[CONTRIBUTION NO. 1561 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient at 25° of Potassium Chloride at Low Concentrations in 0.75 Molar Aqueous Sucrose Solutions

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RECEIVED JULY 27, 1959

The diffusion coefficient of potassium chloride at concentrations between 0.004 and 0.025 molar in 0.75 molar sucrose solution has been determined. The limiting equivalent conductance of potassium chloride in these sucrose solutions has been evaluated. Comparison of the observed and theoretical diffusion coefficients has been made.

The diffusion of potassium chloride at low concentrations in 0.25 molar sucrose solutions by the conductance method was the subject of an earlier communication.[1] Similar determinations in a medium of somewhat higher viscosity is the subject of the present study.

Experimental Results

The method of preparation of solutions and the experimental procedure was identical with that described previously. For theoretical purposes, the limiting conductance of potassium chloride was determined from the measured equivalent conductances given in Table I. The values of the equivalent conductance were found to approach the Onsager limiting equation as the concentration decreased so that a satisfactory extrapolation to zero concentration could be made. The value of Λ^0 obtained from our results agrees closely with the one reported by Stokes and Stokes.[2]

TABLE I

EQUIVALENT CONDUCTANCE OF POTASSIUM CHLORIDE IN 0.75 MOLAR SUCROSE SOLUTIONS ($\Lambda^0 = 85.16$)

c	Λ	c	Λ
0.002	83.05	0.014	79.84
.004	82.20	.016	79.54
.006	81.55	.018	79.24
.008	81.04	.020	78.97
.010	80.60	.030	77.82
.012	80.20	.040	76.68

Following the procedure described by Harned and Nuttall,[3] we have adopted the procedure of substituting the difference in conductance at the bottom and top of the cell for the concentration difference. This method is justified within narrow limits as shown by the data in Table II. This table contains the specific conductances at suitable round concentrations and values of the coefficient $(L'' - L')/(c'' - c')$. This conductance–concentration quotient varies somewhat but is not greater than 0.5% so that no observable error is introduced by substituting conductance differences for concentration differences.

TABLE II

SPECIFIC CONDUCTANCE—CONCENTRATION COEFFICIENT FOR POTASSIUM CHLORIDE IN 0.75 MOLAR SUCROSE SOLUTIONS

c''	$L'' \times 10^3$	c'	$L' \times 10^3$	$\frac{(L'' - L')}{(c'' - c')}$
0.02	1.5794	0.002	0.1661	0.0785
.018	1.4263	.004	.3288	.0784
.016	1.2726	.006	.4893	.0783
.014	1.1178	.008	.6483	.0783
.012	0.9624	.010	.8060	.0782

TABLE III

THEORETICAL AND OBSERVED DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE IN 0.75 MOLAR SUCROSE SOLUTIONS

c	$\overline{\mathfrak{M}}'/c \times 10^{20}$	$\overline{\mathfrak{M}}''/c \times 10^{20}$	$\overline{\mathfrak{M}}/c \times 10^{20}$	$\mathfrak{D}_M \times 10^5$	$\mathfrak{D} \times 10^5$ (Calcd.)	$\mathfrak{D} \times 10^5$ (Obsd.)
0.00414	0.0002	0.0577	22.932	1.0932	1.0960	1.087
.00454	.0002	.0615	22.936	1.0915	1.0945	1.082
.00730	.0002	.0644	22.959	1.0824	1.0864	1.094
.00910	.0002	.0977	22.972	1.0777	1.0823	1.066
.01077	.0002	.1034	22.983	1.0739	1.0790	1.074
.01358	.0003	.1272	23.001	1.0679	1.0738	1.079
.01778	.0003	.1474	23.022	1.0617	1.0686	1.066
.01901	.0003	.1533	23.027	1.0600	1.0671	1.075
.02288	.0003	.1697	23.044	1.0552	1.0630	1.062

$\lambda^0_+ = 41.78$; $\lambda^0_- = 43.38$; $A' = 1.298$; $\mathring{a} = 3.8$; $\mathcal{S}_{(f)} = 0.572$; $\eta_0 = 0.01972$; $D = 72.67$; $T = 273.16$; $R \times 10^7 = 8.3114$; $\mathfrak{D}_0 \times 10^5 = 1.1314$; $\mathcal{S}_{\mathfrak{D}} = 0.747$.

The Diffusion Coefficient and its Theoretical Calculation.—The observed diffusion coefficients at the molecular concentrations, c, are given in the last column of Table III. The values in the next to last column were computed by the use of the equation

$$\mathfrak{D} = 2000RT\,(\overline{\mathfrak{M}}/c)(1 + c\,\partial \ln y_\pm/\partial c) \qquad (1)$$

where $(\overline{\mathfrak{M}}/c)$ is the Onsager and Fuoss[4] mobility term and $(1 + c\,\partial \ln y_\pm/\partial c)$ is the thermodynamic one. For these dilute solutions, the thermodynamic term was computed by the Debye–Hückel equation

$$\log y_\pm = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} \qquad (2)$$

For the evaluation of the mobility term, the theoretical equations as stated by Harned and Owen[5] were employed. The two parts of the mobility term which give the electrophoretic effect are given in columns two and three and the complete mobility term is recorded in column four. The fifth column contains values of the diffusion coefficient by neglecting the variation of $(\overline{\mathfrak{M}}/c)$ with concentration of salt while the sixth column includes this variation. The difference between the values in columns five and six represents the electrophoretic correction. At the bottom of the tables are to be found the quantities necessary for the calculation. Since no transference number data are known for these solutions, we assumed that the limiting transference numbers were identical with those in water. Upon this basis and our value for the limiting equivalent conductance of the salt, the limiting equivalent ionic conductances were computed.

At concentrations from 0.01 to 0.023, the results agree fairly well with the theoretical values. At lower concentrations the results scatter widely. As mentioned in our earlier contribution,[1] it is

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[1] H. S. Harned and J. A. Shropshire, THIS JOURNAL, **80**, 652 (1958).

[2] J. M. Stokes and R. H. Stokes, *J. Phys. Chem.*, **60**, 217 (1950).

[3] H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 736 (1947).

[4] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **34**, 2689 (1932).

[5] H. S. Harned and B. B. Owen, p. 121–122: Equations (4-4-19), (4-4-20), (4-4-20), (4-4-21), "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958.

much more difficult to obtain precise results in these more viscous solutions than in water. We do not yet understand the factors which cause this difficulty. In concluding, it should be noted that at these low concentrations of potassium chloride, we have avoided the difficulties which would be encountered in considering the migration of all the components in this three component system.

Acknowledgment.—This work 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 AT THE UNIVERSITY OF WASHINGTON]

Vapor Pressure of Chromium(II) Bromide

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RECEIVED AUGUST 24, 1959

The vapor pressure of $CrBr_2(s)$ has been measured over the temperature interval 837–1083°K., and thermodynamic properties of the monomeric and dimeric forms have been evaluated relative to the solid.

The vapor pressure of $CrBr_2$ has been measured between 972 and 1083°K. by the transpiration method and in the vicinity of 839°K. by the torsion effusion method.

Experimental Part

The experimental methods and apparatus have been described in earlier papers.[1,2] Argon was used as a carrier gas in transpiration experiments; flow rates between 13 and 60 ml./min. gave the same vapor pressures. The quantity of $CrBr_2$ transported was determined spectrophotometrically, after oxidation to chromate, as described in an earlier study on $CrBr_3$.[3] $CrBr_2$ was prepared in a quartz tube by reaction of HBr with powdered chromium metal at 750°. It was purified by sublimation in high vacuum; analysis gave a chromium content corresponding to 99.3% $CrBr_2$.

With the radiant heating technique employed,[2] the torsion effusion cell could be heated only to 568° at which the vapor pressure of $CrBr_2$ is near the lower limit of the sensitivity of the apparatus. Hence torsion measurements were limited to this one temperature and to a cell with moderately large orifices ($A_0 = 2.60 \times 10^{-3}$ and 3.72×10^{-3} cm.^{2}). The sample was introduced into the cell (in a dry box) through the effusion orifices. Calibration of the apparatus has been described earlier.[2]

Results and Discussion

Results are shown in Fig. 1. The solid line is drawn through the calculated transpiration pressures when the monomer is assumed the only vaporizing species; the dotted line represents the same data if the dimer were the only vapor species. The monomer line is seen to be in better agreement with the absolute pressures obtained by the torsion effusion method (the points grouped at the lowest temperature). We were unable to confirm independently that the torsion pressures shown are a good approximation to equilibrium vapor pressures (steady-state pressures in effusion cells with moderately large orifices will be below equilibrium values if the condensation coefficient is small)[2,4] by repeating the measurement with a cell with smaller orifices since the latter would give a deflection at 568° too small for accurate measurement. Hence the torsion points (Fig. 1) are regarded as lower limiting values; they do correlate well with the transpiration data, however, which suggests they are close to equilibrium. The solid line may be represented by the equation

$$(837\text{–}1083°\text{K.})\ \log P_{\text{mm.}} = -12050T^{-1} + 11.06$$

which, without further knowledge of the mode of vaporization, gives the standard (atm.) free energy of sublimation equation

$$\Delta F^0 = 55{,}100 - 37.4T$$

Recently Schoonmaker, Friedman and Porter[5] have carried out a mass spectrometric analysis of the vapor in equilibrium with $CrBr_2$ at 931°K. Their results indicate about 20% of the vapor to be in the form Cr_2Br_4 at this temperature. They also measured the vapor pressure at this one temperature by conventional effusion technique and report $\Delta F^0 = 17.2$ for the reaction

$$Cr_2Br_4(g) = 2CrBr_2(g) \qquad (1)$$

and, from an estimated ΔS^0 of 32 e.u., calculate ΔH^0 for (1) as 47 kcal.

Using their standard free energy and estimated entropy changes for (1), we have calculated the partial pressures of monomer and dimer for each of our measured vapor pressures ($\Delta F^0 = -RT \ln K_1 = 47{,}000 - 32\ T.$, assumed; ΔC_p for (1) neglected). Data are summarized in Table I. P_{am} represents the apparent pressure of monomer, *i.e.*, as shown in Fig. 1, the pressure calculated from the number of grams of chromium halide transported, assuming

TABLE I

°K.	$P_{am} \times 10^4$, atm.	$K_1 \times 10^4$	$P_m \times 10^5$, atm.	$P_d \times 10^5$, atm.
		Transpiration data		
972	0.603	2.67	4.5	0.76
1000	1.26	5.28	9.3	1.64
1021	2.41	8.60	17.2	3.44
1024	2.48	9.20	17.7	3.41
1024	2.46	9.20	17.8	3.44
1048	4.58	15.6	32.4	6.73
1083	12.8	32.4	84.0	21.8
		Torsion effusion data		
	($P_t \times 10^4$)			
837	0.00607	0.0528	0.055	0.0057
837	.00775	.0528	.069	.0085
838	.00538	.0546	.049	.0048
841	.00640	.0676	.059	.0050

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[1] R. O. MacLaren and N. W. Gregory, *J. Phys. Chem.*, **59**, 184 (1955).

[2] R. J. Sime and N. W. Gregory, *ibid.*, **64**, 86 (1960).

[3] R. J. Sime and N. W. Gregory, THIS JOURNAL, **82**, 93 (1960).

[4] J. H. Stern and N. W. Gregory, *J. Phys. Chem.*, **61**, 1226 (1957).

[5] R. C. Schoonmaker, A. H. Friedman and R. F. Porter, private communication; *J. Chem. Phys.* in press.