difference of nearly 20° in the absolute temperatures, which seems a little large to be ascribed to experimental error. It should be noted, however, that the kinetics of the propylamine decomposition which we find correspond in detail to those for ethylamine found by Schumacher and Wiig,[6] whose rates are also considerably slower than those of Taylor.[7] We also find a somewhat larger temperature coefficient than do Taylor and Achilles; we find about 51 Cal. compared to their 44 Cal., but as it seems to have but little significance the details of the calculation are not given here.

Summary

The thermal decomposition of *n*-propylamine has been extended to low pressures. Below 4 mm. the reaction is first order, but is strongly inhibited by increased surface; this effect diminishes and finally disappears at higher pressures. The reaction is probably a chain.

CAMBRIDGE, MASS. RECEIVED AUGUST 25, 1934

(6) Schumacher and Wiig, *Z. physik. Chem.*, **162A**, 419 (1932).

(7) H. A. Taylor, *J. Phys. Chem.*, **34**, 2761 (1930).

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Vapor Pressures and Activity Coefficients of Aqueous Solutions of Calcium and Aluminum Nitrates at 25°(1)

BY J. N. PEARCE AND L. E. BLACKMAN

In recent papers[2] were reported the vapor pressures and the activity coefficients of aqueous solutions of several strong binary electrolytes. The present paper deals with the results of a similar study of aqueous solutions of calcium and aluminum nitrates.

The apparatus employed is exactly the same as that used in the previous work, except that the number of electrolytic cells has been increased to forty. In this way the volume of electrolytic gas generated per equivalent of silver has been doubled and the errors of measurement have been reduced considerably.

The "analyzed" salts were further purified by repeated crystallization. Nearly saturated mother solutions of each salt were prepared and the weight composition of each was determined accurately by approved methods. Definite weights of these solutions were diluted with conductivity water to give the desired weight molal concentration. The density of each solution was determined accurately by means of a 100-cc. pycnometer recently devised by Pearce. Duplicate weights of the solutions used in the density measurements check easily to one part in one million. All weighings were made with certified brass weights and are corrected for air buoyancy (N. T. P.).

The essential data for the two nitrates are collected in Tables I and II. Each value of p indicated is the mean of three to six independent vapor pressure measurements. The maximum deviation from the mean for any solution did not exceed 0.003 mm. The remaining familiar symbols require no explanation.

TABLE I

VAPOR PRESSURE, ACTIVITY AND FREE ENERGY DATA OF AQUEOUS SOLUTIONS OF CALCIUM NITRATE AT 25°

m	p, mm.	a_1	$h/m^{1/2}$	$\gamma_\pm$	$-\Delta\overline{F}_1$, cal.	$-\Delta F_2^{0.1}$, cal.
0.0	23.752	1.0000	1.365	1.000	....	...
.1	23.659	0.9961	0.868	0.661	2.32	0000
.2	23.566	.9922	.587	.551	4.72	908
.4	23.373	.9841	.405	.452	9.53	1788
.6	23.160	.9751	.286	.396	14.96	2275
.8	22.915	.9647	.190	.356	21.26	2598
1.0	22.638	.9531	.111	.325	28.48	2831
1.5	21.868	.9207	− .016	.351	48.98	3691
2.0	21.002	.8843	− .097	.411	72.88	4479
2.5	20.042	.8438	− .162	.558	100.7	5425
3.0	19.107	.8044	− .198	.684	129.0	6110
3.5	18.118	.7628	− .231	.821	160.5	6708
4.0	17.098	.7198	− .260	1.036	194.9	7359
5.0	15.008	.6319	− .312	1.516	272.1	8433
6.0	13.062	.5499	− .345	2.035	354.5	9280
7.0	11.260	.4741	− .368	2.612	442.4	9999
8.0	9.603	.4043	− .386	3.211	536.8	10603
8.3601[a]	9.041	.3806	− .394	3.486	572.5	10827

[a] Saturated. $a_2 = 27(\gamma m)^4$.

The activity of the water, a_1, in the various solutions may be calculated directly from the

(1) A brief abstract of a dissertation presented to the Graduate College of the State University of Iowa by Leslie Everett Blackman in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

(2) Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932); **55**, 3075 (1933).

TABLE II

VAPOR PRESSURE, ACTIVITY AND FREE ENERGY DATA OF AQUEOUS SOLUTIONS OF ALUMINUM NITRATE AT 25°

m	p, mm.	a_1	$h/m^{1/2}$	$\gamma_\pm$	$-\Delta\overline{F}_1$, cal.	$-\Delta\overline{F}_2^{0.1}$, cal.
0.0	23.752	1.0000	2.895	1.000	....	...
.1	23.648	0.9956	1.236	0.419	2.60	0000
.2	23.500	.9894	0.804	.314	6.33	958
.4	23.235	.9782	.374	.226	13.05	1822
.6	22.860	.9624	.148	.187	22.69	2331
.8	22.405	.9433	− .014	.169	34.61	2780
1.0	21.911	.9224	− .121	.229	47.88	4032
1.5	20.386	.8583	− .340	.505	90.61	6859
2.0	18.561	.7814	− .503	1.302	146.2	9237
2.5	16.678	.7013	− .613	1.870	210.3	11175
3.0	14.860	.6256	− .674	2.815	278.0	12578
3.1607[a]	14.370	.6050	− .678	2.966	297.8	12825

[a] Saturated. $a_2 = 27(\gamma m)^4$.

fractional lowering of the vapor pressure by means of the series relation[3]

$$\ln a_1 = -\frac{p_0 - p}{p_0} - \frac{1}{2}\left(\frac{p_0 - p}{p_0}\right)^2 - \frac{1}{3}\left(\frac{p_0 - p}{p_0}\right)^3 - \dots$$

With increase in concentration successive terms must be added to the series until the addition of a further term produces no change in the value of the logarithm. This procedure becomes tedious and irksome when very soluble salts are employed and a very large number of terms become necessary.

Mathematically considered, the obvious limit of the series for any given concentration is

$$\ln\left[1 - \frac{p_0 - p}{p_0}\right], \text{ or}$$

$$a_1 = [1 - (p_0 - p)/p_0]$$

Thus, the calculation is greatly simplified; the activity of the solvent is simply equal to one minus the fractional lowering of the vapor pressure produced by the salt.

The activity coefficients of the ions were calculated from the activity of the solvent by means of the relation[4]

$$\log \gamma = -\frac{h}{2.303} - \frac{2}{2.303}\int^{m^{1/2}} \frac{h}{m^{1/2}}\,dm^{1/2}$$

where $h = (55.51 \ln a_1/\nu m) + 1$, and νm is the total number of ions from m moles of salt. Randall[5] has shown that if the values of $h/m^{1/2}$ are plotted against the square root of the molality the curves will approach definite limiting values at $m = 0$, which are characteristic for each valence type. These limiting values for calcium nitrate and aluminum nitrate are 1.365 and 2.895, respectively. The plots are shown in Fig. 1. Except for the most dilute solution of each salt, the points fall uniformly on a smooth curve. To calculate the value of the activity coefficient in any solution of molality, m, it is necessary to determine first the value of the integral, or the area under the curve from $m = 0$ up to the desired concentration. This was done by means of a polar planimeter.

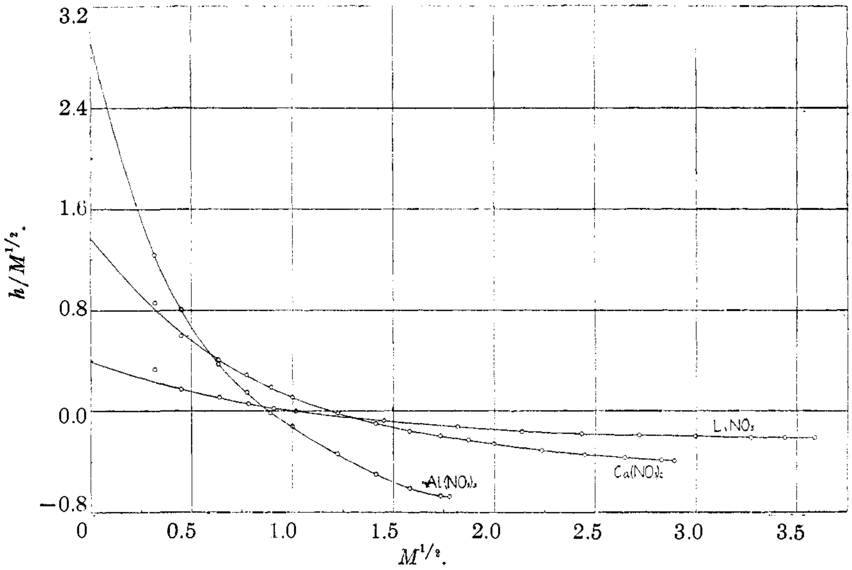

Fig. 1.

The change in free energy accompanying the transfer of one mole of salt from any concentration, m, to one in which the activity of the salt is unity was first calculated by means of the relation $\Delta\overline{F}_2 = RT \ln a_2$, where a_2 is calculated from activity coefficients and molalities by the relation, $a_2 = \nu_+^{\nu_+}\nu_-^{\nu_-}(\gamma m)^{\nu_+ + \nu_-}$. By the proper addition of these free energy changes we obtained the change in free energy accompanying the transfer of one mole of salt from any solution of concentration, m, to one exactly 0.1 m. The change in free energy accompanying the transfer of one mole of water from the pure solvent to any solution in which its activity is a_1 was calculated by means of the relation, $\Delta\overline{F}_1 = RT \ln a_1$. The ac-

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(3) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 274.

(4) Randall and White, THIS JOURNAL, **48**, 2514 (1926).

(5) Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

tivity and free energy data obtained for the two salts are collected in Tables I and II. The variation of the activity coefficients with the concentration is shown in Fig. 2.

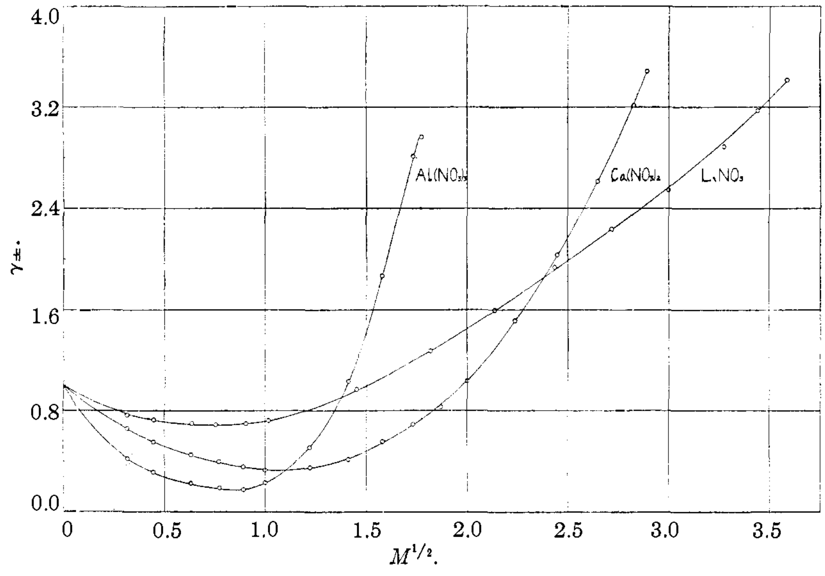

Fig. 2.

The change in the fractional lowering of the vapor pressure with the concentration is shown graphically in Fig. 3. We have included herewith the corresponding plot for solutions of the uni-univalent salt, lithium nitrate. According to Raoult's law, the fractional lowering of the vapor pressure of the solvent is equal to the mole fraction of the solute in the solution. If we assume that the three nitrates are completely dissociated at all concentrations, and, further, that the ions behave as perfect solutes, the fractional lowering produced by the three salts at any concentration should be given by

$$\text{Lithium nitrate } \frac{p_0 - p}{p_0} = \frac{2n_2}{n_1 + 2n_2}$$

$$\text{Calcium nitrate } \frac{p_0 - p}{p_0} = \frac{3n_2}{n_1 + 3n_2}$$

$$\text{Aluminum nitrate } \frac{p_0 - p}{p_0} = \frac{4n_2}{n_1 + 4n_2}$$

Here n_1 is 55.51, or the number of moles in 1000 g. of water, and $2n_2$, $3n_2$, $4n_2$ are the number of moles of ions formed from one mole of the respective salts. The solid curves in Fig. 3 represent what the fractional lowering should be if the ions of the completely dissociated salts formed ideal solutions.

The solution volumes were calculated from the densities by the relation

$$V = (1000 + mM)/d$$

where m is the number of moles of molecular weight M in 1000 g. of water. The volumes of the solutions thus calculated may in turn be expressed as a function of the concentration, that is

$$V = \alpha + \beta m + \gamma m^2$$

Differentiating the latter equation with respect to m gives immediately an expression for calculating the partial molal volumes of the salt, or $V = \beta + 2\gamma m$. Here, α is the volume at $m = 0$, and β and γ are constants characteristic of the salt. The values for the constants were calculated by the method of least squares. The equations for the two salts are

$Ca(NO_3)_2$: $V = 1002.9621 + 37.5265m + 2.1641m^2$

$Al(NO_3)_3$: $V = 1003.0730 + 52.8899m + 5.0894m^2$

Knowing the volume of the solution and the partial molal volume of the salt, we calculated the partial molal volume of the water in each solution by the relation, $V = n_1\bar{v}_1 + n_2\bar{v}_2$. That is, $\bar{v}_2 = (V - n_2\bar{v}_2)/55.51$. The densities of the solutions, the deviations of the calculated solution volumes and the partial molal volumes of the solvent and salts are collected in Tables III and IV.

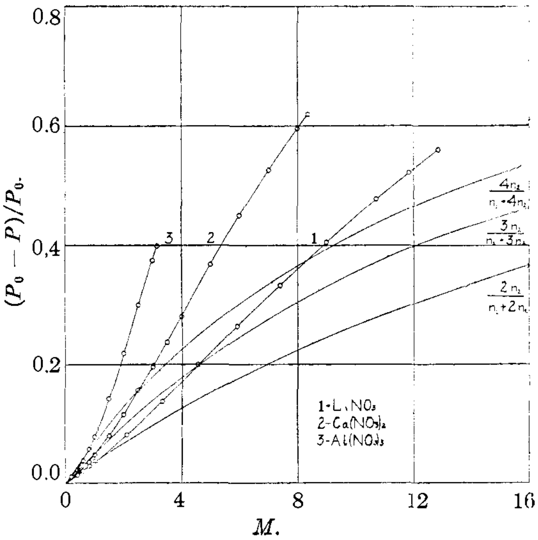

Fig. 3.

TABLE III

THE PARTIAL MOLAL VOLUMES OF CALCIUM NITRATE AND OF WATER IN AQUEOUS SOLUTIONS AT 25°

m	d	$V_{\text{obs.}}$, cc.	ΔV, cc.	$\bar{v}_2$, cc.	$\bar{v}_1$, cc.
0.0	0.997071	1002.938	−0.024	37.526	18.068
.1	1.009670	1006.664	− .072	37.959	18.066
.2	1.022093	1010.494	− .060	38.392	18.065
.4	1.046507	1018.281	− .124	39.258	18.061
.6	1.070371	1026.239	− .018	40.123	18.054
.8	1.093683	1034.373	− .005	40.989	18.043
1.0	1.116449	1042.676	.013	41.875	18.029
1.5	1.170956	1064.210	.089	44.019	17.982
2.0	1.222150	1086.766	.095	46.183	17.914
2.5	1.270014	1110.410	.106	48.347	17.826
3.0	1.314619	1135.148	.130	50.511	17.720
3.5	1.356078	1160.948	.134	52.675	17.593
4.0	1.394473	1187.820	.127	54.839	17.447
5.0	1.462485	1244.785	.089	59.167	17.095
6.0	1.519536	1306.040	.013	63.495	16.666
7.0	1.566558	1371.587	− .099	67.823	16.156
8.0	1.604500	1441.426	− .247	72.151	15.569
8.3601[a]	1.616059	1467.619	− .314	73.710	15.338

[a] Saturated.

TABLE IV

THE PARTIAL MOLAL VOLUMES OF ALUMINUM NITRATE AND OF WATER IN AQUEOUS SOLUTIONS AT 25°

m	d	$V_{\text{obs.}}$, cc.	ΔV, cc.	$\bar{v}_2$, cc.	$\bar{v}_1$, cc.
0.0	0.997071	1002.938	−0.135	52.890	18.068
.1	1.012725	1008.471	.058	53.908	18.068
0.2	1.028301	1013.904	0.049	54.926	18.067
.4	1.058649	1025.077	.034	56.961	18.056
.6	1.087913	1036.659	.020	58.997	18.037
.8	1.116096	1048.651	.009	61.033	18.012
1.0	1.143200	1061.051	− .001	63.069	17.978
1.5	1.206298	1093.842	− .017	68.158	17.864
2.0	1.262843	1129.188	− .022	73.247	17.703
2.5	1.313080	1167.092	− .014	78.337	17.497
3.0	1.357277	1207.551	.004	83.428	17.245
3.1067[a]	1.370250	1221.098	.013	85.062	17.154

[a] Saturated.

Summary

The vapor pressures of aqueous solutions of calcium nitrate and of aluminum nitrate at 25° have been measured for concentrations ranging from 0.1 m to the saturated solution in contact with the solid crystals.

From the vapor pressure data we have calculated the activity of the solvent and the activity coefficients of the ions at each concentration, and the free energy of dilution of both the solute and the solvent. The partial molal volumes of the solvent and salts have been calculated.

IOWA CITY, IOWA RECEIVED AUGUST 29, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Sulfuric Acid Solutions from Electromotive Force Measurements[1]

BY HERBERT S. HARNED AND WALTER J. HAMER

In a recent communication[2] a very comprehensive series of measurements of the cells

$H_2 \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt$ (Type I)

from 0 to 60° and throughout a concentration range from 0.0005 to 7 M was made, and from these the molal electrode potentials of the lead sulfate–lead dioxide electrodes were computed. These results have been supplemented by measurements of the cells

$H_2 \mid H_2SO_4(m) \mid Hg_2SO_4 \mid Hg$ (Type II)

through the same temperature range and through a concentration range of 0.05 to 17.5 M. From the combination of these results, the vapor pressures of the solutions, the activity coefficient of sulfuric acid, the relative partial molal heat content and relative partial molal specific heat of sulfuric acid in aqueous solutions, have been computed throughout the entire concentration and temperature ranges. The molal electrode potential of the mercurous sulfate–mercury electrode has also been evaluated.

Experimental Results

Since the measurements of cells I have already been reported, it is necessary to give only the results of cell II. The apparatus was that described by Hamer.[2] Twice distilled mercury was employed. The mercurous sulfate was prepared by the electrolytic method of Hulett[3] which yields a preparation of fine grains and which shows little or no hysteresis and hydrolyses to a lesser degree than other preparations. This material was di-

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(1) This contribution is part of an investigation of the thermodynamic properties of the electrodes and electrolyte of the lead accumulator. This work was made possible by a grant from the Naval Research Laboratory, Anacostia Station, Washington, D. C., and is published with permission of the Secretary of the Navy.

(2) Hamer, THIS JOURNAL, **57**, 9 (1935).

(3) Hulett, *Phys. Rev.*, **32**, 257 (1911).