[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, DEPARTMENT OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

Activity of Orthophosphoric Acid in Aqueous Solution at 25° from Vapor Pressure Measurements[1]

BY KELLY L. ELMORE, CHARLES M. MASON AND JAMES H. CHRISTENSEN

In research on the preparation of phosphatic fertilizers, there developed a need for certain calculations that could be made only with a knowledge of the activity of orthophosphoric acid in aqueous solution. The present paper describes the derivation of the activity of phosphoric acid in aqueous solutions up to 80 molal from the measured pressure of water vapor over the solutions.

Vapor Pressure Measurements

The vapor pressure of water over solutions of thrice recrystallized phosphoric acid was measured by the isotonic (or isopiestic) method of Robinson and Sinclair.[2] The solutions were free of phosphorus acids of lower oxidation states. For reference standards, potassium chloride and sodium chloride were thrice recrystallized, and sulfuric acid was distilled in an all-glass apparatus. Stock solutions of the materials were analyzed by conventional methods, using atomic weights for 1943 in the calculations.

The apparatus differed from that of Mason[3] only to the extent that the brass equilibration vessel was provided with a liner and a bottle rack of fine silver to permit the use of phosphoric acid in the bottom of the vessel as the liquid medium for heat transfer where the concentration of the experimental solution of phosphoric acid exceeded 8 molal.

The technique was essentially that of Scatchard, Hamer and Wood[4] and of Mason.[3] A few drops of water were placed beneath the liner to ensure complete removal of air from the space between the liner and the outer vessel upon evacuation of the assembly. The evacuated assembly, after standing for an hour to degas the solutions, was re-evacuated, through a small opening, for twenty minutes. Equilibrium between the experimental and reference solutions was established by rocking the vessel through an angle of 15° at 30 cycles per minute for seven days in a water-bath maintained at 25.00 ± 0.01° with the control system suggested by Clapp.[5] This time was determined to be ample by comparison of the sodium chloride–potassium chloride molality ratios with similar ratios obtained by Scatchard, Hamer and Wood.[4]

The isotonic molalities are shown in Tables I and II. From these isotonic molalities the activity, a_1, of the solvent was obtained by the equation

$$\log a_1 = \frac{-\phi_r \nu_r m_r}{2.3026 M} = \log p/p_0 \qquad (1)$$

where ϕ_r, ν_r, and m_r are the osmotic coefficient, number of ions, and molality, respectively, of the reference solution, p and p_0 are the respective vapor pressures of the solution and of pure water, and M is the number of moles corresponding to 1000 g. of solvent (for water M = 55.51). The osmotic coefficients of sulfuric acid solutions, in concentrations up to 4 molal, and of potassium chloride and sodium chloride solutions were obtained from large-scale plots of the values given by Scatchard, Hamer and Wood.[4] Osmotic coefficients for sulfuric acid solutions in concentrations greater than 4 molal were obtained similarly from coefficients calculated from the vapor pressure data of Shankman and Gordon.[6]

TABLE I

ISOTONIC MOLALITIES AND ACTIVITIES OF WATER FOR SOLUTIONS OF ORTHOPHOSPHORIC ACID AT 25°

Reference standards, sodium chloride and potassium chloride.

$m_{H_3PO_4}$	m_{KCl}	m_{NaCl}	a_1 (KCl)	a_1 (NaCl)	a_1 (av.)	a_1 (eq. 9)
0.1659	0.1083	0.1099	0.9964	0.9963	0.9964	0.9964
.1794	.1120	.1166	.9963	.9961	.9962	.9962
.2342	.1490	.1480	.9951	.9951	.9951	.9950
.3034	.1908	.1876	.9937	.9938	.9938	.9938
.3321	.2086	.2180	.9932	.9928	.9932	.9932
.4798	.3018	.2956	.9902	.9902	.9902	.9903
.5899	.3680	.3612	.9881	.9881	.9881	.9881
.6406	.3998	.3915	.9871	.9871	.9871	.9871
.7790	.4910	.4799	.9842	.9842	.9842	.9843
.9040	.5719	.5569	.9817	.9816	.9817	.9818
1.0134	.6390	.6196	.9795	.9796	.9796	.9795
1.0675	.6726	.6535	.9785	.9784	.9785	.9784
1.6103	1.0435	.9993	.9668	.9669	.9669	.9667
1.7602	1.1471	1.0969	.9635	.9636	.9636	.9634
2.0445	1.3580	1.2904	.9569	.9570	.9570	.9570
2.1474	1.4332	1.3592	.9545	.9546	.9546	.9545
2.1645	1.4489	1.3713	.9541	.9542	.9542	.9541
2.5348	1.7269	1.6253	.9453	.9454	.9454	.9452
2.5622	1.7779	1.6763	.9437	.9436	.9437	.9446
2.9366	2.0480	1.9097	.9351	.9352	.9352	.9352
3.0575	2.1448	1.9926	.9320	.9322	.9321	.9321
3.9978	2.9209	2.6669	.9067	.9066	.9067	.9067
4.3306	3.2113	2.9047	.8971	.8973	.8972	.8971
5.5092		3.7763		.8611	.8611	.8612
5.7063	4.4436	3.9129	.8551	.8552	.8552	.8549
6.4949		4.5067		.8285	.8285	.8288
6.5724		4.5694		.8256	.8256	.8262
7.5356		5.2619		.7932	.7932	.7925
8.0280		5.6239		.7757	.7757	
8.5142		5.9769		.7584	.7584	
8.7020		6.1139		.7517	.7517	

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Atlantic City meeting of the American Chemical Society, April, 1946. Article not copyrighted.

[2] R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830–1835 (1934).

[3] C. M. Mason, *ibid.*, **60**, 1638–1647 (1938).

[4] G. Scatchard, W. J. Hamer and S. E. Wood, *ibid.*, **60**, 3061–3070 (1938).

[5] J. K. Clapp, *General Radio Experimenter*, **19**, No. 3, 1–7 (1944).

[6] S. Shankman and A. R. Gordon, THIS JOURNAL, **61**, 2370–2373 (1939).

TABLE II

ISOTONIC MOLALITIES AND ACTIVITIES OF WATER FOR SOLUTIONS OF ORTHOPHOSPHORIC ACID AT 25°

Reference standard, sulfuric acid.

$m_{H_3PO_4}$	$m_{H_2SO_4}$	a_1	$m_{H_3PO_4}$	$m_{H_2SO_4}$	a_1
1.0675	0.5973	0.9782	23.524	10.146	0.3528
1.7602	0.9694	.9633	24.854	10.619	.3289
2.9858	1.6192	.9331	28.202	11.746	.2778
4.3541	2.3082	.8962	28.768	11.861	.2732
5.1875	2.7320	.8690	28.995	12.068	.2649
9.1862	4.5628	.7367	31.044	12.536	.2470
9.5130	4.7401	.7231	31.982	12.827	.2366
10.284	5.0404	.6999	33.305	13.224	.2230
10.903	5.3309	.6774	34.099	13.414	.2167
11.070	5.4010	.6720	35.773	14.064	.1963
11.197	5.4660	.6669	37.824	14.428	.1857
11.938	5.7441	.6452	41.184	15.283	.1625
12.647	6.0190	.6237	43.035	15.733	.1518
13.550	6.4432	.5915	50.010	17.268	.1202
14.057	6.6349	.5765	57.265	18.766	.0957
15.685	7.2422	.5323	64.420	20.024	.0791
15.912	7.3646	.5237	64.659	20.064	.0786
18.034	8.1749	.4677	74.726	21.660	.0627
19.006	8.5554	.4432	120.56	27.01	
20.708	9.1841	.4084	134.00	29.37	
21.327	9.3940	.3937	217.4	33.69	
21.608	9.5043	.3874			

The experimental values for the activity of the water are compared in Fig. 1 with values calculated from the data of Kablukov and Zagvozdkin[7] and of Kasbekar.[8] In general, a_1 was obtained with a precision of one part in ten thousand for concentrations up to 10 molal; with further increase in the concentration of acid the precision lessened until, at 75 molal, it was one part in two hundred. The vapor pressure data of Shankman and Gordon[6] are sparse between 10 and 22 molal sulfuric acid, and their estimated error of 0.01 mm. or less limits the accuracy of the calculated activity of water over phosphoric acid solutions to about 0.5% above 25 molal phosphoric acid. A review of different osmotic coefficients[4,9] for potassium chloride, sodium chloride and sulfuric acid indicates that the error in a_1 for concentrations of phosphoric acid below 25 molal is less than 0.5%.

Activity of Phosphoric Acid in Aqueous Solution

Phosphoric acid is a weak electrolyte with the following dissociation constants: $K_1 = 7.516 \times 10^{-3}$ (ref. 10), $K_2 = 6.226 \times 10^{-8}$ (ref. 11), and $K_3 = 5 \times 10^{-13}$ (ref. 12). Since K_2 and K_3 show that the concentrations of $HPO_4^{=}$ and $PO_4^{\equiv}$ are negligible, the following treatment is based on the assumption that phosphoric acid is a one–one electrolyte.

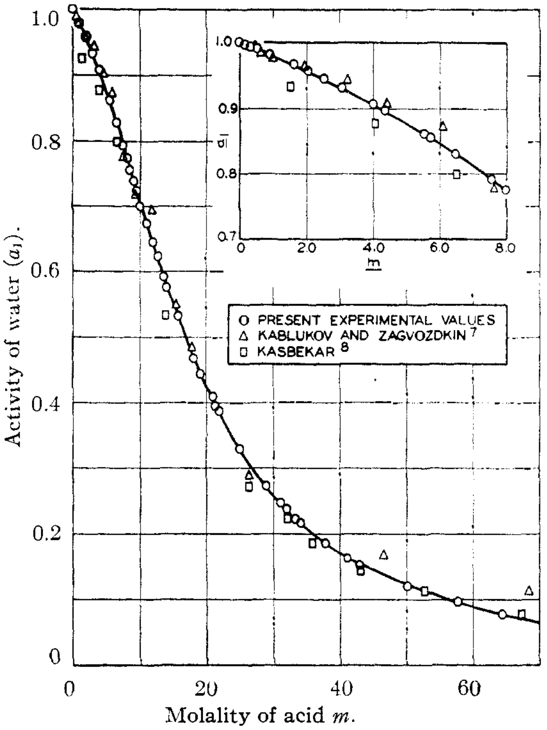

Fig. 1.—Activity of water over orthophosphoric acid solutions at 25°.

Van Rysselberghe[13] has shown that if a_u is taken as the activity of the undissociated part of a partially dissociated electrolyte in water, the Gibbs–Duhem equation for the system becomes

$$\mathrm{d}\log a_u = \frac{M}{m}\left(-\mathrm{d}\log a_1\right) \qquad (2)$$

Equation 2 may be used as a basis for the calculation of a_u if $-\log a_1$ is known as a function of m. Experimental data obtained by the isotonic method are not sufficiently accurate, however, for sharp delineation of the functional relationship between $-\log a_1$ and m below 0.1 molal, particularly as m approaches zero. An examination of published data on the freezing point and electrical conductance of phosphoric acid solutions indicated that the conductance data were the best source of a_u and consequently, by substitution in equation 2, the best source of $-\log a_1$ for concentrations of acid up to 0.1 molal.

For the first ionization of phosphoric acid

$$a_u = \frac{(\alpha m)^2 \gamma_{\pm}^2}{K_1} \qquad (3)$$

or

$$\log a_u = 2\left[1 + \frac{\log \alpha\, \gamma_{\pm}}{\log m}\right] \log m + pK_1 \qquad (4)$$

where α is the degree of dissociation and $\gamma_{\pm}$ is the mean activity coefficient of the ions.

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(7) I. A. Kablukov and K. I. Zagvozdkin, *Z. anorg. allgem. Chem.*, **224**, 315–321 (1935).

(8) G. S. Kasbekar, *J. Indian Chem. Soc.*, **17**, 657–662 (1940).

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943.

(10) L. F. Nims, THIS JOURNAL, **56**, 1110–1112 (1934).

(11) L. F. Nims, *ibid.*, **55**, 1946–1951 (1933).

(12) M. Jowett and H. Miller, *ibid.*, **51**, 1004–1010 (1929).

(13) P. Van Rysselberghe, *J. Phys. Chem.*, **39**, 403–414 (1935).

The degree of dissociation, α, to be used in equations 3 and 4 was determined from the conductance data of Noyes and Eastman[14] for phosphoric acid. The limiting conductance, Λ_0, first was calculated from the conductance data by the method of Shedlovsky.[15] Activity coefficients for the calculation were derived from the Debye–Hückel limiting law. Since there was a deficiency of experimental data in the very dilute region, the value obtained by the method of Shedlovsky ($\Lambda_0 = 378.3$) was adjusted until a plot of the conductance data[14] by the method described by Lugg[16] extrapolated to the value reported by Nims[10] for the first ionization constant of phosphoric acid. Application of the final value, $\Lambda_0 = 379.48$, in the calculation of α, the degree of dissociation, by the methods of Banks[17] and of Shedlovsky[15] yielded similar results. Values of α obtained by the method of Banks[17] and shown in Table III were used in subsequent calculations.

TABLE III

IONIZATION OF PHOSPHORIC ACID

m	α	m	α
0.01	0.6027	0.06	0.3473
.02	.4946	.07	.3301
.03	.4359	.08	.3162
.04	.3970	.09	.3040
.05	.3688	.10	.2938

The activity coefficient of the dihydrogen phosphate ion was calculated from data given by Stokes[18] for the activity coefficients of the potassium and sodium salts and data given by Harned and Owen[9] for the chlorides of potassium and sodium. The calculation was made by a method which has been outlined by Lewis and Randall[19] and which involves the assumption that in solutions of potassium chloride the activity coefficients of chloride ion and potassium ion are identical and equal to the mean ion activity coefficient of the salt. The activity coefficient of the dihydrogen phosphate ion thus calculated substantially followed the Debye–Hückel limiting law up to an ionic strength of 2.0. The mean ion activity coefficient of phosphoric acid therefore was calculated at the reference concentration (0.1 molal H_3PO_4; $\mu \sim 0.03$) by means of the Debye–Hückel limiting law, $\log \gamma_\pm = -0.5085 \sqrt{\alpha m}$, on the assumption that the activity coefficient of hydrogen ion follows the limiting law up to an ionic strength of 0.03.

The calculated values of α and $\gamma_\pm$ were used to evaluate the term, $\log \alpha\gamma_\pm/\log m$, in equation 4. The empirical equation

$$\frac{\log \alpha\gamma_\pm}{\log m} = Am^B + C \sin Dm^E \qquad (5)$$

was found to fit the conductance data in the concentration range from 0.01 to 0.1 molal and to approach zero concentration properly, the constants having the values, $A = 2.9554$, $B = 0.67886$, $C = 0.022$, $D = 46.37$, and $E = 0.86805$.

Calculation of the Activity of Water over Phosphoric Acid in Concentrations up to 0.1 Molal.—To test the validity of equation 5 and the reliability of the calculated values of α and $\gamma_\pm$, the vapor pressure of aqueous solutions of phosphoric acid up to 0.1 molal was calculated from the conductance data. This was done as follows.

Integration of equation 2 yields

$$-\log a_1 = \frac{1}{M}\int m \, \mathrm{d} \log a_u \qquad (6)$$

To evaluate the right-hand term of equation 6, an expression for d log a_u was obtained by differentiating equation 4 after substitution of $\log \alpha\gamma_\pm/\log m$ from equation 5. This operation leads to the relation

$$-\log a_1 = 0.015649m \left\{ 1 + \frac{2.30259ABm^B}{B+1} \left[\frac{1}{2.30259B(B+1)} + \log m \right] \right\} + \frac{2C}{M}\int m \, \mathrm{d}\, (\sin Dm^E \log m) \qquad (7)$$

where the constants have the same values as in equation 5. The last term in equation 7, which is most easily evaluated graphically, affects the calculated values of $-\log a_1$ by about 1% at most, generally less. To compare equation 7 with experimental results, the activity of water over dilute phosphoric acid solutions at the freezing point was calculated from freezing point data given in the International Critical Tables[20] and then recalculated to 25°; partial molal heat values needed in the calculations were derived from the thermochemical data given by Bichowsky and Rossini[21] for phosphoric acid. The activity thus calculated from freezing point data is compared in Fig. 2 with that from equation 7.

It can be demonstrated that the relationship between $-\log a_1$ and m with approach to zero concentration is

$$\lim_{m \to 0} \frac{\mathrm{d}}{\mathrm{d}m}(-\log a_1) = \frac{2}{2.3026M} \qquad (8)$$

With water as the solvent the final expression in equation 8 becomes 0.015649, which is the limiting slope that should be approached by any equation derived from experimental data for the functional relationship between $-\log a_1$ and m

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(14) A. A. Noyes and G. W. Eastman, *Carnegie Inst. Wash. Pub.*, **63**, 262 (1907).

(15) T. Shedlovsky, *J. Franklin Institute*, **225**, 739–743 (1938).

(16) J. W. H. Lugg, THIS JOURNAL, **53**, 1-8 (1931).

(17) W. H. Banks, *J. Chem. Soc.*, 3341–3342 (1931).

(18) J. M. Stokes, *Trans. Faraday Soc.*, **41**, 685–688 (1945).

(19) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, p. 381.

(20) "International Critical Tables," Vol. IV, p. 255.

(21) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

for a one–one electrolyte. This requirement is satisfied by equation 7.

A comparison of the results calculated by equation 7 and the limiting slope from equation 8 is shown in Fig. 2.

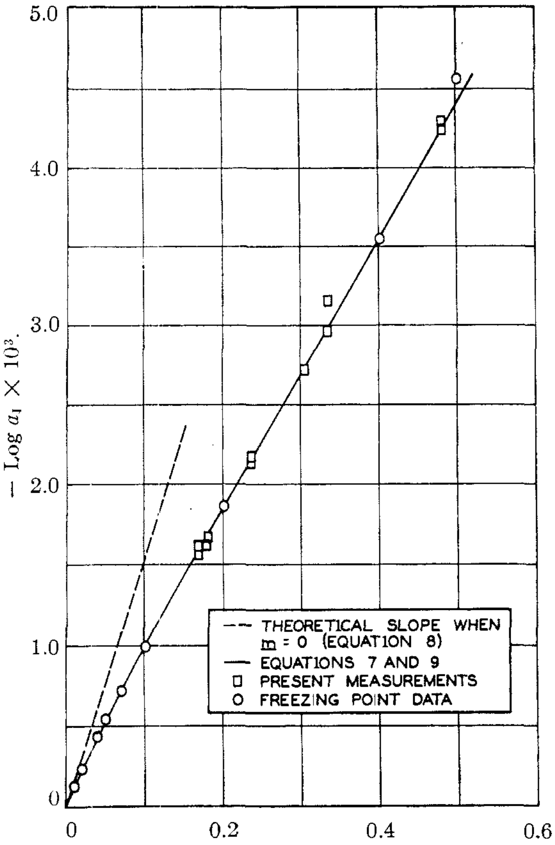

Fig. 2.—Comparison of equations 7 and 9, experimental values, and the theoretical limiting slope for the activity of water over phosphoric acid solutions at 25°.

Calculation of a_u.—Values for the term, $\log \alpha\gamma_\pm/\log m$, as determined from equation 5, were substituted in equation 4 to yield the values of a_u shown in Table IV for concentrations up to 0.1 molal.

For concentrations in the range 0.1 to 7.5 molal, the empirical equation

$$-\log a_1 = Fm^{-1/2} + Gm + Hm^{3/2} + Im^2 \quad (9)$$

was obtained from the isotonic data plus the value derived from equation 7 for a_1 at 0.1 molal. The constants in equation 9 were determined to be $F = 0.0000385103$, $G = 0.00919754$, $H = -0.00144925$ and $I = 0.00108557$. Values of a_1 calculated from equation 9 are compared in Table I and Fig. 2 with the experimental values. Equation 9 and the value of a_u at 0.1 molal from equation 4 were substituted into equation 2 and integrated to give

$$\log a_u = F'm^{-3/2} + G' \log m + H'm^{1/2} + I'm + U \quad (10)$$

for the range 0.1 to 7.5 molal, the constants having the values, $F' = 0.000712466$, $G' = 1.175517$, $H' = -0.241327$, $I' = 0.120512$ and $U = 0.103062$.

For concentrations of 7.5 to 80 molal, equation 2 was evaluated graphically between the limits of 7.5 and m from a large-scale plot of $1/m$ against $-\log a_1$. Table IV shows the calculated activity of phosphoric acid over the three adjoining ranges of concentration, together with correspond-

TABLE IV

ACTIVITY AND RELATIVE PARTIAL MOLAL FREE ENERGY OF PHOSPHORIC ACID IN AQUEOUS SOLUTION AT 25°

Free energy in 15° calories.

m	a_u	$\bar{F}_2 - \bar{F}_2^0$	$-(\bar{F}_1 - \bar{F}_1^0)$	m	a_u	$\bar{F}_2 - \bar{F}_2^0$	$-(\bar{F}_1 - \bar{F}_1^0)$
0.01	0.003969	−3275	0.171	12	80.18	2597	261.2
.02	.01031	−2710	.317	14	125.9	2864	323.6
.03	.01738	−2400	.454	16	187.0	3098	387.3
.04	.02495	−2186	.588	18	265.6	3306	450.1
.05	.03291	−2022	.706	20	358.8	3484	510.4
.06	.04120	−1889	.852	22	471.7	3646	574.6
.07	.04975	−1777	.983	24	603.8	3793	633.9
.08	.05851	−1681	1.11	26	751.4	3922	688.0
.09	.06752	−1596	1.24	28	913.5	4038	746.3
.10	.07688	−1520	1.37	30	1091	4143	803.3
.2	.1605	−1083	2.50	32	1280	4238	854.8
.3	.2493	− 823	3.62	34	1479	4323	906.1
.4	.3417	− 636	4.84	36	1684	4400	956.0
.5	.4373	− 490	6.02	38	1895	4470	1013
.6	.5360	− 369	7.21	40	2111	4534	1048
.7	.6377	− 266	8.41	42	2330	4592	1096
.8	.7425	− 176	9.63	44	2551	4646	1137
.9	.8504	− 96	10.86	46	2775	4696	1174
1.0	.9615	− 23	12.10	48	3001	4742	1219
1.5	1.569	267	18.56	50	3228	4786	1266
2.0	2.275	487	25.46	52	3458	4826	1296
2.5	3.096	669	32.82	54	3690	4865	1333
3.0	4.051	829	40.72	56	3922	4901	1363
3.5	5.165	972	49.13	58	4155	4935	1393
4.0	6.461	1105	58.08	60	4386	4967	1424
4.5	7.968	1229	67.58	62	4615	4997	1459
5.0	9.721	1347	77.66	64	4839	5025	1491
5.5	11.76	1460	88.30	66	5058	5052	1525
6.0	14.12	1568	99.53	68	5271	5076	1551
6.5	16.86	1673	111.4	70	5473	5098	1578
7.0	20.03	1775	123.8	72	5667	5119	1605
7.5	23.71	1875	136.8	74	5850	5138	1631
8.0	27.96	1973	149.7	76	6025	5155	1656
9.0	37.79	2151	177.4	78	6189	5171	1673
10.0	48.97	2305	203.6	80	6343	5186	1698

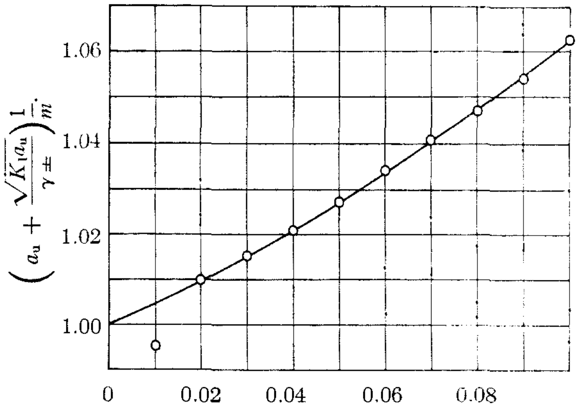

Fig. 3.—Test of calculated value of a_u as a function of m.

ing values for the relative partial molal free energy of the solute and solvent as calculated from the equation

$$\overline{F} - \overline{F}_0 = RT \ln a \qquad (11)$$

Theoretical Check of Calculated Values of a_u.—The function, $\left(a_u + \frac{\sqrt{K_1 a_u}}{\gamma_\pm}\right)\frac{1}{m}$, which is obtained from equation 3 and the total phosphate concentration, m = ($H_2PO_4^-$) + (H_3PO_4), should approach unity as m approaches zero. The values of a_u in Table IV were tested and confirmed by plotting this function against m as shown in Fig. 3. The dislocation of the point at 0.01 molal indicates a slight error in α which is magnified by the very sensitive test.

Acknowledgment.—The assistance of A. D. Jones in many of the calculations and of Winifred M. Blum in the experimental work is acknowledged.

Summary

The vapor pressure (water activity) over orthophosphoric acid in concentrations of 0.16 to 75 molal has been determined at 25°, and the results have been used in the calculation of the activity of the solute and the relative partial molal free energy of both the solute and solvent over the concentration range from 0.01 to 80 molal.

WILSON DAM, ALABAMA

RECEIVED MAY 20, 1946

[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF OSLO UNIVERSITY]

Electrolytic Conductivity of NaOH in H_2O and of NaOD in D_2O at 25°. A Vacuum Distilling Apparatus for Deuterium Oxide

BY ENOK HETLAND

In a previous paper[1] measurements were reported for the conductance of dilute aqueous solutions of the strong acids HCl and DCl at 25°. The present communication presents similar measurements on solutions of NaOH and of NaOD.

If accurate conductance measurements of aquous solutions are to be carried out at low concentrations it is necessary to use water of especially high purity. Also, in the case of alkalies, special precautions were taken to avoid contaminations from the carbon dioxide in the air. For this purpose all measurements were carried out in an atmosphere of hydrogen.

Experimental

Distilling Apparatus.—In order to obtain water of of sufficient purity, a vacuum distilling apparatus, only mentioned in the previous paper, will be described here. Figure 1 shows this apparatus which was built of "Jena Geräteglas." It was evacuated using an ordinary water jet pump. The valves V_1, V_2, V_3 and V_4, each containing an iron core, can be opened by solenoids which are not shown in the drawing. The reservoir K_2 is filled from K_1 by lifting the valve V_1. Radiation from two electric heat elements S-S keeps the water in K_2 boiling. The vapor is condensed in K_4, and the conductivity of the distillate can be measured at any time using the electrodes C. After the apparatus had been in use for some time, and if about 1 mg. of citric acid per liter was added to reservoir K_2 and distillation carried out for a half hour or more, the conductivity was usually below 1.10^{-7} ohm^{-1}. From the bulb K_5 the distillate can be led back to K_2 by opening the valve V_3 or out of the system through V_4. The apparatus can also be emptied through the valve V_2 when necessary. The jet pump was operated continuously during the distillation in order to remove the air and assure that the system contained only water vapor. Uninterrupted, steady boiling in K_2 was obtained by using an electrical heating coil W and a bulb K_3. This provided a flow of steam through the tube T. The first trap F_1 was cooled with an ice–salt mixture, the second F_2 with acetone–carbon dioxide to prevent the heavy water from escaping through the pump. After the apparatus had been in use for some time a new bulb was added to the system parallel to K_2 (not shown in the figure). This allowed greater quantities of water to be distilled in the same run and the boiling became more steady.

Conductivity Cells.—Two cells were used, one of transparent quartz for very dilute solutions and one of "Jena Normalglas" (16 III) for more concentrated solutions. The cell constants were respectively 1.6455 and 65.66. Figure 2 shows the latter. The former, described in the previous paper, had a similar construction. In order to secure uniform concentration of the solution and to be able to renew the solution between the electrodes during the measurements, the mounting of the cell allowed it to be tipped about the axis A-A and then brought back into the original position. The tubes T-T (Fig. 2) connected to each other by the tube U made it possible to carry out the measurements in an atmosphere of hydrogen, to avoid contamination by carbon dioxide and other impurities in the air.

Bridge.—The direct reading bridge was essentially the same as that described by Jones and Josephs.[2] It was, however, not shielded. Shielding of several parts of it was found to have negligible effect. The errors in the bridge readings were far below 0.1% except for the lowest resistances in which case it might reach this value. Precision dial resistance boxes 0.1 to 100,000 ohms were used. Between 100,000 and 1,000,000 ohms, however, a precision binding post box was used. The bridge was connected to a vacuum tube oscillator with a frequency of 1800 cycles per second, and a high resistance telephone without amplifier was used as detector.

Procedure.—At the start of a run the cell was cleaned with water from the vacuum distilling apparatus, two of which were constructed, one for heavy and one for ordinary water. The cell was then dried by evacuating with a water jet pump, filled with pure hydrogen gas to atmospheric pressure, closed with short rubber tubings and Hofmann pinchcocks, weighed and connected to the distilling apparatus by the rubber tubing G_3 in a manner

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(1) O. E. Frivold, O. Hassel and E. Hetland, *Avhandl. Norske Videnskaps-Akad. Oslo, I. Mat.-Naturv. Klasse*, No. 9 (1942).

(2) Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).