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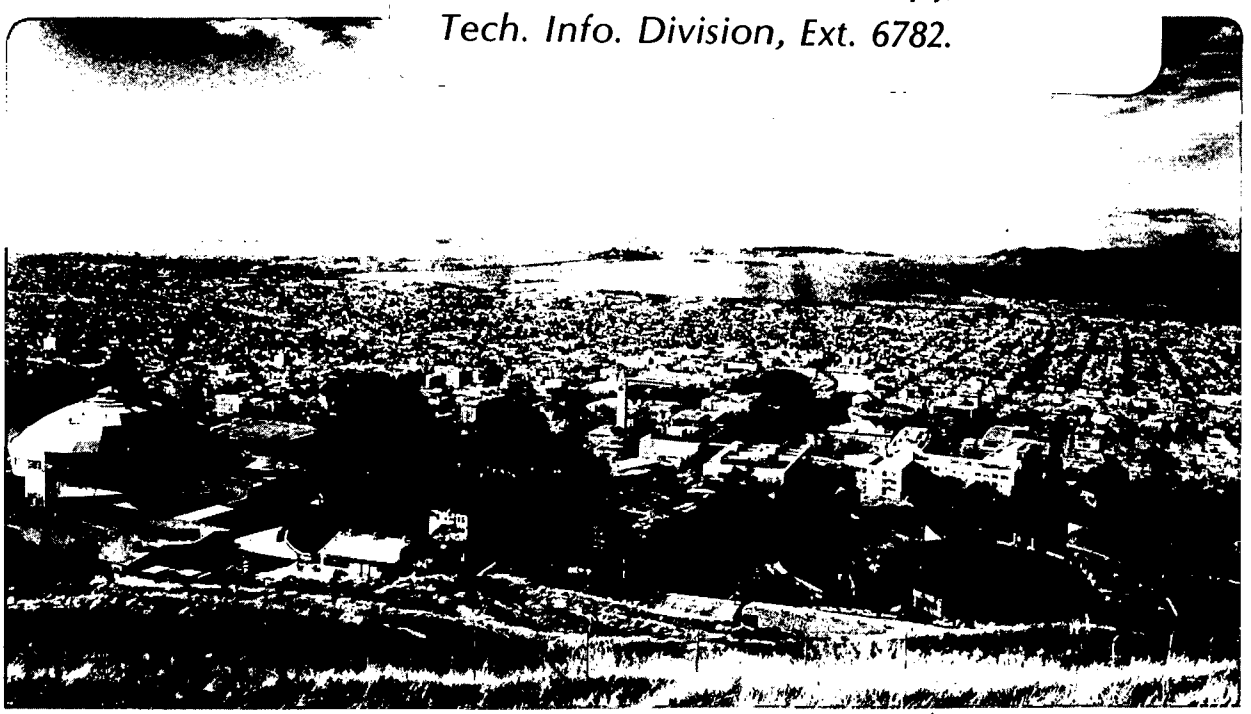

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Thermodynamics of Aqueous Sodium Sulfate

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(Abstract)

The activity coefficient of saturated aqueous Na_2SO_4 is calculated from the properties of the solid and the infinitely dilute solution as well as the solubility. These values are compared with those given by the equation of Rogers and Pitzer which is based on the measured dependence of heat capacity upon molality together with other solution properties at low temperature. Excellent agreement is found from 30 to 280°C. Consequently the equation of Rogers and Pitzer is given an extended range of validity to saturated molality and to 280°C. The trend of solubility with temperature is discussed in relation to the ΔC_p of solution.

Key Words: activity coefficient; electrolyte solutions; solubility; sodium sulfate

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1. Introduction

Recently Rogers and Pitzer[1] measured the heat capacity of aqueous Na_2SO_4 to 200°C and combined these results with literature data on enthalpies and osmotic coefficients at lower temperatures to give equations for the excess Gibbs energy, enthalpy, and heat capacity and for the partial molal heat capacity at zero molality. In view of limitations of the range of input data, validity of the equations for the excess Gibbs energy and the activity coefficient was claimed only to 2.5 mol kg^{-1} below 120°C and to 1.5 mol kg^{-1} from 120 to 200°C. It seems likely, however, that the range of actual validity is wider, and we now explore that question by use of the data on the solubility of Na_2SO_4 which are available to much higher temperature. Since the heat capacity was measured to 200°C, the first and second temperature derivatives of the Gibbs energy are accurately known at that temperature. Even if the equation yields a gradually increasing error in the second derivative, the parent function should remain quite accurate for a considerable range of temperature above 200°C. This we test. Also the comparisons with solubility data test the extrapolation of the molality dependence above the range of measurement.

2. Data and Equations

Schroeder, et al.,[2] measured the solubility of Na_2SO_4 from 150 to 350°C. They also summarized the literature data and obtained curves for the solubility over the full range 0 to 350°C. Recent measurements of Potter and Clynne[3] from 32 to 93°C are presumably more accurate and were adopted below 100°C. Above that temperature the curve of Schroeder, et al., was adopted.

Rogers and Pitzer[1] expressed the standard partial molal heat capacity (at zero molality and saturation pressure) of Na_2SO_4 with the equation

$$C^{\circ}_{p,2} = U_1 + U_2T + U_3T^2 + U_4/(T-263) \tag{1}$$

This equation was integrated twice to yield $(G^{\circ}_T-H^{\circ}_{298})/T$ as follows:

$$H^{\circ}_{T'}-H^{\circ}_{298} = \int_{298}^{T'} C_p dT \tag{2}$$

$$\frac{G_{T'}-H^{\circ}_{298}}{T'} = -\int_{298}^{T'} \frac{H^{\circ}_T-H^{\circ}_{298}}{T^2} dT + S^{\circ}_{298} \tag{3}$$

The value of S°_{298} for $2Na^+ + SO_4^=$ was taken from the CODATA table[4] of 1977 to be 58.41 and 18.83 J K^{-1} mol^{-1}, respectively. The final equation then becomes

$$\frac{G^{\circ}_T-H^{\circ}_{298}}{T} = 990.405 \ln T - 3.39818\ T + 0.001962983\ T^2 + \frac{120470.45}{T} + \frac{6518.67}{263}\left[\frac{T-263}{T}\ln(T-263)-\ln T\right] - 4941.85 \text{ J K}^{-1} \text{ mol}^{-1} \tag{4}$$

Solid Na_2SO_4 exists in several crystalline forms with ranges of metastability as well as true stability. Fortunately the aqueous phase is a catalyst for phase transformation; hence its probable that the solubilities were measured for the stable phases in each range of temperature. Brodale and Giauque[5] examined this situation and give thermodynamic properties for each solid form. They conclude that form V is stable up to 458 K, form IV from 458 to 514 K, and form I above

514 K with forms II and III never stable at least at low pressure. We use the values of $(G_T^\circ - H_0^\circ)/T$ and $(H_T^\circ - H_0^\circ)/T$ as given by Brodale and Giauque. For forms V, IV, and I the reference H_0° is that of form V; hence the heats of transformation are incorporated in their tabulated functions. The remaining quantity required is

$$H_{298}^\circ(aq) - H_0^\circ(c,V) = 20863 \text{ J mol}^{-1}$$

which was obtained as the sum of $H_{298}^\circ - H_0^\circ$ for the solid, 23206 J mol^{-1}, and ΔH_{298}° of solution from Pitzer and Coulter,[6] -2343 J mol^{-1}.

Combination of these quantities yields $\Delta G^\circ/T$ for solution which is related to the solubility m and the mean activity coefficient $\gamma_\pm$ by

$$\Delta G^\circ/T = -R \ln(4m^3\gamma_\pm^3) \tag{5}$$

From the measured solubility the activity coefficient then can be calculated.

Rogers and Pitzer[1] also give equations for the activity coefficient of Na_2SO_4 derived from the change of heat capacity with molality up to 474 K together with literature data on the osmotic coefficient, the heat of dilution, and related quantities up to 393 K. Application of these equations to saturated solutions is a considerable extrapolation beyond the claimed range of validity, but is is interesting to determine their accuracy over this extended domain.

3. Results

Table I gives the results comparing the activity coefficient determined from solubility with that from the solution nonideality equations. The agreement is excellent, not only below 200°C where the test is essentially the extension to higher molality, but also up to 280°C which

involves also an extrapolation upward by 80°C. It is apparent that the two functions are beginning to deviate rapidly above 280°C.

The effects of pressure rapidly become more significant above about 250°C. Strictly speaking, these calculations relate to a hypothetical state at low and constant pressure. The saturation pressure of water is small enough at 200°C that Rogers and Pitzer neglected the effect of its increase above the standard pressure of one atmosphere. While there are no data for Na_2SO_4 in this range, one can make estimates from NaCl and these indicate that increasing pressure should affect the comparison in Table I by no more than about 2% at 250°C but that the effect could easily be 10% at 300°C. Pressure influences both the activity coefficient itself and the standard state $\Delta G°$ of solution. Both effects will tend to raise $\gamma_\pm$ at the higher pressure. These increases should each be a few percent at 250°C with the difference no greater than about 2% as indicated above. The uncertainty of estimate increases rapidly above 250°C.

4. Discussion

A few comments seem worthwhile concerning the qualitative trend of the solubility of sodium sulfate and the ΔC_p of solution. Over the temperature range 30 - 185°C the solubility values in Table I relate to solid form V. The solubility first decreases with temperature, then passes through a minimum and then increases. This indicates an increasing heat of solution and a positive ΔC_p of solution. Yet the data for the standard state at infinite dilution yield a large, negative ΔC_p° of about -200 J K^{-1} mol^{-1}. Thus the apparent molal heat capacity at saturation molality must exceed that for the standard state by more than

200 J K^{-1} mol^{-1}. The equations of Rogers and Pitzer[1] do, indeed, yield this very large increase in apparent molal heat capacity with concentration, as they must to yield the agreement already reported. But it is worthwhile to keep in mind this striking effect when examining solubility data for salts or making estimates of change of solubility with temperature.

The ΔC_p of solution eventually becomes negative even at saturation molality in the higher temperature range where the stable solid is form IV. This may be noted from the data in Table I for the range 200 - 240°C. In this range the standard state ΔC_p° becomes even more negative, about -500 J K^{-1} mol^{-1}. Although the apparent molal heat capacity at saturation is much larger than that for the standard state, that increase is not enough to yield a positive ΔC_p.

5. Conclusions

The activity coefficient equation of Rogers and Pitzer[1] for aqueous Na_2SO_4 is shown to be accurate to about 2% in the extended range to saturation molality up to 200°C. From 200 to 280°C the equation also appears to be accurate to about 2% for the hypothetical low-pressure state. Values for the real state at the saturation pressure of water would be slightly higher but the exact amount of increase can only be estimated at this time.

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Table I. The Activity Coefficient of Aqueous Sodium Sulfate from Two Sources

t_1 °C	m mol kg^{-1}	$\gamma_\pm$ from solution data[a]	$\gamma_\pm$ from solid and solubility[b]
30	3.51_8	0.137_8	0.139_4
40	3.36_6	0.140_6	0.142_4
60	3.14_8	0.140_4	0.141_7
80	3.02_0	0.133_5	0.133_1
100	2.97_0	0.120_0	0.120_2
120	2.95_2	0.104_8	0.104_9
140	2.95_7	0.088_8	0.089_1
160	2.99_9	0.072_5	0.073_3
180	3.06_2	0.057_5	0.058_7
200	3.13_3	0.044_3	0.045_9
220	3.20_3	0.033_4	0.035_0
240	3.20_3	0.025_0	0.026_6
260	2.96_4	0.019_9	0.020_8
280	2.41_5	0.018_1	0.017_9
300	1.69	(0.019_3)	(0.017_5)

[a] From reference 1.

[b] From equation (5) above.

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