approach and other formulations that neglect polarization[8,11] seems to bear out Varshni's[10] contention that the added attraction is offset by added repulsion due to the distortion of the electron clouds in the direction of the bond.

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[CONTRIBUTION NO. 1477 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Diffusion and Activity Coefficient of Sodium Nitrate in Dilute Aqueous Solutions at 25°

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RECEIVED DECEMBER 23, 1957

The diffusion coefficient of sodium nitrate has been determined by the conductance method in the concentration range between 0.001 and 0.011 molar at 25°. From these data, its activity coefficient in very dilute solutions has been computed.

It has been shown that activity coefficients of univalent electrolytes at low concentrations can be evaluated with high accuracy in dilute solutions from diffusion coefficients.[1] The method is very favorable numerically and affords a means of obtaining activity coefficients at low concentrations of many electrolytes for which no other methods are available. In this contribution, this method has been applied to solutions of sodium nitrate at 25°.

The diffusion coefficient in dilute solutions may be computed by the equation[2]

$$\mathfrak{D} = 1000\nu\, RT(\overline{\mathfrak{M}}/c)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) \qquad (1)$$

where $\mathfrak{D}$ is the diffusion coefficient, ν is the number of ions into which the electrolyte dissociates, R is the gas constant in ergs moles deg.$^{-1}$ and T the absolute temperature. $(\overline{\mathfrak{M}}/c)$ is the concentration dependent mobility term and $(1 + c\partial \ln y_{\pm}/\partial c)$ is the thermodynamic term. The equations for computing $(\overline{\mathfrak{M}}/c)$ are given in detail elsewhere[3] and will not be reproduced here. Upon rearrangement, equation 1 becomes

$$\frac{\mathfrak{D}}{1000\,\nu\, RT\,(\overline{\mathfrak{M}}/c)} - 1 \equiv \mathfrak{D}' = c\,\frac{\partial \ln y_{\pm}}{\partial c} \qquad (2)$$

which defines the function $\mathfrak{D}'$. It is observed that c is the molar concentration and $y_{\pm}$ is the activity coefficient on the molar concentration scale. From this equation, we obtain

$$\log y_{\pm} = \frac{\ln y_{\pm}}{2.3026} = 0.8686 \int_0^c \frac{\mathfrak{D}'}{c^{1/2}}\, dc^{1/2} \qquad (3)$$

An important feature of this method is that the limiting value of $\mathfrak{D}'/c^{1/2}$ is fixed and is not dependent upon the diffusion coefficient. Thus

$$\lim_{c=0}\left[\frac{\mathfrak{D}'}{c^{1/2}} = \frac{\partial \ln y_{\pm}}{2\partial c^{1/2}}\right] = -\frac{2.3026}{2}\,\mathcal{S}_{(f)} \qquad (4)$$

where $\mathcal{S}_{(f)}$ is the theoretical slope of the logarithm of the activity coefficient. By plotting $\mathfrak{D}'/c^{1/2}$ against $c^{1/2}$ to this limiting value, the activity coefficient may be obtained by equation 3 by graphical integration.

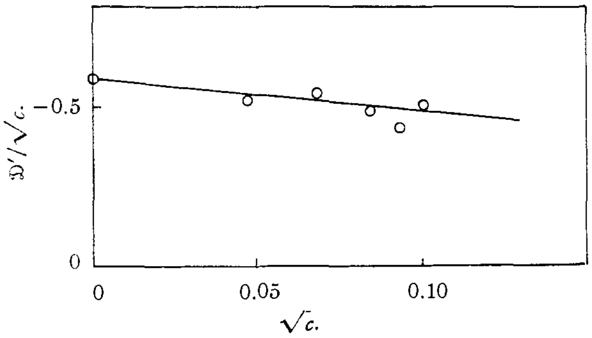

Fig. 1.—Plot for the computation of the activity coefficient of sodium nitrate at 25°.

Table I contains the observed values of the diffusion coefficient of sodium nitrate at the concentrations indicated. It also includes all the data necessary for computing the mobility term $(\overline{\mathfrak{M}}/c)$ according to the equations referred to in reference 3.

TABLE I

COMPUTATION OF $\mathfrak{D}'/c^{1/2}$ USED FOR DETERMINING THE ACTIVITY COEFFICIENT OF SODIUM NITRATE[a]

c	$A'\sqrt{c}$	$\phi(A'\sqrt{c})$	$\Delta\overline{\mathfrak{M}}'/c \times 10^{20}$	$\Delta\overline{\mathfrak{M}}''/c \times 10^{20}$
0.00223	0.0543	1.756	0.022	0.074
.00479	.0788	1.438	.032	.128
.00710	.0969	1.260	.036	.170
.00872	.1074	1.176	.042	.194
.01009	.1155	1.119	.045	.214

$c^{1/2}$	$\mathfrak{D}$(obs.) $\times 10^5$	$(\overline{\mathfrak{M}}/c) \times 10^{20}$	$-\mathfrak{D}'$	$-\mathfrak{D}'/c^{1/2}$
0.0472	1.534	31.707	0.02439	0.5167
.0686	1.516	31.751	.03707	.5408
.0843	1.512	31.786	.04073	.4834
.0934	1.514	31.807	.03997	.4280
.1005	1.498	31.824	.05056	.5033

[a] $\lambda^0_+ = 50.11$; $\lambda^0_- = 71.44$; $\Lambda^0 = 121.55$; $10^3\,\eta = 8.849$; $D = 78.54$; $a = 3.5$ Ångströms; $A' = 1.150$; $\mathcal{S}_{(f)} = 0.5091$.

Figure 1 shows a plot of $\mathfrak{D}'/c^{1/2}$ *versus* $c^{1/2}$ from which the activity coefficients of sodium nitrate at round concentrations recorded in Table II were calculated.

Certain features of this calculation deserve notice. Numerically, the method is very favorable since the limiting value of $\mathfrak{D}'/c^{1/2}$ is known and since the deviation of the activity coefficient from

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(1) H. S. Harned, *Proc. Nat. Acad. Sci.*, **40**, 551 (1954).

(2) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958, p. 121–2, equations (4-4-19), (4-4-20) and (4-4-21).

TABLE II

THE ACTIVITY COEFFICIENT OF SODIUM NITRATE IN DILUTE AQUEOUS SOLUTION AT 25°

c	0.0005	0.001	0.002	0.005	0.010	0.015	0.020
y^{+}	0.9746	0.9696	0.9508	0.9251	0.8933	0.8793	0.8643

unity is measured by the entire area under the graph. It is true that the selection of a value of the distance parameter, a, required for calculating the mobility term is arbitrary, but it should be observed that the variation of this mobility term with concentration is small and is not very sensitive to the value of a.

This investigation was supported in part by the Atomic Energy Commission under Contract AT (30-1)-1375.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Electrical Conductivity of Ag_2HgI_4

BY THEODORE J. NEUBERT AND GEORGE M. NICHOLS

RECEIVED JANUARY 11, 1958

The electrical conductivity of pressed samples of Ag_2HgI_4 has been studied as a function of temperature and time. A.c. measurements were made at a frequency of 1000 sec.$^{-1}$. Curves of steady state log σ *versus* T^{-1} data are similar to curves given by previous workers although there are differences which are described and discussed. The activation energy for the conduction process ($T < 20°$) in β-Ag_2HgI_4 was found to be 12 kcal. mole^{-1}. Transition temperature for temperatures increasing is *ca.* 52°. Measurements made with T-increasing and T-decreasing show a hysteresis the magnitude of which depends upon the rate of temperature change. Sample history and the time-schedule of measurement were found to be very important. Measurements as a function of time upon changing from one temperature to another indicate that in the region of the order-disorder transition (35-52°) resistance values relax more slowly than temperature can be changed. Analysis of the rate of this slow approach to a steady state indicates that both in the approach to order (T-decreasing) and in the approach to disorder (T-increasing) two nucleation steps are involved. The necessity for the two steps is also indicated in the steady state log σ *versus* T^{-1} curves by a secondary inflexion occurring at 48° for T-increasing and showing a constant hysteresis of 8°.

Silver tetraiodomercuroate (Ag_2HgI_4) is a thermochromic compound which exhibits an order-disorder transition[1] in the region of 52°. X-Ray diffraction,[2-6] specific heat,[7] electrical conductivity,[8,9] color transition[5] and dilatometric[10] studies have been reported. It is the purpose of this paper to report some extensions of the electrical conductivity data and to describe attempts to elucidate the approach of conductivity values to a steady state.

Although there are some variations in interpretation of the X-ray diffraction patterns, the order-disorder transition may be pictured (after Ketelaar) as follows. In both the low temperature β-modification (yellow) and the high temperature α-modification (red) iodine ions are cubic close-packed and silver and mercury ions occupy some of the tetrahedral holes. The β-modification has tetragonal symmetry; mercury ions situated at corners of a (cubic) unit cell and silver ions at the mid-points of the vertical faces. As the temperature is raised it becomes possible for silver and mercury ions to occupy each other's lattice sites and also the two extra lattice sites (the top and bottom face centers of the "unit cube") which are unoccupied at lower temperatures. Above 52° mercury ions and silver ions are completely disordered. The α-modification has, therefore, averaged face centered cubic symmetry.

Experimental

Preparation of Stock Material.—Ag_2HgI_4 was precipitated slowly, and with vigorous stirring, from 0.5 *m* $HgI_4^{=}$ solution by addition of the stoichiometric amount of 1 *m* Ag^+ solution. Reagent grade chemicals (KI, HgI_2 and $AgNO_3$) were used. The precipitated powder was washed (10-15 times) by decantation, filtered and dried *in vacuo* over P_2O_5. The preparation was carried out in diffuse light using brown bottles, but otherwise no extraordinary precautions were taken to avoid photochemical effects. Analysis showed the product to contain 1.009 times the theoretical amount of silver, the apparent loss of mercury iodide being presumably the result of too many decantations.

Preparation of Samples.—Samples for conductivity measurement were formed by pressing at room temperature in an evacuable stainless steel die. The piston was one inch in diameter and ram pressures were 20-40 thousand pounds. Measured densities were 5.8-6.0 g. cm.$^{-3}$, depending upon the pressing force and upon whether or not the die was evacuated during pressing. Carefully pressed samples were a uniform yellow-orange color and were semi-translucent, *e.g.*, ordinary typewriting could be read through specimens 1 mm. thick. Before making measurements, new samples were cycled to above and below the transition temperature two or three times in order to relieve strains and improve their homogeneity.

Some measurements were made on cast samples. These were prepared by heating Ag_2HgI_4 powder in glass tubes enclosed in an iron bomb to *ca.* 450°. No specific data for cast specimens will be reported because their stoichiometry was somewhat altered from Ag_2HgI_4 by the casting operation. The results were, in general, very similar to those obtained with pressed specimens.

Conductivity Measurements.—Sample resistances were determined using an essentially symmetrical conductance-capacitance impedance bridge with a Wagner grounding arm. The bridge was constructed in this Laboratory to measure the equivalent parallel resistance (R_p) and equivalent parallel capacitance (C_p) over the wide range of values exhibited by Ag_2HgI_4 in the temperature region $-35°$ to 90°. Although the accessible frequency range was 5 to 300,000 sec.$^{-1}$, only work at 1000 sec.$^{-1}$ is discussed in this paper. Bridge balances at 1000 sec.$^{-1}$ usually could be made to a precision of 0.1% in R_p.

Electrode System.—Samples were introduced into the bridge circuit *via* a three electrode (guarded) cell intended to

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[1] J. A. A. Ketelaar, *Trans. Faraday Soc.*, **34**, 874 (1938).

[2] J. A. A. Ketelaar, *Z. Krist.*, **80**, 190 (1931); **87**, 436 (1934).

[3] L. K. Frevel and P. P. North, *J. Applied Phys.*, **21**, 1038 (1950).

[4] C. E. Olsen and P. M. Harris, *Phys. Rev.*, **86**, 651 (1952).

[5] L. Suchow and P. H. Keck, THIS JOURNAL, **75**, 518 (1953).

[6] S. Hoshino, *J. Phys. Soc., Japan*, **10**, 197 (1955).

[7] J. A. A. Ketelaar, *Z. physik. Chem.*, **B30**, 53 (1935).

[8] J. A. A. Ketelaar, *ibid.*, **B26**, 327 (1934).

[9] L. Suchow and G. R. Pond, THIS JOURNAL, **75**, 5242 (1953).

[10] D. G. Thomas, L. A. K. Stavely and A. F. Cullis, *J. Chem. Soc.*, 1727 (1952).