Determination of T_{50}.—A column of adsorbent 75 ± 2 mm. long was prepared in a chromatographic tube 9 × 130 (outside dia. 11 mm.) then solvent (about 2.5 ml.) was introduced and the time required for it to reach a point 50 mm. from the top of the column was measured with a stop-watch. This value was recorded as T_{50}. This measurement can usually be made in the same determination as S.

Summary

Several silicic acid samples and mixtures containing varying proportions of silicic acid and Celite have been evaluated as chromatographic adsorbents using the terms: S, measuring column packing, V_c and T_{50}, measuring rate of solvent flow, and R, measuring adsorption affinity. A linear relation was found between the composition of the mixtures and some function of each of the terms.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE, NEW ZEALAND]

The Derivation of Water Activities from Electromotive Force Data

BY R. H. STOKES

Introduction

The partial molar free energies of solvent and solute are connected by the Gibbs–Duhem equation

$$n_1 \mathrm{d}\bar{F}_1 = -n_2 \mathrm{d}\bar{F}_2$$

which becomes, for aqueous solutions, using the molality scale

$$55.51 \mathrm{~d} \ln a_W = -m \mathrm{~d} \ln a_2 \qquad (1)$$

a_2 representing the activity of the solute and a_W the water activity. In terms of the osmotic coefficient, $\phi = -(55.51/\nu m)\ln a_W$, and the stoichiometrical activity coefficient, γ, this leads to the equation of Randall and White[1]

$$-\ln \gamma = h + 2\int_0^m (h/\sqrt{m}) \mathrm{~d} \sqrt{m} \qquad (2)$$

where $h = 1 - \varphi$, by means of which water activity data are readily made to yield activity coefficients. The corresponding equation for converting activity coefficients into osmotic coefficients is

$$h = -(1/m)\int_0^m m \mathrm{~d} \ln \gamma \qquad (3)$$

This form is by no means as useful for computational purposes as (2), since the integral forms the whole of the required quantity instead of only a part as in (2). Consequently the graphical integration of m with respect to $\ln \gamma$ must be carried out with great accuracy and is a very time-consuming process. Furthermore, it frequently demands γ values at closer intervals than those experimentally available so that recourse must be had to interpolation formulas. A third disadvantage of equation (3) is that in certain cases where γ is derived from e. m. f. measurements on cells with hydrogen electrodes, the cell reaction involves water. In such cases γ cannot be evaluated without prior knowledge of the water activities and a series of approximations for γ and a_w is necessary until values consistent with (2) and (3) are obtained.

Accordingly the general method now presented, by which water activities may be derived directly from e. m. f. measurements on cells without transference, should be of interest.

Development of Equations

In a complete concentration cell without transference, of the type

$$\text{Electrode A} \,\Big|\, \underset{m_{\text{ref.}}}{\text{Electrolyte solution}} \,\Big|\, \text{Electrode B}—$$
$$\text{Electrode B} \,\Big|\, \underset{m}{\text{Electrolyte solution}} \,\Big|\, \text{Electrode A}$$

the cell reaction may be represented by: 1 molecule electrolyte at concentration m + r molecules of water in solution of concentration $m_{\text{ref.}}$ → 1 molecule electrolyte at concentration $m_{\text{ref.}}$ + r molecules water in solution of concentration m, per n electrons transferred. Here n is the valency of the ion of highest valency present and r is an integer depending on the specific cell used, usually zero, except in certain cells involving hydrogen or metal oxide electrodes.

The free energy change in such a cell is given by

$$-nEF = \bar{F}_2 - \bar{F}_{2\,\text{ref.}} - r(\bar{F}_W - \bar{F}_{W\text{ref.}}) \qquad (4)$$

Differentiating, since $n_{\text{ref.}}$ is constant

$$-nF \mathrm{~d}E = \mathrm{d}\bar{F}_2 - r \mathrm{~d}\bar{F}_W$$

which by equation (1) becomes

$$(nF/RT) \mathrm{~d}E = (55.51/m) \mathrm{~d} \ln a \;+ r \mathrm{~d} \ln a_W$$

$$(F/RT) \mathrm{~d}E = (55.51 + rm)/nm \mathrm{~d} \ln a_W$$

Hence

$$\ln a_w/a_{w\,\text{ref.}} = (F/RT) \int_{m_{\text{ref.}}}^{m} nm/(55.51 + rm) \mathrm{~d}E$$

Defining $m' = nm/(55.51 + rm)$, we have finally

$$\log a_W/a_{\text{ref.}} = F/(2.303\ RT) \int_{m'_{\text{ref.}}}^{m'} m' \mathrm{~d}E \qquad (5)$$

which gives an explicit expression for a_W in terms of the molalities and the electromotive forces. Equation 5 is a generalized form of that used by Åkerlöf and Kegeles[2] for the evaluation of water transfer potentials for the cell

$$H_2 \,\Big|\, \underset{m}{\text{NaOH}} \,\Big|\, Na_xHg - Na_xHg \,\Big|\, \underset{m_{\text{ref.}}}{\text{NaOH}} \,\Big|\, H_2$$

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[1] M. Randall and A. M. White, THIS JOURNAL, **48**, 2514 (1926).

[2] G. Åkerlöf and G. Kegeles, *ibid.*, **62**, 620 (1940).

In every case so far examined it has been found that a simple deviation function, $x = E + f(m')$, can be defined, in such a way that x varies by only a few millivolts over a concentration range where E varies by several hundred millivolts. The form of $f(m')$ is decided by trial: a logarithmic form, $x = E + \log m'$, is usually applicable below $1M$, while at higher concentrations the forms $x = E + b\sqrt{m'}$ or $x = E + cm'$ may be more suitable. We then have

$$\int m'\mathrm{d}E = \int m'\mathrm{d}x - \int f(m').\{\mathrm{d}\,f(m')/\mathrm{d}m'\}\mathrm{d}m' \quad (6)$$

The second term on the right is a simple analytical integral; the first term may be obtained by tabular or graphical integration. *Since the first term contributes only a few per cent. to the total value of* $\int m'\mathrm{d}E$, *it is readily evaluated with all the accuracy inherent in the e. m. f. determinations.* This accuracy is not obtained if the direct integration of m' with respect to E or of m to $\log \gamma$ is attempted.

Examples

(1) **Potassium Chloride.**—By the method outlined above water activities in solutions of potassium chloride have been evaluated at 25° using the e. m. f. measurements of Harned and Cook[3] on cells of the type

$$\mathrm{Ag{-}AgCl}\left|\underset{m_{\mathrm{ref.}}}{\mathrm{KCl}}\right|\mathrm{K_xHg{-}K_xHg}\left|\underset{m}{\mathrm{KCl}}\right|\mathrm{AgCl{-}Ag}$$

In such cells the reaction is simply the transfer of one molecule of salt from concentration m to concentration $m_{\mathrm{ref.}}$ for the passage of one electron. Hence $n = 1$, $r = 0$ and 5 becomes for 25°

$$\log a_{\mathrm{W}}/a_{\mathrm{W\,ref.}} = 0.3046 \int_{m_{\mathrm{ref.}}}^{m} m\mathrm{d}E$$

It is immaterial whether we use the actual e. m. f.'s observed, or add or subtract a constant amount. Therefore equation 5 is applicable either to complete concentration cells or to the half cells which are often in practice measured. The sign of E must be consistent with equation (4) and to achieve this it may be necessary to treat the published E values as negative.

In this case we used the logarithmic deviation functions

$x_1 = E - 0.1066 \log m$, up to $1M$

$x_2 = E - 0.1145 \log m$, from $1M$ to $4M$

The water activity at $0.1M$ was obtained from the value given by Hornibrook, Janz and Gordon.[4] The details of the calculations are presented in Table I, in order to illustrate the very small variation in x and the consequent small contributions of the first term in (5) to the total integral.

(2) **Sulfuric Acid.**—The measurements of Hamer[5] on the cell

$$\mathrm{(Pt)\ H_2|H_2SO_4|PbSO_4|PbO_2|(Pt)}$$

provide a more interesting example. The reaction in this cell is: $H_2 + H_2SO_4 + PbO_2 \rightarrow PbSO_4 + 2H_3O$. Hence in the complete concentration cell the reaction is

$$\underset{m}{\mathrm{H_2SO_4}} + \underset{\substack{\text{in soln. of}\\ \text{concn.}\\ m_{\mathrm{ref.}}}}{\mathrm{2H_2O}} \longrightarrow \underset{m_{\mathrm{ref.}}}{\mathrm{H_2SO_4}} + \underset{\substack{\text{in soln. of}\\ \text{concn.}\\ m}}{\mathrm{2H_2O}}$$

per two electrons transferred, so that in our notation $n = 2$, $r = 2$, $m' = 2m/(55.51 + 2m)$. The integration is made in several steps, using the deviation functions

0.0005 to $0.01M$	$x_1 = E - 0.07445 \log m'$
0.01 to $1M$	$x_2 = E - 0.06207 \log m'$
1 to $7M$	$x_3 = E - 0.75076\, m'$

The value of a_{W} at $0.0005M$ may be put equal to the mole fraction of water without introducing any error in the fifth decimal place; consequently the water activities are in effect evaluated absolutely. It is in cases of this kind, where both solute and solvent are involved in the cell reaction, that the present method is most advantageous. By transforming equation (4) into an equation in a_2 only, instead of a_{W} only, a similar integral formula for the activity coefficient may be obtained.

TABLE I

CALCULATION OF a_{W} IN POTASSIUM CHLORIDE SOLUTIONS AT 25° FROM THE DATA OF HARNED AND COOK

m	E	x_1	$0.3046\int_{0.05}^{m} m\mathrm{d}x_1$	$-\log a_{\mathrm{W}}$
0.05	0	0.13869	....	0.000733
.1	.03263	.13923	+0.000012	.001450
.2	.06478	.13929	+ .000015	.002863
.3	.08332	.13906	− .000002	.004256
.5	.10677	.13886	− .000027	.007051
.7	.12220	.13871	− .000054	.009844
1.0	.13866	.13866	− .000067	.014061
		x_2	$0.3046\int_{1}^{m} m\mathrm{d}x_2$	
1.0	.13866	.13866	....	.01406
1.5	.15768	.13752	− .00043	.02120
2.0	.17165	.13719	− .00061	.02860
2.5	.18274	.13718	− .00062	.03617
3.0	.19203	.13740	− .00043	.04393
3.5	.20030	.13800	+ .00016	.05210
4.0	.20759	.13865	+ .00090	.06042

$x_1 = E - 0.1066 \log m$ from 0.05 to 1 M

$x_2 = E - 0.1145 \log m$ from 1 to 4 M

$$-\log a_{\mathrm{W}}/a_{\mathrm{W}(0.05M)} = 0.3046 \int_{0.05}^{m} m\ \mathrm{d}x_1 + 0.01410\ (m - 0.05)$$

$$-\log a_{\mathrm{W}}/a_{\mathrm{W}(1M)} = 0.3046 \int_{1}^{m} m\ \mathrm{d}x_2 + 0.01515(m - 1)$$

E. m. f. measurements also have been reported[6] on the cell, $\mathrm{H_2|H_2SO_4|Hg_2SO_4{-}Hg}$, in which the cell reaction does not involve water. The deviation functions used in this case were

0.05 to $1M$, $x_1 = E + 0.0622 \log m$

1 to $17.5M$, $x_2 = E + 0.064\sqrt{m}$

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(3) H. S. Harned and M. A. Cook, THIS JOURNAL, **59**, 1290 (1937).

(4) W. J. Hornibrook, G. J. Janz and A. R. Gordon, *ibid.*, **64**, 513 (1942).

(5) W. J. Hamer, *ibid.*, **57**, 9 (1935).

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

TABLE II

ACTIVITIES AND PARTIAL MOLAL HEAT CONTENTS OF WATER IN SULFURIC ACID SOLUTIONS AT 25°

	a_W				$\bar{L}_1$		
m	Cell I	Cell II	Harned and Hamer	Shankman and Gordon	Cell I	Cell II	Calorimetric
0.01	0.99951	.....	0.99960	....	....	.....	....
.02	.99912	.....	.....	....	.....	.....	....
.05	.99801	0.99791	.99819	....	0.57	(0.57)	0.7
.1	.99628	.99616	.9964	....	1.2	1.2	1.2
.2	.99278	.99239	.....	....	1.8	1.8	1.8
.5	.98205	.98198	.9821	....	2.4	2.4	2.1
1	.96217	(.96217)	.9620	....	6.1	6.0	4.9
1.5	.9391	.9392	....	....	11.0	10.8	10.3
2	.9136	.9139	.9136	0.9129	19.2	19.0	19.4
3	.8505	.8508	.8506	.8514	57.2	57.0	52.4
4	.7771	.7776	.....	.7795	111.7	111.3	113.8
5	.6981	.6985	.6980	.7030	181.7	181.9	188.8
6	.6197	.6201	.....	.6252	255.7	255.2	272.3
7	.5453	.5458	.5453	.5497	340.4	339.6	368.7
9	.4175	.....	.....	.4165	....	521	546
11	.3171	.....	.....	.3110	....	714	756
13	.2378	.....	.....	.2304	....	906	958
15	.1763	.....	.....	.1698	....	1149	1150
17	.1289	.....	.....	.1252	....	1393	1338

Cell I : $H_2 \mid H_2SO_4 \mid PbSO_4 \mid PbO_2 \mid Pt$
Cell II: $H_2 \mid H_2SO_4 \mid Hg_2SO_4 \mid Hg$

The values have been calculated relative to $1M$, the value of a_W at $1M$ being taken from the calculations on the lead peroxide cell. The a_W values listed by Harned and Hamer, obtained in part by integrating the activity coefficients in a series of approximations, and in part by combining the measurements on the two types of cell, also agree well with those calculated by the present method. It is most unfortunate that this entirely self-consistent set of a_W values is in very poor agreement with those obtained from direct vapor pressure measurements.[7] These a_W values are compared in Table II.

Partial Molal Heat Content of the Solvent.—When e. m. f. measurements are made over a range of temperature, it is usual to express the e. m. f. as a quadratic in the temperature

$$E = E_{T_0} + a(T - T_0) + b(T - T_0)^2 \qquad (7)$$

the constants E_{T_0}, a and b being obtained by least-squaring the observations with respect to the temperature. Since we are now dealing with variations in both temperature and molality, we shall write (5) in the form

$$\ln a_W/a_{W\text{ref.}} = (F/RT)\int_{m'_{\text{ref.}}}^{m'} m' \, (\partial E/\partial m') \, \mathrm{d}m'$$

From (7)

$$\partial E/\partial m' = \partial E_{T_0}/\partial m' + (T - T_0)\partial a/\partial m' + (T - T_0)^2\partial b/\partial m'$$

Hence

$$\ln a_W/a_{W\text{ref.}} = (F/RT)\left[\int_{m'_{\text{ref.}}}^{m'} m'\mathrm{d}E_{T_0} + (T - T_0)\int_{m'_{\text{ref.}}}^{m'} m'\mathrm{d}a + (T - T_0)^2\int_{m'_{\text{ref.}}}^{m'} m'\mathrm{d}b\right]$$

Since the quantities under the integral signs are now independent of temperature, we may differentiate with respect to T, obtaining an expression for $\bar{H}_1$ the partial molal heat content of the solvent

$$\bar{H}_1 - \bar{H}_{1\text{ref.}} = -RT^2\partial\,(\ln a_W/a_{W\text{ref.}})/\partial T = -F\left[\int_{m'_{\text{ref.}}}^{m'} m'\mathrm{d}E_{T_0} - T_0\int_{m'_{\text{ref.}}}^{m'} m'\mathrm{d}a + (T_0^2 - T^2)\int_{m'_{\text{ref.}}}^{m'} m'\mathrm{d}b\right]$$

The evaluation of $\int m'\mathrm{d}E_{T_0}$ has already been considered; the other two integrals are readily obtained by graphical or tabular integration. As an example the derivation of $\bar{L}_1$ at 25° from the two types of sulfuric acid cell is of interest. For the lead peroxide cell, measurements at high dilutions ($0.0005M$) are available at which the heat content of the solvent is very nearly equal to that of pure water, so that for practical purposes we may take the quantity $\bar{H}_1 - \bar{H}_1$ ($0.005M$) as equal to $\bar{L}_1$. The values in the sixth column, of Table II have been computed in this way. The value at $0.05M$ may then be used as a basis for calculations from the mercurous sulfate cell, giving the seventh column of Table II, the last column of which contains data interpolated from the values (based on calorimetric measurements) quoted by Craig and Vinal.[8] The agreement between the e. m. f. results from the two types of cell is extraordinarily good whilst the calorimetric data are in fair agreement.

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

[8] D. N. Craig and G. W. Vinal, *J. Research Bur. Standards*, **24**, 475 (1940).

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 17*M* yielded results from which the water activity, a_W, can be interpolated at 25°. The saturated solution, however, is approximately 28*M* at this temperature. The electromotive forces of the cell

$$\mathrm{H_2}\left|\underset{m}{\mathrm{NaOH}}\right|\mathrm{HgO{-}Hg}$$

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 29*M* 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 5*M*. 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).