

THE SYSTEM SODIUM SULPHATE-WATER: I. THE DENSITIES AND SPECIFIC VOLUMES OF AQUEOUS SOLUTIONS OF SODIUM SULPHATE BETWEEN 25 AND 40°, AND THE FICTIVE VOLUMES OF SODIUM SULPHATE IN SOLUTION

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In a study of the effect of pressure on the equilibria between salts and their solutions a knowledge of the Fictive Volumes of the salts in solution is of the utmost importance. To determine the fictive volumes, that is to say the increase in volume which an infinitely large volume of the solution undergoes when one gram of the salt is added, it is necessary to know the specific volumes of solutions of the salt at various concentrations to as high a degree of accuracy as possible. Such data were not available in the case of sodium sulphate and it is the object of this paper to supply the need.

Experimental

The work was divided roughly into two parts.

First, the densities, and hence the specific volumes of solutions containing from 1 to 28 per cent of sodium sulphate were accurately determined at 25°. For solutions containing up to 21 per cent of Na₂SO₄ the density could be determined directly at that temperature but in the case of solutions of higher concentration the density was found at 30° and then converted to that at 25°.

Second, by means of a dilatometer the change in specific volume per degree between 25° and 40° was found for each solution. By combining these results it was possible to calculate the specific volume of any solution of sodium sulphate between 25 and 40°.

Density Determinations. The densities of the solutions were found by a pycnometer method. The pycnometers, thermostat tank, balance, and weights were those described by Hall,¹ and his technique and precautionary measures were observed throughout.

The temperature of the bath was checked frequently by a 10-junction copper-constantan thermel, one limb of which dipped into the thermostat near the pycnometer while the other was immersed in melting ice. The thermel was constructed by the author and was calibrated against the Standard 25-junction element of the Bureau of Standards with the kind assistance of Dr. W. P. White. The E. M. F. of the thermel was read with a Wolff potentiometer. The mean fluctuation of the bath was $\pm 0.005^\circ$. The standard cell of the potentiometer was calibrated at the Bureau of Standards.

Sodium sulphate. J. T. Baker's C. P. Analyzed crystalline sodium sulphate decahydrate was used. It was recrystallized from water three times, care being taken each time to free the crystals from adhering solution by suction. The purified crystals were then kept in a vacuum desiccator over

¹ Ralph E. Hall: J. W. Acad. Sci., 14, 167 (1924).

KOH until they were reduced to a fine anhydrous powder. Finally the powdered salt was heated in a platinum vessel to $400\text{--}500^\circ$ for six hours. The loss in weight of the Na_2SO_4 during this operation never exceeded 0.1 per cent.

Solutions. For each determination a fresh solution was prepared directly from salt and water. Here again Hall's method was used and at no time did any trouble arise from the formation of bubbles of air in the solution. When large amounts of the salt were required, however, the salt was weighed directly in the standard flask wherein the solution was prepared. This method proved more reliable than washing the salt into the flask from a separate weighing vessel.

Procedure. Before each experiment the pycnometers were washed out with a chromic acid solution and with distilled water and dried by a current of dried, filtered air. They were then immersed in distilled water, dried with a linen cloth, and suspended on the balance arms. After half an hour, when equilibrium was attained, the difference in weight was taken, double weighings being made in all cases. The constancy of the weight of the solution-pycnometer was comparable with the figures given in Hall's paper. The solution-pycnometer was then filled, immersed in the thermostat, adjusted and weighed as Hall describes. The weight of the solution was corrected for the temperature, pressure, and the humidity of the air in the balance case.

Experiments with pure water gave the volume of the solution-pycnometer and were performed at intervals throughout the work. The results are given in Table I. The volume of the pycnometer at 25° is 55.0365 milliliters and at 30.0° is 55.0448 milliliters.

TABLE I
Calibration of Pycnometer

Temperature	Number of experiment	Weight of water
25°	1	54.8758
	2	54.8758
	3	54.8759
	4	54.8752
	5	54.8751
	6	54.8756
	7	54.8760
25°	Average	54.8756
30°	8	54.8073
	9	54.8068
	10	54.8068
30°	Average	54.8069

In order to avoid any errors due to elastic hysteresis in the glass, the experiments at 25° were all completed before those at 30° were undertaken.

Dilatometer Experiments. The dilatometer, used for the determination of the coefficients of expansion of the different solutions is shown in Fig. 1. It

consisted of a bulb, *A*, some 50 cc in capacity, to which was sealed a graduated capillary tube, *C*, whose internal diameter was about 1 mm. Liquid was introduced into the dilatometer through *C* by withdrawing the air at *B*. The stopcock *D*, was very carefully selected and gave no leakage trouble whatsoever.

The whole was then immersed in a large enclosed bath holding about 5 liters of water which was stirred vigorously. The bath was provided with an electrical heater and a cooling coil. By means of a variable resistance in series with the heater the temperature of the bath could be held within 0.1° of any point for any length of time. The temperature of the bath was read with the thermel described above. The position of the meniscus in the capillary was read with a lens, correct to 0.1 mm of the scale.

Procedure. After the dilatometer had been completely filled and was immersed in the bath at 25° , the stopcock, *D*, was opened and the liquid allowed to run very slowly down the capillary until the meniscus reached a certain definite zero mark. It was essential that the capillary should be absolutely clean and that no liquid should adhere to the upper portions of the capillary tube.

The stopcock was then closed and the whole was kept at 25° until equilibrium was attained, when the position of the meniscus was observed. The temperature was then raised slowly and readings were taken at intervals of 2.5° . In each case half an hour was allowed for the dilatometer to come into equilibrium with its surroundings. Owing to the limited length of the capillary the highest temperature reached was 37.5° , whereafter readings were taken with falling temperature down to 25° . If two readings at the same temperature differed by 0.2 mm., indicating hysteresis of the glass, leakage or formation of bubbles, the run was rejected. This was only necessary in one case.

A thermometer was suspended alongside the capillary and the air temperature was taken at the time of each reading. Hence a stem correction could be made to bring the volume of the liquid in the capillary to the volume it would occupy at the temperature of the bath.

Calibration of the dilatometer. The graduated capillary tube, *C*, was calibrated by means of a weighed thread of mercury. The bore was very regular indeed, the maximum and minimum cross section areas being 1.120 and 1.116 mm² respectively. The mean cross section area of the capillary was taken as 1.118 mm². The capillary was graduated in millimeters. The volume of the dilatometer at 25° was determined by weighing its water content at that temperature. It was 47.394 milliliters.

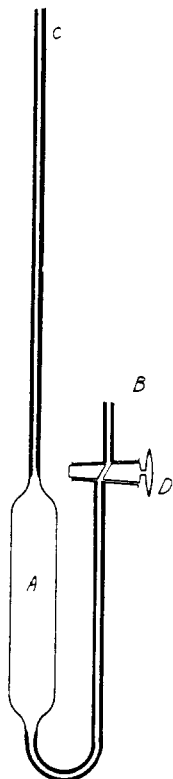


FIG. 1
Diagram of dilato-
meter

To determine the correction to be added for the expansion of the glass, i. e. to convert *apparent* to *real* expansion, several runs were made with pure water whose coefficient of expansion was taken from the Smithsonian tables.

Let $\Delta h''$ represent the observed rise of the water in the capillary for a temperature rise of Δt° and let Δv represent the increase in volume of 1 gram of water for the same change of temperature. Then if M is the mass of water in the dilatometer, $M\Delta v$ is the real expansion.

Also if a is the area of the cross section of the capillary and $\Delta h'$ is the rise in the level of the water which should occur, were there no expansion of the glass,

$$M\Delta v/a = \Delta h'$$

The correction $(\Delta h' - \Delta h'')$, was found for various temperatures and the curve of $(\Delta h' - \Delta h'')$ against temperature was plotted. The curve was accurately represented by the equation

$$(\Delta h' - \Delta h'') = 1.28 (t - 25) \quad (A)$$

Results

The results of the density determinations made at 25 and 30° are given in Table II. The weighings are corrected to vacuum. In Table III the first steps in rounding off the results to even concentrations are given. All the densities are reduced to 25° and in column 2 the corrections necessary to bring the check determinations to the same percentage have been made. Here the experimental consistency may be studied.

TABLE II
Density of Na_2SO_4 solutions
Experimental results

Temp.	Weight of salt	Weight of solution	Concentration per cent (x_2)	Weight of solution in pycnometer	Density
25°	1.0002	102.6038	0.9748	55.3598	1.005878
	2.0005	101.7751	1.9656	55.8503	1.014787
	3.0016	102.9788	2.9148	56.3209	1.023338
	5.0029	104.7829	4.7746	57.2524	1.040268
	4.9999	104.7727	4.7721	57.2524	1.040268
	5.0070	104.9138	4.7725	57.2521	1.040257
	10.1053	108.5147	9.3124	59.5770	1.082500
	11.0037	109.7683	10.0245	59.9497	1.089272
	11.0079	109.9376	10.0129	59.9443	1.089174
	12.9986	104.8549	12.3968	61.2096	1.112164
	15.8300	110.9914	14.2624	62.2206	1.130534
	23.0650	117.1804	19.6833	65.2576	1.185718
	25.0054	118.3059	21.1362	66.1004	1.201028
	25.0074	118.3573	21.1287	66.0955	1.200940
	25.0058	118.3467	21.1293	66.0965	1.200958
30°	30.0248	120.1801	24.9832	68.2497	1.239890
	35.2489	126.0318	27.9683	70.0807	1.273157

TABLE III

Densities of Na_2SO_4 solutions at 25° , all check determinations corrected to the same concentrations

x_2	Density	Final value	Calculated values Eqn. (1)	Obs-Calc $\times 10^1$	Calculated values Eqn. (2)	Obs-Calc $\times 10^1$
0.9748	1.005875	1.005875	1.005925	-50	1.005807	+68
1.9656	1.014787	1.014787	1.014726	+61	1.014725	+62
2.9148	1.023338	1.023338	1.023230	+108	1.023314	+24
4.7730	1.040249	1.040249	1.040083	+166	1.040267	-18
	1.040271					
	1.040261					
	1.040251*					
	1.040248*					
9.3124	1.082501	1.082501	1.082435	+66	1.082590	-89
10.0200	1.089232	1.089236	1.089187	+49	1.089319	-83
	1.089240					
12.3968	1.112164	1.112164	1.112186	-22	1.112218	-54
14.2624	1.130534	1.130534	1.130579	-45	1.130534	0
19.6833	1.185717	1.185717	1.185764	-47	1.185692	+25
21.1362	1.201029	1.201020	1.201010	+10	1.201020	0
	1.201012					
	1.201019					
24.9832	1.242568	1.242569	1.242326	+243	1.242844	-275
27.9685	1.275917	1.275917	1.275359	+558	1.276644	-727

*4th and 5th values were taken from work in which a larger pycnometer was used.

Empirical equations giving the relation between density and concentration in solutions. In order to find the values of the densities of solutions of even concentrations, as are given in Table IV, it was expedient to find a simple equation which would represent density as a function of concentration as accurately as possible. It is usual to employ a power series for this purpose and such may be derived from a difference table or by the solution of simultaneous equations, but the labor involved in the derivation of a cubic or biquadratic is very considerable.

Moreover, when differentiated, as is necessary in the computation of fictive volumes, these power series do not simplify at all. Hence another type of equation was sought.

It was found that the equation

$$\log \rho = ax_2 + b \quad (\text{B})$$

where ρ is the density, x_2 is the percentage of Na_2SO_4 and a and b are constants, fits the observations as well as a cubic equation. In Table III are the calculated values obtained from Equation 1, a logarithmic one, and Equation 2, a cubic one. In columns 5 and 7 the differences between the observed and calculated values are given. These differences, when plotted against the concentration, gave the deviation curves.

The equations from which the final calculations were made were:

$$\text{Eqn. (1) } \log \rho = 0.00381823 x_2 - 0.0011563$$

$$\text{Eqn. (2) } \rho = 0.997077 + 0.00893498 x_2 + 0.00002094 x_2^2 + 0.000006075 x_2^3$$

$$\text{Eqn. (3) } \log \rho = 0.0038256 x_2 - 0.0012570$$

Equation 3 was derived for the range of concentration, 10 to 28 per cent, so that a check on the calculations at higher concentrations might be made. By combining each of these equations with the appropriate deviation curve we calculated the densities corresponding to even percentages of Na_2SO_4 and these are shown together in Table IV. In column 5 the mean of the three sets of values is given and a weighted mean is shown in column 6. When the difficulties of drawing an accurate deviation curve are considered, it will be seen that the agreement among the three interpolations is very satisfactory. The specific volumes of solutions of Na_2SO_4 at 25° are given in column 7.

TABLE IV

Final values of densities and specific volumes of solutions of Na_2SO_4

x_2	Density Eqn. (1)	Density Eqn. (2)	Density Eqn. (3)	Mean	Final values (Weighted mean)	Specific volumes
0					0.997077	
1.0	1.006104	1.006101		1.006102	1.006102	0.993935
2.0	1.015093	1.015096		1.015094	1.015094	0.985130
3.0	1.024115	1.024119		1.024117	1.024117	0.976451
5.0	1.042331	1.042329		1.042330	1.042330	0.959389
10.0	1.089044	1.089043	1.089043	1.089043	1.089043	0.918237
15.0	1.137878	1.137878	1.137880	1.137879	1.137878	0.878827
20.0	1.189036	1.189036	1.189039	1.189036	1.189036	0.841017
21.0	1.199573	1.199570	1.199572	1.199571	1.199570	0.833632
25.0	1.242754	1.242754	1.242754	1.242754	1.242754	0.804664
28.0	1.276276	1.276277	1.276271	1.276276	1.276276	0.783530
(29.0)	(1.287666)		(1.287663)	(1.287664)	(1.287664)	(0.776600)

Results of the Dilatometer Experiments

From experiments the following quantities were obtained directly:

R_0 = the height of the meniscus in the capillary at 25° .

R = height of the meniscus (corrected for stem temperature) at t° .

t = the temperature of the bath.

It was found most convenient to work with $\Delta t = t - 25$, so this quantity will be used throughout.

$R - R_0$ is a function of the apparent expansion and was converted to Δh , a function of the real expansion, by adding the appropriate correction from Equation A.

Then, if a be the cross section of the capillary, V_{25} , the volume of the dilatometer at 25° and $\Delta V/V_{25}$ the relative change in volume or the increase in volume which 1 cc (at 25°) of the solution undergoes when its temperature is raised Δt° ,

$$\Delta V/V_{25} = a\Delta h/V_{25}.$$

TABLE V
Relative changes in volume of solutions of Na_2SO_4 , $\Delta V/V_{25}$

0% Na_2SO_4				1% Na_2SO_4				5.30% Na_2SO_4				10.00% Na_2SO_4			
Temp.	(Obs)	(Calc)	Diff.	Temp.	(Obs)	(Calc)	Diff.	Temp.	(Obs)	(Calc)	Diff.	Temp.	(Obs)	(Calc)	Diff.
25.0	0	-0.002	+2	25.0	0	-0.002	+2	25.0	0	-0.001	+1	25.0	0	+0.001	-1
27.5	0.673	+0.675	-2	27.5	0.709	0.709	0	27.5	0.829	0.830	-1	27.5	0.926	0.925	+1
30.0	1.405	1.406	-1	30.0	1.470	1.473	-3	30.0	1.701	1.702	-1	30.0	1.882	1.881	+1
32.5	2.194	2.192	+2	32.5	2.292	2.289	+3	32.5	2.615	2.615	0	32.5	2.867	2.869	-2
35.0	3.034	3.032	+2	35.0	3.162	3.158	+4	35.0	3.572	3.569	+3	35.0	3.890	3.890	0
37.5	3.925	3.926	-1	37.5	4.078	4.080	-2	37.5	4.564	4.565	-1	37.5	4.944	4.943	+1
14.81% Na_2SO_4				19.81% Na_2SO_4				25% Na_2SO_4				28% Na_2SO_4			
10°	0.000			10°	0.001			10°	0.001			10°	0.003		
10°	0.3929			10°	0.4126			10°	0.4256			10°	0.42967		
10°	0.001099			10°	0.00164			10°	0.00121			10°	0.00105		
Temp.	(Obs)	(Calc)	Diff.	Temp.	(Obs)	(Calc)	Diff.	Temp.	(Obs)	(Calc)	Diff.	Temp.	(Obs)	(Calc)	Diff.
25.0	0	0.000	0	25.0	0	0.001	-1	25.0	0	-0.001	+1	25.0	0	-0.003	+3
27.5	0.992	0.994	-2	27.5	1.044	1.043	+1	27.5	1.070	1.071	-1	27.5	1.075	1.077	-2
30.0	2.018	2.014	+4	30.0	2.104	2.105	-1	30.0	2.158	2.157	+1	30.0	2.168	2.171	-3
32.5	3.054	3.058	-4	32.5	3.183	3.187	-4	32.5	3.256	3.259	-3	32.5	3.282	3.279	+3
35.0	4.128	4.127	+1	35.0	4.294	4.290	+4	35.0	4.381	4.376	+5	35.0	4.404	3.399	+5
37.5	5.221	5.221	0	37.5	5.412	5.412	0	37.5	5.506	5.508	-2	37.5	5.530	5.532	-2

$\Delta V/V_{25}$ was used in all the intermediate steps as it is quite independent of the specific volume of the solutions at 25° and so the slight corrections to bring the observed results to those for even percentages of salt could readily be made by straight interpolation. For each solution observations were taken at six temperatures and quadratic equations were obtained to represent $\Delta V/V_{25}$ as a function of Δt by the method of least squares.

The equations were of the form

$$\Delta V/V_{25} = a' + b't + c't^2 \quad (C)$$

In Table V the results on the relative changes of volume of solutions of Na_2SO_4 are given in a complete form. For each concentration the observed volume changes are shown and alongside them are written the volume changes calculated from the quadratic equation. The column marked "Diff." contains the difference between the observed and calculated values and demonstrates how closely the equations fit. The coefficients a' , b' , and c' are given at the head of each column.

The quantity sought, however, was Δv , the increase in the *specific* volume for a given rise of temperature, or the expansion per gram of solution.

TABLE VI
Calculation of coefficients b and c

x_2	$b' \times 10^3$	$c' \times 10^3$	v (at 25°)	$b \times 10^3$	$c \times 10^3$
0	0.2599	0.00435	1.00293	0.2607	0.00436
1	0.2740	0.00420	0.99394	0.2723	0.00417
5	0.3210	0.00335	0.95938	0.3080	0.00321
10	0.3630	0.00259	0.91824	0.3333	0.00238
15	0.3938	0.00197	0.87883	0.3461	0.00173
20	0.4131	0.00163	0.84102	0.3474	0.00137
25	0.4256	0.00121	0.80466	0.3425	0.00097
28	0.4279	0.00105	0.78353	0.3367	0.00082

TABLE VII

The values of Δv , the increments in volume to be added to the specific volume at 25° to obtain the specific volume at t° .

Concentration per cent	$10^3 \Delta v$			
	$t = 25^\circ$	$t = 30^\circ$	$t = 35^\circ$	$t = 40^\circ$
0	0	1.413	3.043	4.892
1.0	0	1.466	3.140	5.023
5.0	0	1.620	3.401	5.342
10.0	0	1.727	3.571	5.536
15.0	0	1.774	3.634	5.581
20.0	0	1.771	3.611	5.519
25.0	0	1.737	3.522	5.356
28.0	0	1.705	3.449	5.136

It is obvious that $\Delta v/v_{25} = \Delta V/V_{25}$, or $\Delta v = v_{25} \Delta V/V_{25}$, where v_{25} is the specific volume of the solution in question at 25° .

$$\text{Hence if } \Delta v = a + bt + ct^2 \quad (D)$$

$$a = a'v_{25}, b = b'v_{25}, c = c'v_{25}.$$

The calculation of the coefficients, b and c , is given in Table VI. This enables us at once to compute the specific volume of any solution of Na_2SO_4 between 25° and 40° .

In Table VII are given the values of Δv , the amount to be added to the specific volume at 25° to obtain the specific volume at t° .

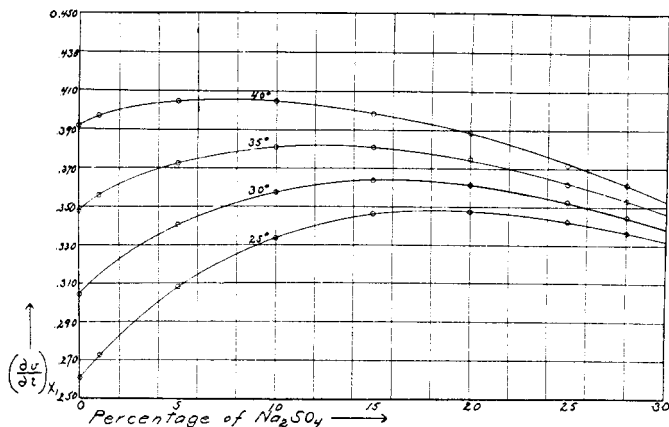


FIG. 2

The expansibilities of sodium sulphate solutions at various concentrations and temperatures.

By differentiating the equation (D)

$$v = a + bt + ct^2$$

$$\text{we obtain } dv/dt = b + 2ct \quad (E)$$

which is the coefficient of expansion of 1 gram of solution.

In Fig. 2 the values of $(b + 2ct)$ at $25, 30, 35$, and 40° are plotted against the percentage of Na_2SO_4 .

Calculations of the Fictive Volumes of Sodium Sulphate in Solution at 25°

Following the practice employed in the foregoing, we decided first to calculate the fictive volumes of the salt in solution at 25° and thereafter to derive the increments in fictive volume with temperature from the expansion equations.

Consider a system of two components, designated by the subscripts 1 and 2. Let m_1 and m_2 be the masses of the components present in a total volume V of the system. Then the fictive volume, v_1 , of component (1) is given by the equation

$$v_1 = \left(\frac{\partial V}{\partial m_1} \right)_{m_2, p, T}.$$

If $x_1 = \frac{100 m_1}{m_1 + m_2}$ and $x_2 = \frac{100 m_2}{m_1 + m_2}$, the percentages of the components pre-

sent are used, it may easily be shown that

$$v_2 = x_1 \frac{dv}{dx_2} + v, \quad v_1 = x_2 \frac{dv}{dx_1} + v. \quad (F)$$

where v is the specific volume of the system. In the present case we have considered Na_2SO_4 as component (2) and H_2O as component (1). It may be emphasized, however, that similar results would have been obtained had the components been $\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ and H_2O .

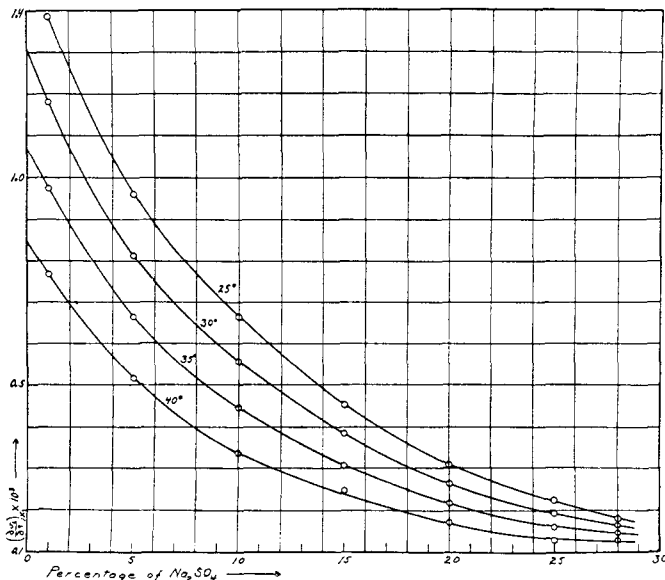


FIG. 3

The fictive expansibilities of sodium sulphate in solution at various concentrations and temperatures.

From the formula connecting density and concentration we have:

$$\log \rho = ax_2 + b$$

$$\text{i. e. } \log (1/v) = ax_2 + b$$

$$\text{Hence } dv/dx_2 = -av \times 2.303 \quad (G)$$

Thus a first approximation to the fictive volume of a salt in solution may be given by the simple formula

$$v_2 = v (1 - 2.303 ax_1) \quad (H)$$

To obtain the highest accuracy from the observations, however, it is necessary to correct dv/dx_2 by a term from the deviation curve. From the deviation curves used for the interpolations described above a correction for $d\rho/dx_2$ was obtained graphically. This, on being multiplied by $-v^2$, gave the term to be added to $-av \times 2.303$ to obtain the best value of dv/dx_2 .

In order to check the values obtained by this method the cubic equation was also differentiated and a corrected value of dv/dx_2 obtained with the aid of the deviation curve.

The results are given in Table VIII.

TABLE VIII
Fictive volumes of Na_2SO_4 in solution at 25°

x_2	v_2 (From Eqn. 4)	v_2 (From Eqn. 2)	v_1 (From Eqn. 3)	v_2 Final values (Weighted Mean)
0				(0.0860)
1.0	0.1140	0.1147		0.1144
2.0	0.1292	0.1287		0.1288
3.0	0.1392	0.1396		0.1394
5.0	0.1570	0.1581		0.1578
10.0	0.1942	0.1942	0.1937	0.1940
15.0	0.2223	0.2227	0.2227	0.2226
20.0	0.2476	0.2478	0.2479	0.2478
25.0	0.2699	0.2694	0.2702	0.2698
28.0	0.2826	0.2820	0.2827	0.2824
30.0				(0.2906)

In columns 2 and 4 are the values calculated with the help of Equations 1 and 3 and their deviation curves, while column 3 gives the figures from the cubic equation 2 and its deviation curve. The weighted mean is printed in column 5. The values in parentheses are the results of extrapolations using Equation K.

The fictive volumes at 25° are represented as a function of concentration with great exactness by the equation

$$\log (v_2 - 0.0860) = 0.58177 \log x_2 + 2.4518 \quad (\text{K})$$

The agreement between observed and calculated values is illustrated in Table IX.

TABLE IX

Comparison of the values of fictive volumes of Na_2SO_4 in solution at 25° with those calculated from Equation K.

x_2	v_2 (From observations)	v_2 (Calculated from Eqn. K)	Diff. $\times 10^4$
1.0	0.1144	0.1143	+1
2.0	0.1288	0.1284	+4
3.0	0.1394	0.1396	-2
5.0	0.1578	0.1582	-4
10.0	0.1940	0.1940	0
15.0	0.2226	0.2228	-2
20.0	0.2478	0.2477	+1
25.0	0.2698	0.2701	-3
28.0	0.2824	0.2826	-2

A glance at Equation K will show that $0.0860 = (v_2)_0$, the fictive volume of the salt at zero concentration. Thus if we write $\Delta v_2 = [v_2 - (v_2)_0]$ we can convert the equation to the form

$$\Delta v_2 = 0.0283 x_2^{0.58177} \quad (L)$$

Although the specific volumes are given confidently to at least 1 part per 100,000, the fictive volumes calculated therefrom can only be written with an accuracy of 0.5 per cent. This is due to the fact that the slopes of the deviation curves influence the final values of the fictive volumes by about 5 per cent and in these deviation curve slopes the uncertainties arise. It should be emphasized that to obtain an accuracy of 1 to 0.1 per cent in the values of the fictive volumes, the specific volumes must be known to 0.001 per cent or closer.

Fictive Volumes and Fictive Expansibilities at Various Temperatures

The fictive volumes at 25° and the coefficients of expansion of the solutions having been obtained, it was a comparatively simple matter to pass to the fictive volumes at other temperatures.

If $(v_2)_{25}$ be the fictive volume at 25° and $(v)_{25}$ be the specific volume at that temperature,

then $(v)_t = (v)_{25} + bt + ct^2$, where b and c are the constants of Eqn. D.

Now $(v_2)_t = x_1 d(v)_t / dx_2 + (v)_t$

$$\begin{aligned} &= x_1 d/dx_2 [(v)_{25} + bt + ct^2] + (v)_{25} + bt + ct^2 \\ &= (v_2)_{25} + t(b + x_1 db/dx_2) + t^2(c + x_1 dc/dx_2). \end{aligned}$$

$$\text{Or } (v_2)_t = (v_2)_{25} + Bt + Ct^2 \quad (M)$$

where $B = b + x_1 db/dx_2$ and $C = c + x_1 dc/dx_2$.

The coefficients, B and C , are readily found from the slopes of the curves of b and c plotted against x_2 at 25°.

The values of the fictive volumes at 25, 30, 35, and 40° are given in Table X.

TABLE X
Fictive volumes of Na_2SO_4 in solution at different temperatures.

x_2	Fictive volumes of Na_2SO_4			
	$t = 25^\circ$	$t = 30^\circ$	$t = 35^\circ$	$t = 40^\circ$
0	0.0860			
1	0.1144	0.1208	0.1262	0.1306
5	0.1578	0.1622	0.1659	0.1689
10	0.1940	0.1970	0.1995	0.2015
15	0.2226	0.2247	0.2264	0.2279
20	0.2478	0.2492	0.2504	0.2514
25	0.2698	0.2708	0.2717	0.2724
28	0.2824	0.2833	0.2840	0.2847

By differentiation of Equation M with respect to temperature, keeping

x_1 constant, we have $\left(\frac{\partial v_2}{\partial t}\right)_{x_2} = B + 2Ct$.

Hence α_2 , the fictive expansibility of Na_2SO_4 in solution is given by

$$\alpha_2 = \left(\frac{\partial v_2}{\partial t} \right)_{x_2} = B + 2Ct.$$

In Fig. 3 the curves of α_2 , as a function of x_2 , are plotted for 25, 30, 35 and 40°

It may easily be shown that the fictive volume of the water, $\frac{\partial V}{\partial m_1} = v_1$, is given by the equation

$$v_1 = v - x_2 \, dv/dx_2$$

A mean of the three values of dv/dx_2 used for the calculations of the fictive volumes of the Na_2SO_4 was used for this computation of v_1 and the results are given in Table XI.

TABLE XI
Calculation of v_1 (fictive volume of H_2O in Na_2SO_4 solutions) at 25°

x_2	$dv/dx_2 \times 10^2$	$x_2 \, dv/dx_2$	v	v_1
0			1.0029	1.0029
1	-.8884	-.0089	.9939	1.0028
2	-.8736	-.0175	.9851	1.0026
3	-.8630	-.0259	.9765	1.0025
5	-.8439	-.0422	.9594	1.0016
10	-.8045	-.0805	.9182	0.9987
15	-.7721	-.1158	.8788	0.9946
20	-.7416	-.1483	.8410	0.9893
25	-.7131	-.1783	.8047	0.9830
28	-.6958	-.1948	.7835	0.9783

Discussion of Results

The immediate purpose of this paper is the provision of thermodynamic data, so that very little discussion of the results will be attempted at this stage but attention may be drawn to the following points.

As would be expected, the specific volumes of the solutions and hence the fictive volumes show no sudden changes at 32.5°, the transition point of the decahydrate to the anhydrous salt. There are, however, strong indications that the salt is very highly hydrated in the dilute solutions at the lower temperatures and that as temperature and concentration increase this hydration gradually diminishes. We wish to use the term hydration, or in general, solvation, in a very broad sense and would define it as follows.

If a molecule or ion of a salt in a solution tends to alter its environment in such a way that the molecules of the solvent are more closely packed around the salt than in the pure solvent the salt is solvated in solution. In other words, if we introduce into water one molecule of a salt which is hydrated in solution, the molecule will hold to itself by attractive forces varying in intensity, n molecules of water.¹ The nature of the attracting forces and the magnitude of n are purposely left indefinite.

¹ A. Eucken: "Fundamentals of Physical Chemistry." (Translated by Jette and LaMer.) p. 245 (1925).

The first indications of a high degree of hydration of the sodium sulphate were found in the very low values of the fictive volume at low concentrations and the rapid rise in fictive volume with increase of concentration. Although the specific volume of Na_2SO_4 in the solid state is 0.375, the fictive volume at zero concentration is only 0.086 while the fictive volume in a 25 per cent solution is 0.27.

On the other hand, in the case of sodium chloride where the specific volume in the solid state is 0.462, the fictive volumes of the salt in solutions containing 0.5 and 25 per cent of NaCl are 0.30 and 0.40 respectively.¹

Perhaps the most striking evidence of the apparent hydration of the salt in the solution is obtained from the curves for the fictive expansibilities in Fig. 3. In this diagram the fictive expansibilities of the Na_2SO_4 , $\partial v_2/\partial t = \alpha_2$ are plotted against x_2 for four different temperatures. From the relative positions of the curves it will be seen that α_2 diminishes as the temperature is raised. Furthermore all the curves appear to converge on a value of α_2 which is of the order of 0.0001.

From the results of Jaeger² on the densities of molten salts we find that dv/dt for liquid Na_2SO_4 at 900° is 0.00023. This value is undoubtedly much higher than dv/dt for the undercooled liquid at 25° . In fact no large error would be made by supposing that at 25° dv/dt is of the order of 0.0001. We might, therefore, state with some degree of certainty that at higher temperatures and concentrations the fictive expansibility of Na_2SO_4 in solution tends to the value of the expansibility of the pure liquefied Na_2SO_4 .

How are we to account for the very large values of the fictive expansibilities of Na_2SO_4 at the lower temperatures and concentrations? An explanation is forthcoming if we consider the fictive expansibility as the result of two factors: (1) the thermal expansion of the pure liquefied solute, and (2) the expansion due to the dissociation of the hydrate complexes as the temperature rises. If the salt is highly hydrated at the low temperatures and concentrations, then, as the temperature is raised, dehydration takes place and is made apparent through a large value of the fictive expansibility of the salt. As the solution becomes more concentrated, the salt is less hydrated and consequently the amount of dehydration per degree rise of temperature falls off and α_2 diminishes. Finally, when the concentration and temperature are high enough, we can assume that we are dealing with the almost anhydrous salt and a fairly constant value of α_2 is obtained.

In the above discussion we have assumed that factor (1) varies very slightly with dilution. Although this is at present not capable of proof, we can see from the flatness of the 40° curve that it is an approximation to the truth.

Thus it is the very rapid diminution in α_2 from its relatively large value at zero concentration and at 25° as temperature and concentration are increased which leads us to confirm the supposition that Na_2SO_4 is highly

¹ Unpublished calculations from the data on the densities of NaCl by Hall: op. cit.

² F. M. Jaeger: *Z. anorg. allgem. Chem.*, **101**, 182 (1917).

hydrated in aqueous solution at low temperatures and concentrations and that this hydration decreases as temperature and concentration are increased.

The complex nature of water itself and the lack of further data prevent us from proceeding further with the discussion at present.

In conclusion the author wishes to take the opportunity of expressing his gratitude to Dr. L. H. Adams for his advice and criticism which have been frequently sought and freely given during the prosecution of the work.

Summary

The densities and specific volumes of solutions of sodium sulphate at 25° and over a range of concentration from 0 to 28 per cent have been determined with an accuracy of 5 to 10 parts per million. The thermal expansibilities have been determined for the same solutions between 25° and 40° with the same accuracy. From these data the fictive volumes of sodium sulphate and water in solutions of sodium sulphate have been calculated.

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