomel electrodes in solutions of various concentrations of potassium chloride and hydrochloric acid are prepared in the same way, but since they are ordinarily used as reference electrodes, over a shorter period of time, a simpler type of vessel suffices. The first form shown in Fig. 5, with a rubber stopper and with a doubly bent side tube to avoid contamination by convection, has proved very convenient.

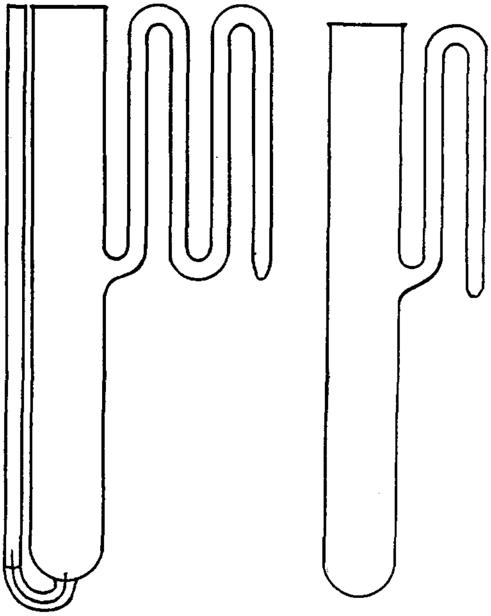

Fig. 5.

The second vessel shown in Fig. 5 is suitable for use with any solid electrode which enters the top through a rubber stopper. Such vessels were used for the silver chloride electrodes which were prepared from platinum gauze, following the suggestion of MacInnes and Parker,[1] by silver plating and then electrolyzing a solution of hydrochloric acid or slightly acidified potassium chloride with the gauze as an anode. Such electrodes, after washing, give constant but not always reproducible potentials. The thermodynamic properties of the silver chloride so produced vary with the method of preparation; therefore these electrodes were never used as standards but the potential of each was measured in 0.1 molal potassium chloride against the tenth normal or normal calomel electrode. The difference of potential between a silver chloride and a calomel electrode in the same chloride solution is independent of the concentration of the solution, over a wide range. This difference, which ordinarily amounts to about 0.046 volt, being determined for each electrode, is added directly

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[1] MacInnes and Parker, THIS JOURNAL, 37, 1445 (1915).

to the electromotive force of the cell of which the silver chloride constitutes one electrode, and the results are, therefore, given as though calomel had been used in place of silver chloride. This procedure has the advantage that in dilute solutions the silver chloride electrode comes more quickly to equilibrium and shows greater constancy than the calomel.

Potentials at Liquid Junctions.—One of the most serious obstacles in the interpretation of exact measurements of e. m. f. is due to uncertainty regarding liquid potentials. It is true that the potential between two dilute solutions may be largely eliminated by interposing between them a saturated solution of potassium chloride. Since the error caused by the assumption of complete elimination is in most cases of the order of one millivolt,[1] the method is useful wherever the highest accuracy is not desired. The use, in place of potassium chloride, of other solutions, such as concentrated ammonium nitrate, leads to much larger errors.

When a direct junction is made between two dilute solutions, the liquid potential varies with the time and with the manner in which the junction is made.[2] It is, therefore, important to establish a method of making reproducible liquid junctions, as well as to determine by experiment or theory the potential at the junction so made.

Bjerrum[3] made liquid contacts in a layer of sand, and adopting this suggestion in our early work we made a very large number of measurements of cells involving liquid potentials, with the apparatus illustrated in Fig. 6. The tube F, G, E was partly filled with sand as shown. Tenth molal hydrochloric acid was placed in the tube E and tenth molal potassium chloride in the tube F. Calomel electrodes containing 0.1 *M* hydrochloric acid and 0.1 *M* potassium chloride were dipped respectively into E and F. The junction was made in the sand at G and this junction could be renewed as often as desired by suction applied to the tube at H. The experimental conditions were varied greatly and several varieties of sand, carefully selected and washed, were used. At no time were reproducible results obtained, nor results which re-

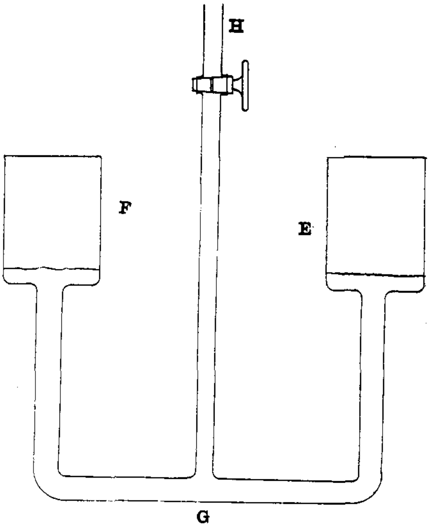

Fig. 6.

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[1] Bjerrum, *Z. physik. Chem.*, **53**, 430 (1905).

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

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

mained constant to 0.0001 volt for more than a minute or two. The potential of the liquid junction first established was surprisingly high (0.030 volt) and fell rapidly without reaching any definite limiting value.

It is interesting to note, however, that when the junction was made in sand between two concentrations of the same solution, even when the liquid potential was greater than the one just mentioned, it remained constant. Thus the electromotive force between calomel electrodes in molal and tenth molal hydrochloric acid with this junction gave 0.1012 volt, and the same reading was obtained for over an hour.

Experiments with this type of junction were finally abandoned and we returned to the old method of dipping a tube containing one solution into a larger tube containing the other. In order, however, to make frequent renewals of the liquid junction many of our measurements were made with the apparatus shown in Fig. 7. The tubes O and R lead to the two solutions between which the junction is to be established. By applying suction at P, and by operating the stopcocks, the solution from R may be drawn through the apparatus, and then the solution from O. A fresh junction at Q can be produced as often as is desired. An additional reservoir of one or both of the solutions may be introduced as at N. The opening at Q should be not less than 2 mm. Although we have not studied the matter carefully, we believe that a smaller aperture leads to less reproducible results. With such "dipping" contacts liquid potentials are established which, while varying very rapidly in the first few seconds, reach a value in the first few minutes that is thoroughly reproducible and nearly constant, although it may vary a few tenths of a millivolt upon standing half an hour. The

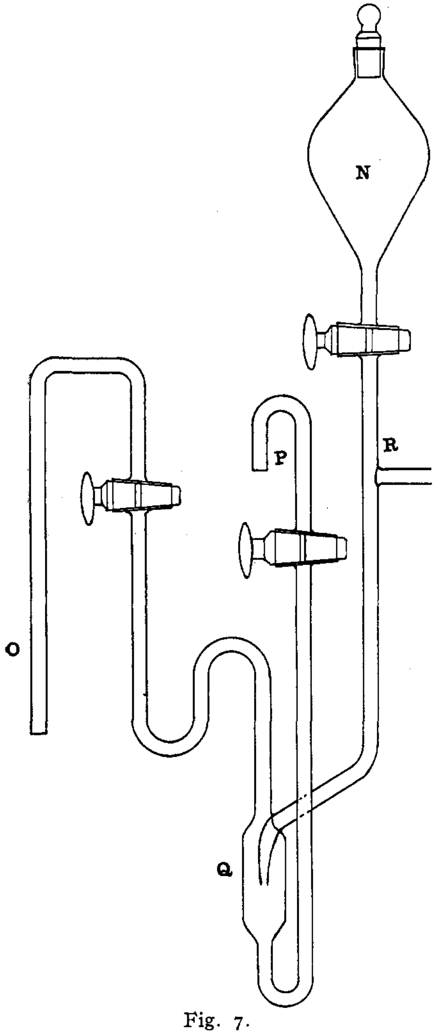

Fig. 7.

value obtained after the first minute or two will be taken as the liquid potential.

Experimental Results.

It will be impossible in the space at our command for us to reproduce the results of our individual measurements, and we shall only give for each cell what seems the best value of e. m. f., together with an estimate of the probable accuracy.

All the measurements are at 25°.

The Difference in Potential between Normal and Tenth-Normal Calomel Electrodes.—Following the practice of Lewis and Randall we shall define the normal calomel electrode as the combination Hg, HgCl, KCl (1.0 *M*), KCl (0.1 *M*). In other words, we shall regard the liquid potential between 0.1 *M* and 1.0 *M* potassium chloride as an integral part of the potential of the normal electrode. The normal calomel electrode will be designated as N. E.

As our final value for the difference between the tenth normal and normal electrodes we find

$$\text{Hg, HgCl, KCl } (0.1\,M),\ \text{N. E.};\quad \mathbf{E} = -\,0.0529. \qquad (1)$$

When **E** is given as positive it indicates that the tendency of the positive current in the cell is to pass from left to right, when negative, from right to left. We have formerly given (L. and R.) the value of 0.0530 and we have occasionally obtained values as low as 0.0528, but the value given is probably correct to within less than 0.0001 volt.

Cells Involving a Liquid Potential between Potassium Chloride and Hydrochloric Acid.—From the formula of Lewis and Sargent[1] we should find (L. and R.) for the liquid potential

$$\text{HCl } (0.1\,M),\ \text{KCl } (0.1\,M);\quad \mathbf{E} = 0.0284.$$

Our earlier measurement of the cell, Hg, HgCl, HCl (0.1 *M*), KCl (0.1 *M*), HgCl, Hg, gave the same value, 0.0284. This was one of the reasons for believing the degree of dissociation in the two electrolytes to be the same. The evidence which we shall present in this paper, however, shows definitely that the degree of dissociation of hydrochloric acid is greater[2] than that of potassium chloride at this concentration. We have not remeasured this combination since our method of establishing junc-

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

[2] For earlier evidence of this character, see Lewis, *Ibid.*, **34**, 1643 (1912). From several considerations, Harned (*Ibid.*, **38**, 1986 (1916)) has arrived at the conclusion that the corrected degree of dissociation of HCl (0.1 *M*) is greater than that of KCl (0.1 *M*) in the ratio 1.034. This is nearly identical with the ratio 1.04 or 1.05 which we shall obtain in the next section. Loomis and Meacham (*Ibid.*, **38**, 2310 (1916)) recently offer evidence in favor of the view that the two degrees of dissociation are very nearly the same. As a matter of fact the difference, though appreciable, is by no means as great as that which would be calculated from conductivity data.

tions has been standardized, but we have studied the similar cell with silver chloride electrodes and have found 0.0278 which, moreover, is the value obtained with calomel electrodes by Bjerrum and also by Myers and Acree.[1] We may therefore take as final values[2]

$$\text{Hg, HgCl, HCl } (0.1\ M),\ \text{KCl } (0.1\ M),\ \text{HgCl, Hg};\ \mathbf{E} = 0.0278 \quad (2)$$

$$\text{Ag, AgCl, HCl } (0.1\ M),\ \text{KCl } (0.1\ M),\ \text{AgCl, Ag};\ \mathbf{E} = 0.0278. \quad (3)$$

The corresponding cell with 0.01 M solutions, in which the two degrees of dissociation are certainly almost identical, affords a better test of the applicability of the formula of Lewis and Sargent, which in this case gives

$$\text{HCl } (0.01\ M),\ \text{KCl } (0.01\ M);\ \mathbf{E} = 0.0274. \quad (5)$$

We have obtained for the cell with silver chloride electrodes

$$\text{Ag, AgCl, HCl } (0.01\ M),\ \text{KCl } (0.01\ M),\ \text{AgCl, Ag};\ \mathbf{E} = 0.0272. \quad (6)$$

Since at this concentration (but no longer at 0.001 M) the difference in solubility between calomel and silver chloride is negligible, we should also find

$$\text{Hg, HgCl, HCl } (0.01\ M),\ \text{KCl } (0.01\ M),\ \text{HgCl, Hg};\ \mathbf{E} = 0.0272. \quad (7)$$

Although we have as yet very little experimental evidence, it seems

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[1] Myers and Acree, *Am. Chem. J.*, **50**, 396 (1913).

[2] In a case like this, where a junction is made between two liquids at the same concentration, but not at the same ion activity, there seems at present no possibility of calculating the liquid potential from any theoretical equation. It is highly desirable that the whole problem of liquid potentials should be subjected to a thorough experimental investigation in order, in the first place, to find the effect of producing the contact in different ways, especially in tubes of different size, and, in the second place, to determine empirically the liquid potential between numerous pairs of electrolytes. In attacking the second problem the method of Lewis and Sargent is of limited applicability, partly because of the instability of ferro- and ferri-cyanides in many solutions, and partly because the degree of dissociation of these salts is hard to calculate. An entirely similar but far more useful method was used some years ago by Lewis and Faragher in a hitherto unpublished investigation. The method consisted in adding to each of the two liquids, between which the liquid potential was to be determined, small amounts of iodine and potassium iodide, such that the activity of I_2 and I^- were the same on both sides. Between two electrodes of platinum-iridium immersed in the two liquids the e. m. f. should be the desired liquid potential. Unfortunately, though numerous measurements were made, they were all with junctions in sand. It is hoped that this work may soon be repeated with the standard liquid junctions described above. In a few cases where chlorides are in question and the activity of chloride ion is known in each solution, the liquid potential may be experimentally determined. Thus in the above case if the activity of chloride ion is known in HCl (0.1 M) and KCl (0.1 M), we obtain Equation 13 of a later section, and combining this with (2) we find for the liquid potential

$$\text{HCl } (0.1\ M),\ \text{KCl } (0.1\ M);\ \mathbf{E} = 0.0266 \quad (4)$$

which proves to be the value given by the unmodified Planck equation. That equation, however, was based upon the assumptions of equal ion concentration and no change of ion mobility with the concentration, neither of which in this case is probably correct.

probable that between any two uni-univalent electrolytes at 0.01 M the liquid potential can be calculated within one- or two-tenths of a millivolt.

Hydrogen and Calomel Electrodes in Hydrochloric Acid and the Free Energy of Dilution of Hydrochloric Acid.—As the result of many measurements of the hydrogen electrode in hydrochloric acid (0.1 M) against silver chloride and calomel electrodes in the same solution, we find as a final result[1]

$$H_2, \text{HCl } (0.1\ M), \text{HgCl}, \text{Hg}; \ \mathbf{E} = 0.3989. \qquad (8)$$

The value was previously given (L. and R.) as 0.3990. This combination has been studied recently by several investigators. Harned[2] found 0.3991; Loomis and Meacham,[3] 0.3988; Ellis,[4] 0.3988. The value above given is undoubtedly correct to 0.0001 volt.

If we combine this with (2) we find

$$H_2, \text{HCl } (0.1\ M), \text{KCl } (0.1\ M), \text{HgCl}, \text{Hg}; \ \mathbf{E} = 0.4267, \qquad (9)$$

and this is precisely the result which we have obtained experimentally in our recent study of this combination. Others have obtained somewhat different values: Loomis and Acree[3] found 0.4269, Myers and Acree[3] 0.4273, and Harned 0.4274. It is evident that different methods of establishing liquid junctions produce in this case materially different results.

In hydrochloric acid (0.01 M) we find as the result of numerous closely agreeing experiments

$$H_2, \text{HCl } (0.01\ M), \text{HgCl}, \text{Hg}; \ \mathbf{E} = 0.5105, \qquad (10)$$

which we believe to be correct within about 0.0001 volt.

Combining this equation with (7) gives

$$H_2, \text{HCl } (0.01\ M), \text{KCl } (0.01\ M), \text{HgCl}, \text{Hg}; \ \mathbf{E} = 0.5377. \qquad (11)$$

This combination we have not recently measured experimentally.[5]

The difference between the values of e. m. f. for Cells 8 and 10, 0.1116, multiplied by $\mathbf{F}'$ (23074) gives for the free energy of dilution

$$\text{HCl } (0.1\ M) = \text{HCl } (0.01\ M); \ \Delta F = 2573 \text{ cal.} \qquad (12)$$

If α_1 and α_2 are the corrected degrees of dissociation at concentrations c_1 and c_2, we have the equation $\Delta F = R'T \ln [(\alpha_2 c_2)^2/(\alpha_1 c_1)^2]$. Our

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[1] All measurements involving the hydrogen electrode are calculated to one atmosphere partial pressure of H_2.

[2] Harned, THIS JOURNAL, 37, 2475 (1915).

[3] Loomis and Meacham, *Ibid.*, 38, 2310 (1916).

[4] Ellis, *Ibid.*, 38, 752 (1916).

[5] It was an error in the preliminary measurement of this cell (L. and R.), to which we have already alluded, which was responsible for error in our previous calculations of the difference in potential between the normal hydrogen and the normal calomel electrodes, and of the dissociation constant of water.

recent calculations of the corrected degree of dissociation of KCl, which will shortly be published, give for 0.1 M, 0.03 M and 0.01M: $\alpha = 0.780$, 0.865 and 0.930, respectively. It is possible that at 0.01 M, α is a trifle greater for hydrochloric acid than for potassium chloride, but the difference is so small and so uncertain in value that we shall assume provisionally for all uni-univalent electrolytes at this concentration, $\alpha = 0.930$. Using this value in the above equation we find for HCl 0.1 M, $\alpha = 0.816$. Since α is nearly a linear function of log c, the value of α for hydrochloric acid at any concentration between 0.01 M and 0.1 M may be calculated by assuming that between these limits the difference between α for hydrochloric acid and for potassium chloride varies linearly with log c. Thus, for example, we find for hydrochloric acid (0.03 M), $\alpha = 0.884$.

The Normal Hydrogen *versus* **the Normal Calomel Electrode.**—We are now in a position to calculate the potential of hydrogen in a solution which is (hypothetical) molal[1] with respect to hydrogen ion, that is, against a solution in which the activity of H^+ is n times as great as in a solution which is $1/n$ molal with respect to H^+, where n is a large number.

From Equation 8 we have

$$H_2,\ HCl\ (0.1\ M),\ HgCl,\ Hg;\ \mathbf{E} = 0.3989.$$

Now from the corrected degrees of dissociation given in the preceding section we find

$$Hg,\ HgCl,\ HCl\ (0.1\ M)\ ||\ KCl\ (0.1\ M),\ HgCl,\ Hg;\ \mathbf{E} = 0.0012, \quad (13)$$

for in this cell in which the liquid potential is eliminated, the total e. m. f. depends upon the difference in the corrected concentration of Cl^- on the two sides, namely, according to the preceding section, 0.0816 in hydrochloric acid and 0.0780 in potassium chloride, and the ratio of these numbers substituted in the ordinary logarithmic formula gives the value (13). We also have from (1)

$$Hg,\ HgCl,\ KCl\ (0.1\ M),\ N.\ E.;\ \mathbf{E} = -0.0529.$$

And finally, taking the corrected concentration of H^+ in HCl (0.1 M) as 0.0816, we find

$$H_2,\ H^+(M)\ ||\ HCl\ (0.1\ M),\ H_2;\ \mathbf{E} = -0.0644, \quad (14)$$

where $\mathbf{E} = 0.05915 \log 0.0816$. Adding all of these equations together we find

$$H_2,\ H^+(M)\ ||\ N.\ E.;\ \mathbf{E} = 0.2828. \quad (15)$$

Similarly we may calculate from the measurement in hydrochloric acid (0.01 M) given in Equation 10. At this concentration we have assumed equal dissociation of hydrochloric acid and potassium chloride. Hence,

$$Hg,\ HgCl,\ HCl\ (0.01\ M)\ ||\ KCl\ (0.01\ M),\ HgCl,\ Hg;\ \mathbf{E} = 0. \quad (16)$$

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[1] See Lewis, THIS JOURNAL, **35**, 25 (1913).

From the degrees of dissociation, 0.930 and 0.780, given above for potassium chloride 0.01 M and 0.1 M, we find[1]

$$\text{Hg, HgCl, KCl } (0.01\ M) \,||\, \text{KCl } (0.1\ M)\text{, HgCl, Hg; } \mathbf{E} = -0.0546. \quad (17)$$

Finally taking the corrected concentration or activity of H^+ in HCl (0.01M) as 0.00930, we have

$$H_2,\ H^+(M) \,||\, \text{HCl } (0.01\ M),\ H_2;\ \mathbf{E} = -0.1202. \quad (18)$$

Adding Equations 1, 10, 16, 17 and 18 we find the identical value which we obtained from measurements in 0.1 M solution, namely,

$$H_2,\ H^+(M) \,||\, \text{N. E.; } \mathbf{E} = 0.2828. \quad (15)$$

Taking the potential of the normal hydrogen electrode as zero, *the potential of the normal calomel electrode is —0.2828.*

The Hydrogen Electrode in Alkaline Solutions.—The potential of hydrogen in potassium hydroxide (0.1 M) against calomel in potassium chloride (0.1 M) has been fully discussed by Lewis and Randall. The agreement between several series of measurements is surprisingly good, and the results are further corroborated by the work of Lorenz and Böhi. We can, therefore, rely within one- or two-tenths of a millivolt upon the final value,

$$H_2,\ \text{KOH } (0.1\ M)\text{, KCl } (0.1\ M)\text{, HgCl, Hg; } \mathbf{E} = 1.0833, \quad (19)$$

or, combining with (1),

$$H_2,\ \text{KOH } (0.1\ M)\text{, KCl } (0.1\ M)\text{, N. E.; } \mathbf{E} = 1.0302. \quad (20)$$

We shall not at present attempt further use of these equations because of uncertainty as to the value of the liquid potential, and especially because we have no information as to the degree of dissociation in potassium hydroxide (0.1 M).

A number of measurements have been made with the corresponding cell containing 0.01 M solutions. Here the difficulty of establishing a liquid junction of definite potential seems to be greater than in the more concentrated solutions, and many of our measurements were made before the difficulties of the liquid-junction problem were fully realized. Our final result, however, is almost certain to be correct within less than one-half a millivolt, namely,

$$H_2,\ \text{KOH } (0.01\ M)\text{, KCl } (0.01\ M)\text{, HgCl, Hg; } \mathbf{E} = 1.0820. \quad (21)$$

For the liquid potential[2] we have, from the formula of Lewis and Sargent,

$$\text{KOH } (0.01\ M)\text{, KCl } (0.01\ M)\text{; } \mathbf{E} = -0.0152. \quad (22)$$

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[1] MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915), have obtained the direct experimental result,

$$\text{Ag, AgCl, KCl } (0.01\ M)\text{, KCl } (0.1\ M)\text{, AgCl, Ag; } \mathbf{E} = -0.0540.$$

If we add to this the liquid potential, namely, 0.0007 (L. and R.) we obtain 0.0547, which is almost identical with the value given in (17).

[2] For this calculation we have taken λ for KCl (0.01 M) as 141.4, and for KOH (0.01 M) as 255.8 (from an unpublished investigation by Randall and Scalione).

Combining (21) and (22) gives

$$H_2,\ KOH\ (0.01\ M)\ ||\ KCl\ (0.01\ M),\ HgCl,\ Hg;\ \mathbf{E} = 1.0972. \quad (23)$$

The liquid potential between KCl (0.1 M) and KCl (0.01 M) (L. and R.) is

$$KCl\ (0.01\ M),\ KCl\ (0.1\ M);\ \mathbf{E} = 0.0007. \quad (24)$$

Now combining (23) with (17), (24) and (1) gives

$$H_2,\ KOH\ (0.01\ M)\ ||\ N.\ E.;\ \mathbf{E} = 0.9904. \quad (25)$$

Taking the degree of dissociation of KOH (0.01 M) as 0.930, we find

$$H_2,\ OH^-(M)\ ||\ KOH\ (0.01\ M),\ H_2;\ \mathbf{E} = 0.1202. \quad (26)$$

Finally, combining (25) and (26), we have for the potential of hydrogen in (hypothetical) molal OH^- against the normal calomel electrode,

$$H_2,\ OH^-(M)\ ||\ N.\ E.;\ \mathbf{E} = 1.1106, \quad (27)$$

or, combining with (15),

$$H_2,\ OH^-(M)\ ||\ H^+(M),\ H_2;\ \mathbf{E} = 0.8278. \quad (28)$$

The Dissociation Constant of Water.—We have mentioned above the source of error in our previous calculation (L. and R.) of the dissociation constant of water. This important constant we may now calculate directly from Equation 28, for in this cell the concentration of H^+ in the presence of OH^- (M) is equal to K_w, the dissociation constant. We therefore have the equation

$$0.8278 = 0.05915 \log K_w;\ K_w = 1.012 \times 10^{-14}. \quad (29)$$

Considering the above-mentioned error in our preliminary publication, it is perhaps unsafe to ascribe too small limits of error to the figures now given, but it is hard to see how any appreciable error could have entered into this calculation, except, possibly, a small error in Equation 23; so that we may consider this value of K_w as correct at least within 2 or 3%.

The concentration of H^+ and of OH^- in pure water at 25° is equal to $\sqrt{K_w}$, or 1.006×10^{-7}.

The Effect of Pressure and Temperature upon the Potential of the Hydrogen Electrode.—The constancy and reproducibility of the hydrogen potential gives, perhaps, sufficient evidence of the reversibility of the hydrogen electrode. This is not only corroborated by the change in potential with change in concentration of H^+ but also by the change of potential with changing pressure and temperature.

The results of our experiments upon the effect of pressure and the effect of changing the partial pressure of hydrogen have been published (L. and R.), and it was shown that the measured potentials at various pressures agree with those calculated from the thermodynamic equation to 0.00001 volt. Since that publication two other investigators, apparently unfamiliar with our work, have studied the subject. Loomis and Acree[1]

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[1] Loomis and Acree, THIS JOURNAL, 38, 2391 (1916).

came to the same conclusion, although their experimental deviations were far greater.[1] Similar experiments were also made by Ellis,[2] but his experimental variations were also considerably greater than our own.

Our experiments on the temperature coefficient of the cell 8 are also described in the former publication (L. and R.), and it was shown that in this manner an extremely exact determination could be made of the heat of formation of aqueous hydrochloric acid, and even a rough determination of its heat capacity. These measurements have also been reproduced and amplified by Ellis who investigated similar cells containing hydrochloric acid from 0.01 to 4.5 *M*.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 301.]

THE PROPERTIES OF MIXED LIQUIDS. III. THE LAW OF MIXTURES. I.

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Numerous attempts have been made to discover just what happens when two or more liquids mix to form a homogeneous system. Since in such cases neither chemical analysis nor the application of the phase rule can give aid, an answer to the question, if obtainable at all, can only be found from a study of the changes in the various physical properties brought about by the mixing.

All work based upon the change in a physical property which is caused by the mixing of one liquid with others, must necessarily depend upon the assumption that a general law exists, by aid of which, if no chemical interaction takes place between the constituents, and the individual constituents themselves, in the mixture, undergo no change in property due to simple contact with the others, it is possible to calculate from the values of that property for the pure constituents, and their amounts present in the system, the magnitude of the property for any one definite mixture. Such a "law of mixtures" has indeed been postulated in all work of this sort, but a survey of the literature fails to show the existence of any very definite or extensive experimental evidence of the general holding or lack of holding of such a law.

The object of this paper is to present the results of an experimental investigation of such a "law of mixtures," with surface tension as the

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[1] These authors attempt to decide the mechanism of the process of the hydrogen electrode from their experiments. It must be emphasized that no measurements of the potential of a reversible electrode give the slightest clue to the mechanism of the electrode process.

[2] Ellis, THIS JOURNAL, 38, 737 (1916).