[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 122.]

THE FREE ENERGY OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION AND THE ACTIVITIES OF ITS IONS.

BY MING CHOW.

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1. Introduction.

The purpose of this research was to determine with the aid of electromotive-force measurements the free energy attending the transfer of potassium hydroxide in aqueous solution from one concentration to another, and from these free-energy decreases to derive the relative activities of the ions of the base and its activity coefficients at various concentrations. The principle of the method is substantially identical with that involved in the investigations of MacInnes and Parker[1] on potassium chloride and of Ellis[2], and of Noyes and Ellis[3] on hydrochloric acid.

With respect to the significance of the term activity, it may be recalled that this is a concept introduced by G. N. Lewis[4] as a quantitative expression of the mass-action effect of imperfect solutes (those which exert an effect not proportional to their concentration), and shown by him to be thermodynamically related to various other properties. Thus the activity is the "effective concentration" from an equilibrium or the thermodynamic standpoint. The most general of the thermodynamic relations, one indeed which may well be regarded as the most concrete definition of activity, is that afforded by the equation

$$-\Delta F = N R T \log (a_1/a_2),$$

in which R is the perfect-gas constant, and $-\Delta F$ represents the decrease in the free energy of the system attending the transfer at the absolute temperature T of N mols of any substance (thus of an ion) from a solution of any concentration in which its activity is a_1 to another solution of any concentration in which its activity is a_2. When dealing with ions we may substitute for their activities a_1 and a_2, the products $\alpha_1 c_1$ and $\alpha_2 c_2$, in which α_1 and α_2 are activity coefficients (analogous to ionization coefficients) representing the factors by which the concentrations c_1 and c_2 of the substance must be multiplied to give the activities of the ions.

The most direct way of determining the free-energy decrease attending

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[1] THIS JOURNAL, 37, 1445–1461 (1915).

[2] *Ibid.*, 38, 737–762 (1916).

[3] *Ibid.*, 39, 2532–2544 (1917).

[4] *Proc. Am. Acad.*, 43, 259–293 (1907); *Z. phys. Chem.*, 61, 129–165 (1908).

the transfer of ions from one concentration to another, and thereby of determining their relative activities, is the measurement of the electromotive force of cells in which such a transfer takes place; for the relation between these quantities is expressed by the simple equation

$$-\Delta F = \mathrm{E\,N\,F},$$

in which E is the electromotive force of a cell in which a given transfer of ions takes place when N faradays or N F coulombs of electricity pass through it.

The cells studied in this investigation were of the type

$$\mathrm{Hg + HgO,\ KOH}(c_1),\ \mathrm{K\ in\ Hg,\ \ KOH}(c_2),\ \mathrm{HgO + Hg}.$$

The potassium amalgam (K in Hg) was used in the form of a dropping electrode. The potassium hydroxide concentrations were varied from 0.003 to 0.84 *N*. The temperature was always 25°.

The investigation was carried out with the aid of a grant made to Prof. A. A. Noyes by the Carnegie Institution of Washington, for which I wish to express my indebtedness. To Professors D. A. MacInnes and A. A. Noyes I wish also to extend my thanks for valuable suggestions in connection with the research and for assistance in the preparation of this article for publication.

2. Preparation of the Substances and Solutions.

The mercury used was purified by blowing air through a mass of it covered with dil. nitric acid, and by distilling it in a current of air at 5–10 mm. pressure.

The mercuric oxide employed was a chemically pure commercial preparation.

The potassium amalgam was made by electrolyzing a pure 2 *N* potassium hydroxide solution (prepared as described below) between a cathode consisting of 250 cc. of mercury placed in the bottom of a 1000 cc. conical flask and an anode of platinum foil immersed in 600 cc. of the alkali solution placed above the mercury, a current of 1.5 amperes being passed for about 2 hours. The amalgam was first washed 3 times with water, and was then separated from the film of liquid and from the solid potassium hydroxide which gradually formed (through action of the moisture), by passing it through capillary tubes successively into 3 evacuated glass flasks. The amalgam was finally collected in a 500 cc. Pyrex flask, to the neck of which was sealed a glass tube carrying a stopcock (as shown in inverted position in Fig. 2 below). This method yielded a liquid amalgam containing about 0.2 atom per cent. of potassium with only a thin film of a white, solid substance. The method seems simpler than that of MacInnes and Parker, and yields equally satisfactory results.

The potassium hydroxide solution was prepared by electrolyzing with a strong current a concentrated solution of potassium hydroxide (purified by alcohol) over a mercury cathode till a large quantity of amalgam crystals had formed. These crystals were separated from the mercury by pouring the mass through a Büchner funnel, were washed with water and transferred to a large resistance glass bottle containing "conductivity water" closed with a stopper carrying a water-sealed exit tube. The decomposition of the amalgam became nearly complete after 3 or 4 days, the action being hastened by placing in the solution a platinum gauze connected with the amalgam by a platinum wire. The solution was then drawn through a tube containing a small asbestos filter into a nitrogen-filled Pyrex flask and the liquid was boiled under reduced pressure to expel the air. The solution was kept under nitrogen, and the flask was

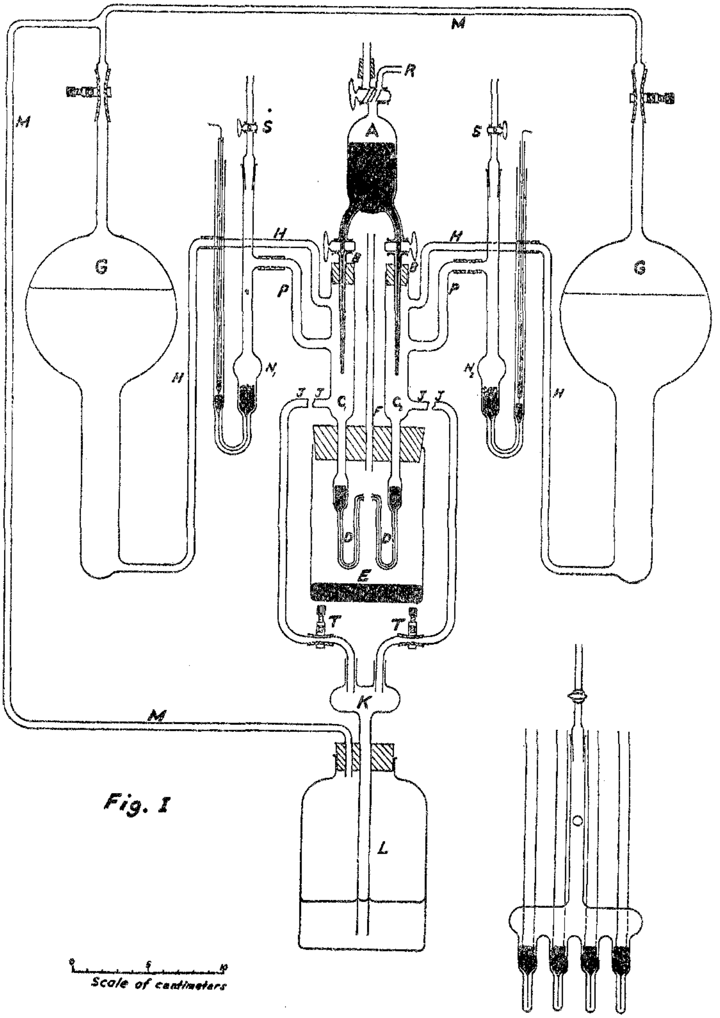

Fig. 1

fitted with tubes so that portions of it could be drawn off when needed without coming into contact with the air. The potassium hydroxide solutions so obtained were 0.5 to 0.8 *N*. They were standardized by titration with a weighed portion of constant-boiling hydrochloric acid, prepared as described by Hulett and Bonner,[1] with the help of methyl red, using a weight buret. The more dilute solutions were made by adding weighed portions of this stock solution to conductivity water in a weighed flask, boiling them under reduced pressure, and weighing the flask again to determine the exact concentration.

3. Description of the Apparatus.

The whole apparatus is shown in Fig. 1.

The vessel A is the reservoir containing the amalgam. This vessel was connected below with 3 capillary tubes, of which only 2 (lettered B) are shown in the figure. These passed through rubber stoppers into the cells C, through which the dropping amalgam fell through the overflow tubes D into the vessel E, open to the atmosphere through the tube F. These amalgam electrodes are described in detail in Section 4 below.

The 3 potassium hydroxide solutions of different concentrations were contained in 3 Pyrex glass bulbs G (of which only two are shown) From these the solutions flowed through the connecting tubes H H into cells C, and emerged from them through the outlet J into the larger tube K and the bottle L. The space above the liquid in vessels G and L was filled with nitrogen at atmospheric pressure, which was kept constant automatically because of the free communication between these vessels through the tubes M.

The 3 half-cells N_1, N_2, N_3 (of which only 2 are shown), containing the mercury, mercuric oxide, and potassium hydroxide solution previously saturated with it, were connected through tubes P with the 3 cells C containing the dropping electrodes. The half-cells were made of Pyrex glass, each having 4 separate electrode compartments at the bottom, as shown in the sketch in the lower right-hand part of the figure, which represents an elevation at right angles to that in the main drawing.

4. The Amalgam Electrodes.

The first experiments were made with a flowing amalgam electrode of the cup form used by Lewis and Kraus,[1] Lewis and Keyes,[2] and MacInnes and Parker;[3] but it was not possible to find the conditions under which satisfactory results could be secured. A modified form of dropping electrode was therefore devised. This consisted simply of a small tube of about one mm. bore, to the lower end of which was joined a slightly tapering capillary tube about 1.5 cm. long and of such diameter that 14 g.

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[1] THIS JOURNAL, 31, 390 (1909).

[2] *Ibid.*, 32, 1462 (1910).

[3] *Ibid.*, 34, 120 (1912).

or one cc. of pure mercury flowed through it per minute when there was a column of mercury 19 cm. in height above the capillary. Three of these capillary tubes were made of such dimensions as to give an equal outflow of mercury. These were joined, each through a stopcock, to the bottom of a glass cylinder (A in the figure) which served as a reservoir for the amalgam.

The following table shows typical results which were obtained with dropping electrodes of this kind, and also the best results which were observed with flowing electrodes of the cup type. The cell measured was $Hg + HgO$, $NaOH$ (0.25 *M*), $Na_{0.0006}\,Hg$, $NaOH$ (0.04 *M*), $HgO + Hg$. The first column gives the time in minutes after the flow was started; the second column the electromotive force in millivolts shown by the capillary dropping electrode, and the third column that shown by the flowing cup electrode. The results have no absolute significance, as the concentrations were only roughly determined.

TABLE I.

Constancy of the Electromotive Force with Dropping Electrodes.

	Electromotive force.	
Time. Min.	Dropping electrode. Mv.	Cup electrode. Mv.
1.5	93.78	83.0
3.0	93.79	88.5
4.0	93.80	90.0
5.0	...	90.8
6.0	...	91.7

5. Method of Procedure.

In making a series of measurements the amalgam was first introduced into the receiver A. This was first thoroughly cleaned and dried, care being taken that none of the stopcock grease got into the tubes. The capillary tubes were then completely filled with pure, dry mercury up to and through the stopcocks. The reservoir was connected, as shown in Fig. 2, with the inverted glass flask U containing the stock of amalgam through a tube V closed with rubber stoppers at both ends and provided with a side-arm with a stopcock. The whole arrangement was evacuated through the side-arm, and the stopcock W was opened, allowing the amalgam to flow down into the reservoir A. The flask and connecting tube were then removed and dry nitrogen was admitted to the empty space in the reservoir; a collapsible rubber bulb filled with dry nitrogen being attached to the tube R, so as to keep the pressure equal to that of the atmosphere.

The mercuric oxide half-cells were set up as shown in Fig. 1. The potassium hydroxide solutions used in them were previously boiled to expel air, and shaken for 5 to 10 hours under nitrogen in sealed Pyrex glass pipets with a little mercury and the mercuric oxide. The whole mixture was then charged into the half-cells up to the level of the side-arms by breaking off the tips of the pipets, air being excluded by previously filling the cells with nitrogen.

The potassium hydroxide solutions were then introduced into the apparatus. The overflow tubes D were filled with mercury, serving as a seal for the 3 cells C; and these were completely filled with the 3 potassium hydroxide solutions to be investigated. The bulbs G were charged with the solutions and connected with the cells C, as were also the mercuric oxide half-cells N. The reservoir A containing the amalgam was set in place, with its capillaries dipping into the solutions, and by slight suction applied at the stopcock S the half-cells N and the connecting tubes H and P were completely filled with the solutions.

The whole apparatus (except the tube K and the bottle L) was supported on a frame within a thermostat, with the water standing at the level of the bottom of the rubber stoppers in the cells C.

In making an experiment, the solutions were started flowing through the apparatus, by opening the screw-clamps T, at a rate of about 50 cc. per minute through each cell. After half a minute the amalgams were allowed to flow in through the fully opened stopcocks, at the rate of about one cc. per minute into each cell. Measurements of the electromotive force between the mercuric oxide half-cells N_1 and N_2, and between N_2 and N_3, were then made as rapidly as possible, the flow of the amalgam and the measurements being continued for about 4 minutes. The latest form of a Leeds and Northrup potentiometer was used for the measurements.

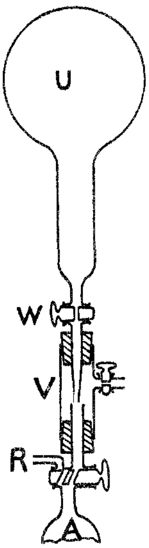

Fig. 2.

6. Measurements with the Hydrogen Mercuric-Oxide Cell.

Measurements of the electromotive force of the cells H_2 (1 atm.), NaOH (0.001 to 0.3 N), HgO + Hg were made primarily to test the reproducibility of the mercuric oxide electrode; but, since the results have interest as giving the free-energy change attending the reaction

$$H_2 + HgO = Hg + H_2O,$$

they will be presented in some detail.

The hydrogen half-cell used was the same as that described in the following article. The sodium hydroxide solution was prepared by the same method as was used for the potassium hydroxide, and the mercuric oxide half-cells were also made up just as has been already described.

The values adopted for the electromotive force were those observed after the readings had remained constant within a few hundredths of a millivolt for an hour or more, which occurred within 2 hours after the cell was set up. These values were not changed more than a few hundredths of a millivolt by shaking the mercury half-cells, which was done in all cases. They were also corrected for instrumental errors as described by Ellis.[1] Two standard cells certified by the Bureau of Standards were used, which agreed with each other within 0.05 millivolt.

The following table contains the results. The first column shows the number of mols of sodium hydroxide per 1000 g. of water. The second column gives the mean value in millivolts of the electromotive force of the cell at 25° derived from the values observed with the 4 mercuric oxide electrodes, and reduced to a hydrogen pressure of one atmosphere (taking into account the barometric pressure and the vapor pressure of the solution). The last column of the table gives the average deviation from their mean of the 4 values observed with the separate mercuric oxide electrodes.

Table II.

Electromotive Force of the Hydrogen Mercuric Oxide Cell at 25°.

Mols NaOH per 1000 g. of water.	Electromotive force. Mv.	Average deviation. Mv.
0.316	926.40	0.03
0.101	926.37	0.04
0.0316	926.44	0.02
0.0103	926.08	0.05
0.00310	926.37	0.08
0.00105	926.66	0.11

It will be seen that the average deviations from the mean of the observed values for the 3 more concentrated solutions are less than 0.05 millivolt, and also that these 3 values agree with each other within nearly the same limit. This shows that the mercuric oxide electrodes, as well as the hydrogen electrode, were giving values reproducible within 0.03 to 0.05 millivolt. The somewhat greater variations in the more dilute solutions are probably due to their sensitiveness to slight concentration changes.

The average of the first 3 values is 0.92640 volt. This multiplied by 193,000 coulombs (equivalent to 2 faradays) gives 178,800 joules as the free-energy decrease attending the reaction H_2 (1 atm.) + $HgO(s)$ = $Hg(l)$ + $H_2O(l)$. These values agree closely with the results of Brönsted,[2] which lead to the value 0.9266 for the electromotive force of the cell H_2 (1 atm.), NaOH (0.672 *M*), HgO + Hg at 25°.

7. Measurements with the Mercuric-Oxide Amalgam Cells.

Three sets of measurements were made. In each set observations were made of the electromotive force of the combinations of mercuric oxide half-cell N, through the amalgam electrodes in C_1 and C_2 with mercuric

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[1] This Journal, 38, 749 (1916).

[2] *Z. phys. Chem.*, 65, 86 (1909).

oxide half-cell N_2, and of the combination of the half-cell N_2 through the amalgam electrodes in C_2 and C_3 with the half-cell N_3. Just before the amalgam and the potassium hydroxide solutions were started flowing, the 4 electrodes in each of the mercuric oxide half-cells were compared with each other. The average deviation of the 4 electrodes from the mean commonly amounted to 0.05 millivolt. That one which had the electromotive force nearest to the mean was alone used for the measurements of the combination cells.

Immediately after the flow of the amalgam was started the electromotive force was unsteady but within half a minute it had become constant and remained so within a few hundredths of a millivolt for about 3 minutes. When the amalgam had mostly dropped into the solution, the values usually increased by 0.2 to 0.3 millivolt. The values of the electromotive force adopted were those observed soon after they became constant.

Table III contains the observed electromotive forces E in volts for the 3 sets of measurements, and the corresponding free-energy decreases ($-\Delta F$) in joules attending the transfer of 1 KOH from the solution whose concentration c_1 is given in the first column to the solution whose concentration c_2 is given in the second column. In the last column are given the activity coefficient ratios α_1/α_2 calculated by the equation

$$-\Delta F = R\,T \log (c_1\alpha_1/c_2\alpha_2)^2,$$

in which the quantities α really represent the geometrical means $(\alpha_{K}\alpha_{OH})^{1/2}$ of the activity coefficients of the two ion constituents.

TABLE III.

Electromotive Force of the Mercuric Oxide-Amalgam Cells.

Mols KOH per 1000 g. water.		Electromotive force.	$-\Delta F =$	
c_1.	c_2.	E.	96500 E.	α_1/α_2.
0.8394	0.09396	0.10807	10429	0.917
0.09396	0.01054	0.10636	10264	0.889
0.4506	0.04407	0.11134	10744	0.854
0.04407	0.004474	0.11310[a]	10914	0.917
0.2895	0.02978	0.10772	10395	0.837
0.02978	0.003473	0.10730	10355	0.941

[a] This value was obtained by introducing hydrogen electrodes in place of the mercuric-oxide electrodes.

8. The Activity Coefficients.

In order to show the degree of concordance of the 3 sets of measurements and to combine them into a single series, the activity coefficients were plotted as ordinates against the square roots of the concentrations as abscissas. To obtain absolute values of the activity coefficients it is assumed that the value at the lowest concentration, 0.0035 molal, is 0.980, which is the value derived for the conductance ratio of potassium hydroxide at 18° from the conductivity data of Kohlrausch[1] and the ion conductances at zero concentration of Johnston.[2] This value, 0.980, is intermediate between those adopted in the previous articles from this laboratory for the activity coefficient of potassium chloride[3] (0.979 at 0.001 molal) and for that of hydrochloric acid[4] (0.985 at 0.0034 molal). The method of plotting was to locate first the point $\alpha = 0.979$, $c = 0.00347$, and then the points corresponding to the last 2 activity ratios in Table III, and to draw a curve through them; then to locate on this curve the point for $c = 0.00447$, and to locate without reference to the curve the other 2 points corresponding to the 2 activity ratios given in the middle rows of the table, and to draw the best representative curve through the 5 independent points; and, finally, to bring into the plot, by proceeding in the same way, the first 2 activity ratios given in the table. A second graph was plotted independently by another person in an exactly similar way except that the logarithms of the concentration (instead of its square-roots) were plotted as abscissas.

The activity coefficients read off from the 2 plots at certain round concentrations, and the means of the 2 values at each concentration, are given in Table IV. It should be noted that these activity coefficients α are really the geometrical means $(\alpha_K \alpha_{OH})^{1/2}$ of the activity coefficients of the two ion constituents, and that they represent the activity coefficients of either ion constituent only under the assumption that the two are equal. In the last 2 columns of the table are given the values of the conductance-viscosity ratio $(\Lambda\eta/\Lambda_0\eta_0)$ and of the conductance ratio (Λ/Λ_0) calculated from the conductance values of Kohlrausch[1] at 18°, the Λ_0 value (237) for 18° derived by Johnston,[5] and the viscosity data of Kanitz[6] at 25°.

TABLE IV.

The Activity Coefficients of Potassium Hydroxide.

Mols per 1000 g. of water.	Activity coefficients.			Conductance-viscosity ratio.	Conductance ratio.
	I.	II.	Mean.		
1.00	0.800	0.786	0.793	0.877	0.776
0.70	0.772	0.772	0.772	0.880	0.804
0.50	0.764	0.766	0.765	0.884	0.831
0.30	0.770	0.768	0.769	0.889	0.855
0.20	0.795	0.791	0.793	0.891	0.870
0.10	0.845	0.847	0.846	0.910	0.900
0.03	0.921	0.919	0.920	0.939	0.936
0.01	0.960	0.961	0.961	0.963	0.962
0.003	0.983	0.981	0.982	0.980	0.980

[1] "Landolt u. Börnstein, Tabellen," 1912, p. 1104

[2] THIS JOURNAL, 31, 1015 (1909).

[3] See Ellis, *ibid.*, 38, 760 (1916).

[4] Noyes and Ellis, *ibid.*, 39, 2543 (1917).

[5] THIS JOURNAL, 31, 1015 (1909).

[6] *Z. phys. Chem.*, 22, 340 (1897).

It will be seen from these results, as was found by Ellis in the case of hydrochloric acid, that:

(1) The activity coefficient at first decreases with increasing concentration, but passes through a minimum at a concentration of about 0.5 molal, and then increases rapidly.

(2) Up to concentrations of 0.5 molal the activity coefficient has a much smaller value than the conductance-viscosity ratio (thus 7% smaller at 0.1 molal, and 11% smaller at 0.2 molal), thus again showing that this ratio, even at these moderate concentrations, is not even an approximate measure of the effective ionization of largely ionized substances.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 123.]

THE ACTIVITIES OF THE IONS IN SOLUTIONS OF MIXED ELECTROLYTES.

BY MING CHOW.

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1. Introduction.

This investigation consisted in measurements of the electromotive force of voltaic cells of the type

$$H_2 \text{ (1 atm.)}, HCl\ (c_1) + KCl\ (c_2), Hg_2Cl_2 + Hg,$$

in which the separate concentrations c_1 and c_2 were varied, but their sum $c_1 + c_2$ was kept constant, namely, in these experiments, at 0.1 *N*. The purpose of the research was to determine directly the value of the product of the activities of the hydrogen ion and chloride ion, and to draw conclusions as to the separate activities of these two ions in the mixture.[1]

A similar research with the same object in view has already been published by Loomis, Essex, and Meacham;[2] but as it was found possible in the present investigation to secure more constant and reproducible electromotive forces, and as the data lead to conclusions somewhat different from those drawn by these authors, it seems desirable to present here the results of my measurements. Reference should also be made to the work of Harned,[3] who measured the same type of cell, but kept the concentration of the hydrochloric acid, not that of the mixed electrolytes, constant.

This research was carried out at the suggestion of Prof. A. A. Noyes,

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[1] In regard to the concept of activity and activity coefficients here employed, see the first section of the preceding article.

[2] THIS JOURNAL, 39, 1133 (1917).

[3] *Ibid.*, 38, 1988 (1916).