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THE ACTIVITIES OF THE IONS OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION

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Introduction

This work is a revision of that of Chow[1] on the measurement of the electromotive force of concentration cells of potassium hydroxide for the purpose of determining the activities of the ions. Chow's results were based on single measurements for each pair of concentrations and were made with a form of electrode which has since been found to be unreliable.

The principle involved is the same as that used by MacInnes and Parker[2] on potassium chloride solutions, by Ellis, and Noyes and Ellis[3] on hydrochloric acid and by MacInnes and Beattie[4] on lithium chloride. The cells were of the type, $H_2 \mid KOH\ (c_1) \mid KHg_x \mid KHg_x \mid KOH\ (c_2) \mid H_2$, in which the net effect of passing 1 faraday from left to right is the transfer of one mole of potassium hydroxide from a concentration C_1 to a concentration C_2. The electromotive force is given by the expression,[2] $E = 2\,RT/F\,ln\text{-}\alpha_1\,C_1/\alpha_2\,C_2$ where α_1 and α_2 are the mean activity coefficients of the two ions in the two solutions of concentration C_1 and C_2, respectively; R, T, and F have the usual significance.

Apparatus

The apparatus used is shown in Fig. 1. The amalgam was contained in the vessel A and was run into the cell through the capillary tubes B. This form of electrode was found by Chow[1] and Beattie[4] to be preferable to the cup electrode used by MacInnes and Parker.[2] The amalgam dropped into the bent arms D and overflowed into the vessel E which was open to the atmosphere. A difference of level of the mercury in D kept the solution from flowing out. The potassium hydroxide solutions, which were contained in the flasks G, flowed in through the tubes H to the cell and out through the tubes J into the bottle L. The rate of flow of the solutions was determined by the pinchcocks T. L was nearly filled with nitrogen at atmospheric pressure at the start. The tubes M, which allowed gas to flow into the space above the solutions in the flasks G, maintained atmospheric pressure in the flasks, for as solution ran out of G into L, an equal volume of gas was displaced through tubes M into the top of G. This equalization of pressure was a very necessary condition in order to maintain atmospheric pressure in the hydrogen electrodes N_1 and N_2, which were connected as shown with the central tubes C_1 and C_2. The hydrogen electrodes consisted of 3 platinized platinum gauze strips connected through a glass seal in the tubes passing through the rubber stopper. The hydrogen, which was first bubbled through some of the same solution as contained in the cell, was led in by the tubes P and out by R which prevented air from diffusing

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[1] Chow, This Journal, **42**, 488 (1920).

[2] MacInnes and Parker, *ibid.*, **37**, 1445 (1915).

[3] Ellis, *ibid.*, **38**, 737 (1916). Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[4] MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).

back. No water seal was necessary as long as the gas was kept bubbling at a moderate rate.

The whole apparatus was held in a frame and placed in a thermostat with the water level nearly up to the tops of the tubes C. A high quality of commercial potentiometer was used to measure the electromotive force, and was standardized by 2 standard cells which had just been received from the Bureau of Standards. The temperature of the thermostat water was maintained at 25° within 0.02°.

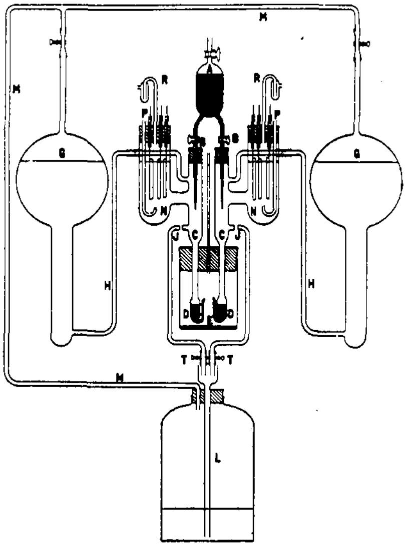

Fig. 1.

Method of Procedure

The method of making the measurements was as follows. The flasks G of Fig. 1 were filled with nitrogen and then with the respective potassium hydroxide solutions of the 2 concentrations, care being taken to exclude air completely. The hydrogen electrodes were washed several times with their respective solutions and set in place after the tubes C and N had been filled. The amalgam container A was filled from a reservoir. The tubes C_1 and C_2 were filled to the top by increasing the pressure in N_1 and N_2 slightly and the stoppers on the tubes B of the amalgam container put in place so that no gas remained in the tops of C_1 and C_2. Hydrogen was then passed in to bring the electrodes to equilibrium, which usually occurred in $^1/_2$ to 1 hour. When 3 N potassium hydroxide solution was used, however, nearly 3 hours was necessary to attain equilibrium.

After this equilibrium was established the flow of the solutions was started at the rate of about 80 cc. per minute, by opening the pinchcocks T, and the amalgam was run in through the fully opened stopcocks in tubes B at the rate of about 1 cc. per minute. Hydrogen was allowed to bubble in continuously and rapidly enough to prevent air from being sucked back when the level dropped in N_1 and N_2, as it did slightly. This slight change of level did not affect the hydrogen electrodes, for they checked as well after the run as before. Measurements of the electromotive force were made between one hydrogen electrode of N_1 and one of N_2. The time of the run was from 4 to 5 minutes and measurements were taken continuously. The potential usually stayed constant to 0.1 millivolt for about 3 minutes, after which it varied up or down. In some cases it was constant for the entire run.

Preparation of Materials

The potassium amalgam was made by electrolyzing potassium into pure mercury from a solution of pure potassium hydroxide. The amalgam was then separated from the solution as completely as possible by passage through a capillary tip, and then placed in a 500cc. Pyrex flask, provided with a capillary stopcock. The flask was sealed and allowed to stand for 2 or 3 days to dry. The amalgam contained approximately 0.2% by weight of potassium. Amalgams of 0.02% and 0.002% by weight were made by dilution of the 0.2% solution with pure mercury. These were also kept in sealed containers provided with stopcocks. Potassium hydroxide contaminated the amalgam in the containers but when the amalgam was drawn off through the capillary stopcocks it came out almost as clean as pure mercury.

The more dilute amalgam was used with the dilute solutions and the more concentrated amalgams with the more concentrated solutions. The electromotive force is independent of the concentration of the amalgam provided it is the same in both cells, but it was found that the electromotive force was much steadier when this approximate adjustment of amalgam concentration to solution concentration was made. The most concentrated amalgam, when used with the 0.01 and 0.001 N solutions, gave an electromotive force value which averaged about that obtained with the dilute amalgam, but it was very unsteady.

The potassium hydroxide solutions, with the exception of the 3 N solutions, were prepared in the apparatus shown in Fig. 2. This consists of two Pyrex flasks A and B of 1 liter and 3 liters capacity, respectively, joined by a 12mm. tube as near the bottom as possible. About 500 cc. of pure dry mercury was used, sufficient to fill well above the connecting tube. The 3-liter flask was first evacuated, then filled with nitrogen, and finally with conductivity water (collected hot and boiled under reduced pressure) which was forced in, out of contact with air and while still hot. A very strong solution of pure potassium hydroxide was next added to flask A, which was fitted as a simple electrolytic cell. Potassium was electrolyzed into the mercury as cathode. The current was usually limited to 2 or 3 amperes, as too strong a current gave a concentrated viscous amalgam. More potassium hydroxide solution was added as it was used up. The whole apparatus was mounted in a box and rocked back and forth (about one cycle in 10 seconds), thus circulating the amalgam produced in A throughout B. The decomposition of the amalgam in B was aided by the platinized platinum electrode E which was short circuited with the amalgam. This electrode was, in fact, necessary to produce reasonably rapid solution of the potassium. To prevent air from entering B the water seal C was used. This was made as shown to allow for the large fluctuations in volume as the mercury flowed back and forth between the flasks A and B. Five to 6 days were necessary to produce a 1 N solution. This apparatus gave an exceptionally pure solution of potassium hydroxide. A test with barium hydroxide showed the absence of carbonate, and there must have been a minimum of dissolved air since at no time did the solution come in contact with the atmosphere, and hydrogen was constantly forming at the electrode E. The solutions, which were perfectly clear, were withdrawn from the electrolyzer into a flask fitted with a short tube and one reaching to the bottom resembling a wash bottle.

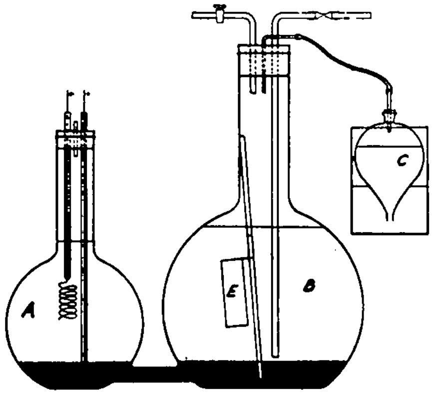

Fig. 2.

The 3 N solutions were made from a solution of the purest potassium hydroxide obtainable,[5] by adding solid barium hydroxide to precipitate the carbonate. Tests were made for carbonate at frequent intervals and when it had all been precipitated and a slight excess of barium was present, the solution was filtered. The small excess of barium was precipitated while filtering and a final solution obtained which gave no test for either carbonate or barium. This solution was then boiled for over an hour under reduced pressure to free it from dissolved air. The presence of oxygen in the concentrated solutions is not so harmful, however, as in the dilute solutions. Further, two determina-

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[5] A commercial quality "purified by alcohol."

tions of the electromotive force of the cell with solutions made by electrolysis and by precipitation checked within the experimental error.

These conc. solutions were analyzed as follows. A weighed quantity (30 to 40 g.) was titrated nearly to the end-point by a weighed quantity of constant-boiling hydrochloric acid which had been standardized to 0.01% by precipitation of the chloride as silver chloride. The small amount of residual base was titrated with approximately 0.03 *N* acid, using methyl red as indicator. In general, but a few cubic centimeters of these solutions were necessary, so that the accuracy of weighing determined the accuracy of analysis. Results that check more closely than within 0.05% were consistently obtained.

Other solutions were made by gravimetric dilution of one of the strong solutions with hot conductivity water. All manipulation was performed out of contact with air, in flasks resembling wash bottles with stopcocks in each arm, and all solutions were boiled under reduced pressure before the final weighing. They were kept in an atmosphere of nitrogen, and were never allowed to stand for more than 4 days before use, and frequently not longer than one day. However, no difference was found between solutions 4 days old and 1 day old, as shown by two determinations of the electromotive force made to test this point.

Measurements

Fifteen successful sets of measurements were made, giving 7 determinations which were checked once and in one case twice. The check measurements were in every case made with solutions for which separate analytical data were obtained. The results are given in Table I. The concentrations were within 2 to 3% of round numbers and activity coefficient ratios were calculated with these values. The concentrations in moles of potassium hydroxide per 1000 g. of water are given in the first two columns. The measured electromotive force is given in the third

TABLE I

ELECTROMOTIVE FORCES OF POTASSIUM HYDROXIDE CONCENTRATION CELLS AT 25°

Concentrations Moles KOH per 1000 g. of H_2O		Measured e.m.f.	Activity-coeff. ratio
C_1	C_2	E	$\frac{\alpha_1}{\alpha_2}$
3.000	0.2915	0.1416	1.530
2.955	0.2963	0.1395	1.515
0.992	0.0996	0.1172	0.983
0.995	0.0992	0.1170	0.972
0.992	0.0996	0.1169	0.977
0.300	0.0998	0.05361	0.945
0.300	0.1000	0.05345	0.943
0.2963	0.0282	0.1138	0.872
0.3000	0.0299	0.1110	0.865
0.0992	0.00989	0.1110	0.865
0.0996	0.00984	0.1110	0.857
0.0288	0.00286	0.1120	0.879
0.0299	0.00293	0.1130	0.882
0.0100	0.000991	0.1147	0.924
0.0100	0.001000	0.1149	0.936

column, and the activity coefficient in the fourth, calculated from the equation, $E = 2RT/F \ln \alpha_1 C_1/\alpha_2 C_2 = 0.1183 \log \alpha_1 C_1/\alpha_2 C_2$, where R, the gas constant, is taken as 8.316, T as 298.1, and F as 96,500.

The activity-coefficient ratios calculated in this manner are not directly comparable on account of the differences in concentrations. They were corrected to even concentrations by the following method. A curve was plotted of activity against the square root of the concentration (the latter being used instead of the concentration itself in order to reduce the size of the plot), using values from determinations in which the concentrations were nearest to round numbers. This gave the slope of the curve with more accuracy than sufficient to find the correction which must be added or subtracted to give the activity coefficient at the nearest round number. The maximum concentration difference to be corrected was only 6% and a difference of 1% in the concentration in general affected the activity-coefficient ratio to less than 0.1%. In Table II these mean values are given. There are also included in this table the values of the free energies of dilution for the approximate concentrations indicated.

TABLE II

ACTIVITY-COEFFICIENT RATIOS AND FREE ENERGY OF DILUTION OF POTASSIUM HYDROXIDE AT 25°

Concentrations Moles of KOH per 1000 g. of H_2O C_1	C_2	Mean activity-coeff. ratio $\frac{\alpha_1}{\alpha_2}$	Free energy of dilution F(joules)
3.0	0.30	1.522	13, 500
1.0	0.10	0.978	11,300
0.30	0.10	0.944	5,160
0.30	0.03	0.870	10,730
0.10	0.01	0.861	10,670
0.03	0.003	0.880	10,780
0.01	0.001	0.930	11,060

To find the activity coefficient itself we must make some assumption in regard to the relation of activity and concentration at some one point. We assumed, therefore, that the activity is equal to the "concentration" of the ions in the most dilute solution (0.001 N), the "concentration" being computed in the familiar manner from conductance data. The ionization at 0.001 N was derived from the equivalent conductance value of Kohlrausch[6] and the conductance at infinite dilution given by Johnston[7] which results in the figure 0.989. Using this value the activity coefficients given in Table III, second column, were calculated. The third column of Table III contains the activity coefficients determined by Chow.[1] In the fourth column are given the conductance ratios, using again Kohl-

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[6] Kohlrausch and Holborn, "Das Leitvermögen der Elektrolyte," B. G. Teubner, 1916.

[7] Johnston, THIS JOURNAL, 31, 1010 (1909).

rausch's values, and the fifth column contains the conductance-viscosity ratio, using the viscosity data of Kanitz.[8]

TABLE III

MEAN ACTIVITY COEFFICIENTS OF THE IONS OF POTASSIUM HYDROXIDE AT 25°

Concentrations Moles of KOH per 1000 g. of H_2O	Activity coeff.	Activity coeff. (Chow)	Conductance ratio	Conductance-viscosity ratio
3.0	1.136	...	0.593	(0.871)[a]
1.0	0.775	0.793	0.776	0.877
0.3	0.748	0.769	0.855	0.889
0.1	0.792	0.846	0.900	0.910
0.03	0.857	0.920	0.936	0.939
0.01	0.920	0.961	0.962	0.963
0.003	0.974	0.982	0.980	0.980
0.001	0.989	...	0.989	0.989

[a] Value for viscosity extrapolated from 2 *N* to 3 *N*.

It should be noted that this activity coefficient is the square root of the product of the activity coefficients of the two ions and equal to that of either ion only when the activities are equal.

Discussion of Results

It is seen that there is a great difference (2 to 8%) between our values and those of Chow.[1] We believe that this is due principally to his having taken insufficient care to exclude air from his solutions. It is exceedingly important to have no dissolved oxygen in the solution, for oxygen reacts with the potassium of the amalgam, decreasing its concentration and at the same time increasing the concentration of the solution. The percentage effect is greater in the dilute solutions which, therefore, produce a smaller measured electromotive force and hence smaller activity ratio; Chow's results are in this direction.

Chow also used mercuric oxide electrodes instead of hydrogen electrodes and the former appear to be unreliable. For example, it was found by the present author that when the mercuric oxide was shaken with the potassium hydroxide for one week instead of one day, which was Chow's procedure in obtaining the equilibrium mixture for the electrodes, a difference in the electromotive force of from 1 to 6 millivolts was observed. There are 2 forms of mercuric oxide, red and yellow, and they have different solubilities and hence different free energies.[9] The yellow form, which consists of the smaller particles, is the more soluble. When red mercuric oxide is shaken with potassium hydroxide it slowly changes over to a certain extent to the yellow form and at a rate dependent on the concentration of the potassium hydroxide. In strong alkali (1.0 *N*), the change is comparatively slow; in 2 weeks there is hardly a perceptible

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[8] Kanitz, *Z. physik. Chem.*, **22**, 340 (1897).

[9] Fuseya, THIS JOURNAL, **42**, 368 (1920).

change in color, but it is decidedly evident after 2 months. In the more dilute solutions (for example, in 0.001 *N*), however, shaking overnight is sufficient to change an appreciable amount of the red to the yellow form. The rate of change of one form to the other appears to be roughly inversely proportional to the concentration of the alkali. With this variable factor it can be readily seen that no true equilibrium can be expected. Even if each were shaken long enough to attain equilibrium, the difference of the free energies of the mercuric oxide on the two sides of the cell would invalidate the resultant electromotive force. The constancy of the potential of the cell, $H_2 | KOH | HgO | Hg$, with change in the concentration of the potassium hydroxide, obtained by Chow,[1] can probably be explained by the fact that too short a time of shaking the mercuric oxide with the alkali was allowed, so that the red form had not yet changed to the yellow.

It is seen that the degree of ionization and the activity coefficient are far from equal except at very low concentrations and in a small range at 1.8 *N* where the activity-coefficient curve rises again. The minimum at 0.42 *N* has an activity coefficient 19% less than the "degree of ionization" and at 3.0 *N* the activity coefficient is 30% greater. The curve has the typical form found by other investigators for the uni-univalent type of electrolyte, resembling most nearly that of lithium chloride.

The activity coefficients given in Table III are estimated to be reliable to 0.5% on the average, the maximum divergence between the corrected activity-coefficient ratios for the two runs on the same concentrations being 0.6%.

Sincere appreciation is rendered Dr. D. A. MacInnes for his kind help and suggestions during the course of this work.

Summary

The electromotive forces of cells of the type, $H_2 | KOH (c_1) | KHg_x | KHg_x | KOH (c_2) | H_2$, have been measured at 25° for concentrations of potassium hydroxide ranging from 3 *N* to 0.001 *N*. The activity coefficients of the ions of the solution at various concentrations and the free energy of dilution between various concentrations have been calculated and tabulated. Data given by Chow[1] have been found to be incorrect.

The relation between the activity and concentration for potassium hydroxide has been found to be similar to that for other uni-univalent electrolytes.

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