The author wishes to thank Dr. R. A. Robinson for valuable assistance in the preparation of this paper.

Summary

A method is described by which the activities and the partial molal heat contents of the solvent may be computed directly from the electromotive forces of cells without transference. The method is applied to data for potassium chloride and sulfuric acid and values at 25° are tabulated.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

Isopiestic Vapor Pressure Measurements on Concentrated Solutions of Sodium Hydroxide at 25°

BY R. H, STOKES

Our knowledge of the vapor pressures of sodium hydroxide solutions at 25° is surprisingly incomplete, as has recently been remarked by Williamson.[1] Thus the dynamic vapor pressure measurements of Hayward and Perman[2] were made between 30 and 80, whilst the electromotive force measurements of Åkerlöf and Kegeles[3] between 0.1 and $17M$ yielded results from which the water activity, a_W, can be interpolated at 25°. The saturated solution, however, is approximately $28M$ at this temperature. The electromotive forces of the cell

$$H_2 \left| \begin{matrix} NaOH \\ m \end{matrix} \right| HgO\text{–}Hg$$

which were measured by Shibata and Murata[4] at 25° should give the water activities, since the cell reaction is presumably $H_2 + HgO \rightarrow H_2O + Hg$. Williamson,[1] however, has pointed out serious discrepancies between these values and existing direct determinations.

The present paper gives the results of isopiestic vapor pressure measurements on sodium hydroxide solutions from 2 to $29M$ at 25°, from which water activities and activity coefficients are derived.

Experimental

Sodium Hydroxide.—A saturated lye was prepared from "Baker's Analyzed" C. P. pellets, and, after settling, was filtered through a sintered-glass funnel into a nickel crucible inside a desiccator. This was connected to a hydrogen supply, and samples were drawn off when required by inserting a delivery tube through the lid of the desiccator into the crucible, against a stream of hydrogen. The solution was then forced out by hydrogen pressure. The delivery tube was removed when not in use, in order to minimize contamination of the solution. Analysis of the stock solution showed the presence of carbonate equivalent to 0.14% of the total alkali, which is consistent with the results reported by Han and Chao.[5]

Sulfuric acid was prepared from "Baker's Analyzed" C. P. material, in the form of a 70% solution which was stored in a special vessel from which it could be run out with the minimum exposure to the air. The solution was analyzed by weight-titration against 5- to 10-g. portions of pure sodium carbonate; the end-point was slightly exceeded, and the carbon dioxide boiled out, after which a small back-titration to the brom thymol blue end-point was made with 0.2 N sodium hydroxide. The analyses were reproducible to 0.05%. Other solutions were prepared by weight-dilution of the main stock, with check analyses. The apparatus used for equilibration of the solutions was of the usual form,[6] with platinum containers for the sulfuric acid solutions and silver for the sodium hydroxide. The sulfuric acid solutions were weighed out in the usual way, but the sodium hydroxide was run direct from the storage vessel into the tared dishes, which were then immediately set in position on the copper block and the desiccator closed and evacuated. In this way the exposure of the sodium hydroxide solutions to the air was reduced to a matter of 30 seconds. An analysis of a sample which was put through this process in a blank run showed the presence of 0.2% of the total alkali as carbonate. After the establishment of equilibrium, all four dishes were weighed, the initial and final weights of the sulfuric acid dishes giving their equilibrium composition. The sodium hydroxide dishes had not been weighed initially because of the risk of carbon dioxide contamination during weighing; therefore the equilibrium composition was determined by analysis as follows: the dish and its contents were transferred bodily to a beaker, diluted and titrated just past the end-point with sulfuric acid from a weight buret. After boiling out carbon dioxide a small back titration was made; thus the analysis gave the total alkali present. It was known, however, that the equilibrium solution contained approximately 0.2% of carbonate, the effect of which on the isopiestic ratio required consideration. A small amount of sodium carbonate was added to one of a pair of dishes containing sodium hydroxide solutions, and the normal course of equilibration and analysis was followed. It was found that the addition of 1.65% carbonate reduced the apparent isopiestic ratio calculated in the form $m_{H_2SO_4}/m_{NaOH}$ by 0.0041 at $5M$. The presence of 0.2% carbonate is therefore not likely to affect the ratios by more than 0.0005, which is of the order of the experimental error. The sulfuric acid used in analyzing the sodium hydroxide solutions was prepared from the same stock solution as was used in the sulfuric acid dishes, so that a slight error in the original analysis of the main stock would have practically no effect on the isopiestic ratios. Agreement between the duplicate dishes was usually better than 0.1% and often better than 0.03%. All molalities and analyses were based on vacuum corrected weighings. The experimental results are reported in Table I.

Calculation of Results.—Since the curve of the isopiestic ratio is very smooth and varies

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(1) A. T. Williamson, *Trans. Faraday Soc.*, **40**, 421 (1944).

(2) A. M. Hayward and E. P. Perman, *Trans. Faraday Soc.*, **27**, 59 (1931).

(3) G. Åkerlöf and G. Kegeles, THIS JOURNAL, **62**, 620 (1940).

(4) E. Shibata and F. Murata, *J. Chem. Soc. Japan*, **52**, 393 (1931).

(5) J. E. S. Han and T. Y. Chao, *Ind. Eng. Chem., Anal. Ed.*, **4**, 229 (1932).

(6) R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

TABLE I

ISOPIESTIC SOLUTIONS OF SODIUM HYDROXIDE AND SULFURIC ACID AT 25°

m_{NaOH}	$m_{H_2SO_4}$	m_{NaOH}	$m_{H_2SO_4}$	m_{NaOH}	$m_{H_2SO_4}$
1.988	1.673	2.115	1.772	2.322	1.928
3.240	2.589	3.865	3.040	4.000	3.141
4.382	3.425	4.647	3.619	5.682	4.376
6.358	4.881	6.509	5.002	6.693	5.144
7.838	6.056	8.803	6.865	10.037	7.937
10.927	8.744	12.551	10.228	13.621	11.240
15.601	13.029	18.140	15.082	19.596	16.184
19.642	16.194	21.986	17.831	23.872	18.990
23.896	19.012	25.826	20.103	26.316	20.346
26.693	20.553	26.802	20.601	26.912	20.691
27.262	20.880	27.447	20.950	28.745	21.650

only from 0.751 to 0.836 in the concentration range studied, the thirty-three points obtained were sufficient to define the curve. In Table II values of the isopiestic ratio $m_{H_2SO_4}/m_{NaOH}$, the water activity a_W, and the stoichiometrical activity coefficient γ, are given at round molalities. The water activities in sulfuric acid solutions above $4.5M$ were interpolated from the tables given by Shankman and Gordon[7]; at lower concentrations values were derived by combining the measurements of Scatchard, Hamer and Wood[8] on the isopiestic ratio $m_{NaCl}/m_{H_2SO_4}$ with those of Olynyk and Gordon[9] on the vapor pressures of sodium chloride solutions. The data of Shankman and Gordon are somewhat sparse in the range 15 to $20M$ sulfuric acid, though the deviation function which they used makes it possible to estimate a_W with reasonable accuracy. The isopiestic ratios, however, are known with an accuracy considerably exceeding that of the direct a_w values for sulfuric acid.

The activity coefficients of sodium hydroxide were computed relative to $2M$ by the equation of Randall and White.[10] At certain parts of concentration range the term $2\int \frac{h}{\sqrt{m}}\, d\sqrt{m}$ was replaced by the equivalent forms $\int \frac{h}{m}\, dm$ and $\int h\, d\ln m$, which were better adapted to tabular integration. The value of γ at $2M$ was taken as 0.711 from the previous work of Åkerlöf and Kegeles.[3]

Comparison with Other Work.—The a_W values interpolated to 25° from the data of Åkerlöf and Kegeles are included in Table II for comparison. It must be remembered that at high concentrations the water activity is very sensitive to small errors in the electromotive force. Even so, the agreement cannot be considered satisfactory. By taking the electromotive force results of Harned and Hamer[11] as standards for sulfuric acid the agreement is somewhat improved up to $8M$ sodium hydroxide but is even worse at higher concentrations. The vapor pressures up to $4M$ relative to $0.05M$ deduced by Harned and Hecker[12] from earlier measurements on cells of the type used by Åkerlöf and Kegeles are reasonably consistent with those in Table II, the average difference being 0.001 in a_W. The work of Hayward and Perman[2] between 30 and 80° has been used by Williamson[1] to estimate values at 25°, in the range 20–$28M$. These values are uniformly higher than the present results, by 0.012 in a_W. The e. m. f. measurements of Shibata and Murata[4] lead to a_W values very much lower than ours, the differences being of the order of 0.01. The e. m. f. of their cell was not very sensitive to the sodium hydroxide concentration, changing by only about 35 millivolts over the concentration

TABLE II

WATER ACTIVITIES, OSMOTIC COEFFICIENTS AND ACTIVITY COEFFICIENTS OF SODIUM HYDROXIDE SOLUTIONS AT 25°

m_{NaOH}	R	$a_W{}^a$	φ	γ	$a_W{}^b$
2.0	0.8414	0.9296	1.013	(0.711)	0.9296
2.5	.8235	.9096	1.052	.745	....
3.0	.8062	.8884	1.095	.788	.8880
3.5	.7937	.8661	1.140	.839	....
4.0	.7856	.8420	1.193	.904	.8406
4.5	.7800	.8164	1.251	.984	....
5.0	.7752	.7898	1.310	1.074	.7883
6.0	.7687	.7334	1.434	1.302	.7303
7.0	.7688	.6734	1.568	1.608	.6688
8.0	.7736	.6106	1.712	2.02	.6049
9.0	.7816	.5472	1.859	2.57	.5409
10.0	.7906	.4859	2.003	3.27	.4796
11.0	.8007	.4280	2.141	4.16	.4231
12.0	.8106	.3748	2.270	5.25	.3730
13.0	.8196	,3271	2.386	6.56	.3299
14.0	.8278	.2851	2.488	8.08	.2896
15.0	.8332	.2488	2.574	9.79	.2526
16.0	.8357	.2178	2.644	11.64	.2187
17.0	.8354	.1920	2,694	13.55	.1881
18.0	.8324	.1702	2.731	15.5	....
19.0	.8285	.1516	2.756	17.5	....
20.0	.8234	.1357	2.772	19.4	....
21.0	.8173	.1220	2.781	21.4	....
22.0	.8102	.1103	2.781	23.2	....
23.0	.8024	.1003	2.775	25.0	....
24.0	.7945	.0917	2.764	26.6	....
25.0	.7854	.0841	2.749	28.2	....
26.0	.7764	.0773	2.733	29.7	....
27.0	.7675	.0712	2.716	31.2	....
28.0	.7591	.0659	2.696	32.5	....
29.0	.7512	.0610	2.677	33.9	....

$R = m_{H_2SO_4}/m_{NaOH}$

[a] a_W values from corresponding sulfuric acid solutions.
[b] a_W values of Åkerlöf and Kegeles.

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(7) S. Shankman and A. R. Gordon, THIS JOURNAL, **61**, 2370 (1939).

(8) G. Scatchard, W. J. Hamer and S. E. Wood, *ibid.*, **60**, 3061 (1938).

(9) P. Olynyk and A. R. Gordon, *ibid.*, **65**, 224 (1943).

(10) M. Randall and A. M. White, *ibid.*, **48**, 2514 (1926).

(11) H. S. Harned and W. J. Hamer, *ibid.*, **57**, 27 (1935).

(12) H. S. Harned and J. C. Hecker, *ibid.*, **55**, 4838 (1933).

range 0.5 to 27*M*; consequently great accuracy cannot be expected from the method. Even so, the fact that their results are all low suggests that the cell reaction is not simply

$$HgO(s) + H_2(g) \longrightarrow H_2O(l) + Hg$$

but may be affected by such factors as partial adsorption of water by the electrode material with formation of hydroxides of mercury, or allotropic changes in the mercuric oxide as the concentration changes.

Acknowledgment.—The author wishes to acknowledge of the kind assistance of Dr. R. A. Robinson throughout the course of this work.

Summary

From isopiestic measurements at 25° on concentrated solutions of sodium hydroxide and sulfuric acid, values of the water activities and activity coefficients of sodium hydroxide have been calculated between 2 and 29*M*.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE STATE UNIVERSITY OF IOWA]

Solvate Formation by Certain Tetrahalides in Liquid Sulfur Dioxide

BY P. A. BOND AND WM. E. BELTON

Studies which have been made on the solubilities of the tetrahalides of the fourth periodic group in sulfur dioxide have resulted in the discovery of several systems where two liquid phases are in equilibrium with a single gas phase. Bond and Beach,[1] Bond and Stephens[2] and Bond and Crone[3] have reported upon systems formed by stannic chloride, stannic bromide, carbon tetrachloride, titanium tetrachloride and titanium tetrabromide with sulfur dioxide and have described these systems in terms of solubility and temperature. For each of these solutes the two liquid layers are well defined with the exception of those for stannic chloride which were found to be metastable. A solution of zirconium chloride did not form two liquid layers but gave a crystalline solvate having the composition $ZrCl_4 \cdot SO_2$.

Presence of this solvate suggested the possible occurrence of similar compounds of other tetrahalides with sulfur dioxide. These were found and this paper concerns itself with their isolation and the determination of their composition.

Analyses of the lower or heavy layers separated at a temperature slightly above the quadruple point gave the same composition as that of the respective solvates. These results do not, however, agree with those obtained previously by Bond and co-workers. In each case the composition of the lower layer as formerly reported showed a higher percentage of the tetrahalide than indicated for the solvates here investigated. For $TiCl_4$–SO_2 the percentages were 94.5 against 85.6, for $TiBr_4$–SO_2 96 against 92, and for $SnBr_4$–SO_2 94.07 against 93.2. The last two values are rather close. The fairly easy formation of metastable phases in the case of the titanium tetrahalide systems might have led to inaccuracy in tracing the curves, but this does not seem to be a complete explanation, for in the system $SiCl_4$–SO_2, Bond and Stephens,[2] no reasonable composition could be given for a solvate which would contain 99% $SiCl_4$ as required by the determined quadruple point. Further research on these systems is indicated, with especial attention to the possibility of the lowering of the melting point of the solvate by dissolved tetrahalide and the occurrence of a eutectic point between the quadruple point and the melting point of the tetrahalide.

Some research has also been done upon the vapor pressures of the solvates and their solutions. The results are incomplete and are not here reported.

Experimental

The liquid sulfur dioxide and the tetrahalides were prepared and purified according to the methods used by Bond and co-workers.[1,2,3] All apparatus used in the preparation of solutions and in the analyses of the compounds was designed to prevent the absorption of water from the air as was done in previous investigations.

The apparatus used to determine the composition of the solid phase is shown in Fig. 1. The flask A was prepared by closing one end of a 25-mm. glass tube 9.5 cm. in length and attaching an additional piece of glass rod to the sealed end to give additional weight and thus allow it to sink in a bath of acetone–solid carbon dioxide. A hollow ground glass stopper, C, was provided which served also as an inlet tube for the sulfur dioxide. Its elongated open tip extended well into the tube A so that the gas was delivered below the exit tube D.

After cleaning and drying at 110°, the flask was weighed while submerged in a bath of acetone cooled with solid carbon dioxide. This was accomplished by suspending it by a fine nichrome wire from the stirrup of an analytical balance placed above the bath. When the weight of the flask had been determined, it was removed from the bath and a portion of pure tetrahalide added. The flask was then closed and weighed in the bath at the same temperature. In order to ensure the largest possible contact of the solidified tetrahalide with the solvent, the flask was rotated and cooled slowly so that the solidified material was distributed on the sides as well as the bottom of the tube.

Pure dry sulfur dioxide was now passed through the center tube, C, and liquefied in the flask which had been replaced in the bath. When sufficient sulfur dioxide had been liquefied, the flask was detached, stoppered, removed from the bath and allowed to warm slightly until solution had occurred. It was then replaced in the bath and permitted to come to equilibrium at the desired temperature

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[1] Bond and Beach, THIS JOURNAL, **48**, 348 (1926).

[2] Bond and Stephens, *ibid.*, **51**, 2910 (1929).

[3] Bond and Crone, *ibid.*, **56**, 2028 (1934).