[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE ACTIVITY COEFFICIENT OF BARIUM HYDROXIDE IN AQUEOUS SOLUTION AT 25°

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The present communication is concerned with the calculation of the activity coefficient of barium hydroxide in aqueous solution at 25° through the concentration range of 0 to the saturated solution from electromotive force measurements of the cells.

$$H_2 \mid Ba(OH)_2\ (m) \mid Ba_xHg \mid Ba(OH)_2\ (m_0) \mid H_2$$

Materials and Experimental Procedure

The concentrated barium hydroxide solutions made from a high grade analyzed chemical were allowed to stand for a week until all carbonate had settled. The clear solutions were carefully drawn off and kept in bottles containing carbon dioxide-free air. The concentrations were determined by titration with hydrochloric acid standardized by gravimetric analysis. Weight burets were employed. Dilute solutions were prepared by addition of known weights of boiled water *in vacuo*. Since measurements of cells of this type are among those most difficultly reproducible, the sources of error lie in the operation of the cells and not in the knowledge of the concentrations of the solutions.

A 0.2% barium amalgam was made by electrolysis of a saturated solution of barium hydroxide. This was withdrawn into an evacuated flask which was then inverted and allowed to stand for twenty-four hours or more until all the usual solid impurities had risen to the surface. This amalgam was then diluted to 0.1% by withdrawal into an equal volume of mercury in a similar vessel.

The cells were similar in design to those previously described by Harned[2] and by Åkerlöf[3] with one modification. It was found by Lucasse[4] that alkaline earth metal amalgams which flowed from the ordinary type of drawn capillary tubes did not function well in cells of this type. He found that amalgam vessels with turned up capillaries which had not been drawn to fine tips functioned in a much more satisfactory manner. Our experience confirmed this point, so that this type of amalgam vessel was employed.

All solutions were boiled *in vacuo* to remove dissolved air, and all pre-

[1] The present communication was constructed from part of a Dissertation to be submitted to the Graduate School of Yale University in partial fulfilment of the Degree of Doctor of Philosophy, June, 1932.

[2] Harned, THIS JOURNAL, **47**, 676 (1925).

[3] Åkerlöf, *ibid.*, **48**, 1160 (1926); Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[4] Lucasse, THIS JOURNAL, **47**, 743 (1925).

cautions accompanying the manipulation of cells of this type were observed. The measurements were made at 25 ± 0.02°.

It should be mentioned that these cells are among the most difficult to manipulate. Very small quantities of dissolved air caused large errors. The average error in reproducibility is estimated to be ±0.3 mv. Therefore, we have relied on a large number of measurements in order to minimize the accidental variations.

Method of Calculation and Results

The electromotive force of the cell

$$H_2 \mid M(OH)_2\ (m) \mid M_xHg \mid M(OH)_2\ (m_0) \mid H_2$$

is given by the equation

$$E = 0.08873 \log \frac{\gamma m}{\gamma_0 m_0} + 0.05915 \log \frac{a_{H_2O(m_0)}}{a_{H_2O(m_0)}} \quad (1)$$

In general, it is necessary to know the activity of water in the hydroxide solution in order to obtain γ. As shown by Harned,[2,5] the second term on the right of equation (1) may be evaluated from the electromotive forces by an arithmetical calculation. This procedure was adopted for the cells containing barium hydroxide and it was found that the numerical value of this term was less than the experimental error in the determination of E throughout the moderate concentration range of 0 to 0.23 molal. Indeed, this factor does not exceed 0.1 mv.

Table I contains the measurements. m is the molality, c the concentration in moles per liter of solution, d the density of the solution determined for the purposes of the calculations to follow, and E the observed electromotive forces of the cell containing 0.12 M barium hydroxide as the reference solution, so that m_0 always equaled 0.12 M. The sixth column contains the number of cells measured at each molality and the seventh column contains the total deviation in millivolts of these measurements. In order to render the results more consistent, E was plotted against log m, and the smoothed out results given in the fifth column were read off the plot.

The values of the activity coefficients were obtained by employing Hückel's equation

$$\log \gamma = -\frac{0.708\sqrt{6c}}{1 + A\sqrt{6c}} + B(6c) - \log(1 + 0.054m) \quad (2)$$

where A and B are constants. In order to evaluate A and B, three electromotive forces are necessary, and these were read off the curve at 0.01, 0.06, and 0.12 molal. Since the method of obtaining A and B from cells of this type has been previously described,[6] we shall not discuss the matter further. A and B were found to be 0.696 and 0.0113, respectively. The eighth column of the table contains the values of γ computed by equation

[5] Harned and Schupp, This Journal, **52**, 3886 (1930).

[6] Hückel, *Physik. Z.*, **26**, 93 (1925); Harned, This Journal, **48**, 326 (1926).

TABLE I

ACTIVITY COEFFICIENTS OF BARIUM HYDROXIDE IN AQUEOUS SOLUTIONS AT 25° FROM MEASUREMENTS OF CELLS

$H_2 | Ba(OH)_2\ (m) | Ba_xHg | Ba(OH)_2\ (0.12) | H_2$

m	c	d	E (obs.)	E (curve)	No. of cells	Deviation, mv.	γ (Hückel)	γ (obs.)	γ (curve)
0.0	....	0.9970	......	......	.	...	..	..	..
.00245	0.002445	.9977	−0.1245	−0.1238	2	0 1	0.834	0.820	0.835
.00390	.00389	.99795	− .1078	− .1078	1	.0	.799	.795	.795
.00409	.00408	.9980	− .1069	− .1062	2	.4	.795	.776	.790
.00500	.00499	.99815	− .0976	− .0993	2	.2	.780	.808	.773
.00603	.00601	.99835	− .0928	− .0927	1	...	.761	.760	.761
.00621	.00619	.9984	− .0922	− .0918	2	.7	.759	.749	.757
.00793	.00790	.9987	− .0840	− .0836	2	.5	.735	.726	.733
.00991	.00988	.9991	− .0762	− .0761	3	.2	.713	.711	.713
.01	.009974	.9991	......	− .0758	.	...	(.712)	..	(.712)
.01132	.01129	0.9993	− .0725	− .0718	2	.2	.699	.685	.697
.01509	.01505	1.0000	− .0630	− .0628	2	.3	.668	.657	.661
.01577	.01573	1.0002	− .6020	− .0614	2	1.0	.663	.647	.658
.02015	.02010	1.0010	− .0540	− .0537	2	0.3	.635	.622	.627
.02037	.02030	1.0010	− .0537	− .0533	1	...	.634	.620	.626
.02045	.02040	1.0011	− .0523	− .0532	2	.7	.633	.640	.623
.02050	.02045	1.0011	− .0528	− .0531	2	.8	.633	.631	.623
.03077	.03070	1.0029	− .0397	− .0404	2	.5	.585	.580	.579
.03089	.03082	1.0029	− .0399	− .0402	2	.7	.585	.576	.580
.03915	.03906	1.0045	− .0327	− .0329	2	.7	.556	.558	.553
.04083	.04074	1.0048	− .0314	− .0316	2	.2	.552	.552	.549
.04970	.04960	1.0065	− .0254	− .0256	2	1.5	.528	.531	.527
.05000	.04990	1.0065	......	− .0254	.	...	(.527)	..	(.526)
.05323	.05312	1.0071	− .0233	− .0234	2	0.9	.519	.522	.521
.06000	.05988	1.0083	......	− .0200	.	...	(.505)	..	(.505)
.06150	.06140	1.0086	− .0197	− .0193	1	...	.502	.496	.501
.06162	.06151	1.0087	− .0191	− .0192	2	.1	.502	.503	.502
.06210	.06198	1.0087	− .0187	− .0189	2	.0	.501	.504	.502
.07152	.07140	1.0105	− .0151	− .0149	2	.3	.484	.481	.483
.07983	.07970	1.0120	− .0121	− .0118	2	.9	.471	.465	.469
.08015	.08002	1.0121	− .0117	− .0117	1	...	.471	.469	.469
.08154	.08141	1.0123	− .0111	− .0111	2	.8	.469	.468	.468
.09167	.09153	1.0142	− .0072	− .0078	1	...	.455	.460	.453
.09764	.09750	1.0153	− .0057	− .0060	2	.1	.448	.452	.446
.1055	.1054	1.0168	− .0036	− .0038	2	1.1	.439	.445	.437
.1200	.1199	1.0194	......	.0000	.	...	(.424)	(.424)	(.424)
.1476	.1475	1.0246	+ .0060	+ .0060	2	0.5	.402	.402	.402
.1781	.1780	1.0303	+ .0112	+ .0112	2	.3	.382	.382	.382
.1890	.1890	1.0322	+ .0133	+ .0130	1	...	.376	.380	.377
.1996	.1996	1.0346	+ .0144	+ .0144	2	.2	.371	.370	.370
.2296	.2296	1.0397	+ .0185	+ .0185	2	.1	.357	.358	.358

(2), the ninth column contains the values computed by equation (1) by employing the value at m_0 equals 0.1200 of 0.424 computed by equation

(2), and the tenth column similar values computed from the smoothed results.

The agreement of the smoothed out values with those computed by the equation is good. All three series of γ values agree well in the more concentrated solutions. In the dilute solutions, the behavior of the directly observed values in column (9) is somewhat erratic.

Summary

1. Measurements of the cells

$$H_2 \mid Ba(OH)_2\ (m) \mid Ba_xHg \mid Ba(OH)_2\ (0.12M) \mid H_2$$

through a concentration range from 0.002 to 0.23 M at 25° have been made.

2. The densities, d_{25}, of aqueous barium hydroxide solutions at 25° have been determined and are given to within $\pm$ 1 in the fourth decimal place by the equation

$$d_{25} = 0.9970 + 0.1878m$$

3. The activity coefficient of barium hydroxide in aqueous solution has been evaluated by employing Hückel's equation, which upon substitution of the numerical values of the constants A and B becomes

$$\log \gamma = -\frac{0.708\sqrt{6c}}{1 + 0.696\sqrt{6c}} + 0.0678c - \log(1 + 0.054m)$$

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THE HEATS OF SOLUTION OF GASEOUS METHYLAMINE

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Object of the Investigation.—In a previous paper[1] there were presented some preliminary values for the total heats of solution of gaseous monomethylamine in water at different concentrations of methylamine produced. These preliminary data were included at that time to give an idea of the order of magnitude of this heat effect and to present a more complete listing of the thermodynamic properties of methylamine with the view of using this substance as a refrigerating fluid. Since the appearance of that paper, more reliable data have been obtained; these are presented in the present paper.

Existing Data.—Besides the preliminary data of Felsing and Thomas, there are listed but few determinations or calculations of this heat effect in the literature. Bonnefoi[2] presents two experimental values and Moore and Winmill[3] present a calculated value; the values given by Bonnefoi are 11,780 and 12,400 cal./mole of methylamine when the ratio of moles of

[1] Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

[2] Bonnefoi, *Ann. chim. phys.*, **23**, 362 (1905).

[3] Moore and Winmill, *J. Chem. Soc.*, **101**, 1667 (1912).