

Diffusion Coefficients of Potassium Sulfate in Water

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The differential diffusivities of the system K_2SO_4 -water have been measured at 25° C., at varying concentrations up to saturation, using an interferometric technique. Diffusivities over the range 15–50° C. were also determined at a concentration of 10.09 grams/100 grams H_2O and the results correspond to an equation of the form:

$$\Delta\eta \times 10^8 = 8.1 + 0.071t$$

The activation energy for diffusion for this concentration and temperature range is approximately 4.8 kcal./mole.

DIFFUSIVITY VALUES for the system K_2SO_4 -water were measured with a Zeiss diffusion interferometer. The experimental procedure has previously been described in detail (7). The method consists in bringing the two liquids concerned into contact by sliding the upper and lower portion of a diffusion cell into alignment. Then the free diffusion taking place is followed by an interferometric technique, the fringe patterns being recorded photographically. The limits of the technique are fixed by the minimum and maximum suitable refractive index differences (7).

In this particular method, by using sufficiently small concentration differences, a linear variation of diffusivity with concentration can be assumed and thus values of the differential diffusivity can be determined directly at the mean value \bar{c} of the concentration range Δc . It is possible to measure differential diffusivities in this system with concentration ranges down to 0.35 grams K_2SO_4 /100 grams H_2O , representing a shift of about 4 fringes. It is considered that at fringe shifts smaller than this, the error in analysis far outweighs any gain in reducing Δc . The results obtained usually represent Δc values of two grams K_2SO_4 /100 grams H_2O except at the extremes of the concentration range where various solutions were diffused into pure water and saturated solution. The accuracy is estimated to be $\pm 2\%$.

The method is, in comparison with other diffusion methods, rapidly carried out; each run including the analysis takes about three hours. It was found that, when working with this system, it did not matter whether the method of Longworth (6) in which the difference in fringe numbers is kept constant, or Creeth (1), in which analysis the fringe pair are maintained symmetrical with respect to the centre of the pattern, was chosen. Both gave results that fell within the estimated error range of $\pm 2\%$.

The differential diffusion coefficients for potassium sulfate in water at 25° C. are listed in Table I. The diffusivity increases quite sharply with decreasing concentrations below about three grams K_2SO_4 /100 grams H_2O , but, as saturation is approached, the diffusivity becomes almost independent of concentration. This behavior is typical of many electrolytes in water. It is interesting to note that a correlation of the form:

$$\frac{D}{D_0} = 1 - 0.41c^{0.22}$$

where c is the solution concentration in moles/liter and D_0 is the diffusivity at infinite dilution as predicted by the Nernst equation, fits the data quite accurately. This is similar in form to the empirical correlation reported by Emanuel and Olander (2) for the diffusion of copper sulfate in water.

Also shown in Table I is a value obtained by Gillam (3) using a modified Lamm interferometric method. This is an integral coefficient for the range 0–6.0 grams K_2SO_4 /100 grams water at 25° C. The value is some 2% high at the mean of this concentration range as would be expected for an integral coefficient.

Figure 1 shows an Arrhenius plot of differential diffusivities over the temperature range 15 to 50° C. with solution concentrations of 9.110 grams/100 grams H_2O and 11.07 grams/100 g H_2O ($\bar{c} = 10.09$ grams/100 grams H_2O). These values of diffusivity correspond to diffusion from saturated to slightly unsaturated solution at 20° C. and should give good approximations to diffusivity at saturation over this temperature range. This is due to the small change in diffusivity with concentration at concentrations approaching saturation as indicated in Table I. The activation energy for diffusion at these concentrations is calculated to be 4.8 kcal./mole.

The theories of liquid state phenomena suggest that diffusivity, viscosity, and absolute temperature are related by an expression of the form $(D\eta/T) = \text{constant}$. This relationship is considered to apply to diffusion of large

Table I. Diffusivity of Potassium Sulfate in Water at 25° C.

c Grams/100 Grams H_2O	\bar{c} Grams/100 Grams H_2O	Diffusion Coefficient, Cm. ² /Sec. $\times 10^8$
0	0	15.70 ^a
0.347	0.174	13.30
0.683	0.342	12.94
2.034	1.017	12.30
3.733	1.865	11.96
2.011	3.040	11.28
6.00	3.00	11.55 ^b
1.939	5.015	10.70
2.264	7.116	10.29
1.790	10.00	9.88
1.750	10.95	9.86
2.128	11.06	9.84
0.430	11.30	9.80

^a Nernst limiting value. ^b Based on reference (3).

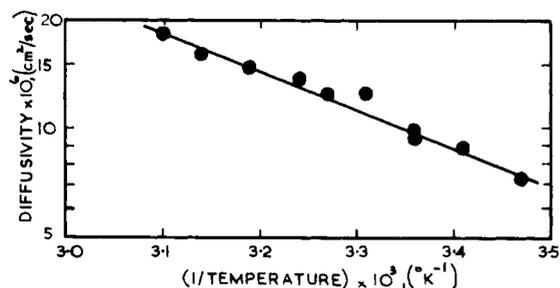


Figure 1. Plot of $\log D$ vs. $1/T$ for near-saturated potassium sulfate solutions

molecules through nonelectrolytes. However, a similar empirical equation has also been found to exist in certain concentrated electrolyte systems over a limited range of temperature and concentration (7). This gives rise to a useful working correlation which is particularly valuable considering the lack of diffusivity data and the complexity of theoretical equations for electrolytes (4). Figure 2 shows a plot of $D\eta$ against t , the temperature in degrees centigrade and gives rise to a correlation of the form:

$$D\eta \times 10^8 = 8.1 + 0.071 t$$

In this plot, the viscosity values are in poises and are available in the literature (5). The correlation is suitable for calculating differential diffusivity values for this system at concentrations approaching saturation and over the temperature range, 15–50°C.

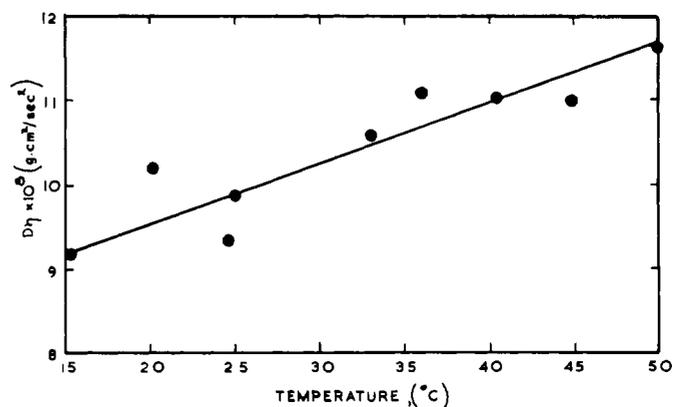


Figure 2. Plot of $D\eta$ vs. temperature for potassium sulfate

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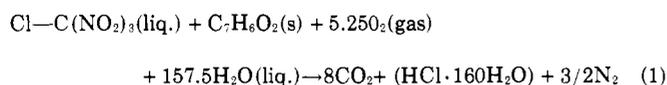
Heat of Formation of Trinitrochloromethane by Combustion Calorimetry

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The energy of combustion of liquid trinitrochloromethane with benzoic acid as fuel was determined in a rotating bomb calorimeter. The standard heat of formation at 25°C. was calculated using a computer program which has been developed for compounds containing C, H, O, N, and Cl. The heat of formation of trinitrochloromethane is -5.57 ± 0.18 kcal./mole (± 0.18 is estimated standard deviation of the mean). Some other properties—such as vapor pressure, latent heat of vaporization, density, refractive index, freezing point, surface tension, and heat capacity—for better characterization of trinitrochloromethane were also measured and are reported.

THE REACTION was carried out in an oxygen atmosphere using benzoic acid as the fuel. The equation of the idealized heat of reaction from which the heat of formation is determined is:



Difficulties were encountered in determining the proper ratio of trinitrochloromethane to benzoic acid for a complete reaction; 45% trinitrochloromethane produced a clean com-

bustion. Noticeable amounts of carbon and, in some instances, unburned trinitrochloromethane appeared in the bomb after the combustion if the trinitrochloromethane content was under 45%. Chlorine gas liberated in the reaction was converted to the chloride ion by adding arsenious acid solution to the bomb (8).

EXPERIMENTAL

Material. Trinitrochloromethane was synthesized and purified by distillation and vapor-liquid chromatography. No impurity was detected by either the gas chromatograph or