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Aqueous solution of sodium sulfate. Determination of the dissolution enthalpy at 25, 27.5 and 45°C[☆]

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Abstract

The dissolution enthalpy of sodium sulfate in water was measured until saturation at 24.4, 27.5 and 44.3°C using a C80D differential calorimeter (Setaram).The experimental data were fitted using Pitzer's ion interaction model and the value of the dissolution enthalpy per mole of salt at infinite dilution was found at each temperature, by treating $(\Delta_{diss}H)^{\infty}$ as an adjustable parameter.

Keywords: Dissolution enthalpy; DSC; Sodium sulfate

1. Introduction

The phase diagram of the $(H_2O + Na_2SO_4)$ system exhibits the presence of two hydrates: $Na_2SO_4 \cdot 7H_2O$ (metastable) and $Na_2SO_4 \cdot 10H_2O$ (stable) [1]. Fig. 1 shows the part of the solubility diagram useful to our study [2, 3]. A three-phase metastable system $\{(Na_2SO_4 \cdot 7H_2O)$, anhydrous Na_2SO_4, saturated solution$\}$ is characterised by a temperature $t_A = 24.4$ °C and a maximum solubility $\hat{m}_A = 3.64$ mol of Na_2SO_4 per kg of water (point A). A three-phase stable system $\{(Na_2SO_4 \cdot 10H_2O)$, anhydrous Na_2SO_4, saturated solution$\}$ is characterised by a temperature $t_B = 32.38$°C and a maximum solubility $\hat{m}_B = 3.49$ mol of Na_2SO_4 per kilograms of water (point B). The line AB represents a metastable equilibrium between the anhydrous sulfate and the saturated solution. The shaded area A'ABB' represents a one-phase metastable solution.

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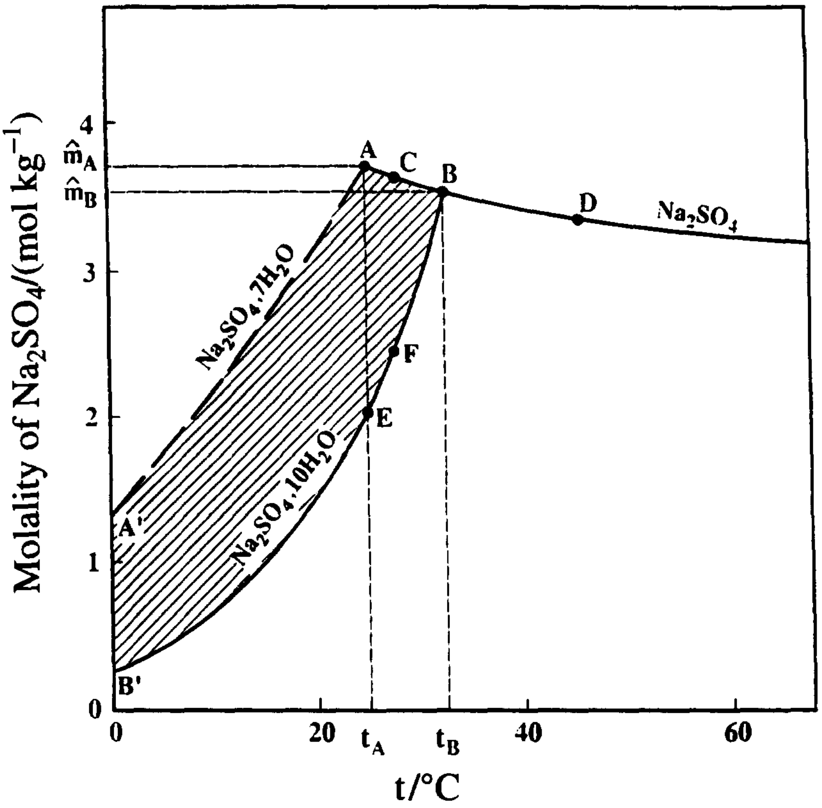

Fig. 1. Solubility diagram of $(H_2O + Na_2SO_4)$: molality $\hat{m}(Na_2SO_4)$ against temperature t, where t/°C = T/K − 273.15.

We have carried out three series of measurements corresponding to the temperatures: $t_A = 24.4$°C, $t_C = 27.5$°C and $t_D = 44.3$°C. Two multiphase equilibria states may be expected at each temperature t_A and t_C: stable equilibria respresented by points E and F; and metastable equilibria represented by points A and C. At t_D the equilibrium is stable and is represented by point D.

2. Experiments

We measured the dissolution enthalpy of sodium sulfate in water at 24.4, 27.5 and 44.3°C using a C80 differential calorimeter (Setaram). A mass m_1 of sodium sulfate and a mass m_0 of twice distilled water were introduced in the mixing cell. A mass $(m_1 + m_0)$ of water was introduced in the reference cell. The working temperature was fixed and then, when thermal equilibrium was reached, mixing was achieved using the inverting mechanism, which is driven by an electric motor.

The calorimeter was calibrated by measuring the heat of fusion of indium and by measuring the heat of dissolution of NaCl at 25°C. The precision of the results is about 2%. The lower value of the salt molality (0.28) was defined by the calorimeter sensitivity. Reagent grade Na_2SO_4 (Aldrich) was dried at 110°C.

3. Results

The initial system consists of n_1 moles of pure solid sodium sulfate and n_w moles of water and the measured enthalpy variation is ΔH_{exp}. This system may be scaled and described by the following equivalent systems. The first consists of 1 mol of sodium sulfate and $n'_w = n_w/n_1$ mol of water. The enthalpy variation is then $\Delta H = \Delta H_{exp}/n_1$. The second system consists of 1 kg of water and n_1/k mol of sodium sulfate where k is the number of kilograms of water of the initial system ($k = n_w M_w$). The enthalpy variation is then $\Delta \hat{H} = \Delta H_{exp}/k$.

The experimental results are reported in Tables 1–3 and the variations of $\Delta \hat{H}$ versus n_1/k are represented in Figs. 2–4. We observe that the three plots have the same shape, an initial decrease of enthalpy followed by a plateau level. The presence of a plateau indicates, on the one hand, that the solubility of sodium sulfate does not increase above

Table 1
The dissolution enthalpy of Na_2SO_4 in water at 24.4°C: $n_1/k = n_1/(n_w M_w)$, $M_w = 0.0180153$ kg mol^{-1} and $\Delta \hat{H} = \Delta H_{exp}/k = \Delta H_{exp}/(n_w M_w)$

n_w/mol	$n_1 \times 10^3$/mol	n_1/k/(mol kg^{-1})	ΔH_{exp}/J	$\Delta H_{exp}/n_1$/ J (mol Na_2SO_4)$^{-1}$	$\Delta \hat{H}$/ J (kg H_2O)$^{-1}$
0.2942	1.4952	0.2821	−3.05	−2038	−575
0.2942	2.2583	0.4261	−6.49	−2873	−1224
0.2776	2.8609	0.5721	−10.44	−3650	−2088
0.1110	1.7437	0.8716	−8.56	−4910	−4281
0.0942	1.7324	1.0211	−9.51	−5490	−5607
0.1388	2.9545	1.1816	−17.71	−5994	−7083
0.0555	1.4980	1.4983	−10.70	−7143	−10702
0.0531	1.5156	1.5840	−11.09	−7317	−11590
0.1110	3.5895	1.7942	−28.47	−7931	−14230
0.0419	1.5564	2.0629	−13.29	−8538	−17614
0.0416	1.6247	2.1654	−13.76	−8470	−18343
0.0833	3.7817	2.5206	−35.19	−9306	−23455
0.0416	2.1661	2.8877	−21.29	−9829	−28383
0.0555	3.2628	3.2625	−33.09	−10141	−33087
0.0559	3.3093	3.2863	−32.57	−9842	−32343
0.0603	3.8471	3.5431	−37.16	−9659	−34223
0.0615	4.0935	3.6915	−41.06	−10030	−37028
0.0555	4.0590	4.0606	−36.78	−9061	−36794
0.0559	4.4934	4.4573	−36.19	−8054	−35899
0.0416	3.6880	4.9167	−27.95	−7578	−37261
0.0352	3.5247	5.5516	−22.80	−6468	−35911

Table 2
The dissolution enthalpy of Na_2SO_4 in water at 27.5°C: $n_1/k = n_1/(n_w M_w)$, $M_w = 0.0180153$ kg mol^{-1} and $\Delta\hat{H} = \Delta H_{exp}/k = \Delta H_{exp}/(n_w M_w)$

n_w/mol	$n_1 \times 10^3$/mol	n_1/k/(mol kg^{-1})	ΔH_{exp}/J	$\Delta H_{exp}/n_1$/ J(mol Na_2SO_4)$^{-1}$	$\Delta\hat{H}$/ J(kg H_2O)$^{-1}$
0.2793	2.8686	0.5695	−11.46	−3995	−2276
0.0948	1.7754	1.0396	−10.28	−5789	−6018
0.0531	1.5121	1.5790	−11.29	−7466	−11788
0.0420	1.5543	2.0530	−13.22	−8503	−17457
0.0848	3.7795	2.4742	−34.58	−9150	−22638
0.0562	3.0995	3.0588	−30.35	−9792	−29956
0.0559	4.0421	4.0100	−36.29	−8958	−35925
0.0352	3.5226	5.5508	−22.94	−6511	−36143

Table 3
The dissolution enthalpy of Na_2SO_4 in water at 44.3°C: $n_1/k = n_1/(n_w M_w)$, $M_w = 0.0180153$ kg mol^{-1} and $\Delta\hat{H} = \Delta H_{exp}/k = \Delta H_{exp}/(n_w M_w)$

n_w/mol	$n_1 \times 10^3$/mol	n_1/k/(mol kg^{-1})	ΔH_{exp}/J	$\Delta H_{exp}/n_1$/ J(mol Na_2SO_4)$^{-1}$	$\Delta\hat{H}$/ J(kg H_2O)$^{-1}$
0.2942	2.2576	0.4260	−13.16	−5828	−2483
0.2776	2.8602	0.5720	−17.13	−5989	−3426
0.1110	1.7402	0.8699	−11.47	−6591	−5734
0.0832	1.7719	1.1813	−12.48	−7043	−8320
0.0555	1.5008	1.5011	−11.20	−7463	−11202
0.0555	1.8324	1.8331	−14.37	−7842	−14376
0.0416	1.6254	2.1657	−13.44	−8269	−17908
0.0416	1.6810	2.2398	−13.81	−8215	−18401
0.0416	1.8922	2.5233	−16.01	−8461	−21349
0.0416	2.1647	2.8866	−18.69	−8634	−24923
0.0558	3.3579	3.3422	−26.44	−7874	−26316
0.0555	4.0815	4.0795	−27.53	−6745	−25517
0.0563	4.5039	4.4421	−28.14	−6248	−27754
0.0432	3.8288	4.9194	−21.94	−5730	−28189

a certain n_1/k value, and on other hand, that the solid which is in equilibrium with the saturated solution is Na_2SO_4.

Each temperature has a corresponding solubility limit, characterised by a molality $(\hat{m}_1)_{sat}$. Thus, one can distinguish two cases: when $n_1/k \leqslant (\hat{m}_1)_{sat}$, the final system corresponds to an aqueous solution where the total amount of salt has been dissolved; and when $n_1/k > (\hat{m}_1)_{sat}$, the final system consists of a saturated solution with at least one solid phase.

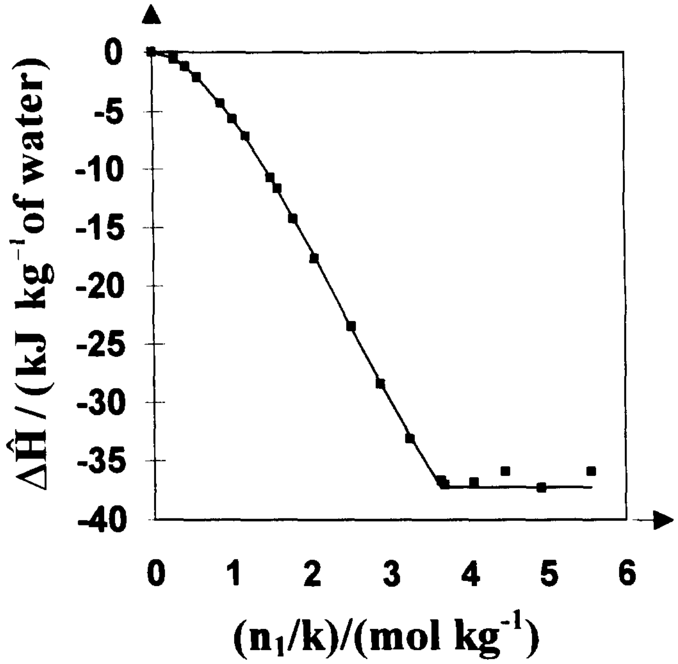

Fig. 2. Variations of $\Delta\hat{H}$ versus n_1/k at 24.40°C: ■, $\Delta\hat{H}$ experimental; — $\Delta\hat{H}$ calculated. With $n_1/k = [n_1/(n_w M_w)]$, $M_w = 0.0180153$ kg mol^{-1}, $\Delta\hat{H} = \Delta H_{exp}/k = \Delta H_{exp}/(n_w M_w)$.

Thus, the plots show that the solubility limits $(\hat{m}_1)_{sat}$ obtained at 24.4 and 27.5°C are approximately $(\hat{m}_1)_{sat} = 3.64$ mol of Na_2SO_4 per kg of water and $(\hat{m}_1)_{sat} = 3.57$ mol of Na_2SO_4 per kg of water. The saturated solutions are represented by points A and C on Fig. 1.

4. Discussion

The thermodynamic properties of aqueous solutions of strong electrolytes are represented using the unsymmetric convention and the molality scale. According to this convention, if the complete dissolution of n_1 moles of sodium sulfate in n_w moles of water is considered, the relative enthalpy L is defined by

$$L = H(n_w, n_1) - n_w h_w^* - n_1 \bar{h}_1^\infty \qquad (1)$$

where $H(n_w, n_1)$ is the total enthalpy of the solution, h_w^* the molar enthalpy of water and $\bar{h}_1^\infty$ the partial molar enthalpy of sodium sulphate at infinite dilution.

An apparent molar property is defined for a binary solution by the following equation

$${}^{\Phi}Z = [Z(n_w, n_1) - Z(n_w, 0)]/n_1 \qquad (2)$$

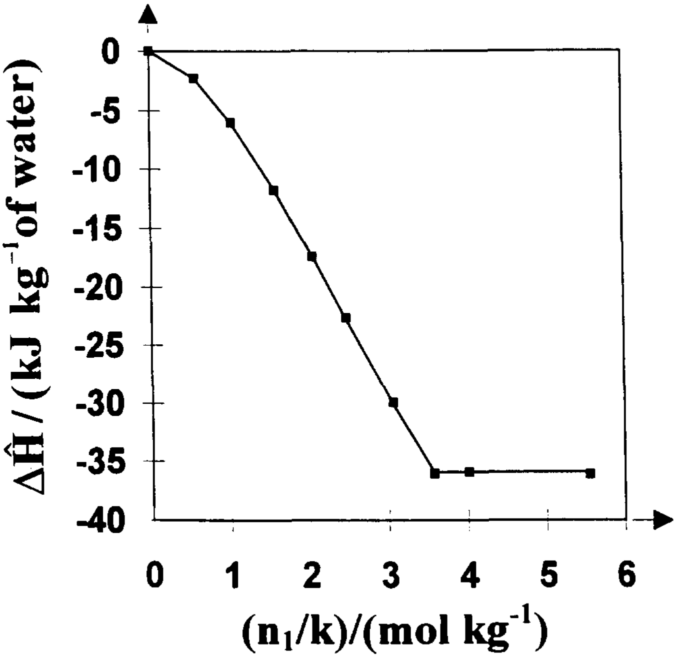

Fig. 3. Variations of $\Delta\hat{H}$ versus n_1/k at 27.50°C: ■, $\Delta\hat{H}$ experimental; — $\Delta\hat{H}$ calculated. With $n_1/k = [n_1/(n_w M_w)]$, $M_w = 0.0180153\ \mathrm{kg\ mol^{-1}}$, $\Delta\hat{H} = \Delta H_{exp}/k = \Delta H_{exp}/(n_w M_w)$.

where $Z(n_w, n_1)$ is an extensive property. In such conditions

$$ {}^{\Phi}H = [H(n_w, n_1) - n_w h_w^*]/n_1 \tag{3}$$

$$ {}^{\Phi}L = L(n_w, n_1)/n_1 \quad (\text{since } L(n_w, 0) = 0) \tag{4}$$

The initial total enthalpy is

$$H_i = n_w h_w^* + n_1 h_1^* \tag{5}$$

where h_w^* is the molar enthalpy of pure water and h_1^* the molar enthalpy of pure sodium sulfate.

The measured dissolution enthalpy ΔH_{exp} is expressed by

$$\Delta H_{exp} = H(n_w, n_1) - n_w h_w^* - n_1 h_1^* \tag{6}$$

Hence

$$\Delta H_{exp}/n_1 = {}^{\Phi}H - h_1^* \tag{7}$$

If we consider Eq. (2), we have also

$$L/n_1 = {}^{\Phi}H - \bar{h}_1^{\infty} = {}^{\Phi}L \tag{8}$$

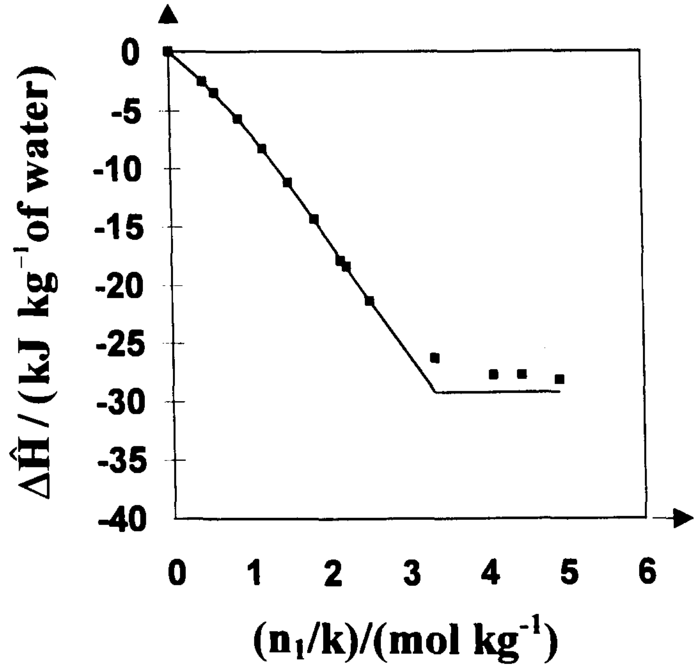

Fig. 4. Variations of $\Delta\hat{H}$ versus n_1/k at 44.30°C: ■, $\Delta\hat{H}$ experimental; — $\Delta\hat{H}$ calculated. With $n_1/k = [n_1/(n_w M_w)]$, $M_w = 0.0180153\ \mathrm{kg\ mol^{-1}}$, $\Delta\hat{H} = \Delta H_{exp}/k = \Delta H_{exp}/(n_w M_w)$.

The molar dissolution enthalpy at infinite dilution is expressed by

$$(\Delta_{diss}H)^{\infty} = \bar{h}_1^{\infty} - h_1^{*} \tag{9}$$

Hence

$$\Delta H_{exp}/n_1 = {}^{\Phi}L + (\Delta_{diss}H)^{\infty} \tag{10}$$

and

$$\Delta\hat{H} = (n_1/n_w M_w)[{}^{\Phi}L + (\Delta_{diss}H)^{\infty}] \tag{11}$$

The relatively enthalpy L can be calculated from the excess Gibbs energy of the solution

$$L = G^E - T(\partial G^E/\partial T)_{p,\hat{m}_1} \tag{12}$$

We have chosen to represent G^E with Pitzer's model [4] which also provides a representation of ${}^{\Phi}L$ versus composition and adjustable parameters.

For a 1–2 electrolyte

$${}^{\Phi}L = L/n_1 = 3(A_H/2b)\ln(1 + bI^{1/2}) - 4RT^2[\hat{m}_1 B^L_{MX} + 2\hat{m}_1^2 C^L_{MX}] \tag{13}$$

with $B^L_{MX} = B^{(0)L}_{MX} + (2B^{(1)L}_{MX}[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})])/\alpha^2 I$, where I is ionic strength $= 3\hat{m}_1$, $b = 1.2\ \mathrm{kg^{1/2}\ mol^{-1/2}}$ and $\alpha = 2\ \mathrm{kg^{1/2}\ mol^{-1/2}}$. We have fitted experi-

Table 4
Results of the experimental data fitting with Pitzer's model considering $(\Delta_{\mathrm{diss}}H)^{\infty}$ as an adjustable parameter

T/K	$B^{(0)\mathrm{L}} \times 10^2$	$B^{(1)\mathrm{L}} \times 10^1$	$C^{\mathrm{L}} \times 10^3$	$(\Delta_{\mathrm{diss}}H)^{\infty}$/kJ mol^{-1}	$(\Delta_{\mathrm{diss}}\hat{H})_{\mathrm{sat}}$/kJ (kg H$_2$O)$^{-1}$
297.55	0.1953	0.1167	−0.1212	−0.987	−36.580
300.35	0.1918	0.1024	−0.1252	−2.060	−36.034
317.45	0.1228	0.0716	−0.0773	−7.235	−26.944

mental data considering $(\Delta_{\mathrm{diss}}H)^{\infty}$ as an adjustable parameter. The results are reported in Table 4. The calculated values of $\Delta\hat{H}$ are represented in Figs. 2–4. The results of the fitting show that $(\Delta_{\mathrm{diss}}H)^{\infty}$ is well represented by

$$(\Delta_{\mathrm{diss}}H)^{\infty}/(\mathrm{J\,mol^{-1}}) = 9139 - 312.5\,(T/\mathrm{K}) \tag{14}$$

From Eq. (9) we obtain

$$(\partial(\Delta_{\mathrm{diss}}H)^{\infty}/\partial T) = (\partial \bar{h}_1^{\infty}/\partial T)_P - (\partial h_1^{*}/\partial T)_P \tag{15}$$

The molar heat capacities are defined by $Cp_1^{\ominus} = (\partial \bar{h}_1^{\infty}/\partial T)_P$ and $Cp_1^{*} = (\partial h_1^{*}/\partial T)_P$, where $Cp_1^{\ominus}$ is the standard molar heat capacity of Na_2SO_4 in the solution and Cp_1^{*} is the standard molar heat capacity of Na_2SO_4 (pure solid). The NBS values [5] of these heat capacities are (at $T = 298.15$ K) $Cp_1^{\ominus} = -201$ J K^{-1} mol^{-1} and $Cp_1^{*} = 128$ J K^{-1} mol^{-1}. Then

$$(Cp_1^{\ominus} - Cp_1^{*})_{\mathrm{NBS}} = -329\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

The experimental value is obtained from Eq. (14)

$$(Cp_1^{\ominus} - Cp_1^{*})_{\mathrm{EXP}} = -312\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

Our value is in very good agreement with the NBS value.

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