Osmotic Coefficients of Aqueous Solutions of Seven Compounds at 0°C

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Aqueous sulfuric acid and urea have been used as isopiestic standards to derive the 0°C osmotic coefficients for NaCl, KCl, $CaCl_2$, Na_2SO_4, and $MgSO_4$.

A number of low-temperature isopiestic comparisons of single salt solutions have been made in this laboratory as part of a larger program to determine activity coefficients in aqueous mixed salt solutions at temperatures from 25°C down to the freezing point. Although these results are not of the highest precision possible, they temporarily fill a gap in a temperature region which is of great interest in the study of natural brines and for which there is at present a general shortage of thermodynamic data. The osmotic coefficients at 15°C of aqueous solutions of seven compounds have been tabulated *(1)*. The results at 0°C for the same compounds are reported here.

Experimental

Materials. The chemicals were purified as described previously *(1)*.

Apparatus and procedure. Comparisons were made in an ice-water bath mounted on a mechanical shaker, using the apparatus previously described *(1)*. The reference materials were urea and sulfuric acid for water activities (a_w) of 0.861 or greater, this limit being set by the solubility limit of urea. At lower a_w it was necessary to rely solely on sulfuric acid as a reference. The freezing point measurements of Scatchard and Prentiss *(6)* on so-

Table I. Isopiestic Motalities at 0°C

Urea	H_2SO_4	NaCl	KCl	$CaCl_2$	Na_2SO_4	$MgSO_4$
0.7645		0.4038	0.4110			
0.9572		0.5011	0.5126			
		0.6740			0.6640	
		0.7290	0.7523	0.4959		1.209
		0.8581			0.8836	
		0.8881			0.9252	
		0.9290				1.478
2.045		1.018	1.059			
		1.096				1.663
2.526	1.033		1.291	0.7840	1.357	1.776
2.952		1.408	1.483			
		1.436				1.987
	1.450	1.826		1.066		
4.548		2.020	2.167			
		2.704	2.965			
	2.075	2.767		1.500		
7.374		2.935				
	2.186	2.957		1.580		
		3.037				3.068
8.539		3.278	3.664			
8.698		3.326	3.724			
8.799		3.352	3.77			
10.738		3.868				
	2.966	4.190		2.116		
	3.086	4.399				
	3.576	5.238		2.536		
	4.087	6.100				
	4.096	6.100		2.874		
	5.205			3.585		
	5.491			3.761		
	6.930			4.612		
	7.837			5.106		
	8.173			5.296		
	8.313			5.368		
	8.974			5.723		
	9.129			5.803		
	9.591			6.058		
	10.130			6.363		
	10.500			6.583		
	10.832			6.775		
	10.959			6.867		
	11.138			6.972		

Table II. Osmotic Coefficients at 0°C

Molality	Urea	H_2SO_4	NaCl	KCl	$CaCl_2$	Na_2SO_4	$MgSO_4$
0.1	0.994	0.680	0.931	0.926	0.862	0.779	0.605
0.2	0.989	0.669	0.923	0.911	0.866	0.729	0.565
0.3	0.984	0.670	0.917	0.912	0.874	0.696	0.544
0.4	0.979	0.674	0.913	0.897	0.882	0.671	0.530
0.5	0.974	0.679	0.912	0.892	0.895	0.649	0.520
0.6	0.970	0.685	0.911	0.888	0.922	0.629	0.517
0.7	0.965	0.693	0.911	0.885	0.951	0.612	0.517
0.8	0.960	0.704	0.912	0.883	0.980	0.598	0.520
0.9	0.956	0.716	0.914	0.881	1.011	0.587	0.526
1.0	0.951	0.728	0.915	0.879	1.042	0.578	0.532
1.5	0.930	0.791	0.928	0.876	1.208	0.552	0.578
2.0	0.913	0.864	0.950	0.883	1.393		0.675
2.5	0.897	0.946	0.977	0.892	1.600		0.795
3.0	0.882	1.036	1.005	0.901	1.828		0.975
3.5	0.870	1.130	1.040	0.912	2.063		
4.0	0.857	1.226	1.080	0.926	2.300		
4.5	0.846	1.322	1.118		2.542		
5.0	0.836	1.416	1.158		2.777		
5.5	0.826	1.502	1.200		2.995		
6.0	0.818	1.584	1.245		3.197		
6.5	0.811	1.661			3.341		
7.0	0.803	1.733			3.455		
7.5	0.795	1.801					
8.0	0.790	1.862					
8.5	0.784	1.920					
9.0	0.780	1.972					
10.0	0.773	2.066					

dium chloride and potassium chloride were also used, but osmotic coefficients derived from this source were limited to concentrations of 1.1*m* or less.

In assigning osmotic coefficients to urea there are two choices. The first values reported by Stokes *(8)* were based on freezing point measurements and a later set *(7)* was based on values extrapolated from higher temperatures using heat data. The first set gave results more consistent with those for the sulfuric acid and the sodium and potassium chloride data than did the second set. The freezing point data for urea, corrected for temperature, were therefore used here, although the difference between the two sets at 0°C was never more than 0.005 in the osmotic coefficient.

The osmotic coefficients for sulfuric acid at 25°C, ϕ_{25} *(5)*, were corrected to 0°C using the thermodynamic data of Giauque et al. *(2)*. The osmotic coefficient, ϕ_0, at 0°C and any given molality *m* was calculated from the expression:

$$\phi_0 = \phi_{25} + \frac{55.51 \times 25}{\nu m R \times 298.16 \times 273.16}\left\{-\bar{L}_1 + 25\bar{J}_1\right\} \qquad (1)$$

where R is the gas constant (8.314 $J\ K^{-1}\ mol^{-1}$), $\bar{L}_1$ is the relative partial molal heat content of the solvent water in the solution in $J\ mol^{-1}$, $\bar{J}_1$ is the temperature coefficient of $\bar{L}_1$ in $J\ K^{-1}\ mol^{-1}$, and ν has a value of 3.

The osmotic coefficients calculated from Equation 1 were lower by about 0.002 on the average than those reported earlier by Glueckauf and Kitt *(3)*. This difference was less than the experimental error in the present work and the 1960 values were (rather arbitrarily) used as standards.

Table III. Water Activity of Saturated Solutions at 0°C

Solid phase	*m*	a_w
$Na_2SO_4 \cdot 10W$	0.35	0.987
$MgSO_4 \cdot 7W$	1.82	0.959
KCl	3.77	0.883
Urea	10.7	0.861
$NaCl \cdot 2W$	6.10	0.760
$CaCl_2 \cdot 6W$	5.37	0.426
$H_2SO_4 \cdot 2W$	43.5	0.002

Results and Discussion

The results of the isopiestic comparisons are summarized in Table I. The original purpose of the work was not to obtain extensive intercomparisons among all seven compounds and for this reason some of the comparisons were made in the absence of either of the primary standards. When this was the case, the osmotic coefficients were estimated by interpolating isopiestic ratios between the standards and the salts in such sets of results. The salts $CaCl_2$, Na_2SO_4, and $MgSO_4$ all super-saturated very readily, and measurements are reported to concentrations well above their solubility limits. Such results are useful in treating mixed salt measurements, where osmotic and activity data are often needed at ionic strengths higher than those corresponding to saturated solutions of single salts. The osmotic coefficients are listed in Table II at rounded concentrations. The average amount by which the isopiestic ratios in Table I deviate from the smoothed ratios used to obtain the results in Table II was ±0.0038. This imprecision is indicative only of the internal consistency of the isopiestic ratios and, until independent activity standards at 0°C are available, it would seem reasonable to regard the ratios (or osmotic coefficients) as being accurate to not better than ±0.004. Jakli and Van Hook *(4)* have recently published the osmotic coefficients of, among other salts, calcium chloride as a function of temperature. Their extrapolated values at 0° agree with mine to within 0.004 at all concentrations up to 7*m*.

It is often useful to know the water activity of a saturated solution at some given temperature. The water activities of saturated solutions of the compounds studied here are given in Table III, along with their approximate concentrations.

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Potassium Sulfate Crystal Growth Rates in Aqueous Solution

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The growth kinetics of potassium sulfate crystals grown from aqueous solution at 20°C have been determined under carefully controlled conditions of temperature and supersaturation. The growth process is diffusion-controlled, being dependent on solution velocity up to about 140 mm/s, and shows an overall second-order dependence on supersaturation. However, the order changes from 2.0 for growth along the (001) crystallographic axis to 1.4 along the (100). Overall growth rates computed from the measured axial growth rates compare well with those measured in a multiparticle system in a fluidized bed crystallizer.

Potassium sulfate (mol wt = 174.26) crystallizes in the anhydrous form from aqueous solution as crystals belonging to the orthorhombic system. A common habit of this salt grown at low supersaturation is shown in Figure 1. The predominant crystallographic faces are (010) and (021).

The solubility of potassium sulfate in water over the temperature range $20 < \theta < 60°C$ may be represented by the equation:

$$c^* = 0.067 + 0.0023\theta - 0.000006\theta^2 \qquad (1)$$

An empirical correlation *(6)* between diffusivity and viscosity over the temperature range $15 < \theta < 50°C$ is:

$$D\eta \times 10^{13} = 8.1 + 0.071\theta \qquad (2)$$

where $D = m^2/s$ and $\eta = N\ s/m^2$. The activation energy of diffusion has been determined *(6)* as 20 kJ/mol.

Other relevant properties include: crystal density, $\rho_c = 2660\ kg/m^3$, density of saturated solution at 20°C, $\rho_s = 1082\ kg/m^3$, viscosity of saturated solution at 20°C, $\eta_s = 1.2 \times 10^{-3}\ N\ s/m^2$.

Growth Rate Measurements

The growth rates of single crystals of potassium sulfate were measured by a technique previously described *(1, 2, 4)*. Briefly, a crystal was mounted on a wire in a glass cell, through which a solution flowed under carefully controlled conditions. Any chosen face or edge could be observed, with a traveling microscope reading ±0.01 mm, and its rate of advance measured. Solutions were prepared from recrystallized potassium sulfate and deionized water and filtered through a No. 4 (30 μm) sintered glass filter. Seed crystals were carefully selected from batches grown in a laboratory-scale fluidized bed crystallizer *(1, 5)* by hand picking from a close sieve cut (22/25 mesh BS, mean size 650 μm). Slightly elongated crystals with well-defined faces, free from inclusions and outgrowths were chosen. These crystals were then grown to a larger size (~3 mm long, 1 mm wide) in the fluidized bed crystallizer at 20°C using a low supersaturation ($\Delta c \sim 0.008$ kg K_2SO_4/kg H_2O; $S \sim 1.07$) to avoid the production of inclusions and irregular growths.

The seed crystal, fixed on the wire with its longest axis vertical, was dipped into deionized water to remove any surface impurities and then introduced into the cell when the solution temperature had achieved a constant value of 20°C. The circulation velocity was adjusted to the desired value. The washing process removed the sharp edges and corners from the crystal so a short period of time (at least 15 min) was allowed for the crystal to "heal" itself before growth rate measurements were commenced. In view of the fact that several crystallographic

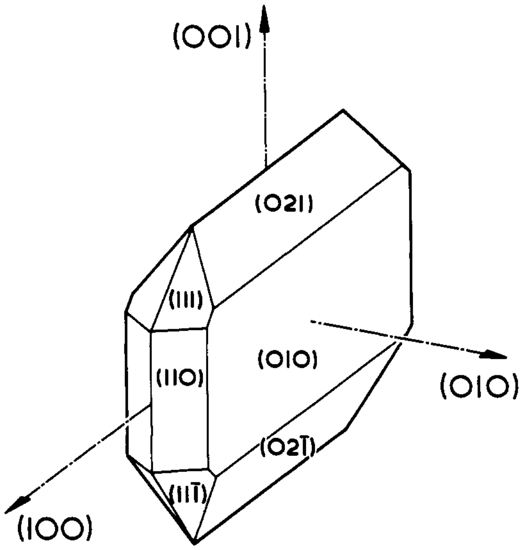

Figure 1. Typical habit of a potassium sulfate crystal grown from aqueous solution at low supersaturation

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