

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON]

Partial Molal Volumes of Nickel Sulfate Solutions

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Densities of nickel sulfate solutions have been determined at $25 \pm 0.02^\circ$.

Materials, Apparatus, Method.—Mallinckrodt Analytical Reagent nickel sulfate was thrice recrystallized from distilled water. A stock solution was prepared by dissolving the purified salt in redistilled water. The nickel sulfate content was determined by precipitation of the nickel dimethylglyoxime salt from weighed samples of the stock solution. The precipitates were filtered into weighed Gooch crucibles and brought to constant weight at 105° .¹ The accepted value was the average of three analyses in which the maximum deviation was less than 0.08% of error. Molal solutions in low concentrations were prepared by diluting weighed samples of stock solution to volume in calibrated flasks at 25° , then weighing the diluted solutions. In this way both molar and molal concentrations were obtained. The concentrated solutions were made up to volume, then weighed portions were analyzed. A saturated solution was prepared by allowing a warm concentrated nickel sulfate solution to cool to 25° , thus permitting it to come to equilibrium with the solid phase which separated. Weighed samples of the supernatant liquid were analyzed as previously. The solubility was found to be 28.42 g. of (± 0.02) nickel sulfate per 100 g. of solution.

For density determinations, Weld precision specific gravity bottles of approximately 25-ml. capacity were used. All weighings were corrected to vacuum. The density given for each concentration is the average of two series of determinations. The maximum deviation between each series is 0.005%.

Apparent molal volumes have been calculated from the equation

$$\phi = \frac{F}{d} - \frac{1000}{md} \frac{d - d_0}{d_0} \quad (1)$$

where ϕ is the apparent molal volume, F the formula weight of nickel sulfate, d_0 the density of water, 0.99707, d the density of the solution and m the molal concentration. Densities and the corresponding values of ϕ are shown in Table I.

(1) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936, p. 684.

TABLE I

Concentration		d_{25}	ϕ	$\delta\phi$
Molar	Molal			
0.06343	0.06357	1.00758	-10.98	-0.01
.34504	.34537	1.05250	- 5.92	+ .10
.74331	.74465	1.11332	- 1.64	- .24
1.1612	1.1659	1.17592	+ 0.77	+ .07
1.6448	1.6575	1.24685	2.90	+ .06
2.0538	2.0774	1.30646	4.12	+ .09
2.3467	2.3806	1.34889	4.84	+ .01
2.5246	2.5658	1.37460	5.22	- .09

From the data, an equation expressing ϕ as a function of m was found by the method of averages,² employing finally the principle of least squares to obtain best values of the coefficients

$$\phi = -14.88 + 15.10m^{1/2} + 1.80m - 2.14m^{3/2} \quad (2)$$

In column 5 are shown the deviations, $\delta\phi$, of the observed values from those calculated by equation (2).

Redlich³ has on the basis of the Debye-Hückel theory given as a limiting relationship

$$\phi = \phi_0 + kw^3/c^{1/2} \quad (3)$$

where $w = 1/2 \sum \nu_i z_i^2$; ν_i is the number of ions of species i and z is the valence. Assuming $k = 1.86$, expressing ϕ as a function of m and applying the equation to nickel sulfate, a bi-bivalent electrolyte, the equation becomes

$$\phi = \phi_0 + 14.88m^{1/2} \quad (4)$$

The slope, $d\phi/dm^{1/2}$, as m approaches 0, is 15.1 for equation (2) as compared to 14.88 in equation (4). The deviation in slope from that corresponding to $k = 1.86$ is within limits of experimental error, thus further confirming the validity of the limiting equation, (3). The partial molal volume at zero concentration was determined as -14.88 ml. per gram formula weight.

Summary

1. Densities at 25° of nickel sulfate solutions ranging from 0.0634 molar to 2.525 molar (saturated) have been determined.

2. The solubility of nickel sulfate at 25° was determined: 28.42 g. per 100 g. of solution.

3. Nickel sulfate was found to conform to the limiting equation as developed from Debye-Hückel theory.

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(2) Lipka, "Graphical and Mechanical Computation," John Wiley and Sons, Inc., New York, N. Y., 1918, p. 163.

(3) Redlich, *J. Phys. Chem.*, **44**, 619 (1940).