at −195.8°; argon, nitrogen, carbon monoxide and oxygen at −183°; carbon dioxide at −78°; normal butane and sulfur dioxide at 0°. The following adsorbents have been used: two copper catalysts, glaucosil, pumice, nickel oxide supported on pumice, nickel on pumice, dry powdered bacteria, chromic oxide gel, "glowed" chromic oxide, potassium chloride, copper sulfate pentahydrate, anhydrous copper sulfate, two silica gel samples, activated charcoal, and two Darco samples (activated carbons). All adsorbents except charcoal gave S-shaped isotherms, and the values for the surface area evaluated from the different isotherms for the same adsorbent were consistent with each other.

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[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, THE STATE UNIVERSITY OF IOWA]

Vapor Pressures and Partial Molal Volumes of Aqueous Solutions of the Alkali Sulfates at 25°[1]

BY J. N. PEARCE[2] AND H. C. ECKSTROM[3]

The vapor pressures of aqueous solutions of a number of electrolytes have been measured in this Laboratory. The data were used to calculate the thermodynamic functions useful in the study of solutions. Since all of the electrolytes previously studied had univalent anions, it seemed desirable to extend the measurements to electrolytes having divalent anions. For this purpose, the three most important alkali sulfates were chosen since the cations were common to many of the electrolytes previously studied.

The method used for measuring the vapor pressures was that developed by Pearce and Snow[4] with a few minor modifications mentioned in later publications by Pearce and students. The densities of the solutions were determined by means of a 100-ml. pycnometer.

The lithium, sodium and potassium sulfates of C. P. grade were recrystallized from distilled water and dried to constant weight. Solutions of the desired molality were made by adding the necessary weight of water to a known weight of anhydrous salt. The molality of the saturated solutions at 25° was determined gravimetrically by precipitating the sulfate ion as barium sulfate.

The vapor pressure data obtained are collected in Tables I, II and III. Column 4 contains values for $h/m^{1/2}$ where $h = (55.51 \ln a_1/\nu m) + 1$ and ν is the number of ions from one molecule of electrolyte. The values of the activity of the solvent, in column 5, have been calculated

TABLE I

VAPOR PRESSURES AND ACTIVITIES OF AQUEOUS SOLUTIONS OF LITHIUM SULFATE AT 25°

m	p_1, mm.	$(p_1^\circ - p_1)/p_1^\circ$	$h/m^{1/2}$	a_1	$\gamma_\pm$
0.0	23.752	0.0000	1.365	1.0000	1.000
.1	23.651	.0043	0.668	0.9958	0.445
.2	23.554	.0083	.502	.9917	.377
.4	23.360	.0165	.363	.9835	.321
.6	23.164	.0248	.293	.9752	.287
.8	22.962	.0333	.244	.9668	.272
1.0	22.757	.0419	.208	.9581	.260
1.5	22.220	.0645	.145	.9355	.246
2.0	21.646	.0887	.100	.9113	.241
2.5	21.071	.1129	.072	.8871	.240
3.0944[a]	20.363	.1427	.045	.8573	.241

[a] Saturated.

TABLE II

VAPOR PRESSURES AND ACTIVITIES OF AQUEOUS SOLUTIONS OF SODIUM SULFATE AT 25°

m	p_1, mm.	$(p_1^\circ - p_1)/p_1^\circ$	$h/m^{1/2}$	a_1	$\gamma_\pm$
0.0	23.752	0.0000	1.365	1.0000	1.000
.1	23.652	.0042	0.696	0.9958	0.433
.2	23.567	.0078	.616	.9922	.353
.4	23.393	.0151	.468	.9849	.283
.6	23.227	.0221	.401	.9779	.246
.8	23.072	.0286	.367	.9714	.221
1.0	22.927	.0347	.346	.9653	.200
1.5	22.565	.0500	.300	.9500	.166
1.9641[a]	22.239	.0637	.271	.9363	.145

[a] Saturated.

TABLE III

VAPOR PRESSURES AND ACTIVITIES OF AQUEOUS SOLUTIONS OF POTASSIUM SULFATE AT 25°

m	p_1, mm.	$(p_1^\circ - p_1)/p_1^\circ$	$h/m^{1/2}$	a_1	$\gamma_\pm$
0.0	23.752	0.0000	1.365	1.0000	1.000
.1	23.656	.0040	0.791	0.9960	0.419
.2	23.565	.0076	.625	.9923	.322
.4	23.399	.0149	.486	.9851	.257
.6	23.239	.0216	.422	.9784	.208
.6889[a]	23.172	.0244	.405	.9756	.196

[a] Saturated.

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(1) Part of the dissertation presented to the Graduate College of the State University of Iowa by Hartley C. Eckstrom in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Deceased November 14, 1936.

(3) Present address: Department of Chemistry, Brown University, Providence, Rhode Island.

(4) Pearce and Snow, *J. Phys. Chem.*, **31**, 281 (1927).

from $a_1 = p_1/p_1^\circ$ by assuming the vapors dilute enough to behave as a perfect gas. The well-known relation of Randall and White,[5] was used

$$\log \gamma_\pm = -\frac{h}{2.303} - \frac{2}{2.303}\int_0^{m^{1/2}} \frac{h}{m^{1/2}}\,dm^{1/2} \quad (1)$$

to calculate the values of the geometric-mean activity coefficients, $\gamma_\pm$.

In Fig. 1 $h/m^{1/2}$ is plotted against $m^{1/2}$. The areas under each curve are determined by a polar planimeter. These areas are used in equation (1) since the integral is most easily evaluated graphically.

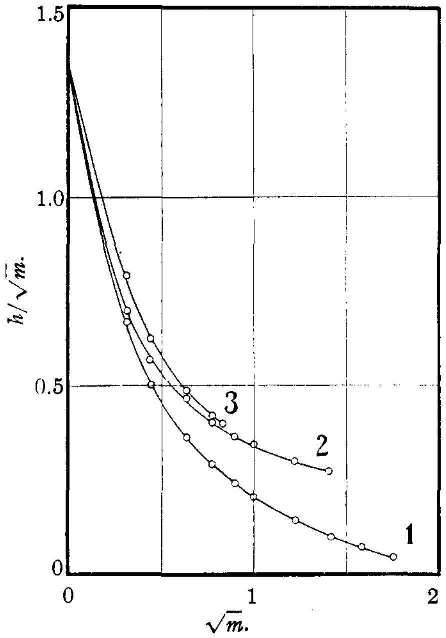

Fig. 1.—The variation of $h/m^{1/2}$ and $m^{1/2}$: 1, Li_2SO_4; 2, Na_2SO_4; 3, K_2SO_4.

No plot has been given for the values of $\gamma_\pm$ since the curves are typical of those previously obtained. Since the values are all calculated from the h-function they all fall on a smooth curve. The values descend but do not pass through a minimum. The values of $\gamma_\pm$ for lithium sulfate have no doubt approached the minimum and would increase if the salt were more soluble. The values of $\gamma_\pm$ given in this paper are lower in all cases than those obtained by Åkerlöf[6] who used e. m. f. methods.

The present authors have decided that the h-function used with vapor pressures does not give a satisfactory method of determining $\gamma_\pm$. This may be explained by considering the shape of the curve obtained by plotting $h/m^{1/2}$ against $m^{1/2}$, Fig. 1. The curve in the dilute solution range cannot be determined with certainty since very small errors in p_1 are greatly magnified. The area is the largest under this part of the curve. This leads to an accumulative error in each successive value of $\gamma_\pm$. In almost all of the previous papers by Pearce and students and also in the present paper the values of $\gamma_\pm$ have not agreed with those obtained by e. m. f. methods. In some cases very great discrepancies appear. However, the vapor pressures are accurate within the limits of the experimental error (±0.004 mm.). The junior author has found that values of $\gamma_\pm$ from e. m. f. data yield vapor pressures which are in agreement with measured vapor pressures, within experimental error, but the reverse calculation does not yield satisfactory values of $\gamma_\pm$. It is pos-

Table IV

Apparent and Partial Molal Volumes of Aqueous Solutions of Lithium Sulfate at 25°

m	d	$c^{1/2}$	$\phi_{obsd.}$, cc.	$\phi_{calcd.}$, cc.	$\bar{v}_2$, cc.	$\bar{v}_1$, cc.
0.0	0.997074	0.00000	...	12.91	12.91	18.07
.1	1.006475	.31552	15.55	15.61	16.96	18.07
.2	1.015627	.44583	16.64	16.73	18.65	18.06
.4	1.033366	.62923	18.33	18.33	21.05	18.05
.6	1.050531	.76899	19.59	19.55	22.89	18.03
.8	1.067219	.88586	20.62	20.58	24.42	18.01
1.0	1.083423	.98798	21.54	21.49	25.76	17.99
1.5	1.122184	1.2021	23.43	23.40	28.57	17.93
2.0	1.158514	1.3782	25.02	24.98	30.85	17.86
2.5	1.192680	1.5293	26.38	26.36	32.79	17.78
3.0944[a]	1.231000	1.6860	27.69	27.79	34.75	17.55

[a] Saturated.

Table V

Apparent and Partial Molal Volumes of Aqueous Solutions of Sodium Sulfate at 25°

m	d	$c^{1/2}$	$\phi_{obsd.}$, cc.	$\phi_{calcd.}$, cc.	$\bar{v}_2$, cc.	$\bar{v}_1$, cc.
0.0	0.997074	0.00000	...	12.09	12.09	18.07
.1	1.009664	.31552	15.63	15.66	17.48	18.07
.2	1.021889	.44579	17.24	17.18	19.80	18.06
.4	1.045658	.62910	19.35	19.37	23.14	18.04
.6	1.068593	.76863	21.06	21.08	25.84	18.02
.8	1.090777	.88520	22.54	22.52	27.94	17.99
1.0	1.112294	.98688	23.82	23.81	29.88	17.96
1.5	1.163430	1.1994	26.49	26.54	33.97	17.87
1.9641[a]	1.207404	1.3617	28.70	28.67	37.10	17.77

[a] Saturated.

Table VI

Apparent and Partial Molal Volumes of Aqueous Solutions of Potassium Sulfate at 25°

m	d	$c^{1/2}$	$\phi_{obsd.}$, cc.	$\phi_{calcd.}$, cc.	$\bar{v}_2$, cc.	$\bar{v}_1$, cc.
0.0	0.997074	0.00000	..	33.70	33.70	18.07
.1	1.010722	.31529	36.97	36.97	38.65	18.07
.2	1.023981	.44487	38.40	38.37	40.82	18.06
.4	1.049670	.62651	40.37	40.40	43.86	18.04
.6	1.074320	.76392	42.01	41.98	46.33	18.02
.6889[a]	1.085004	.81692	42.62	42.60	47.26	18.01

[a] Saturated.

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(5) Randall and White, This Journal, **48**, 2514 (1926).

(6) Åkerlöf, *ibid.*, **48**, 1160 (1926).

sible to change the shape of the h-curve slightly and obtain better values for $\gamma_{\pm}$ without disregarding any of the experimental points. However, it does not seem that such a method is either desirable or accurate.

The density data, and apparent and partial molal volumes are collected in Tables IV, V and VI. The values of $c^{1/2}$ are the square roots of the molar concentration. The values of the apparent molal volume, $\phi_{\text{obsd.}}$, are calculated from

$$\phi_{\text{obsd.}} = (V - n_1v_1)/n_2$$

where V is the total volume of solution containing 1000 g. of water, n_1v_1 is the volume of 1000 g. of water, and n_2 the moles of solute present. The values of the partial molal volumes of the solute, $\bar{v}_2$, have been calculated by following Gucker's method,[7] previously used by the present authors in an earlier publication.[8] When $\phi_{\text{obsd.}}$ is plotted against $\sqrt{c}$, Fig. 2, curves result that are practically straight lines. The empirical equations for the three curves are of the form $\phi = \alpha + \beta c^{1/2} + \gamma c$ where α, β and γ are determined by the method of least squares. The resulting equations are

$$\phi_{\text{calcd.}} = 12.9093 + 8.47832c^{1/2} + 0.204579c, \text{ for } Li_2SO_4$$
$$\phi_{\text{calcd.}} = 12.0853 + 11.0675c^{1/2} + 0.818758c, \text{ for } Na_2SO_4$$
$$\phi_{\text{calcd.}} = 33.6991 + 10.0393c^{1/2} + 1.04131c, \text{ for } K_2SO_4$$

These three equations were used to calculate $\bar{v}_2$, partial molal volume of the solute, by employing Gucker's equation

$$\bar{v}_2 = \phi + c^{1/2}\left[\frac{1000 - c\phi}{2000 + c^{3/2}\dfrac{\partial\phi}{\partial c^{1/2}}}\right]\frac{\partial\phi}{\partial c^{1/2}} \qquad (2)$$

These values of $\bar{v}_2$ appear in column 6 and are plotted in Fig. 2 against m.

The partial molal volumes of the solvent, $\bar{v}_1$, are calculated from the equation $\bar{v}_1 = (V - n_2\bar{v}_2)/n_1$ and appear in column 7. These are also plotted in Fig. 2 against m. It was not possible to show the curve for potassium sulfate since it coincides with that of sodium sulfate.

The junior author is indebted to Professors W. G. Eversole and Louis Waldbauer for their helpful criticism in the writing of this manuscript.

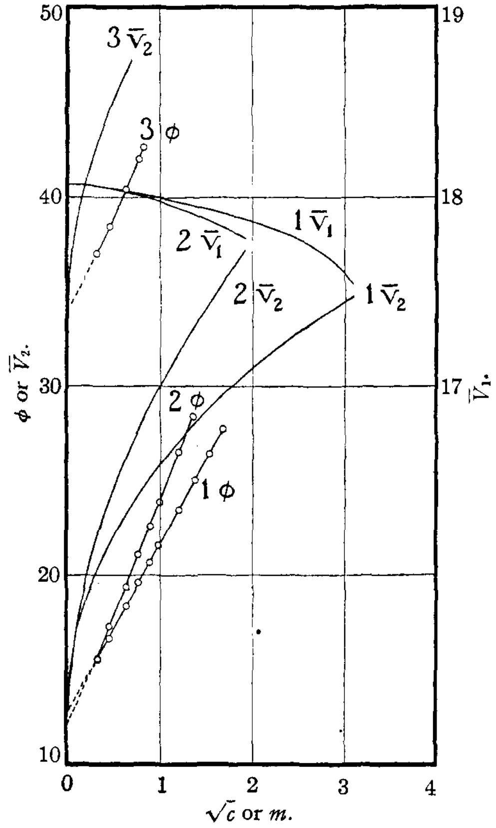

Fig. 2.—The variation of the apparent molal volumes with the square root of the molar concentration and of the partial molal volumes of solute and solvent with the molal concentration: 1, Li_2SO_4; 2, Na_2SO_4; 3, K_2SO_4.

Summary

The vapor pressures and the densities of aqueous solutions of the alkali sulfates have been determined at 25°. From these data have been calculated the activity of the solvent, the geometric mean activity coefficients, the partial and apparent molal volumes of the dissolved electrolytes.

BROWN UNIVERSITY

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(7) Gucker, *J. Phys. Chem.*, **38**, 307 (1934).

(8) Pearce and Eckstrom, *ibid.*, **41**, 563 (1937).