409. *The Interpretation of Soret-effect Measurements on Aqueous Electrolyte Solutions by the Tanner Method.*

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Calculation of Soret coefficients from optical measurements of the refractive-index gradients within a pure Soret effect cell by Tanner's method [1, 2] is subject to several possible errors. These have been examined in the light of new experimental results for a range of salt solutions. In particular, it appears that the recorded temperature interval across the cell may have been too high, and the calculated Soret coefficients too low, in some earlier work. Averaging the refractive-index gradients across the cell instead of using the values obtaining at the centre of the cell has a similar effect. Revised Soret coefficients and heats of transfer are tabulated for a number of salt solutions.

An important method of studying the thermal migration (pure Soret effect) occurring in a column of liquid in which a vertical temperature gradient exists is to measure the change in refractive-index gradient along the column, conveniently by Tanner's method [1, 2] in which the deviation of a narrow beam of parallel light during its passage through the cell is observed. This deviation affords the refractive-index gradient at any horizontal plane in the cell; this gradient is an average value over a small vertical distance within the column of liquid, since the beam has a finite width and leaves the cell at a lower level than that at which it enters. Tanner's optical system, based on Thovert's,[3] was such that this

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[1] Tanner, *Trans. Faraday Soc.*, 1927, **23**, 75.

[2] *Idem, ibid.*, 1953, **49**, 611.

[3] Thovert, *Ann. Chim. Phys.*, 1902, **26**, 366; 1914, **2**, 369.

average gradient could be obtained simultaneously at a number of horizontal planes within the cell, by measuring the deflection (from a suitable reference line) of successive points along a slit image. When the column is isothermal, the image is horizontal, one end corresponding to the upper and the other to the lower boundary surface of the column. If the upper end of the column is heated, the whole image is shifted rapidly downwards to form initially a displaced image, horizontal in the centre, with the tips bent upwards or, more often, downwards. Usually, there is a slow further displacement as the concentration changes in the solution, until the steady-state equilibrium is established. The final image is approximately horizontal, and displaced uniformly from the initial isothermal image.

The experimental quantities are the observed displacements of successive points on the slit image as a function of time and position in the cell, and the temperature interval between the upper and lower boundary surfaces of the column of solution. In principle, these can be used to calculate: (a) An ordinary diffusion coefficient D, which is an average value over a small temperature range. This may be obtained from the rate at which any given point on the image is displaced after the initial rapid displacement due to the temperature gradient.[2,4] (b) The ratio D'/D of the thermal coefficient D' to the ordinary diffusion coefficient, most satisfactorily defined as:

$$\frac{D'}{D} = \frac{1}{N_1(1-N_1)}\left(\frac{\mathrm{d}N_1}{\mathrm{d}T}\right)_{\text{stat.}} = -\frac{1}{N_2(1-N_2)}\left(\frac{\mathrm{d}N_2}{\mathrm{d}T}\right)_{\text{stat.}} = -\frac{1}{m}\left(\frac{\mathrm{d}m}{\mathrm{d}T}\right)_{\text{stat.}}$$

where N_1 is the mole fraction of solvent, N_2 that of solute, m the molality of the solution, and the differential terms are the concentration gradients when the final steady state has been reached.

Some time ago, through the courtesy of Dr. C. C. Tanner, it became possible to study the Soret effect in a number of electrolyte solutions of interest in connection with other work on non-isothermal systems. Since then advances have been made in the descriptive theory of the pure Soret effect, and on re-examining these experimental results it became clear that care is necessary in converting them into values of D'/D. Tanner, in his earlier work, measured the displacement of what he termed the " crest " of the curved slit image relative to the position of the image when the contents of the cell were isothermal. That is, he measured the central, initially straight portion and ignored the curved ends of the image. He was only interested in the final displacement in the steady state and obtained this by empirical extrapolation from the " crest displacements " in the later stages of the experiment. Unfortunately the results are expressed in the form $c^{-1}(\mathrm{d}c/\mathrm{d}T)_{\text{stat.}}$ where c is the molarity of the solution. It is necessary therefore to convert his data on to a molality basis before values of D'/D can be obtained.[5] In his second paper,[2] the principal aim was the calculation of D from the rate of the displacement of the image before the establishment of the steady state; an approximate solution [6] of the differential equation governing the thermal migration process was used; this does not predict the observed curvature of the image at the edges, and Tanner therefore calculated an *average* displacement of the beam from his observations. If $Y_{\xi t}$ is the displacement at time t of the image point corresponding to the light passing through the cell, of total height a, at a level x above the base ($\xi = x/a$), the mean displacement calculated from observations at r points along the image is $r^{-1}\Sigma Y_{\xi t}$. A simple application of the de Groot equation suggests that:

$$\frac{r_1^{-1}\Sigma Y_{\xi t} - r_2^{-1}\Sigma Y_{\xi\infty}}{r_3^{-1}\Sigma Y_{\xi T} - r_2^{-1}\Sigma Y_{\xi\infty}} = \exp\left(-t/\theta\right)$$

where $Y_{\xi T}$ and $Y_{\xi\infty}$ are the displacements at an image point corresponding to the horizontal plane ξ, at the time T when the temperature gradient has just been fully established,

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[4] Tyrrell, *Trans. Faraday Soc.*, 1956, **52**, 940.

[5] Alexander, *Z. phys. Chem.* (*Leipzig*), 1954, **203**, 181.

[6] de Groot, " L'Effet Soret," North Holland Publ. Co., Amsterdam, 1945.

and in the steady state respectively, and t is the time elapsed since the system ceased to be isothermal. θ is a " characteristic time constant " for the apparatus defined by a^2/π^2D. In fact, θ is found not to be constant unless the observed differences in the mean displacements at time t and at time ∞ are adjusted by means of a small additive or subtractive constant, the " bias correction." Apart from the " bias correction," the effect of the averaging process is usually such that

$$r_3{}^{-1}\Sigma Y_{\xi T} - r_2{}^{-1}\Sigma Y_{\xi\infty} < Y_{0\cdot5,T} - Y_{0\cdot5,\infty}$$

where $Y_{0\cdot5,T}$ is the displacement at the centre of the cell immediately after the establishment of the temperature gradient. Since the ratio D'/D is calculated from this final difference, Tanner's second method of calculation should normally give lower results than his first. In fact it can be shown [4] that the first is more correct. The image displacement at the centre of the cell remains almost constant, and equal to that arising from the temperature gradient alone, as long as the time t elapsed since the application of the temperature gradient remains less than $0{\cdot}1\theta$. It can be shown graphically by the Schmidt method [7] that the uniform temperature gradient was established within 1 minute in all the present experiments on the determination of the Soret coefficient. Since θ is usually of the order of 70—100 minutes for aqueous electrolytes, an observation of the constant deflection at the centre of the image between 2 and 7 min. from the commencement of the experiment gave a measure of the temperature gradient within the cell. Thus, if attention is confined to the displacements at the centre of the exploring beam, the temperature and concentration effects can easily be separated.[8]

In order to obtain D'/D from the measured displacements it is usually considered sufficient to know $(\partial\mu/\partial w)_T$ (where μ is the refractive index of the solution and w the concentration), and the temperature interval across the cell as recorded by some conventional device. Tanner, for example, used a pair of calibrated mercury-in-glass thermometers. The refractive index of a solution varies with the concentration of the solute approximately according to the equation : [9]

$$\mu - \mu_0 = aw + bw^2 + cw^3 + \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where μ_0 is the refractive index of the solvent, w the concentration, and a, b, c, etc., are empirical constants. Tanner limited the series to two terms, and obtained on differentiation

$$(\partial\mu/\partial w)_T = a + 2bw \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

He expressed w as the molar fraction of solute, and obtained a and b by measuring the refractive index of the solution whose Soret effect had been studied, of a solution of half this concentration, and of the solvent. Since eqn. (1), and more so eqn. (2), is not exact it is desirable to examine the magnitude of the error introduced by this procedure. It is also possible that the measured temperature interval τ_M may be more or less high. This can easily be tested if $(\partial\mu/\partial T)_w$ is known for the solution. The initial constant displacement at the centre of the slit image is proportional to $(\partial\mu/\partial T)_w \cdot \tau$ and hence the true value of τ at the start of the experiment may be found.

The measurements on electrolyte solutions available to us have been examined in the light of the above considerations and it has been shown that there is a tendency to underestimate the correct value of D'/D corresponding to a given set of experimental results. The best values of this quantity have been calculated for a number of electrolyte solutions, and these, where possible, have been converted into values of the heats of transfer.

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[7] Ingersoll, Zobell, and Ingersoll, " Heat Conduction," McGraw-Hill Book Co., New York, 1948, p. 209; cf. Tanner, " The Soret Effect," Part II, I.C.I. Central Agricultural Control Report, August, 1952.

[8] Thomaes, *Physica*, 1951, **17**, 885.

[9] Partington, " Advanced Treatise on Physical Chemistry," Longmans, Green and Co., London, 1953, Vol. IV, p. 76.

EXPERIMENTAL

Soret effects were measured at 25—35° in Dr. Tanner's laboratory, the apparatus and techniques described by him [2] being used. Almost all the values of dμ/dm used were obtained from measurements at 30° on a Hilger-Chance refractometer, with a V cell for liquids and the green mercury line (5461 Å). Temperature coefficients of refractive index were obtained later with a Zeiss Pulfrich refractometer, from measurements of refractive index at 26° and 34°, with the same light source except where otherwise stated. No special precautions were taken in these experiments, and the temperature of the solution in the cell was assumed to be that of the circulating water in the refractometer. The accuracy of the measurements was checked with distilled water, and with " AnalaR " benzene dried over sodium. With the sodium *D* line as source, $\Delta\mu/\Delta T$ was found to be $-11{\cdot}4 \times 10^{-5}$ deg.$^{-1}$ for water; Flatow [10] found $-11{\cdot}54 \times 10^{-5}$ at 30°. For benzene, a value of -61×10^{-5} deg.$^{-1}$ was obtained. Between 10° and 30° Weegman [11] found $-64{\cdot}5 \times 10^{-5}$, and between 20° and 30° $-63{\cdot}2 \times 10^{-5}$. Measurements on salt solutions were repeated several times, and the mean values obtained (Table 1) are not more than 2—3% in error. This accuracy is adequate for the present purpose.

The salts used were selected because of their relevance to certain other problems and not as part of a systematic programme of work on the Soret effect. The reason for the choice of quaternary halides will be clear from the following paper.

Tetramethyl- and tetraethyl-ammonium bromides (from B.D.H.) were purified by dissolution in absolute alcohol and precipitation with ether after filtration. The other substituted ammonium salts used were chosen partly because of their accessibility. *NNN*-Trimethylanilinium bromide was prepared by treating ethyl α-bromopropionate with dimethylaniline at 160° for 8 hr.[12] and purified as described above (Found: Br, 37·2. Calc. for $C_9H_{14}NBr$: Br, 37·0%). 1-Ethylpyridinium bromide was prepared by refluxing pure pyridine with excess of dry ethyl bromide for 30 min., cooling, filtering, and dissolving the solid salt in absolute alcohol.[13] Precipitation with ether gave a high yield of the deliquescent salt (Found: Br, 42·8. Calc. for $C_7H_{10}NBr$: Br, 42·6%). The analytical discrepancy was probably due to the absorption of water. 1-Ethylquinolinium iodide was made [14] by warming quinoline with excess of dry ethyl iodide: excess of ethyl iodide was distilled off the solid yellow product, which was then purified in the usual manner (Found: I, 44·5. Calc. for $C_{11}H_{12}NI$: I, 44·5%). Sodium, potassium, silver, barium, and ammonium nitrate, and potassium bromide and iodide solutions, were made from dried " AnalaR " reagents in redistilled water. Magnesium nitrate solution was prepared by adding excess of dry " AnalaR " magnesium oxide to a known amount of pure pure nitric acid, filtration, and dilution. Commercial lithium hydroxide was used without purification.

RESULTS AND DISCUSSION

Errors in the Determination of dμ/dm.—If μ can be expressed as a quadratic function in m (molality) the quantity $(\mu - \mu_0)/m$ should be a linear function of m. For aqueous silver nitrate this is not quite correct (see Figure, where the straight line was obtained from the experimental points by the method of least squares). If

$$(\mu - \mu_0)/m = a + bm,$$

then

$$[(\mu - \mu_0)/m]/\mathrm{d}m = b$$

and

$$\mathrm{d}\mu/\mathrm{d}m = mb + (\mu - \mu_0)/m$$

If the " least squares " line is used in calculating dμ/dm, the result will be in error for two reasons. The quantity b differs appreciably from the slope of the experimental curve except in the 2—3 molal region, where the estimate of $(\mu - \mu_0)/m$ is most seriously in error. This error in $[(\mu - \mu_0)/m]$ is not greater than about 1% at worst. The largest error introduced by using the " least squares " line, *i.e.*, by assuming μ to be simply a quadratic function of m, rather than the experimental curve, occurs at the higher concentrations

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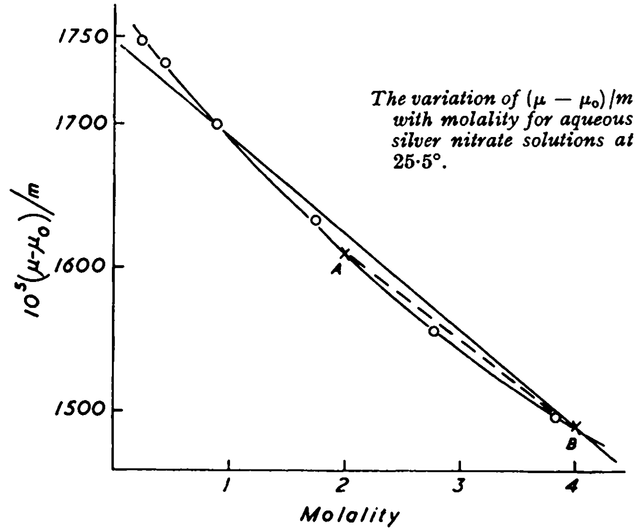
[10] Flatow, *Ann. Physique*, 1903, **12**, 85.
[11] Weegman, *Z. phys. Chem.*, 1888, **2**, 237.
[12] Bischoff, *Ber.*, 1898, **31**, 3017.
[13] Trowbridge and Diehl, *J. Amer. Chem. Soc.*, 1897, **19**, 563.
[14] Dehn and Cope, *ibid.*, 1926, **48**, 2636.

where the slopes of the curve and the straight line diverge most markedly. At 4 molal, the error in calculating $d\mu/dm$ from the line rather than the curve is of the order of 4%. However, the method of estimating $d\mu/dm$ used by Tanner (see above) introduces a smaller error than this, since it is equivalent to substituting the chord A—B for the tangent to the curve at B. Since other, larger sources of error are inherent in the Tanner method this procedure has been used in the present work.

Measurement of the Temperature Interval in Soret-effect Experiments.—The temperature interval in the cell immediately after the establishment of the uniform temperature gradient (τ_C) has been calculated from the experimental values of $\Delta\mu/\Delta T$, and the deflection of the central portion of the slit image measured between 2 and 7 min. after the start of the experiment. The value obtained has been compared with that recorded on the mercury-in-glass thermometers. The bulbs of these were placed in pockets, the ends of which were formed by the back surfaces of the silver plates forming the upper and the lower boundary surface of the cell. The quantities τ_M are the temperature intervals recorded on these thermometers after stem corrections had been applied. The results are shown in Table 1. Obviously τ_C should not be greater than τ_M and the only exception to this was found with potassium iodide solution where the initial deflection was unusually large. Surprisingly, τ_C was usually appreciably less than τ_M, *i.e.*, the temperature gradient within the cell at the beginning of the experiment corresponded to a smaller temperature interval than that recorded on the thermometers. This conclusion was re-inforced by an experiment in which the cell was filled with distilled water and the temperature gradient applied. A value for $\Delta\mu/\Delta T$ of -9.8×10^{-5} deg.$^{-1}$ (λ 5461 Å) was calculated from the



The variation of $(\mu - \mu_0)/m$ with molality for aqueous silver nitrate solutions at 25·5°.

TABLE 1. *Comparison of observed and calculated temperature intervals in Tanner Soret-effect cell for different aqueous electrolytes.*

Solute	Molality	$10^5\,\Delta\mu/\Delta T$ (deg.$^{-1}$)	τ_M	τ_C	Solute	Molality	$10^5\,\Delta\mu/\Delta T$ (deg.$^{-1}$)	τ_M	τ_C
$NaNO_3$ ...	4·625	−19	9·78	8·5	$Ba(NO_3)_2$ ...	0·386	−13	10·25	9·6
	2·153	−17	9·88	9·0	KBr	2·204	−15	9·98	8·5
KNO_3......	3·405	−17	9·88	8·9	KI	2·203	−17	10·02	14·6
	2·159	−16	9·91	8·8	NMe_4Br......	2·514	−14	9·95	9·1
NH_4NO_3	5·037	−19	9·95	8·7		1·135	−13	9·97	9·1
	2·794	−16	9·92	9·9	NEt_4Br ...	1·801	−14	9·92	9·9
$AgNO_3$ ...	2·130	−15	9·60	9·1	1-Ethylquinolinium iodide	0·517	−13	10·04	9·0
	0·393	−13	10·58	8·9					

observed image deflection (which was independent of ξ) and the measured temperature interval. This was appreciably less than it should have been. At 30°, at λ 4800 Å, $d\mu/dT = -11{\cdot}82 \times 10^{-5}$, and at λ 5890 Å, $d\mu/dT = -11{\cdot}54 \times 10^{-5}$ deg.$^{-1}$ (ref. 10). The temperature gradient in this experiment was undoubtedly uniform across the cell and less than that indicated by the thermometers.

Values of p and D'/D.— $p(= \tau D'/D)$ can be calculated from experimental measurements without introducing any difficulties connected with the correct value of the temperature interval τ. Table 2 shows values of this quantity obtained: (i) ($\bar{p}_1$) by Tanner's averaging method, modified to include the " bias correction " in the average value of the final beam displacement; (ii) ($\bar{p}_2$) as in (i) but omitting the " bias correction " (this appears to have been the method used in his later work by Tanner); and (iii) from the deflection at the *centre* of the image, this being termed p and being the correct quantity to use in the calculation of D'/D.

TABLE 2. *Calculation of $\tau D'/D$ by various methods, and estimates of D'/D.*

Salt	Molality	$10^3\bar{p}_1$ (cm.)	$10^3\bar{p}_2$ (cm.)	10^3p (cm.)	$10^3D'/D$ (deg.$^{-1}$)
$NaNO_3$	4·625	26·6	25·8	25·8	3·0
	2·153	19·1	18·2	19·0	2·1
KNO_3	3·405	37·6	37·4	41·2	4·6
	2·159	22·7	21·8	24·7	2·8
NH_4NO_3	5·037	5·62	5·62	5·9—6·4	0·7 *
	2·794		No Soret effect observed		
$AgNO_3$	2·130	57·0	55·9	74·0	8·1
	0·393	27·8	27·2	36·0	4·0
$Ba(NO_3)_2$	0·386	37·8	37·8	41·2	4·3
$Mg(NO_3)_2$	2·143		No Soret effect observed		
LiOH	4·473	31·9	31·9	37·6	3·8 †
KBr	2·204	11·6	11·9	15·3	1·8
KI	2·203	6·27	6·10	6·33	0·63 †
NMe_4Br	2·514	49·0	48·5	59·5	6·5
	1·135	38·8	40·2	41·6	4·6
NEt_4Br	1·801	81·6	80·1	86·9	8·7
1-Ethylquinolinium iodide	0·517	100·4	100·2	106·6	12 ‡
1-Ethylpyridinium bromide	2·015	51·0	51·0	51—58	5·1—5·8 *
$NPhMe_3Br$	0·533	59·6	59·1	70·2	7·0

* The displacement of the central image varied in these cases over a short distance and the choice of a unique value was impossible.

† Calc. from τ_M rather than τ_C. Apart from KI this was because no value of $\Delta\mu/\Delta T$ was available.

‡ The steady state equilibrium had not been completely attained.

Calculation of D'/D from p involves the problem of the correct value of the temperature interval discussed in the previous section. The values shown in Table 2 have been calculated, except where otherwise stated, from τ_C. The calculation is slightly complicated because the measured temperature interval may change by a small amount during the long period required for the establishment of the steady state. The change in τ_C due to this slight drift has been assumed to be proportional to that in τ_M.

The experimental values of $\bar{p}_1$ and $\bar{p}_2$ are, to some extent, subjective quantities. It is never possible to observe the whole image throughout an experiment; the portion whose position can be recorded varies during a given experiment, and from one experiment to another. Thus, in different runs the relative weights given to the observations at the centre and to those at the ends of the slit image will vary, and the " average displacements " will not be strictly comparable. Usually, though not invariably, they were less than that at the centre of the image, and values of D'/D calculated from either $\bar{p}_1$ or $\bar{p}_2$ are likely to be lower than the true value. Thus Tanner's latest values [2] for potassium and barium chloride solutions are probably too low. The Soret coefficients recorded in the earlier paper,[1] if corrected to a molality basis, are undoubtedly more correct. They may still be less than the true values however, because of the possibility that the temperature interval had been over-estimated (see above).

Calculation of Heats of Transfer from D'/D.—The heats of transfer of the ions of a completely dissociated binary electrolyte is related to D'/D by the equation :[15]

$$(\nu_+Q_+^* + \nu_-Q_-^*) = \nu RT^2[1 + m(\partial \ln \gamma_\pm/\partial m)_{Tp}] \cdot D'/D$$

where ν_+ and ν_- are the numbers of positive and negative ions and ν is the total number of ions per molecule. The activity coefficient on the molality scale is known for many salts at 25°, and $m(\partial \ln \gamma_\pm/\partial m)_{Tp}$ can be obtained graphically from these results without serious error. In the present experiments the mean temperature was 30°. The change in $m\partial \ln \gamma_\pm/\partial m$ with temperature is given by :

$$m \cdot \frac{\partial}{\partial T}\left(\frac{\partial \ln \gamma_\pm}{\partial m}\right) = m \cdot \frac{\partial}{\partial m}\left(\frac{\partial}{\partial T} \cdot \ln \gamma_\pm\right) = -\frac{m}{\nu RT^2} \cdot \frac{\partial \bar{L}_2}{\partial m}$$

where $\bar{L}_2$ is the relative partial molar heat content of the solute. For a 2 molal potassium bromide solution, this is about -18×10^{-4} deg.$^{-1}$, the heat data of Hammerschmid and Robinson[16] being used. The change in $m\partial \ln \gamma_\pm/\partial m$ for a temperature change from 25° to 30° is about $-0{\cdot}009$ which corresponds to a change in the term $[1 + m\partial(\ln \gamma_\pm)_{Tp}/\partial m]$ of about 1%. Therefore, except for substances with exceptionally large heats of dilution, the error in using activity coefficients obtained at 25° instead of at 30° is small compared with the uncertainty in D'/D (see also Chapman and Tyrrell[17]).

Values of the quantity $(\nu_+Q_+^* + \nu_-Q_-^*)$ calculated from values of D'/D and from published activity coefficient values[18] are shown in Table 3. There is no extensive series of similar values with which these can be compared exactly. That calculated by Alexander[19] from Tanner's earlier values refers to slightly higher mean temperatures : he calculated mean heats of transfer $Q_\pm^*$ defined for a uni-univalent electrolyte as $(\nu_+Q_+^* + \nu_-Q_-^*)/\nu$, and his tabulated values should therefore be doubled for comparison with the data of Table 3. There is a slight error in Alexander's definition of the heat of transfer since equation (3) of this paper should read $s_\pm = x^{-1}(1 - x) \cdot \text{grad } x/\text{grad } T$, not $s_\pm = x^{-1}(1 - \nu x) \cdot \text{grad } x/\text{grad } T$. Consequently his values are slightly higher than they should be (1% in error at 1 molal, 4% in error at 2 molal, 6% at 3 molal, and 7·5% at 4 molal for a uni-univalent electrolyte). After this small correction his values are somewhat larger than the present ones. Qualitatively, this would be expected, for heats of transfer increase with temperature,[5] but too little is known at present about the magnitude of this change for a quantitative comparison between the two sets of values to be possible. In some cases the difference is rather greater than might reasonably be expected from this cause alone.

Calculation of the Ordinary Diffusion Coefficient D.—This calculation was done for a number of the above solutions both by Tanner's method[2] and by the method described recently by one of us.[4] As in the case of 2·2 molal potassium bromide there examined, the two methods gave similar but not identical results. The values obtained were all of the right order of magnitude (~10^{-5} cm.^{2} sec.$^{-1}$) but in many cases reliable isothermal data for comparison do not exist. The error in the second method could be estimated from the variation of the values of the characteristic time θ calculated from successive observations. This appeared to be of the order of 3—4% at least, even in the most favourable cases.

Conclusions.—There seems no doubt that this optical method of measuring Soret coefficients in the form described by Tanner[2] may give low results, for two reasons. The method of averaging displacements across the cell usually yields a mean value lower than the correct one measured at the centre of the cell. In addition, there is considerable evidence that, in certain experiments, though not in all, the temperature interval recorded

[15] Haase, *Trans. Faraday Soc.*, 1953, **49**, 724.

[16] Hammerschmid and Robinson, *J. Amer. Chem. Soc.*, 1932, **54**, 3120.

[17] Chapman and Tyrrell, *Trans. Faraday Soc.*, 1956, **52**, 1218.

[18] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955.

[19] Alexander, *Z. phys. Chem.* (*Leipzig*), 1954, **203**, 228.

TABLE 3. $(\nu_+Q_+^* + \nu_-Q_-^*)$ *at a mean temperature of* 30°, *calculated from values of* D'/D *obtained in Table* 2.

Salt	Molality	$1 + m(\partial \ln \gamma_\pm/\partial m)$	$(\nu_+Q_+^* + \nu_-Q_-^*)$ (cal. mole^{-1})
$NaNO_3$	4·625	0·743	800
	2·153	0·793	610
KNO_3	3·405	0·418	700
	2·159	0·525	540
NH_4NO_3	5·037	0·529	130
	2·794	—	zero
$AgNO_3$	2·130	0·480	1400
	0·393	0·750	1100
$Ba(NO_3)_2$	0·386	0·515	1200
$Mg(NO_3)_2$	2·143	—	zero
LiOH	4·473	0·884	1200
KBr	2·204	1·000	660
KI	2·203	1·048	240

on the mercury-in-glass thermometers was greater than that between the upper and the lower boundary surface of the liquid column. Both errors would combine to give low values for D'/D. The first was not operative in Tanner's earlier work;[1] the second may have been, though its influence cannot be judged from the published data. In any event, its magnitude would be expected to vary from experiment to experiment, since it would depend largely on the goodness or otherwise of the thermal contact between the thermometer bulb and the metal parts of the experimental cell. A better method of measuring the initial thermal gradient would undoubtedly be that used here, *viz.*, measurement of the initial displacement of the centre of the beam image from its original position when the cell was isothermal, provided that more accurate values of $(\partial\mu/\partial T)_m$ could be obtained.

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