boiling point at 760 mm. pressure is found to be 57.0°.

These results are found to be in fair agreement with those of Stock, but are considered more accurate. The values of Becker and Meyer are clearly too high.

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Note on the Calculation of Activity Coefficients and of Molal Volumes

BY O. REDLICH, P. ROSENFELD AND W. STRICKS

Recently Pearce and Blackman[1] published measurements on vapor pressures and specific gravities of aqueous solutions of calcium and aluminum nitrates. On this occasion, they find that the series given by Lewis and Randall[2] for the activity of the solvent can be represented by the formula $\ln a_1 = \ln [1-(p_1^0-p_1)/p_1^0]$. We may add, moreover, that $a_1 = p_1/p_1^0$, this relation being the *origin* of the above mentioned series.

Further, Pearce and Blackman develop the solution volume (*i. e.*, the volume of the quantity containing 1000 g. of water) in a series in terms of the molarity: $V = \alpha + \beta m + \gamma m^2$. On a previous occasion it has been shown that a similar series can by no means account for the behavior of dilute solutions of strong electrolytes[3]; on the basis of the Debye-Hückel theory it can be proved that a term with $m^{3/2}$ is indispensable. So it is not at all surprising that the differences between observed and calculated values in Tables III and IV show a distinct trend.

The constants α, β and γ are determined by Pearce and Blackman according to the method of least squares. The authors calculate in fact the constant α also from their measurements on solutions of calcium and aluminum nitrate, ignoring completely that this constant representing the volume of 1000 g. of water is determined by the specific gravity of pure water. This quantity, however, is not actually measured by the authors, but forms the basis of their measurements (the volume of the pycnometer being determined by means of it); it cannot be legitimately derived therefore from their results. The procedure applied by them leads to the consequence that the specific volume of water depends on the nature of substances which are dissolved in zero concentration (volume of 1000 g. water = 1002.9621 cc. from calcium nitrate solutions, and 1003.0730 cc. from aluminum nitrate solutions).

Calculating the apparent molal volume of calcium nitrate from the data of Pearce and Blackman and plotting this quantity against square root of concentration (the usefulness of such proceedings being shown in the papers mentioned above), we obtain a curve which is markedly convex toward the $c^{1/2}$ axis for dilute solutions; we do not know any other strong electrolyte of similar behavior. Therefore we evaluated the data given for solutions of calcium nitrate by some former observers and by "I. C. T.," Vol. III; none of these data give a curve of apparent molal volume of similar curvature. The differences between the values of Pearce and Blackman and the older figures are considerable. We have not found adequate data for a comparison in the case of aluminum nitrate.

A paper on the calculation of activity coefficients, to be published shortly in the *Sitzungsber. Akad. Wiss. Wien*, will contain a few additional remarks.[4]

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Addition.—We are much obliged to the Editor for the opportunity of examining the contribution of Professor Pearce, "The Vapor Pressures and the Activity Coefficients of Aqueous Solutions of Calcium and Aluminum Nitrate at 25° (Correction)," before its publication. In view of this contribution we would wish only to state that the activity coefficients of calcium nitrate at 25°, calculated from freezing points and used by us as reference values, are to be published in Landolt-Börnstein, "Tabellen," III. Ergänzungsband; the differences between the values at freezing temperature and at 25° have been derived from heats of dilution [E. Lange, H. Streeck, *Z. physik. Chem.*, **A157,** 1 (1931)] and from specific heats [C. Marignac, *Ann. chim. phys.*, [5] **8,** 410 (1876);

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[1] J. N. Pearce and L. E. Blackman, THIS JOURNAL, **57**, 24 (1935).

[2] G. N. Lewis and M. Randall, "Thermodynamics," New York, 1923, Chapter XXII, Eqn. (34). A misprint in this equation, reproduced in the German translation (Wien, 1927), was retained by J. N. Pearce, M. D. Taylor and R. M. Bartlett, THIS JOURNAL, **50**, 2951 (1928), and was corrected in later papers without a special reference. The series, appropriate only in the case of very dilute solutions, has repeatedly been applied by Pearce and collaborators to rather concentrated solutions.

[3] O. Redlich and P. Rosenfeld, *Z. Elektrochem.*, **37**, 705 (1931); *cf. Z. phys. Chem.*, **A155**, 65 (1931).

[4] The activity coefficients of $LiNO_3$, NaCl, NaBr, KI, $HClO_4$, calculated by us from vapor pressures given by Pearce and collaborators, are to be found in Landolt-Börnstein-Roth-Scheel, "Tabellen," III. Ergänzungsband (to be published). The differences between the activity coefficients of these authors and our results are considerable.

"I. C. T.," Vol. V, p. 123]. Concerning the reliability of Marignac's data, *cf.*, *e. g.*, T. W. Richards and A. W. Rowe [THIS JOURNAL, **43**, 776 (1921)].

NOVEMBER 20, 1935

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The Vapor Pressures and the Activity Coefficients of Aqueous Solutions of Calcium and Aluminum Nitrate at 25° (Correction)

BY J. N. PEARCE

Shortly after the publication of the paper[1] on "The vapor pressures and the activity coefficients of aqueous solutions of calcium and aluminum nitrate," two of my students discovered an unfortunate error in the activity coefficients of the ions of these salts. This error arose through the use of an erroneous conversion factor for planimeter readings. All of these data have been recalculated and replotted independently by these students, and the results have been checked by the writer. The corrected data are given in the accompanying tables.

In making these calculations we have assumed that the activity of the solvent, a_1, is equal to the relative humidity, or $a_1 = p_1/p_1^0$. The activity coefficients have been calculated by means of the equation of Randall and White,[2] namely

$$\log \gamma = -h/2.303 - 2/2.303 \int_0^{m^{1/2}} (h/m^{1/2})\mathrm{d}m^{1/2}$$

where $h = 55.51 \ln a_1/\nu m + 1$. The value of the integral was determined by means of a polar

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	1.0000	....	...
.1	23.659	0.9961	0.8686	0.3894	2.32	...
.2	23.566	.9922	.6075	.3250	4.72	911
.4	23.373	.9841	.4043	.2754	9.53	1849
.6	23.160	.9751	.2861	.2585	14.96	2458
.8	22.915	.9647	.1902	.2574	21.26	2962
1.0	22.638	.9531	.1109	.2644	28.48	3406
1.5	21.868	.9207	− .0159	.2940	48.98	4316
2.0	21.002	.8843	− .0979	.3381	72.88	5077
2.5	20.042	.8438	− .1626	.3971	100.7	5759
3.0	19.107	.8044	− .1976	.4556	129.0	6328
3.5	18.118	.7628	− .2306	.5290	160.5	6868
4.0	17.098	.7198	− .2603	.6171	194.9	7379
5.0	15.008	.6319	− .3125	.8441	272.1	8334
6.0	13.062	.5499	− .3446	1.1240	354.5	9167
7.0	11.260	.4741	− .3677	1.4688	442.4	9917
8.0	9.603	.4043	− .3869	1.9034	536.8	10616
8.3601[a]	9.041	.3806	− .3950	2.0957	572.5	10865

[a] Saturated. $a_2 = 4(\gamma m)^3$.

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.	$-\Delta F_2^{0.1}$, cal.
0.0	23.752	1.0000	2.895	1.000	....	...
.1	23.648	0.9956	1.2315	0.1970	2.60	...
.2	23.500	.9894	0.5790	.1711	6.33	1311
.4	23.235	.9782	.3723	.1291	13.05	2285
.6	22.860	.9624	.1474	.1355	22.69	3363
.8	22.405	.9433	− .0146	.1517	34.61	4313
1.0	21.911	.9224	− .1202	.1718	47.88	5137
1.5	20.386	.8583	− .3382	.2587	90.61	7065
2.0	18.561	.7814	− .5034	.4102	146.2	8845
2.5	16.678	.7013	− .6088	.6382	210.3	10422
3.0	14.860	.6256	− .6762	.9599	278.0	11823
3.1607[a]	14.370	.6050	− .6786	1.0608	297.8	12183

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

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[1] Pearce and Blackman, THIS JOURNAL, **57**, 24 (1935).

[2] Randall and White, *ibid.*, **48**, 2514 (1926).