[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Interpretation of Diffusion Data for Some Strong Electrolytes

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I. Introduction

In the theory[1] consisting of combining Fick's law of diffusion with the thermodynamic idea that the driving force per unit mass of solute is equal to the gradient of the Gibbs chemical potential, one finds that the coefficient of diffusion D of a binary electrolyte is given by the formula

$$D = 2RT\frac{\Omega}{C}(1 + C\,\partial \log f/\partial C)10^3 \qquad (1)$$

in which R is the gas constant, T the absolute temperature, Ω/C the mobility or velocity due to unit force, C the concentration in moles per liter, f the mean activity coefficient of the ions. At infinite dilution Ω/C reduces to the classical Nernst expression which, for a uni-univalent electrolyte, is

$$10^{20}\lim_{C=0}\Omega/C = 1.074\,\frac{\Lambda^0_+\Lambda^0_-}{\Lambda^0_+ + \Lambda^0_-} \quad \text{(c. g. s. units)} \qquad (2)$$

where the limiting equivalent conductivities Λ^0_+ and Λ^0_- are expressed in reciprocal ohms. As explained by Onsager and Fuoss[1] the factor $1 + C\partial \log f/\partial C$ allows "for the interionic attraction reducing the thermodynamic tendency of the ions to separate by diffusion." For the factor Ω/C Onsager and Fuoss[1] give a theory in which they "compute the effect of interaction on the mobility of the migrating ions." The result of this theory for a uni-univalent electrolyte at 18° is

$$10^{20}\Omega/C = 1.074\,\frac{\Lambda^0_+\Lambda^0_-}{\Lambda^0_+ + \Lambda^0_-} - 9.60\left(\frac{\Lambda^0_+ - \Lambda^0_-}{\Lambda^0_+ + \Lambda^0_-}\right)^2$$
$$\frac{\sqrt{2C}}{1 + A\sqrt{2C}} + 15.6\ C\varphi(A\sqrt{2C}) \qquad (3)$$

in which A is a specific constant for the electrolyte and $\varphi(A\sqrt{2C})$ is a function defined by

$$\varphi(x) = e^{2x}Ei(2x)/(1 + x)^2 \qquad (4)$$

with

$$Ei(y) = \int_y^\infty e^{-t}\frac{dt}{t} = -0.5772 - \log y + y - \frac{y^2}{2.2!} + \frac{y^3}{3.3!} - \cdots \qquad (5)$$

For salts such as potassium chloride and potassium nitrate, which are both considered in the present paper, the difference $\Lambda^0_+ - \Lambda^0_-$ is small and Ω/C varies with concentration only on account of the last term in formula (3). For sodium chloride, however, the second term on the right-hand side of this formula is not negligible. As indicated on Fig. 7 of the paper of Onsager and Fuoss,[1] their theory predicts an increase of Ω/C with concentration for both potassium and sodium chloride, but these authors have not shown that, when Ω/C is calculated from the experimental values of D according to formula (1), one finds that, for sodium chloride, this mobility Ω/C decreases steadily as concentration rises, while for potassium chloride an increase of Ω/C of the order required by the theory appears only at concentrations higher than 2 molar. They mention, however, that "at higher concentrations, we meet with quite appreciable deviations, particularly in the case of sodium chloride, and our theory of Ω/C is definitely not adequate." They also state that viscosity and hydration are the probable causes for the deviations. Whether the limiting law for Ω/C is verified or not is doubtful on account of the lack of accurate diffusion data at very low concentrations. A comparison between experimental and calculated coefficients of diffusion such as that presented by Onsager and Fuoss[1] on Fig. 8 of their paper can hardly be considered as a conclusive test of the theory. In the present paper we compare theoretical and "experimental" values of Ω/C after elimination of the thermodynamic factor $2RT(1 + C\,\partial \log f/\partial C)$ from the measured values of D. To the two cases considered by Onsager and Fuoss (potassium and sodium chloride at 18°) we are adding potassium chloride at 25° and potassium nitrate at 18°. Diffusion data for potassium chloride at 25° recently have been published by McBain and Dawson.[2] The dependence on concentration of these new data is of the same type as that exhibited by Clack's data[3] at 18°, a fact which entitles us to reject most of the previous data for potassium chloride (see

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(1) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932). The first complete proof that the affinity of diffusion is measured by the gradient of the Gibbs chemical potential is due to Defay [Compt. rend. du 2^{me} Congrès National des Sciences, Brussels, 1935, p. 317] whose reasoning is based upon DeDonder's theory of affinity [see DeDonder and Van Rysselberghe, "Thermodynamic Theory of Affinity, a Book of Principles," Stanford University Press, 1936.]

(2) McBain and Dawson, *Proc. Roy. Soc.* (London), **148A**, 32 (1935). It should be noted that the legend of the vertical coördinate axis of Fig. 3 of this paper was given erroneously as "cm.^{2}/sec. × 10^5" instead of "cm.^{2}/day."

(3) Clack, *Proc. Phys. Soc.* (London), **36**, 313 (1924).

Fig. 1 of McBain and Dawson[2]). For potassium nitrate we use Clack's diffusion coefficients[3] and Robinson's activity data.[4] The latter were not available at the time of the publication of the paper of Onsager and Fuoss.[1] Following these authors, who used Harned's activity data[5] for 25°, we likewise use Robinson's data for 25° in order to study diffusion coefficients at 18°, hence neglecting the small difference due to heats of dilution. We also present a quantitative investigation of the effect of viscosity on diffusion.

II. Comparison between Measured and Calculated Diffusion Mobilities

1. **Potassium Chloride.**—At 25° we have[5,6]

$$\log f = -\frac{0.820\sqrt{2C}}{1 + 0.76\sqrt{2C}} + 0.0394 \times 2C$$

and hence

$$1 + C\partial \log f/\partial C = 1 - \frac{0.410\sqrt{2C}}{(1 + 0.76\sqrt{2C})^2} + 0.0788\ C$$

At infinite dilution we have, according to the data of MacInnes, Shedlovsky and Longsworth[7] at 25° and other standard data

$$10^{20}\Omega/C = 34.84 \text{ and } 2RT = 4.842 \times 10^{10} \text{ at } 18°$$
$$10^{20}\Omega/C = 40.22 \text{ and } 2RT = 4.958 \times 10^{10} \text{ at } 25°$$

Experimental values of Ω/C are then deduced from the measured coefficients of diffusion by means of formula (1). *Theoretical* values of Ω/C are given by the following equations, the second term on the right-hand side of formula (3) being neglected

$$10^{20}\Omega/C = 34.84 + 15.6\ C\varphi(0.76\sqrt{2C}) \text{ at } 18°$$
$$10^{20}\Omega/C = 40.22 + 18.6\ C\varphi(0.76\sqrt{2C}) \text{ at } 25°$$

In the tables we give: in column 1 the concentration C of the salt in moles per liter; in column 2 the measured coefficient of diffusion D in cm².∕sec. × 10⁵; in column 3 the difference Δ_m between the experimental values of $10^{20}\Omega/C$ and the value at infinite dilution (c.g.s. units); in column 4 the difference Δ_c between the Onsager–Fuoss values of $10^{20}\ \Omega/C$ and the value at infinite dilution; in column 5 the differences Δ_{I} calculated by means of the formula

$$\Delta_{\text{I}} = (1/\eta - 1) \lim_{C=0} \Omega/C\ 10^{20} \qquad (6)$$

in which η is the viscosity of the solution referred to water; in column 6 the differences Δ_{II} calculated by means of the formula

$$\Delta_{\text{II}} = \frac{1}{\eta}\left[\lim_{C=0} \Omega/C\ 10^{20} + \Delta_c\right] - \lim_{C=0} \Omega/C\ 10^{20} \qquad (7)$$

The difference defined by formula (6) corresponds to the hypothesis that the mobility Ω/C might be given by the simple formula

$$\Omega/C = \frac{1}{\eta} \lim_{C=0} \Omega/C \qquad (8)$$

The difference defined by formula (7) corresponds to the hypothesis that the mobility Ω/C might be given by the formula

$$\Omega/C = \frac{1}{\eta}(\Omega/C)_c \qquad (9)$$

in which $(\Omega/C)_c$ is the mobility calculated in the Onsager–Fuoss theory.

The results obtained for potassium chloride at 18 and at 25° are reported in Tables I and II, respectively. They are also represented graphically on Figs. 1 and 2.

TABLE I

DIFFUSION OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION AT 18°

1 C	2 D	3 Δ_m	4 Δ_c	5 Δ_{I}	6 Δ_{II}
0	1.69	0	0	0	0
0.05	1.55	+0.76	+0.46	+0.03	+0.49
.1	1.52	+ .18	+ .66	+ .07	+0.73
.2	1.50	− .29	+ .87	+ .14	+1.01
.4	1.50	− .41	+1.06	+ .30	+1.39
.6	1.53	− .18	+1.16	+ .45	+1.64
.8	1.55	− .25	+1.20	+ .57	+1.79
1.0	1.58	− .30	+1.22	+ .64	+1.88
1.5	1.65	− .26	+1.29	+ .71	+2.03
2.0	1.74	+ .09	+1.43	+ .64	+2.10
2.5	1.83	+ .50	+1.70	+ .43	+2.14
3.0	1.93	+1.05	+1.96	+ .09	+2.05
3.5	2.03	+1.50	+2.30	− .38	+1.89
4.0	2.13	+1.99	+2.62	−1.05	+1.49

TABLE II

DIFFUSION OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION AT 25°

1 C	2 D	3 Δ_m	4 Δ_c	5 Δ_{I}	6 Δ_{II}
0	1.99	0	0	0	0
0.1	1.89	+1.92	+0.79	+0.04	+0.83
.2	1.88	+2.00	+1.04	+ .05	+1.09
.5	1.83	−0.47	+1.33	+ .12	+1.45
1.0	1.86	− .50	+1.45	+ .20	+1.65
1.5	1.99	+ .47	+1.54	+ .12	+1.66
2.0	2.31	+5.04	+1.70	− .12	+1.58

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(4) Robinson, THIS JOURNAL, **57**, 1165 (1935).

(5) Harned, *ibid.*, **51**, 416 (1929).

(6) Onsager and Fuoss[1] write (see formulas 4.13.22) $B = 0.071$ for KCl, $B = 0.129$ for NaCl, while we get from Harned's data $B = 0.0171 \times \log 10 = 0.0394$ for KCl and $B = 0.032 \times \log 10 = 0.0739$ for NaCl. Other misprints are 10^{10} instead of the correct 10^{13} in formula (4.13.19), $\varphi(0.76\sqrt{m})$ instead of the correct $\varphi(0.76\sqrt{2m})$ and 10^{22} instead of the correct 10^{20} in the two formulas at the bottom of page 2768.

(7) MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

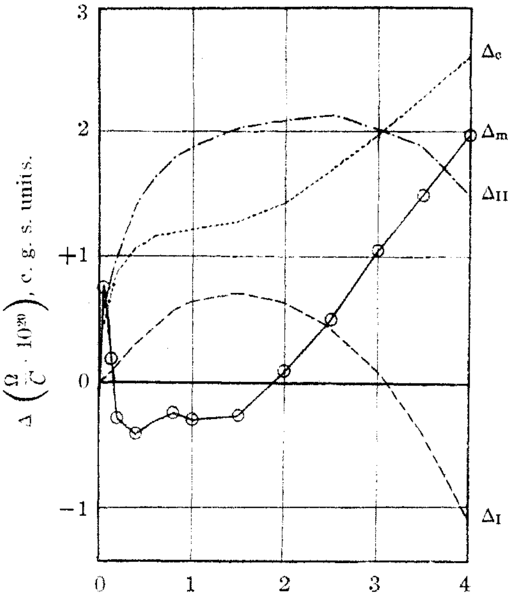

Fig. 1.—Diffusion of KCl at 18°. At infinite dilution $\Omega/C = 34.84 \times 10^{-20}$.

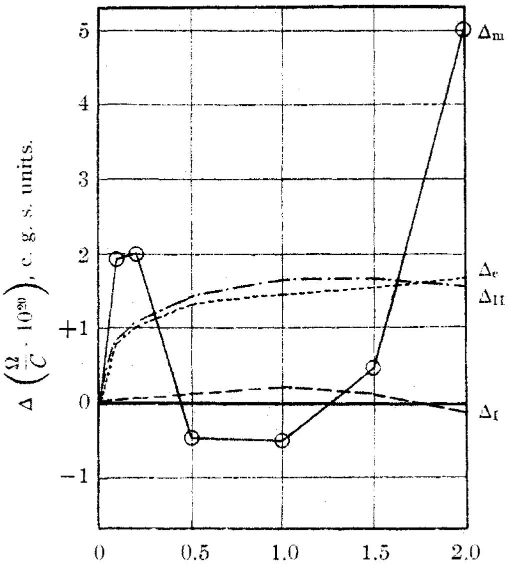

Fig. 2.—Diffusion of KCl at 25°. At infinite dilution $\Omega/C = 40.22 \times 10^{-20}$.

2. Sodium Chloride.—At 25° we have[5,6]

$$\log f = -\frac{0.820\sqrt{2C}}{1 + 0.84\sqrt{2C}} + 0.0739 \times 2C$$

and hence

$$1 + C\partial \log f/\partial C = 1 - \frac{0.410\sqrt{2C}}{(1 + 0.84\sqrt{2C})^2} + 0.1478\,C$$

At infinite dilution we have, for 18°

$$10^{20}\,\Omega/C = 28.01 \text{ with } 2RT = 4.842 \times 10^{10}$$

Formula (1) yields *experimental* values of Ω/C and *theoretical* values are given by the equation

$$10^{20}\,\Omega/C = 28.01 + 15.6\,C\varphi(0.84\sqrt{2C}) - 0.39\,\frac{\sqrt{2C}}{1 + 0.84\sqrt{2C}}$$

TABLE III

DIFFUSION OF SODIUM CHLORIDE IN AQUEOUS SOLUTION AT 18°

1 C	2 D	3 Δ_m	4 Δ_c	5 Δ_I	6 Δ_{II}
0	1.35	0	0	0	0
0.05	1.26	+0.10	+0.33	−0.11	+0.22
.1	1.24	− .10	+ .46	− .24	+ .22
.2	1.22	− .58	+ .59	− .39	+ .19
.4	1.20	−1.64	+ .70	− .82	− .14
.6	1.21	−2.16	+ .76	−1.33	− .61
.8	1.22	−2.70	+ .76	−1.62	−1.00
1.0	1.23	−3.27	+ .75	−2.17	−1.48
1.5	1.26	−4.42	+0.79	−3.33	−2.63
2.0	1.29	−5.46	+1.05	−4.67	−3.79
2.5	1.33	−6.17	+1.33	−5.95	−4.91
3.0	1.36	−6.96	+1.65	−7.42	−6.20
3.5	1.39	−7.66	+1.98	−8.82	−7.47
4.0	1.43	−8.17	+2.29	−10.17	−8.71
4.5	1.46	−8.72	+2.61	−11.53	−10.00
5.0	1.49	−9.26	+2.93	−12.71	−11.11

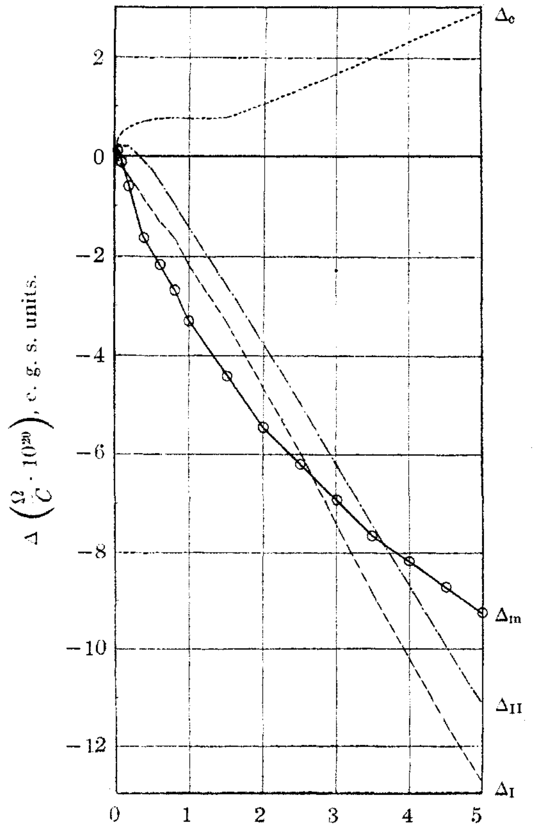

Fig. 3.—Diffusion of NaCl at 18°. At infinite dilution $\Omega/C = 28.01 \times 10^{-20}$.

Differences Δ_I and Δ_{II} have also been calculated according to formulas (6) and (7). The results are reported in Table III and represented graphically on Fig 3.

3. **Potassium Nitrate.**—Activity coefficients of potassium nitrate in aqueous solutions up to 3.5 molal have been measured by Robinson.[4] It is difficult to describe these data by means of a formula of the Hückel type with two parameters A and B

$$\log_{10} f = -0.356 \frac{\sqrt{2C}}{1 + A\sqrt{2C}} + B \times 2C$$

The activity coefficient of potassium nitrate decreases steadily as concentration rises and at low concentrations the application of a formula without the linear term $2BC$ would require impossibly small values of the parameter A. In order to calculate the function φ (κa) of the Onsager–Fuoss theory for this salt we have followed a suggestion due to Guggenheim[8] and have adopted for $A\sqrt{2}$ the value *one*. One readily sees that we could have used this same value of $A\sqrt{2}$ for both potassium and sodium chloride without modifying more than by a negligible amount the calculated values of Ω/C. The factor $1 + C\partial \log f/\partial C$ has been obtained graphically from Robinson's experimental curve for f (after the usual conversion of activity coefficients γ into the corresponding f's and of molalities into concentrations). We get experimental values of Ω/C from formula (1) and theoretical values are given by the equation

$$10^{20} \frac{\Omega}{C} = 34.00 + 15.6\ C\varphi(\sqrt{C})$$

for 18°, the second term on the right-hand side of formula (3) being neglected. Differences Δ_I and Δ_{II} also have been calculated according to formulas (6) and (7). The results are reported in Table IV and represented graphically on Fig. 4.

TABLE IV

DIFFUSION OF POTASSIUM NITRATE IN AQUEOUS SOLUTION AT 18°

1 C	2 D	3 Δ_m	4 Δ_c	5 Δ_I	6 Δ_{II}
0	1.53	0	0	0	0
0.05	1.45	−0.18	+0.62	+0.11	+0.72
.1	1.43	+ .24	+ .72	+ .20	+0.93
.2	1.39	+ .72	+ .96	+ .45	+1.42
.4	1.34	+1.53	+1.17	+ .76	+1.96
.6	1.30	+2.33	+1.29	+1.02	+2.34
.8	1.27	+3.55	+1.37	+1.16	+2.57
1.0	1.24	+4.80	+1.40	+1.30	+2.76
1.5	1.19	+7.36	+1.43	+1.30	+2.79
2.0	1.15	+11.64	+1.47	+0.83	+2.34
2.5	1.17	+18.14	+1.71	+0.28	+2.00

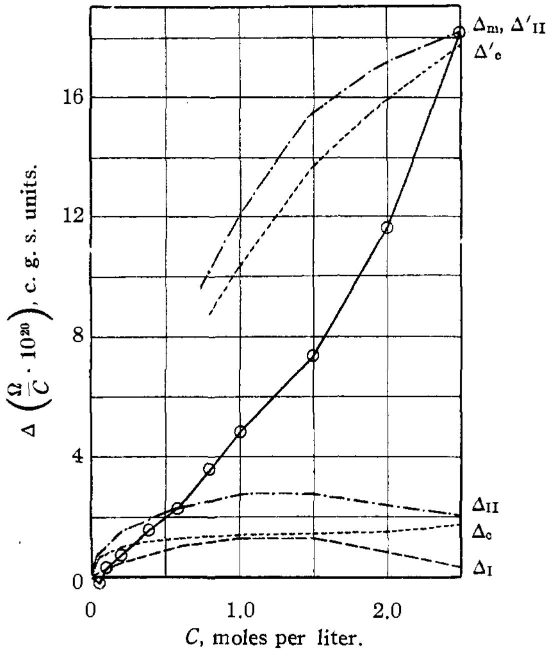

Fig. 4.—Diffusion of KNO_3 at 18°. At infinite dilution $\Omega/C = 34.00 \times 10^{-20}$.

III. Discussion

Close inspection of the tables will make the following points clear.

1. With potassium chloride Ω/C varies very slightly with concentration. Although the calculated increments Δ_c are of the right order of magnitude at high concentrations the behavior of Δ_m is not reproduced correctly at low concentrations. Consideration of the increments Δ_I and Δ_{II} shows that viscosity corrections are not sufficient to explain the experimental Δ_m, whether the corrections are applied to the limiting value of Ω/C or to the Onsager–Fuoss value corresponding to each particular concentration. The diffusion coefficient D of potassium chloride is seen to depend mostly on the activity factor $1 + C\,\partial \log f/\partial C$.

2. With concentrated sodium chloride Ω/C differs by as much as 30% from its limiting value in a direction *opposite in sign* to that predicted by the Onsager–Fuoss theory. The simple viscosity correction applied to the limiting value of Ω/C reproduces the experimental Δ_m's correctly both in sign and order of magnitude. When the viscosity correction is applied to the Onsager–

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(8) Guggenheim, *Phil. Mag.*, [7] **19**, 588 (1935).

Fuoss values of Ω/C a slight improvement is obtained in the agreement at high concentrations, but at low concentrations the differences Δ_I are more nearly correct. Such a situation greatly reduces the significance of the Onsager–Fuoss theory of diffusion.

3. With potassium nitrate the experimental increments Δ_m are unexpectedly large; in concentrated solutions they are nearly ten times as large as the Δ_c's calculated from the Onsager–Fuoss theory. The increments Δ_I and Δ_{II} are in the right direction, Δ_m coinciding exactly with Δ_c at a concentration of 0.6 molar. In view of the arbitrary choice of the parameter A ($A\sqrt{2C} = \kappa a = \sqrt{C}$ or $a = 3$ Å.) we have repeated the calculation of Δ_c with a value of a such that Δ_{II} is identical with Δ_m at $C = 2.5$ moles/liter. We found $a = 0.6$ Å., $A\sqrt{2C} = \kappa a = 0.2\sqrt{C}$. Such a value of a yields the Δ_c' and Δ_{II}' values reported in Table V and represented on Fig. 4. At concentrations smaller than 0.8 the values calculated with $\kappa a = \sqrt{C}$ given in Table IV are themselves larger than the corresponding Δ_m's showing that it is impossible to interpret the mobility of potassium nitrate in terms of a constant value of the ionic diameter a. This difficulty is similar to that encountered in the interpretation of activity data for this salt.

TABLE V

DIFFUSION OF POTASSIUM NITRATE IN CONCENTRATED AQUEOUS SOLUTIONS AT 18°

1 C	2 Δ_c'	3 Δ_{II}'	4 Δ_m
0.8	8.74	10.19	3.55
1.0	10.30	12.00	4.80
1.5	13.69	15.52	7.36
2.0	15.91	17.14	11.64
2.5	17.72	18.14	18.14

In all cases studied in this paper the variation with concentration of the thermodynamic factor $1 + C\partial \log f/\partial C$ is found to be at least as important as the variation of the mobility factor Ω/C. The importance of the thermodynamic factor is particularly striking in the case of salts exhibiting a minimum in the activity coefficient curve. Such salts also exhibit a minimum in the curve for the coefficient of diffusion, as is borne out by potassium and sodium chloride studied in this paper and also by magnesium chloride and magnesium nitrate for which diffusion coefficients have been reported recently by Öholm.[9] With cadmium and magnesium sulfates the diffusion coefficients also exhibit minima, as has been observed by Davies,[10] while the activity coefficients decrease steadily as concentration rises, finally reaching practically constant values.

The remarks made in the present discussion apply to strong electrolytes. It is interesting to examine, at least approximately, the behavior of a typical non-electrolyte such as sucrose. The coefficient of diffusion is given by the formula

$$D = RT\frac{\Omega}{C}(1 + C\partial \log f/\partial C)10^3 \qquad (10)$$

The variation of Ω/C with concentration is much larger than in the case of electrolytes and cannot be accounted for quantitatively by means of the simple viscosity correction as is shown in Table VI obtained by means of various data in the "I. C. T." and Landolt–Börnstein–Roth "Tables."

TABLE VI

DIFFUSION OF SUCROSE IN AQUEOUS SOLUTIONS AT 20°

C, moles/liter	D, cm.^{2}/day	$\frac{\Omega}{C} \times 10^{20}$ c.g.s.	$\frac{1}{\eta}\text{lin}\frac{\Omega}{C} \times 10^{20}$
0	0.380	8.97	8.97
0.25	.368	8.15	6.35
0.50	.353	7.45	4.90
2.00	.272	4.76	0.08

The results indicate that the agreement between measured and calculated Ω/C might be satisfactory in very dilute solutions for which, unfortunately, good experimental data are lacking. Let us note that in the various attempts at applying the Stokes–Einstein law of diffusion to molecular solutions[11] better results might have been obtained by introducing the thermodynamic factor $1 + C\,\partial \log f/\partial C$. We would have

$$D = \frac{RT}{N}\frac{1}{6\pi\eta r}(1 + C\partial \log f/\partial C) \qquad (11)$$

in which N is Avogadro's number, and r the radius of the solute molecules. Comparison with formula (10) gives

$$\frac{\Omega}{C} = \frac{10^3}{N6\pi\eta r} \qquad (12)$$

IV. Summary

1. The diffusion mobilities of potassium chloride, sodium chloride and potassium nitrate in aqueous solution are calculated from the experimental diffusion coefficients and the thermodynamic factors $1 + C\,\partial \log f/\partial C$.

2. The diffusion mobilities are compared with theoretical values obtained in three different man-

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[9] Öholm, *Finska Kemistamfundets Medd.*, **45**, 71 (1936).

[10] Davies, *Phil. Mag.*, [7] **15**, 489 (1933).

[11] See for instance Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1931, Vol. II, 2d. ed., pp. 1026–1028.

ners: (a) by means of the Onsager–Fuoss theory of diffusion; (b) by applying the simple viscosity correction to the mobility at infinite dilution; (c) by applying the viscosity correction to the Onsager–Fuoss mobilities.

3. It is shown that the viscosity correction is at least as important as the Onsager–Fuoss interionic effects and that, with sodium chloride, the correct sign for the variation of the mobility cannot be obtained without the viscosity correction.

4. Remarks are made concerning the minima in the diffusion and activity coefficient curves and concerning the diffusion of sucrose. A modified form of the Stokes–Einstein law of diffusion is proposed.

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

Hydrogen as Carrier Gas for the Catalytic Dehydrogenation of Borneol to Camphor

BY B. E. CHRISTENSEN, E. C. GILBERT AND MAX BOCEK

In connection with another investigation it became necessary to convert borneol quantitatively into camphor. Since oxidation or dehydrogenation in the vapor phase appeared to have many advantages over other methods available, attack upon the problem was made from this aspect.

Although there are numerous references (largely patents) to the vapor phase dehydrogenation of borneol to camphor, the majority deal with the use of copper in some form as the catalyst.[1] Examination of these references, however, reveals data of highly conflicting and contradictory nature, one reporting 100% conversion,[1a] while others[1e] found only traces, and one of the latest[1i] states that reduced copper is a poor catalyst from the standpoint of yield.

In the hope of clearing some of the contradictory points and establishing conditions under which the method might be used reliably, extensive experiments have been carried out in this Laboratory with different catalysts and carrier (diluent) gases. In this paper the results obtained with reduced copper are reported.

Preliminary tests were made with many forms of this catalyst. Using a spongy form obtained by the reduction of fused cupric oxide, conversions of 96–100% were observed at 360°, confirming to some extent the work of Aloy and Brustier.[1a] Repeated tests under these conditions indicated, however, that the high catalytic efficiencies could not be maintained over any period of time and that the color of the copper gradually changed with use. This discoloration could not be restored by further reduction with hydrogen.

Since it was believed that either undesired decomposition products of borneol (due to the high concentration of borneol) or oxidation of the catalyst by traces of oxygen were responsible for the discoloration and diminishing catalytic activity, experiments were next attempted using carrier gases. Others have shown that borneol vapor diluted with benzene gave yields around 86%[1h] while another process using carbon dioxide[1d] (no data given) has been patented.

Although hydrogen is a product of the reaction and in excess logically should retard its progress, this gas would prevent oxidation of the catalyst while also serving as a diluent for the borneol vapor. Attempts made to use hydrogen as the carrier gas met with immediate success, making it possible to maintain the catalyst at high efficiency through many runs, and, under the optimum conditions, apparently minimizing side reactions, so that the product was uniformly of high quality.

Experimental

A borneol reservoir was maintained at any desired temperature by an air-bath. From this, borneol vapor was passed over the catalyst either by its own vapor pressure or by a stream of diluent or carrier gas. Approximately 2–3 g. samples of borneol were generally used. The temperature of the catalyst was controlled by an electric furnace and was measured by a thermocouple. The volume of carrier gas was measured by a calibrated flow-meter.

The catalyst in every run reported in this part of the work consisted of spongy copper prepared by the reduction of fused copper oxide with hydrogen at 200°. The volume

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(1) (a) Aloy and Brustier. *Bull. soc. chim.*. **9**, 733 (1911): (b) Aloy and Brustier. *J. pharm. chim.*, **10**, 42 (1914): (c) French Patent 353.919: *C. A.*. **1**, 383 (1907): (d) British Patent 17.573, Aug. 31. 1906: *C. A.*. **1**, 2320 (1907): (e) Ikeda, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **7**, 1 (1927); (f) Masumoto. *Mem. Coll. Sci. Kyoto Imp. Univ.*. **9A**, 219 (1925): (g) Japanese Patent 99.469. Feb. 9. 1933: *C. A.*. **28**, 2373 (1934); (h) Shoruigin and Makarov-Zemlyanski. *Zhur. Prikladnoi Khim.*. **4**, 68 (1931); (i) Sivov, Korotaeva and Kochneva. *J. Chem. Ind.* (*Moscow*). **3**, 52 (1933); *C. A.*. **28**, 138 (1934).