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THERMODYNAMIC STUDY OF ALKALI SULPHATES

CALCULATION OF ENTHALPY, ENTROPY AND GIBBS FREE ENERGY

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ABSTRACT

Joined with measures of specific heat at low temperature, a calorimetric study of alkali sulphates from ordinary temperature to 1500 K has allowed the calculation of enthalpy, entropy and Gibbs free energy of these salts. The value of entropy at melting point is compared with the value assessed by an acoustical method.

INTRODUCTION

In this paper, we give the values of the three state functions enthalpy, entropy and Gibbs free energy of alkali sulphates reduced to absolute zero. These functions have the characteristic of being directly accessible through calorimetric measures. Furthermore, by studying the speed of sound in liquid alkali sulphates, we determined the values of entropy at their melting points and it is interesting to note that the values obtained by both calorimetric and acoustic methods approximate each other.

METHOD

Low-temperature measurements were made by Paukov and coworkers[1–4] between about 10 and 298 K. The authors measured $C_p(T)$ directly in an adiabatic calorimeter[5]. The differences in experimental values as compared with smoothed values of $C_p(T)$ do not exceed 0.06 at very low temperatures and 0.011 in the 50–300 K field. Between 400 and 1500 K measurements were made by enthalpymetry in an ice calorimeter by the drop method[6]. The sample heated beforehand above its melting point to eliminate any trace of water, is enclosed in a container made of platinum kept in the oven by a metal wire of which the breaking by electric short circuit causes the drop in the calorimetric tube. Enthalpic values in the case of sulphates are given with differences from 0.03 to 0.07 for the lowest temperatures and from 0.01 to 0.02 to the highest temperatures.

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The method used for determining the speed of sound in liquid sulphates is an impulsion method which is similar to that worked out by Litowitz et al.[7] on the one hand and Petit and Blanc[8] on the other. Each pulse from the electronic circuit is sent on the one hand in the fixed length sample under study and on the other in an acoustic delay line constituted by a variable length of water.

The pulse from the delay line is made to coincide with the signal emitted by the sample by adjusting the length of water. To avoid any ambiguity, the measurements are taken from the first signal emitted by the salt and the delay line. The accuracy of speed is from 1 to 4 m sec^{-1} for values between 1000 and 2000 m sec^{-1} inclusive[9].

RESULTS AND ARGUMENTS

Enthalpy values were smoothed in the shape of polynome by the method of least squares which seems most appropriate in the case of a considerable number of experimental points. The form of expressions for sulphates was previously dealt with in earlier publications[6].

TABLE I

VALUES OF ENTHALPY, ENTROPY AND GIBBS FREE ENERGY FOR Li_2SO_4

1 cal = 4.184 J. $\Delta H = H^\circ - H^\circ_0$; $\Delta S = S^\circ - S^\circ_0$; $\Delta G = G^\circ - G^\circ_0$.

$T(K)$	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	$-\Delta G/T$ (cal mol^{-1} K^{-1})
274	3790	24.9	11.1
390	7184	35.1	16.7
506	11363	44.5	22.0
622	15910	52.6	27.0
738	20870	59.9	31.6
796	23647	63.5	33.8
Transition temperature: (848 ± 2) K Transition enthalpy: (6110 ± 100) cal mol^{-1} Transition entropy: (7.2 ± 0.1) cal mol^{-1} K^{-1}			
849	32581	74.1	35.8
909	35895	77.9	38.4
969	39078	81.3	41.0
1029	42130	84.4	44.6
1089	45051	87.1	45.7
1119	46462	88.4	46.9
Melting temperature: (1130 ± 3) K Melting enthalpy: (2230 ± 100) cal mol^{-1} Melting entropy: (1.97 ± 0.1) cal mol^{-1} K^{-1}			
1131	49251	90.9	47.3
1203	52827	93.9	50.0
1275	56402	96.8	52.6
1347	59978	99.5	55.0
1419	63553	102.1	57.3
1455	65341	103.4	58.5

Data regarding temperatures between 298 and 400 K inclusive are obtained by extrapolating enthalpic curves relating to higher temperatures. These values agree very satisfactorily with those determined by adiabatic calorimetry between 298 and 700 K by Schmidt[10].

The results obtained and shown in Tables 1–5 were calculated from a standard thermodynamic relationship giving values of enthalpy, entropy and Gibbs free energy.

Entropic values calculated by acoustical method are deduced from a similar method as that proposed by Cantor[11]. He assumed that the entropy of the liquid consists of the sum of one part of internal movements contributions in the ions (S_i) together with the entropy of the quasi-lattice liquid (S_r).

Under that assumption the Debye temperature, θ_D, may be defined for the quasi-lattice by an expression analogous to that used for a solid lattice[12]:

$$S_r = 3nR(4/3 - \log \theta_D/T)$$

$$\theta_D = h/k(3N/4\pi)^{1/3}(n/V)^{1/3}u$$

R, k, h, N are the gas constant, the Boltzmann constant, the Planck constant and the

TABLE 2

VALUES OF ENTHALPY, ENTROPY AND GIBBS FREE ENERGY FOR Na_2SO_4

1 cal = 4.184 J.

T (K)	ΔH (cal mol^{-1})	ΔS (cal mol^{-1})	$-\Delta G/T$ (cal mol^{-1} K^{-1})
274	4849	33.7	16.0
326	6516	39.3	19.3
378	8223	44.2	22.4
430	10081	48.8	25.3
482	12104	53.2	28.1
508	13155	55.3	29.4
Transition temperature: (515 ± 1) K			
Transition enthalpy: (1650 ± 90) cal mol^{-1}			
Transition entropy: (3.2 ± 0.2) cal mol^{-1} K^{-1}			
516	15129	59.2	29.8
648	20465	68.4	36.8
780	26151	76.3	42.8
912	32184	83.5	48.2
1044	38567	90.0	53.1
1143	43582	94.6	56.5
Melting temperature: (1155 ± 2) K			
Melting enthalpy: (5580 ± 130) cal mol^{-1}			
Melting entropy: (4.83 ± 0.11) cal mol^{-1}			
1156	49842	100.0	56.9
1220	52966	102.7	59.2
1284	56091	105.1	61.4
1348	59215	107.5	63.6
1412	62340	109.8	65.6
1460	64683	111.4	67.1

Avogadro number, respectively

n is the number of ions per molecule; here $n = 3$

V is the molar volume

u is the speed of sound at temperature T

S_i is essentially the sum of the vibration and rotation entropies calculated from the standard relationship[13] of the shape:

$$S = R(\log Z + T(\partial \log Z/\partial T)_V)$$

Z being the partition function of vibration or rotation. Table 6 gives the values of the various entropies and the total entropy calculated for liquid sulphates at their melting points. Agreement between these results is satisfactory. Nevertheless comparison remains tricky, as Cantor's assumptions are arbitrary, in particular the definition of θ_D (which does not result from structural considerations). Furthermore

TABLE 3

VALUES OF ENTHALPY, ENTROPY AND GIBBS FREE ENERGY FOR K_2SO_4

1 cal = 4.184 J.

T (K)	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	$-\Delta G/T$ (cal mol^{-1} K^{-1})
274	5331	39.3	19.9
394	9232	51.1	27.6
514	13714	61.0	34.3
634	18515	69.4	40.2
754	23769	76.9	45.4
814	26716	80.7	47.9
Transition temperature: (855 ± 1) K			
Transition enthalpy: (2140 ± 70) cal mol^{-1}			
Transition entropy: (2.5 ± 0.1) cal mol^{-1} K^{-1}			
856	31103	85.9	49.6
956	35576	90.8	53.6
1056	40235	95.5	57.4
1156	45080	99.9	60.9
1256	50111	104.0	64.1
1306	52697	106.0	65.7
Melting temperature: (1341 ± 2) K			
Melting enthalpy: (8795 ± 150) cal mol^{-1}			
Melting entropy: (6.6 ± 0.1) cal mol^{-1} K^{-1}			
1342	63378	114.0	66.8
1370	64748	115.0	67.8
1398	66118	116.0	68.7
1426	67488	117.0	69.7
1454	68858	118.0	70.6
1468	69543	118.4	71.0

entropic values determined with the assistance of sound velocity imply free rotations in liquid sulphates which is not confirmed by the studies of geometrical obstruction or free volume[14].

CONCLUSION

It may be noted that the values obtained from our calorimetric measurements in the case of Na_2SO_4 are in agreement with those recently published[15]. The acoustic methods, however, appear to be able to produce an order of magnitude only.

TABLE 4

VALUES OF ENTHALPY, ENTROPY AND GIBBS FREE ENERGY FOR Rb_2SO_4
1 cal = 4.184 J.

T (K)	ΔH ($cal\ mol^{-1}$)	ΔS ($cal\ mol^{-1}\ K^{-1}$)	$-\Delta G/T$ ($cal\ mol^{-1}\ K^{-1}$)
274	5694	44.5	23.8
406	10184	57.8	32.8
571	16602	71.1	42.0
703	22286	80.0	48.3
825	28748	88.4	54.0
901	32451	92.7	56.6
Transition temperature: (931 ± 4) K			
Transition enthalpy: (1039 ± 180) cal mol^{-1}			
Transition entropy: (1.12 ± 0.2) cal mol^{-1} K^{-1}			
932	35360	95.8	57.8
1016	39208	99.8	61.2
1100	43212	103.6	64.3
1184	47372	107.2	67.2
1268	51690	110.7	70.0
1310	53907	112.4	71.3
Melting temperature: (1339 ± 2) K			
Melting enthalpy: (9180 ± 200) cal mol^{-1}			
Melting entropy: (6.9 ± 0.2) cal mol^{-1} K^{-1}			
1340	64691	120.5	72.2
1368	66074	121.5	73.2
1396	67457	122.5	74.2
1424	68840	123.5	75.2
1452	70223	124.5	76.1
1466	70914	125.0	76.6

TABLE 5

VALUES OF ENTHALPY, ENTROPY AND GIBBS FREE ENERGY FOR Cs_2SO_4
1 cal = 4.184 J.

$T(K)$	ΔH $(cal\ mol^{-1})$	ΔS $(cal\ mol^{-1}\ K^{-1})$	$-\Delta G/T$ $(cal\ mol^{-1}\ K^{-1})$
274	5863	48.0	26.6
410	10498	61.6	36.0
546	15756	72.7	43.8
682	21577	82.2	50.5
818	28198	91.0	56.5
886	31963	95.4	59.3
Transition temperature: (~940) K Transition enthalpy: (600 ± 130) cal mol^{-1} Transition entropy: (0.64 ± 0.1) cal mol^{-1} K^{-1}			
941	35894	99.7	61.6
1009	38987	102.9	64.2
1077	42251	106.0	66.8
1145	45687	109.1	69.2
1213	49293	112.2	71.5
1247	51160	113.7	72.6
Melting temperature: (1274 ± 3) K Melting enthalpy: (8620 ± 170) cal mol^{-1} Melting entropy: (6.8 ± 0.1) cal mol^{-1} K^{-1}			
1275	61343	121.7	73.6
1315	63318	123.2	75.0
1355	65294	124.7	76.5
1395	67270	126.1	77.9
1435	69245	127.5	79.3
1465	70727	128.5	80.3

TABLE 6

VALUES OF THE VARIOUS ENTROPIES AND THE TOTAL ENTROPY CALCULATED FOR ALKALI SULPHATES AT THEIR MELTING POINTS

Salt	T_F (K)	u_F $(m\ sec^{-1})$	*Entropy* $(cal\ mol^{-1}\ K^{-1})$				
			$S_{vib.}$	$S_{rot.}$	S_t	$S_{tot.}$	$S_{calor.}$
Li_2SO_4	1130	2371	19.9[a]	24.26	52.5	96.7	90.9
Na_2SO_4	1155	2053	20.2	24.31	56.7	101.2	99.9
K_2SO_4	1341	1743	22.7	24.76	65.0	112.5	114.0
Rb_2SO_4	1339	1363	22.7	24.76	69.5	117.0	120.5
Cs_2SO_4	1274	1200	22.0	24.60	71.6	118.2	121.7

[a] Vibration frequencies were selected in Ref. 13; the distance S–O is 1.50 Å.

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