381. *Diffusion Coefficients for Aqueous Silver Nitrate Solutions at 25°, 35°, and 45° from Diaphragm-cell Measurements.*

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The diaphragm-cell method has been applied to aqueous silver nitrate solutions, up to 4M, at three temperatures. A calibration method for use at temperatures other than 25° has been worked out, in which potassium chloride solutions are used. The differential diffusion coefficients (*D*) obtained for silver nitrate solutions agree well at 25° with recent Rayleigh fringe values for concentrations between 0·1 and 1M in spite of the fact that the large variation of *D* with concentration for this system makes the diaphragm-cell method less suitable than for most systems to which it has been previously applied. Comparison with optical data is also possible at 45°; here the diaphragm-cell values are undoubtedly high in dilute solutions (<0·5M). This may be due to an extension, with increasing temperature, of the concentration range at which surface effects in the diaphragm become important.

The diaphragm-cell method of measuring diffusion coefficients as developed by Stokes[1] requires very simple equipment and yet appears to have an accuracy not far short of that expected from the best optical methods (Gouy fringe, integral fringe, methods) for those solutions of electrolytes to which it has been applied, provided that the concentration range examined does not extend below 0·1M. For analytical reasons it would not, in general, be easy to study nitrates and these would in any case be expected to give more difficulty than, for example, chlorides or bromides because of the steady decrease in their differential diffusion coefficients with increasing concentration. This is true for silver nitrate also, for which no analytical difficulties exist. However, when this work began, no modern values of the differential diffusion coefficients of silver nitrate in water were available, except for very dilute solutions, and as they were required for some work then in progress on the Soret effect in silver nitrate solutions[2] it was decided to examine the possibility of using the method in a less favourable case than those to which it had hitherto been applied. Further, a possible method of calibrating the cell at temperatures other than 25° has been examined. Subsequently a limited number of values derived from Rayleigh fringe data[3] have become available with which the present values can be compared.

Experimental

The apparatus, its manipulation, and the method of cell calibration followed the descriptions given by Stokes.[1] As recommended by this author, the upper compartment of the cell was always filled initially with pure water, and the lower one with the solution of the particular concentration being studied. The potassium chloride used in the calibration was analysed by weight titration with standard silver nitrate solution. The end-point was detected by measuring the potential of an amalgamated silver electrode with respect to a calomel half-cell connected to the titration vessel by an ammonium nitrate–agar bridge. This electrode system, due originally to Clark,[4] gives a sharp and reproducible change in the e.m.f. at the end-point. Silver nitrate analyses were done in the same way, with potassium chloride solution as the titrant. Successive analyses were reproducible to better than 0·1%. To convert molal concentrations into the molarities used in the calculations, solution densities are needed. Data for potassium chloride and for silver nitrate (except at very high concentrations) at 25° were available.[5] Other values, measured pyknometrically, are shown in Table 1.

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[1] Stokes, *J. Amer. Chem. Soc.*, (*a*) 1950, **72**, 763; (*b*) 1950, **72**, 2243; (*c*) 1951, **73**, 3527.

[2] Tyrrell, Firth, and Kennedy, *J.*, 1961, 3432.

[3] Longsworth, in " Structure of Electrolyte Solutions," ed. Hamer, John Wiley, New York, 1959, p. 183.

[4] Clark, *J.*, 1926, 749.

[5] Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 388; 1933, **55**, 4124.

TABLE 1.

Density measurements on potassium chloride and silver nitrate solutions (g. ml.$^{-1}$).

(a) $AgNO_3$ (m = mole per kg. of water)						(b) KCl (m = mole per kg. of water)			
T = 25°		T = 35°		T = 45°		T = 35°		T = 45°	
m	Density	m	Density	m	Density	m	Density	m	Density
6·3628	1·7050	0·0528	1·0018	0·0250	0·9940	0·1273	1·0003	0·0453	0·9919
6·5220	1·7206	0·3242	1·0391	0·0363	0·4958	0·4043	1·0122	0·1484	0·9966
7·9882	1·8431	0·8234	1·1047	0·1406	1·0098	0·5141	1·0174	0·3287	1·0049
		1·7361	1·2195	0·2648	1·0231	0·7728	1·0280	0·7873	1·0241
		3·0562	1·3728	0·6664	1·0800	1·3905	1·0541	1·6943	1·0607
		4·5879	1·5330	0·9751	1·1186	1·6698	1·0650	2·7899	1·1012
		4·9303	1·5664	1·7149	1·2115	2·1853	1·0847	4·1372	1·1476
		5·4776	1·6190	1·8658	1·2287	2·8960	1·1102		
		7·7709	1·8164	2·5906	1·3141	4·6322	1·1675		
		7·9030	1·8312	3·5720	1·4208				
				4·3137	1·4976				
				5·6324	1·6240				
				7·1870	1·7598				

Calibration of Cell at 35° *and* 45°.—The experimental data are the duration (t) of the experiment, the initial (c_2, invariably zero) and final (c_4) concentrations in the top compartment, and the corresponding quantities (c_1, c_3) in the lower one. It can be shown that, for practical purposes,[1,6] a " cell integral diffusion coefficient," $\bar{D}$, defined as:

$$\bar{D} = \frac{1}{c_{m''} - c_{m'}} \int_{c_{m'}}^{c_{m''}} D \, dc, \tag{1}$$

where $c_{m''} = \frac{1}{2}(c_1 + c_3)$, $c_{m'} = \frac{1}{2}(c_2 + c_4)$, is given by:

$$\bar{D} = \frac{1}{\beta_T t} \ln \frac{c_1 - c_2}{c_3 - c_4}, \tag{2}$$

where β_T is the cell constant at temperature T, a quantity having the dimensions of an inverse area and dependent upon the dimensions of the cell and the nature of the diaphragm. It is convenient to define an " integral diffusion coefficient," $\bar{D}^0{}_c$, by the equation:

$$\bar{D}_c{}^0 = \frac{1}{c} \int_0^c D \, dc. \tag{3}$$

It follows from (1), (2), (3) that

$$\bar{D}^0{}_{c_{m''}} = \bar{D} + \frac{c_{m''}}{c_{m'}} (\bar{D}^0{}_{c_{m'}} - \bar{D}). \tag{4}$$

$\bar{D}^0{}_c$ is known [1] as a function of c at 25° for the potassium chloride–water system, and $\bar{D}$ can therefore be found for any pair of $c_{m'}$, $c_{m''}$ values. Thus from experiments with potassium chloride solutions in the cell, β_{25} can be obtained. This is the customary procedure. $\bar{D}^0{}_c$ is not available at other temperatures but Longsworth [7] has obtained the differential diffusion coefficients at 35° and 45° in 1·0-, 2·0-, 3·0-, and 4·0-molal solutions of potassium chloride in water by the Rayleigh fringe method. At these temperatures, β_{25} was chosen as a first approximation for both β_{35} and β_{45} for the calculation of $\bar{D}$ from the experimental data. $\bar{D}^0{}_c$ values, and differential diffusion coefficients, were then calculated in the normal fashion, by using the limiting Nernst value of the diffusion coefficient appropriate to the temperature being studied. These last were calculated from the limiting conductivities tabulated in Appendix 6—2 of reference 8. The provisional values of the differential diffusion coefficient were plotted on large-scale graphs against $c^{\frac{1}{2}}$, and values at molarities corresponding to 1-, 2-, 3-, and 4-molal solutions were interpolated, or, in the case of 4-molal solutions, obtained by a short extrapolation. The resulting values were compared with those obtained by Longsworth

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[6] Gordon, *Ann. N.Y. Acad. Sci.*, 1945, **46**, 285.

[7] Longsworth, *J. Phys. Chem.*, 1957, **61**, 1557.

[8] Robinson and Stokes, " Electrolyte Solutions," Butterworths Scientific Publns., London, 1955.

(Tables 2 and 3). The ratios of corresponding values in each of the two sets were virtually independent of concentration, and the estimates of β_{35} and β_{45} were adjusted correspondingly. These improved estimates of the cell constants were applied afresh to the experimental measurements, and new values of the differential diffusion coefficients were produced for comparison. The procedure was repeated until no further change in β_{35} or β_{45} was required.

TABLE 2.

Cell constant at 35° and 45°. Comparison between coefficients derived from diaphragm cell data on KCl solutions (D_{exp}) and Longsworth's optical values[7] (D_{L}). All diffusion coefficients in cm.^{2} sec.$^{-1}$ × 10^{-5}.

(*a*) $T = 35°$

		$\beta_{35} = \beta_{25}$		$\beta_{35} = 0{\cdot}9944\beta_{25}$		$\beta_{35} = 0{\cdot}9932\beta_{25}$
Molality	D_{L}	$D_{\text{exp.}}$	$D_{\text{L}}/D_{\text{exp.}}$	$D_{\text{exp.}}$	$D_{\text{L}}/D_{\text{exp.}}$	$D_{\text{exp.}}$
1·0	2·340	2·309	1·013	2·332	1·003	2·342
2·0	2·443	2·413	1·012	2·435	1·003	2·441
3·0	2·547	2·516	1·013	2·540	1·003	2·548
4·0 *	2·630	2·600	1·012	2·625	1·002	2·630
		Mean = 1·013		Mean = 1·003		

(*b*) $T = 45°$.

		$\beta_{45} = \beta_{25}$		$\beta_{45} = 0{\cdot}9944\beta_{25}$		$\beta_{45} = 0{\cdot}9948\beta_{25}$
Molality	D_{L}	$D_{\text{exp.}}$	$D_{\text{L}}/D_{\text{exp.}}$	$D_{\text{exp.}}$	$D_{\text{L}}/D_{\text{exp.}}$	$D_{\text{exp.}}$
1·0	2·825	2·785	1·014	2·827	0·999	2·821
2·0	2·929	2·900	1·010	2·935	0·998	2·930
3·0	3·036	2·996	1·013	3·040	0·999	3·034
4·0 *	3·116	3·077	1·013	3·126	0·997	3·120
		Mean = 1·013		Mean = 0·999		

* Values obtained by short extrapolations.

TABLE 3.

Differential diffusion coefficients for aqueous KCl solutions at 35° and 45° (cm.^{2} sec.$^{-1}$ × 10^5).

Molarity	0·00	0·10	0·20	0·50	1·00	2·00	3·00
D_{35}	(2·478)	$2{\cdot}37_0$	$2{\cdot}32_0$	$2{\cdot}31_1$	$2{\cdot}34_5$	$2{\cdot}45_8$	$2{\cdot}57_5$
D_{45}	(3·012)	$2{\cdot}79_7$	$2{\cdot}77_9$	$2{\cdot}77_9$	$2{\cdot}82_2$	$2{\cdot}94_4$	$3{\cdot}05_8$

On the third approximation, excellent agreement was obtained, especially at 35°. Even at 45°, however, the deviations were not large enough to be serious. It is clear from Table 2*b* that further approximation steps would not have been helpful, and in the subsequent work on silver nitrate the ratios $\beta_{35}/\beta_{25} = 0{\cdot}9932$, $\beta_{45}/\beta_{25} = 0{\cdot}9948$ were used. It might be expected that a regular progression in β_T with T would have been observed, but this was not so. A possible cause is that the cell had been repaired between the experiments at 35° and those at 45°, with a consequent slight change in the dimensions.

All cell constants change slowly with time owing to gradual erosion of the disc by the action of the stirrers,[1] and, as is customary, β_{25} was measured at regular intervals and the appropriate value to use in a given experiment derived from a plot of β_{25} against age of cell. If β_{35} or β_{45} was needed, the above ratios were used to calculate them from β_{25}.

Table 3 shows values of differential diffusion coefficients at 35°, 45°, for the potassium chloride–water system at smoothed molarity values. These were obtained incidentally as a result of the calibration method adopted.

Diffusion Coefficients of Silver Nitrate Solutions.—Table 4 shows the initial concentration (molarity) in the lower compartment (c_1), $\bar{D}$ the cell integral diffusion, and $c_{m''}$, together with the final value of $\bar{D}^0{}_{c_{m''}}$, the integral diffusion coefficient, at 25°, 35°, and 45°.

Differential diffusion coefficients have been obtained from these by plotting $\bar{D}^0{}_c$ against $c^{\frac{1}{2}}$, and applying equation (5) which is a consequence of equation (3):

$$D = \bar{D}^0{}_c + \frac{c^{\frac{1}{2}}}{2} \cdot \frac{d\bar{D}^0{}_c}{dc^{\frac{1}{2}}}. \qquad (5)$$

TABLE 4.

Cell integral ($\bar{D}$) and integral diffusion coefficients ($\bar{D}^0{}_c$) for silver nitrate solutions at 25°, 35°, and 45° (cm.^{2} sec.$^{-1}$ × 10^5).

$T = 25°$				$T = 35°$				$T = 45°$			
c_1	$\bar{D}$	$c_{m''}$	$\bar{D}^0{}_{c_{m''}}$	c_1	$\bar{D}$	$c_{m''}$	$\bar{D}^0{}_{c_{m''}}$	c_1	$\bar{D}$	$c_{m''}$	$\bar{D}^0{}_{c_{m''}}$
0·05367	$1{\cdot}65_6$	0·04838	$1{\cdot}66_6$	0·05123	$2{\cdot}08_5$	0·04536	$2{\cdot}09_6$	0·1361	$2{\cdot}51_6$	0·1207	$2{\cdot}53_5$
0·09151	$1{\cdot}63_3$	0·07856	$1{\cdot}64_9$	0·1431	$2{\cdot}04_3$	0·1301	$2{\cdot}05_5$	0·3053	$2{\cdot}43_1$	0·2684	$2{\cdot}46_3$
0·1828	$1{\cdot}59_9$	0·1582	$1{\cdot}61_7$	0·2037	$2{\cdot}01_6$	0·1810	$2{\cdot}03_3$	0·5113	$2{\cdot}34_0$	0·4574	$2{\cdot}38_0$
0·2154	$1{\cdot}59_5$	0·1965	$1{\cdot}60_8$	0·5447	$1{\cdot}90_4$	0·4897	$1{\cdot}93_3$	0·5373	$2{\cdot}34_7$	0·4730	$2{\cdot}38_7$
0·3726	$1{\cdot}55_0$	0·3203	$1{\cdot}57_4$	0·8494	$1{\cdot}81_9$	0·7848	$1{\cdot}85_0$	0·9842	$2{\cdot}19_5$	0·8765	$2{\cdot}25_4$
0·5429	$1{\cdot}49_6$	0·4970	$1{\cdot}52_0$	1·2409	$1{\cdot}71_9$	1·1257	$1{\cdot}76_7$	1·3213	$2{\cdot}11_4$	1·1903	$2{\cdot}17_7$
0·6334	$1{\cdot}47_9$	0·6334	$1{\cdot}48_9$	1·9489	$1{\cdot}56_0$	1·7927	$1{\cdot}65_3$	1·4102	$2{\cdot}07_9$	1·2885	$2{\cdot}14_0$
0·8264	$1{\cdot}45_1$	0·7508	$1{\cdot}47_9$	2·7920	$1{\cdot}46_9$	2·5766	$1{\cdot}53_3$	1·5346	$2{\cdot}05_3$	1·3751	$2{\cdot}12_7$
0·9103	$1{\cdot}42_6$	0·7967	$1{\cdot}46_7$	3·3011	$1{\cdot}40_2$	3·0294	$1{\cdot}47_5$	2·1856	$1{\cdot}91_5$	1·9574	$2{\cdot}00_6$
0·9318	$1{\cdot}42_6$	0·8093	$1{\cdot}46_8$	4·1850	$1{\cdot}28_3$	3·9403	$1{\cdot}33_6$	3·1929	$1{\cdot}72_4$	2·9016	$1{\cdot}82_4$
0·9584	$1{\cdot}41_1$	0·8462	$1{\cdot}45_2$	4·6198	$1{\cdot}22_5$	4·2888	$1{\cdot}30_6$	3·8007	$1{\cdot}63_1$	3·4559	$1{\cdot}74_3$
1·2678	$1{\cdot}37_5$	1·1028	$1{\cdot}42_3$					4·2898	$1{\cdot}58_4$	4·0094	$1{\cdot}67_1$
1·3559	$1{\cdot}35_0$	1·2250	$1{\cdot}39_1$								
1·8468	$1{\cdot}27_6$	1·6380	$1{\cdot}33_4$								
1·8905	$1{\cdot}28_7$	1·6729	$1{\cdot}34_3$								
2·3808	$1{\cdot}20_6$	2·0771	$1{\cdot}27_9$								
2·4401	$1{\cdot}19_9$	2·2372	$1{\cdot}25_1$								
2·8332	$1{\cdot}14_6$	2·5109	$1{\cdot}22_1$								
3·4906	$1{\cdot}09_2$	3·2641	$1{\cdot}14_8$								

TABLE 5.

Differential diffusion coefficients for aqueous silver nitrate solutions (cm.^{2} sec.$^{-1}$ × 10^5).

Molarity	$T = 25°$	$T = 35°$	$T = 45°$	Molarity	$T = 25°$	$T = 35°$	$T = 45$
0·000	(1·768)	(2·212)	(2·682)	0·5000	$1{\cdot}41_2$	$1{\cdot}77_6$	$2{\cdot}20_4$
0·050	$1{\cdot}62_8$	$2{\cdot}04_8$	$2{\cdot}54_6$	0·9674 §	—	—	$1{\cdot}97_6$ (1·999)
0·0998 *	—	—	$2{\cdot}48_4$ (2·386)	0·9761 §	$1{\cdot}26_7$ (1·275)	—	—
0·1000	$1{\cdot}59_4$	$2{\cdot}02_0$	$2{\cdot}48_4$	1·000	$1{\cdot}25_8$	$1{\cdot}58_0$	$1{\cdot}96_0$
0·1004 *	$1{\cdot}59_3$ (1·584)	—	—	1·500	$1{\cdot}14_4$	$1{\cdot}43_0$	$1{\cdot}76_8$
0·1975 †	—	—	$2{\cdot}40_0$ (2·331)	2·000	$1{\cdot}04_7$	$1{\cdot}30_4$	$1{\cdot}60_0$
0·1989 †	$1{\cdot}54_2$ (1·537)	—	—	2·500	$0{\cdot}96_2$	$1{\cdot}18_8$	$1{\cdot}45_4$
0·2000	$1{\cdot}54_1$	$1{\cdot}95_0$	$2{\cdot}39_6$	3·000	$0{\cdot}88_5$	$1{\cdot}06_8$	$1{\cdot}33_0$
0·4897 ‡	—	—	$2{\cdot}20_5$ (2·194)	3·500	$0{\cdot}81_4$	$0{\cdot}94_3$	$1{\cdot}21_0$
0·4928 ‡	$1{\cdot}41_6$ (1·425)	—	—	4·000	$0{\cdot}74_7$	$0{\cdot}81_9$	$1{\cdot}10_2$

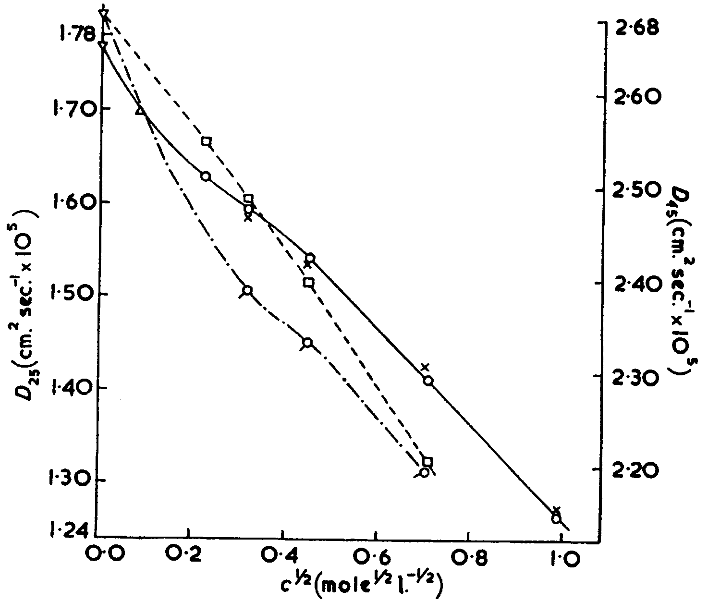
* 0·1009-molal. † 0·2006-molal. ‡ 0·5017-molal. § 1·0078-molal.

Values from integral fringe measurements [3] are shown in parentheses. Nernst values at 35° and 45° are derived from values of ionic mobilities interpolated from data at 0°, 18°, 25°, and 100° in Appendix 6—2 of reference 8.

These are shown in Table 5 at rounded values of molarity, and at the molarity values corresponding to the molalities at which Longsworth's silver nitrate values (shown in parentheses) are valid. All these were obtained by interpolation on a large-scale plot.

The interpolation errors alone in the present work make the third place uncertain, but probably not to more than $\pm 0{\cdot}002$. Comparison of the data at the concentrations marked * † ‡ § shows that at both 25° and 45° the diaphragm-cell values are higher at low concentrations, and lower at higher concentrations, than those found by Longsworth.[3] The discrepancies are most serious at low concentrations at 45°.

The major difficulty in deriving differential coefficients from the integral coefficients in Table 4 lies in the fact that $\bar{D}^0{}_c$ decreases monotonically as the concentration increases. As a result, $\mathrm{d}\bar{D}^0{}_c/\mathrm{d}c^{\frac{1}{2}}$ is always large and negative, the term $|\frac{1}{2}c^{\frac{1}{2}}\,\mathrm{d}\bar{D}^0{}_c/\mathrm{d}c^{\frac{1}{2}}|$, which appears in equation (5), increasing with c. It is not easy to measure $\mathrm{d}\bar{D}^0{}_c/\mathrm{d}c^{\frac{1}{2}}$ accurately, but, if the second term in (5) is small in comparison with the first, this difficulty is not serious. For most aqueous electrolyte systems to which the diaphragm cell method has been applied, $\bar{D}^0{}_c$ initially decreases rapidly with c, passes through a broad minimum at $c \approx 0{\cdot}2$—$0{\cdot}5$, and thereafter increases slowly. Consequently, $|\frac{1}{2}c^{\frac{1}{2}}\,\mathrm{d}\bar{D}^0{}_c/\mathrm{d}c^{\frac{1}{2}}|$ is never large in comparison with $\bar{D}^0{}_c$. For example, we have plotted Stokes's values [1b] of $\bar{D}^0{}_c$ for aqueous sodium chloride against $c^{\frac{1}{2}}$. In a 3-molar solution this plot gave $\bar{D}^0{}_c$ as $1{\cdot}50_2 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, and $\frac{1}{2}c^{\frac{1}{2}}\,\mathrm{d}\bar{D}^0{}_c/\mathrm{d}c^{\frac{1}{2}}$ as $+0{\cdot}036$ in the same units, there being considerable uncertainty in the latter as can be seen from the fact that Stokes gives a value $D = 1{\cdot}54_4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ for this solution, as against $D = 1{\cdot}53_8 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ obtained by inserting the above figures in equation (5). For 3M-silver nitrate at 25° the corresponding figures are $1{\cdot}17_2$ and $(-0{\cdot}28_7) \times 10^{-5}$ cm.^{2} sec.^{1}, *i.e.*, the relatively uncertain correction term amounts to 25% of $\bar{D}^0_c$ instead of the mere 2% for sodium chloride. It is interesting [9] that the diaphragm-cell diffusion coefficients for aqueous sodium chloride are about 1% below those derived from Gouy fringe measurements in this concentration region, though clearly errors in the correction term above are unlikely to be solely responsible for this difference. For silver nitrate, however, errors in the determination of $d\bar{D}^0_c/dc^{\frac{1}{2}}$ would be expected to be more important. At 25°, agreement between the optical data and the present measurements is certainly as good as can be expected in view of this difficulty. This can most conveniently be seen by inspection of the annexed Figure. If either set of values for concentrations above 0·1-molar is to be reconciled with Harned and Hildreth's conductimetric data,[10] and with the limiting Nernst value, the curve of D against $c^{\frac{1}{2}}$ must have the curious kinked form shown. Clearly, either set could be fitted adequately to the values of D at very low concentrations; the optical data would lead to a slightly more pronounced " kink " in the curve. At higher concentrations the latter are slightly higher than the present values, but the discrepancy, which is small, does not appear to increase with concentration, at least between 0·5- and 1·0-molar. On this evidence, the diaphragm-cell data at 25° can be accepted as reliable to better than 1 part in the second decimal place even in this highly unfavourable case. At 35°, the same form for the plot of D against $c^{\frac{1}{2}}$ is found and, although no other values are available for comparison, the coefficients obtained (Table 5) are probably as accurate as those at 25°.



Comparison of diffusion coefficients obtained for aqueous silver nitrate solutions at 25° and 45°, from diaphragm cell and Rayleigh fringe measurements.[3]

▽ Nernst limiting values. ○ Diaphragm cell (full line drawn through these points) at 25°. △ Conductimetric,[10] at 25°. × Rayleigh fringe, at 25°. □ (and broken line) Diaphragm cell, at 45°. ρ (and dash-dot line) Rayleigh fringe,[3] at 45°.

The left-hand ordinate refers to data at 25°, and the right-hand one to those at 45°.

The greater discrepancies at low concentrations at 45° are very obvious from the Figure,

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[9] Harned, *Discuss. Faraday Soc.*, 1957, **24**, 1957.

[10] Harned and Hildreth, *J. Amer. Chem. Soc.*, 1951, **73**, 3292.

which also shows that the diaphragm-cell values no longer give the " kinked " form of curve, still present in the plot of Longsworth's optical values, and are higher than would be expected if such a curve still applied. At 25°, high values are commonly obtained if solutions below 0·05-molar are studied by this method, an effect ascribed to surface effects within the pores of the diaphragm. It seems possible that a similar phenomenon persists up to 0·5-molar at 45°, at least for the silver nitrate–water system, the values given in Table 5 for concentrations below this being too high. No effect of this kind was observed with certainty in the potassium chloride studies used for calibration; this is not surprising since the most dilute solution at which comparisons were made was 1-molal. If it exists, it would of course affect some of the coefficients shown in Table 3. For concentrations above 0·5-molar in the silver nitrate–water system the deviations at the two points where comparison is possible are no greater than might be expected from the computational difficulty discussed in the preceding paragraph. The diaphragm-cell values at 45° for solutions in this concentration range are therefore probably reasonably reliable.

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