667. Optical Studies of the Soret Effect. Part I. A Modified Optical Beam-displacement Method and its Application to Aqueous Silver Nitrate Solutions.

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An optical method of studying the Soret effect is described; it involves a modified Tanner cell. Results for m- and 2m-silver nitrate at a mean temperature of 25°, obtained for different applied temperature gradients, have been used in calculating Soret coefficients by different methods. The results obtained from a given set of data were not quite identical, principally because of theoretical difficulties. A satisfactory method of calculation is described which gives values of this parameter which are independent of cell height, of the position of the exploring beam in the cell, and of temperature gradient, and the advantages of using a cell with a small separation between the hot and the cold plate with this beam-displacement method are demonstrated. Soret coefficients for solutions between 0·1m and 8m at several mean temperatures have been obtained, and entropies of transfer for silver nitrate have been calculated as a function of solution concentration at 25°.

The Soret phenomenon, that is, the partial separation of the components (demixing) of a binary solution under the influence of a temperature gradient, has recently attracted increasing attention, both experimentally and from the theoretical point of view.[1,2] The

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[1] Bierlein, *J. Chem. Phys.*, 1955, **23**, 10.

[2] Agar, *Trans. Faraday Soc.*, 1960, **56**, 776.

primary aim of experimental work in this field is to deduce the Soret coefficient (σ), which may be conveniently defined [3] as

$$\sigma = -\frac{1}{m}\left(\frac{\text{grad } m}{\text{grad } T}\right)_{\text{stat.}}, \tag{1}$$

from the experimental results. In equation (1) the suffix "stat." denotes that the concentration gradient is measured in the time-invariant steady state in which the flow of matter caused by the temperature gradient is balanced by the flow in the reverse direction under the influence of the concentration gradient. Usually the temperature gradient is applied to a vertical column of the liquid solution in such a way as to eliminate as far as possible the effects of convection, and the concentration changes are followed by measuring the change of some physical property with time. For dilute electrolyte solutions, measurements of the ratio of the resistances of the upper and the lower half of the Soret cell have been used successfully; [4-7] for somewhat more concentrated solutions it has been suggested [7,8] that an adaptation of Harned and French's conductimetric method [9] of studying the isothermal diffusion of dilute electrolytes would be satisfactory. For even more concentrated solutions of electrolytes, and for non-electrolyte mixtures, optical methods have been quite widely used. These fall into two main classes:

(i) Interference ("integral fringe") methods. Longsworth [10] used a twin Soret cell in conjunction with a Rayleigh interferometer for a detailed study of several concentrated aqueous electrolytes. He showed that an integrated diffusion equation due to Bierlein [1] gave a good but not perfect representation of the rate at which the steady state was attained. In an attempt to minimize first-order variations in σ with temperature, fringe patterns formed at planes disposed symmetrically about the cell centre were used. A second method in which refractive-index differences at two planes placed symmetrically above and below the cell centre were measured directly in a conventional Soret cell [11] gave results for fairly concentrated potassium chloride solutions which agreed well with those found by Longsworth.[12]

(ii) Beam displacement methods. In these the refractive-index gradient in the unequally heated liquid column is measured. Tanner [13,14] measured this gradient as a function of cell height over almost the whole height of the cell. Other workers have usually limited their observations to measuring either the average refractive-index gradient over a large part of the cell height [15,16] or that over a limited region explored by a narrow horizontal light beam entering the cell at a known level.[17]

In diffusion work, interference-fringe methods are preferred because of the accuracy with which fractional fringe shifts can be measured. However, in studies of the Soret effect other difficulties tend to reduce this advantage. For example, Longsworth [10] was unable to design a twin cell with fully satisfactory thermal properties. Also the cell must be fairly tall, and, for adequate sensitivity, quite a large temperature interval must be used. Furthermore, the optical equipment used must be of high quality. Beam-displacement methods, on the other hand, are less demanding in the last respect and possess one great advantage which has hitherto been almost entirely ignored. Since the

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[3] Cf., *e.g.*, Tyrrell, *Trans. Faraday Soc.*, 1960, **56**, 770.

[4] Agar, "The Structure of Electrolytic Solutions," ed. Hamer, Wiley, New York, 1959, p. 213.

[5] Agar and Turner, *Proc. Roy. Soc.*, 1960, *A*, **255**, 307.

[6] Snowden and Turner, *Trans. Faraday Soc.*, 1960, **56**, 1409.

[7] Snowden and Turner, *Trans. Faraday Soc.*, 1960, **56**, 1812.

[8] Agar and Turner, *J. Phys. Chem.*, 1960, **64**, 1000.

[9] Harned and French, *Ann. New York Acad. Sci.*, 1945, **44**, 267.

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

[11] Chanu and Lenoble, *Compt. rend.*, 1955, **260**, 949; *J. Chim. phys.*, 1956, **53**, 309.

[12] Tyrrell, "Diffusion and Heat Flow in Liquids," Butterworths, London, 1961.

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

[14] Tanner, *Trans. Faraday Soc.*, 1953, **49**, 611.

[15] Korsching, *Z. Naturforsch.*, 1955, **10a**, 242.

[16] Bierlein, Finch, and Bowers, *J. Chim. phys.*, 1957, **54**, 872.

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

gradient of refractive index is measured, it is the temperature *gradient* which determines the sensitivity, not the temperature interval between the cell plates as in the integral-fringe methods described. Hence, if the distance between the cell plates is reduced, the temperature interval between them can be reduced in the same proportion without loss of sensitivity. It has been reported[16] that the value of σ calculated from beam-displacement measurements with the available equations depends on the temperature interval used and it would seem to be advantageous to reduce it as far as possible. Further, the time required for a given experiment is proportional to the square of the cell height, while the greater the area : height ratio the smaller is the likelihood that convective remixing will affect the results. The only experimental work on these lines reported hitherto is that of Whitaker and Pigford[18] who used a brass cell with a plate distance of only 2 mm. However they were concerned mainly with a broad study of non-electrolyte pairs and it is difficult to judge the real potentialities of the method from their results.

Some years ago a paper from this laboratory[19] described the results of some Soret coefficient measurements obtained on the second apparatus designed by Tanner.[14] On this basis, modified cells have been designed and their performances evaluated by using them to study the Soret coefficients of silver nitrate solutions of different concentrations over a range of mean temperatures with different temperature gradients. These solutions were chosen because the original cell was not well adapted to work with non-aqueous solutions, while silver nitrate in water has a relatively large Soret coefficient. Also, some diffusion measurements are available on this system, and this permits Soret coefficients to be calculated from the experimental data on one type of modified cell by several methods. Since isopiestic activity coefficients are available at 25° for silver nitrate solutions from 0·1 molal upwards,[20] it has been possible to obtain the sum of the ionic entropies of transfer ($S^*_+ + S^*_-$) from the calculated Soret coefficients.

EXPERIMENTAL

The optical system is shown in Fig. 1. A horizontal adjustable slit A is illuminated through condenser lens B by a high-pressure mercury arc C (Mazda type ME-D). Behind the slit A are placed a Compur shutter and a Wratten green filter (No. 77) (D) which transmits light of λ 5461 Å. Light from this slit is rendered parallel by the lens E (*f* 12 cm.) and then passes through a horizontal double slit F (cf. Thomaes[17]) whose vertical position relative to the optic axis could be adjusted accurately. The Soret cell G was placed immediately after the double slit, and the light issuing from it was focused by a Zeiss achromat H of 50 cm. focal length on to a vertical graticule scale I placed in the image plane. The diffraction image of A formed in this plane had a strong central band which was split into a sharp interference pattern. This was photographed against the scale lines of the graticule by a low-power microscope objective attached to a plate camera, arranged so that a number of successive exposures could be made on the same plate. Ilford Selochrome plates were used, with a high-contrast developer. Under the conditions of exposure and development adopted, the photographic image consisted of three dark bands on a transparent background, the marks on the graticule showing as clear lines in the darkened areas. Displacements of the fringe pattern were measured by using a travelling microscope (5 × magnification), with any convenient line in the graticule as a reference line. After a little experience, the position of the fringe pattern relative to the graticule could be determined with a reproducibility of 10 microns. During the course of an experiment no change in the width of the fringe pattern could be detected; it was simply displaced as a whole.

The original cell used, shown in Fig. 2a, was that designed and described by Tanner.[14] In the later work on m-silver nitrate a redesigned glass cell chamber was used with the same silver discs. The plane glass windows in the new chamber were small and circular, and the inner surfaces were arranged to be 7·63 cm. apart, that is, they formed tangents to the circular silver plates (Fig. 2b). They were sealed in position by small O ring seals, and the cell was

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[18] Whitaker and Pigford, *Ind. Eng. Chem.*, 1958, **50**, 1026.

[19] Tyrrell, Chapman, and Wilson, *J.*, 1957, 2135.

[20] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1954, Appendix 8–10.

therefore suitable for use with non-aqueous solutions.[21] A somewhat more uniform temperature gradient was obtained in a rectangular cell of a radically different design, but other factors prevented its extensive use. On the whole, the cell of circular section has many advantages over other forms.

The temperatures of the upper and the lower plate were controlled by circulating through them water from thermostat baths of large capacity, and were measured by multi-junction thermocouples (copper–constantan, 5 junction) placed in the sockets shown in Fig. 2. At the beginning of an experiment, the two plates were held at the same temperature until thermal equilibrium was reached. Then, by operating a series of quick-release valves (Saunders) in the pumping system, water at the higher temperature was passed through the upper plate, and that at the lower temperature through the lower plate. To minimise heat losses from the cell, the whole of the optical layout was enclosed in an air-thermostat maintained at the mean temperature of the experiment with an accuracy of $\pm 0{\cdot}2^\circ$.

FIG. 1. *Optical system (vertical section).*

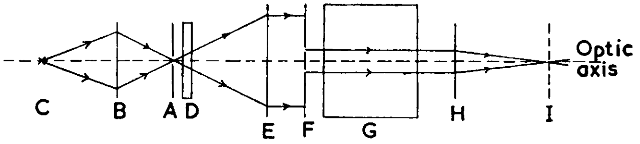
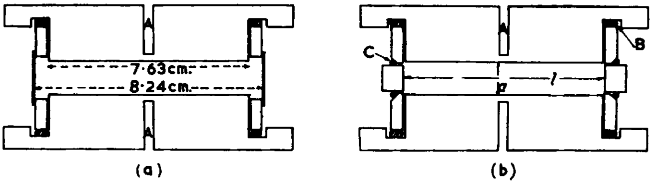


FIG. 2. *Experimental Soret effect cells.*

(a) *Unmodified Tanner cell.* (b) *Modified cell with small tangential windows.*

The upper half of the cell is separated from the lower half by three Tufnol (or Nylon) spacing rods outside the circular glass wall of the cell. These are not shown.



A,A *Thermocouple pockets.* B *Large* ○ *rings.* C *Small* ○ *rings round the windows.*

Before an experiment, the lower plate of the cell was set up at the correct height and levelled to 30 seconds of arc by means of a precision clinometer. The body of the cell was then assembled, and the top plate dropped into position and compressed lightly against the three Tufnol (or Nylon) spacing rods. The cell was filled with de-aerated solution, and the pressure on the top plate adjusted until the distance between the top and the bottom surface was within 10 microns of the desired value at a number of points on the periphery of the cell. These measurements, of course, also gave an accurate measure of the cell height. By this means, both plane-bounding surfaces in the cell were made horizontal and parallel to the highest degree of accuracy available to us. It was not possible to ensure that the cell walls were also vertical to the same degree of precision. Finally, the double slit was adjusted to a known position relative to the base of the cell, also with an accuracy of 10 microns.

Bierlein, Finch, and Bowers [16] have described a similar optical arrangement in which the position of the interference pattern in the beam passing through the cell is compared with that of a similar undeflected beam which has passed through air. In this way small shifts due to changes in the mechanical or optical parts of the apparatus were said to be eliminated. We have tried incorporating such a device in the present apparatus, but found that the only shifts observed in the reference pattern were due to changes in the mercury arc during the warming-up stage. By ensuring that the lamp had been running for some time before observations were begun, the observed shifts in the reference beam in the present apparatus were found to be negligible and this refinement was unnecessary in our experimental conditions.

Solutions were made up by weight from "AnalaR" silver nitrate and distilled water (which

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[21] Tyrrell and Faine, unpublished work.

had been passed through a mixed-bed ion exchange column). Refractive indices were measured on a Bellingham and Stanley refractometer of an improved Pulfrich pattern. The refractive-index increment with concentration was obtained from measurements on a series of solutions whose composition increased successively by 0·5 molality unit. Between 0 and 1 molal this quantity remained constant, and was used in interpreting Soret effect measurements on solutions up to 0·5m. At concentrations above 1m, it slowly decreased, and, from this concentration upwards, the mean of the increments measured between $(x - 0{\cdot}5)$ and x, x, and $(x + 0{\cdot}5)$, was assumed to be the value characteristic of an x-molal solution. The change with temperature was found from the observed constant deflection of a beam entering the 10 mm. cell at $\xi_1 = 0{\cdot}5$ in the time interval between the establishment of the temperature gradient and the onset of demixing in this plane. This was not noticeable when $t < 0{\cdot}1\theta$, or less than 10 minutes from the time at which the temperature gradient was first applied.

RESULTS AND DISCUSSION

Temperature Distribution in the Soret Cells.—The temperature coefficient of refractive index ($\mathrm{d}n/\mathrm{d}T$) for water is known accurately,[22] and, when the cell is filled with water, the temperature gradient at any given plane can be deduced from the deflection of a light beam passing through the cell at that plane. Strictly, because of the finite width of the beam and the bending of the beam within the cell, the average temperature gradient over a small vertical height in the cell is found by using the equation

$$\mathrm{d}T/\mathrm{d}\xi = Z_\xi(a/lf)(\mathrm{d}n/\mathrm{d}T)^{-1}, \qquad (2)$$

where ξ is the " reduced height " in the cell defined as the ratio z/a (z is the height of the plane explored above the bottom of the cell which has a total height a); the effective optical path length within the cell is l, and the focal length of the image-forming lens H is f; and Z_ξ is the observed deflection for light passing through the plane identified as ξ. By using a series of identical double slits arranged one above the other and suitably masked, it was possible to explore the temperature gradient at a number of planes in the cell in a relatively short time.

Some early experiments were carried out with the cell shown in Fig. 2a. The temperature gradient within this cell did not vary by more than 1—2% over the region $\xi = 0{\cdot}2$—$0{\cdot}8$, but the average value calculated from eqn. (2) by using the geometrical distance between the inner surfaces of the windows as a measure of l was considerably less than that calculated from the thermocouple readings. By means of the latter, the effective optical path length in the cell could be calculated and was found to be very close to the diameter (7·63 cm.) of the silver discs. This observation is important in assessing some of the earlier work done with this type of cell.[14,19] This uncertainty was absent in the modified cell shown in Fig. 2b, but the temperature gradient in it was rather less uniform and not quite symmetrical about the median plane of the cell (Fig. 3). A similar cell in which the distance (a) between the discs was reduced to 2 mm. was also examined. With a total temperature interval between the thermocouples of 1·96°, the temperature gradient in the cell was substantially constant at all planes and ~1% less than that calculated from the thermocouple readings and the cell height. This corresponds to a temperature difference of 0·01° between the thermocouples and the disc faces, which would not be surprising.

Measurement of Soret Coefficients.—The total refractive-index gradient ($\mathrm{d}n/\mathrm{d}\xi$) in the cell, when this is filled with a solution, is the sum of two terms, one arising from the concentration gradient and the other from the temperature gradient, and can be expressed as

$$\frac{\mathrm{d}n}{\mathrm{d}\xi} = \frac{\mathrm{d}N}{\mathrm{d}\xi}\left(\frac{\partial n}{\partial N}\right)_T + \tau\left(\frac{\partial n}{\partial T}\right)_N$$

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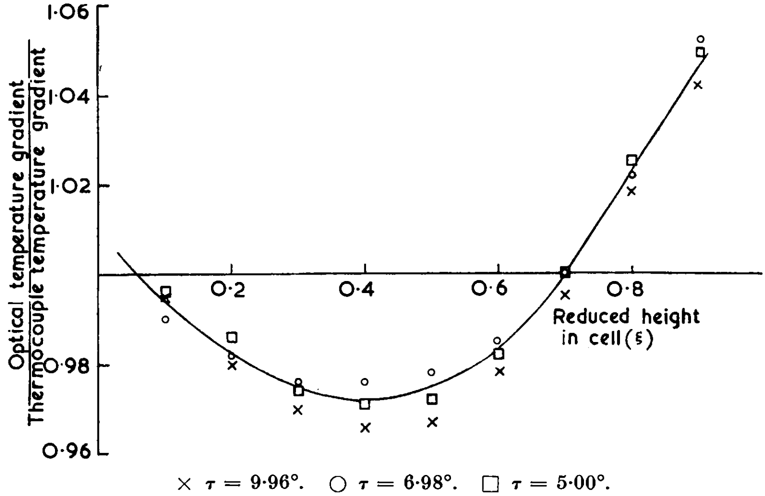
[22] Tilton and Taylor, *J. Res. Nat. Bur. Stand.*, 1938, **20**, 419.

where N is the mole fraction, and τ the temperature interval across the cell, the temperature gradient being assumed to be constant at all points in the cell. As shown in the previous section this constancy does not always exactly hold. The gradient of concentration in the cell can only be obtained in terms of the Soret coefficient from the diffusion equation (J_i = flow of component i per unit area per unit time, ρ is the density of the solution),

$$J_i = -\frac{D\rho}{a}\left(\frac{dN_i}{d\xi} + \sigma\tau N_i(1 - N_i)\right),$$

integrated subject to the boundary conditions appropriate to the cell. A full solution of this problem has not been achieved, but several approximate forms have been proposed [1,2,23] of varying degrees of complexity, all of which assume that the temperature gradient, the diffusion coefficient D, and the Soret coefficient are constant throughout the cell. A useful approximate form which can be derived from either Bierlein's [1] or Agar's [2] treatment is (cf. ref. 12, p. 202):

FIG. 3. *Vertical variation of temperature gradient in modified, water-filled, Tanner cell.*



$$Z_{\xi,t} = \frac{lf}{a}\left[K_2 - \sigma\tau K_1\left\{1 - \frac{2}{\pi}\sum_{j=1}^{\infty}[1 - (-1)^j]\frac{1}{j}\sin j\pi\xi \exp(-j^2t/\theta)\right\}\right]. \qquad (3)$$

$Z_{\xi,t}$ is the observed deflection at time t of a beam passing through the cell in the plane ξ; $K_1 = N_i^0(1 - N_i^0)(\partial n/\partial N_i)_T$; $K_2 = \tau(\partial n/\partial T)_N$; and $\theta = a^2/\pi^2 D$. The series converges most rapidly when $\xi = \frac{1}{3}, \frac{2}{3}$, and at these planes equation (3) can be replaced by

$$Z_{\xi,t} - Z_{\xi,\infty} = \frac{4lf}{\pi a}\sigma\tau K_1 \sin\pi\xi \exp(-t/\theta) \qquad (4)$$

after a very short time. In this, $Z_{\xi,\infty}$ is the steady-state deflection, since, from (3), when $t = \infty$, we have

$$Z_{\xi,\infty} = \frac{lf}{a}(K_2 - \sigma\tau K_1). \qquad (5)$$

Elsewhere in the cell the higher terms in the sum of equation (3) remain important for longer.

If the diffusion constant, and hence θ, is unknown, a plot of ln $(Z_{\xi,t} - Z_{\xi,\infty})$ against t

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[23] de Groot, " L'Effet Soret," North Holland, Amsterdam, 1947.

should be linear with a slope of $(-1/\theta)$, except when t is small, and an intercept at $t = 0$ from which σ can be calculated (method 1). Alternatively, if an independent value of D is available, $Z_{\xi,t}$ should be a linear function of $\exp(-t/\theta)$, the slope being proportional to σ (method 2). Extrapolation of this linear plot to $t = \infty$ yields a value of $Z_{\xi,\infty}$ derived from measurements of $Z_{\xi,t}$ in the earlier stages of the experiment. Both this extrapolated value and the directly observed one can be used in equation (5) to calculate σ (methods 3 and 4 respectively). They should, of course, be the same, but there are some experimental difficulties in the way of a direct observation of $Z_{\xi,\infty}$ and Bierlein, Finch, and Bowers[16] in their work on n-heptane–benzene mixtures preferred to use the extrapolated value which they found to differ significantly from the directly measured one. In methods 1 and 2, direct determination of the Soret coefficient from the plot involves the term ($\sin \pi\xi$). The entrance plane at which the centre of the beam impinges on the cell can be determined quite accurately, but, through the cell, the beam follows a parabolic path and emerges at a plane lower than that at which it has entered. If the entrance plane is at ξ_1 and the exit plane at ξ_2, it can be shown that[24]

$$\xi_1 - \xi_2 = \frac{l}{2naf} \cdot Z_{\xi,t}, \tag{6}$$

where n is the refractive index of the solution in the cell. The observed deflection in the image plane is proportional to the average refractive-index gradient over the path explored; provided that ξ_1 and ξ_2 are not very different this is given by equation (3) with ξ replaced by $(\xi_1 + \xi_2)/2$. From equation (6),

$$\bar{\xi} \equiv \frac{\xi_1 + \xi_2}{2} = \xi_1 - \frac{l}{4naf} \cdot Z_{\xi,t},$$

$Z_{\xi,t}$ is a function of time and ($\sin \pi\bar{\xi}$) must also vary during the experiment. However, a large proportion of the observed deflection in the image plane is due to the temperature gradient, and this remains constant during the establishment of the Soret equilibrium. For the purpose of calculating σ by methods (1) or (2) it is reasonable to take the value of $Z_{\xi,t}$ to be used in equation (6) as the mean between that due to the temperature effect alone and that observed when the steady-state equilibrium has been reached. Strictly, the plots used in methods (1) and (2) should not be exactly linear because of this time-variation of $Z_{\xi,t}$, but the effect is too small to be seen; the choice of $\bar{\xi}$ to be inserted in equation (3) does, however, make a small difference to the calculated Soret coefficients.

Experiments on the rate of attainment of the steady state have been carried out on m- and 2m-solutions. At $\xi = \frac{1}{3}$, $\xi = \frac{2}{3}$, the plots of $\log (Z_{\xi,t} - Z_{\xi,\infty})$ against time were accurately linear for $t > 0{\cdot}1\theta$. Fig. 4 shows a plot of $Z_{\xi,t}$ against $\exp(-t/\theta)$ for a m-solution, θ having been calculated from Longsworth's value[25] of the diffusion coefficient at 25°. The observed value of $Z_{\xi,\infty}$ agreed closely with the extrapolated value derived from a least-squares analysis of the data from an earlier stage of the experiment. Similar results were obtained for 2m-solutions except that the extrapolated value of $Z_{\xi,\infty}$ was consistently 2—4% below the measured value. Parasitic remixing processes in the cell would have produced the opposite effect. However, it was found that small changes in the value chosen for θ changed the slope and intercept of the exponential plot significantly without noticeably affecting the linearity. The only value of the diffusion coefficient available to us was derived from some diaphragm-cell measurements,[26] a method which is not very suitable for use with this solution, and it is possible that it was slightly in error.

Table 1 shows some isothermal diffusion measurements derived from the slopes of

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

[25] Longsworth, " The Structure of Electrolytic Solutions," ed. Hamer, Wiley, New York, 1959, p. 194.

[26] Firth, unpublished work.

the logarithmic plots which may be compared with Longsworth's value of 1·276 × 10^{-5} cm.^{2} sec.$^{-1}$.

TABLE 1. *Diffusion coefficients for* m-*silver nitrate solutions from Soret effect measurements.* $T_m = 25°$ *at centre of cell* ($\xi = 0·5$). *Cell:* 1 *cm. high, thick windows.*

Plane of entry, ξ_1	0·321	0·655	0·321	0·655	0·321	0·655
Temperature gradient (° C cm.$^{-1}$)	10·01	10·00	7·01	7·00	5·00	5·00
Calc. diffusion coeff. (10^{-5} cm.^{2} sec.$^{-1}$)...	1·208	1·246	1·268	1·279	(1·335)	1·27

When the temperature gradient was high, the measured diffusion coefficient was below the true value, and it increased towards the correct one as the temperature gradient was reduced. The value in parentheses is exceptionally high, and may indicate that there was some convective remixing in the cell during this experiment, though there is little evidence in the Soret coefficients calculated from these measurements that the experiment was abnormal (cf. Table 2).

An investigation of the effect of the size of the temperature interval upon the magnitude of the calculated Soret coefficient derived from data of the kind available here may be vitiated by an incorrect choice of the mean temperature in the cell. The mean refractive-index gradient over a limited vertical height in the cell has usually been measured in this work at $\xi \sim \frac{1}{3}$ or $\frac{2}{3}$, these values being chosen to make the higher terms in the sum appearing in equation (3) diminish to insignificance as rapidly as possible. At first sight, it might be assumed that, since the local refractive-index gradient is being measured, the calculated Soret coefficient values must refer to the region explored. If this were the case, it would be correct to keep the mean temperature at this plane the same from one experiment to another. If this is done for investigations at $\xi = \frac{1}{3}$, the temperature at the centre of the cell will be higher than that at the plane explored, and will fall as the temperature interval across the cell decreases. When the region round $\xi = \frac{2}{3}$ is studied, the temperature at the cell centre will be less and will rise as the temperature interval is decreased. However, this simple view can hardly be correct since the cell is bounded at $\xi = 0$, $\xi = 1$, and the diffusion processes at any plane cannot be independent of those proceeding elsewhere in the cell. A solution of the diffusion equation for the case of a variable Soret coefficient has not been satisfactorily achieved though an attempt has been made by one of us [27] assuming a linear variation of σ with temperature. It is difficult to estimate the effect of some of the approximations used in this treatment on the final result but we have concluded that, no matter where the refractive-index gradient is measured in the cell, the Soret coefficient calculated from the data refers to that at the cell centre. If this is so, the temperature at $\xi = 0·5$ should be kept constant when changing

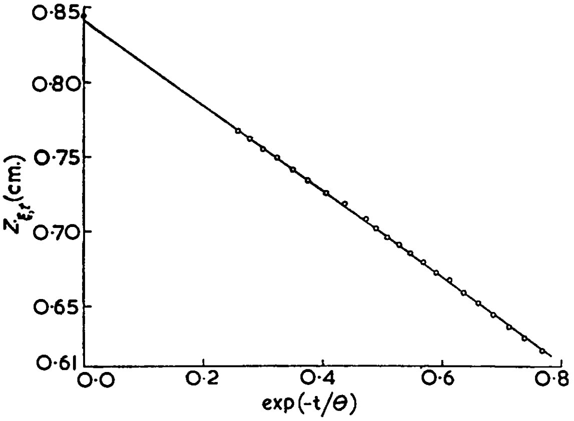

FIG. 4. *The rate of attainment of Soret equilibrium in aqueous* m-*silver nitrate* ($\tau = 10·00°$; $\xi_1 = 0·655$; 25° *at* $\xi = 0·5$).

Plot of $Z_{\xi,t}$ *against* exp ($-t/\theta$) *with* $D = 1·276 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ (Longsworth, ref. 24).

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[27] Kennedy, Ph.D. Thesis, Sheffield, 1960.

the temperature interval. Soret coefficients, calculated by methods (1) and (3) only, from experiments on 2m-solutions in which the exploring beam entered the cell at $\xi = \frac{1}{3}$, the temperature in this plane being unchanged, showed a marked decrease with the size of the temperature interval, especially when method (1) was used. A linear extrapolation to zero temperature gradient gave a value of about 7·3 × 10^{-3} deg.$^{-1}$ but the uncertainty in this figure is quite large. A more extensive study with m-solutions, for which a reliable value of the diffusion coefficient is available, was then carried out with modified Tanner cells having a = 10 mm. and a = 2 mm. Results on the first cell are given in Tables 1 and 2. Soret coefficients calculated by the four methods described are shown in Table 2

TABLE 2. *Soret coefficients for aqueous* m-*silver nitrate calculated from results obtained from a modified Tanner cell* (a = 10 mm.).

Plane of entry, ξ_1	Temp. gradient (° c cm.$^{-1}$)	Approx. ξ at which $T = 25°$	Calc. Soret coefficients (deg.$^{-1}$ × 10^3)							
			Method 1		Method 2		Method 3		Method 4	
0·321	10·02	$\frac{1}{3}$	4·69	(4·28)	4·68	(4·29)	4·67	(4·42)	4·65	(4·42)
0·655	10·27	$\frac{2}{3}$	3·87		3·90		4·18		4·20	
0·321	7·00	$\frac{1}{3}$	4·51	(4·27)	4·50	(4·28)	4·36	(4·35)	4·38	(4·37)
0·655	7·00	$\frac{2}{3}$	4·03		4·07		4·34		4·36	
0·321	4·49	$\frac{1}{3}$	4·49	(4·31)	4·55	(4·33)	4·49	(4·44)	4·36	(4·33)
0·655	5·01	$\frac{2}{3}$	4·14		4·11		4·40		4·30	
0·321	10·01	$\frac{1}{2}$	4·54	(4·33)	4·49	(4·31)	4·42	(4·39)	4·30	(4·32)
0·655	10·00	$\frac{1}{2}$	4·13		4·13		4·37		4·34	
0·321	7·01	$\frac{1}{2}$	4·42	(4·28)	4·43	(4·31)	4·45	(4·39)	4·45	(4·41)
0·655	7·00	$\frac{1}{2}$	4·14		4·16		4·34		4·37	
0·321	5·00	$\frac{1}{2}$	4·44	(4·32)	4·49	(4·36)	4·37	(4·37)	4·48	(4·42)
0·655	5·00	$\frac{1}{2}$	4·21		4·23		4·37		4·37	

Notes. Method 1: From intercept of log $(Z_{\xi,\infty} - Z_{\xi,t})$ against time. Method 2: From slope of $Z_{\xi,t}$ against exp $(-t/\theta)$ with independent value of diffusion coefficient. Method 3: From measured steady-state deflection. Method 4: From steady-state deflection obtained by extrapolation from plot used for method 2.

Figures in parentheses represent the mean value of the pair.

for observations taken at $\xi = \frac{1}{3}$, $\xi = \frac{2}{3}$, with three different temperature gradients. In half the experiments, the temperature at the plane explored was held at 25°; in the other half, the temperature at the cell centre was kept at this value. For the first set the Soret coefficients calculated by methods (1) and (2) are considerably larger from data obtained at $\xi_1 = 0{\cdot}321$ than at $\xi_1 = 0{\cdot}655$, the difference falling slightly with the temperature gradient. Differences of this kind are too large to be explicable in terms of the uncertainty in ξ due to the bending of the beam in its passage through the cell as discussed earlier. The mean of each pair of values, however, varies very little with the temperature gradient. The differences between the pairs of coefficients calculated by methods (3) and (4) are not so marked; indeed, except when the temperature gradient had its largest value, they were scarcely significant. Once again, the change in the mean of each pair with temperature gradient was small, but the mean value for all observations, calculated by these methods, was distinctly larger than the similar figure calculated by methods (1) and (2); if appreciable convective remixing had occurred during the experiments, it should have been smaller. The same general pattern emerges from a study of the second group for which the temperature at $\xi = \frac{1}{2}$ was kept constant, though the differences between pairs of values, calculated by methods (1) and (2), from data at $\xi_1 = 0{\cdot}321$, and at $\xi_2 = 0{\cdot}655$ are somewhat less than before. For methods (3) and (4), the differences are even smaller. These results are consistent with the view that the calculated value of the Soret coefficient is characteristic of that at the centre of the cell and that, even on this assumption, equation (3) is not entirely adequate to describe the variation in the refractive-index gradient with time (cf. Longsworth [10]).

The mean values in the second set display an independence of the temperature gradient similar to that found for the first. Furthermore, if all the results are examined, it will be seen that methods (1) and (2) on the one hand, and methods (3) and (4) on the other, nearly always give calculated coefficients in close agreement for any given set of experimental results. This shows that these experimental results are consistent with Longsworth's measurements on the isothermal diffusion coefficient of m-silver nitrate, and it thus reinforces the conclusion drawn from the data in Table 1.

Because of experimental difficulties, the planes explored in the upper and the lower section of the cell were not quite symmetrical about the centre. Since the calculated coefficients probably refer to the value at the cell centre rather than to that characteristic of the plane explored, this small defect should be less important for the second set of results in Table 2, and the following discussion is confined to these. The mean of all the values shown in parentheses derived by methods (1) and (2) is 4·31 × 10^{-3} deg.$^{-1}$, the standard deviation of this mean being 0·011 × 10^{-3} deg.$^{-1}$. For methods (3) and (4) the corresponding quantities, in the same units, are 4·38 and 0·014 respectively. This difference is significant, but again has the wrong sign to be explicable in terms of convective remixing in the cell. The conditions in the cell used in this work were quite different from those employed by Agar and Turner,[5] who used a cell with a much smaller diameter and much more dilute solutions; both of these factors might tend to favour some remixing by convection, and hence higher Soret coefficients from data obtained exclusively in the early stages of the experiment than from measurements on the system in the steady state. The simplest explanation for the present observations is that equation (2) is not quite adequate except when *t* approaches infinity. On this view, methods (3) and (4) are the most reliable for the interpretation of beam-displacement data. If this is correct, it is clearly desirable to reduce the duration of the experiments as far as possible by reducing the height of the cell to the lowest practicable value, at least in experiments such as these where the denser component becomes concentrated at the cold wall.

TABLE 3. *Soret coefficients for aqueous* m-*silver nitrate, calculated* (*method* 3) *from results obtained with a modified Tanner cell* (*a* = 2 mm.).

$\xi_1 = \frac{2}{3}$		$\xi_1 = \frac{1}{2}$		$\xi_1 = \frac{1}{3}$		Whole cell	
Temp. grad. (° c cm.$^{-1}$)	σ (10^{-3} deg.$^{-1}$)	Temp. grad. (°c cm.$^{-1}$)	σ (10^{-3} deg.$^{-1}$)	Temp. grad. (° c cm.$^{-1}$)	σ (10^{-3} deg.$^{-1}$)	Temp. grad. (° c cm.$^{-1}$)	σ (10^{-3} deg.$^{-1}$)
9·95	4·42	9·75	4·35	—	—	9·29	4·36
9·20	4·35	9·76	4·38	—	—	—	—
7·00	4·42	7·17	4·38	7·05	4·40	6·82	4·33
7·02	4·34	7·35	4·35	6·95	4·38	—	—
5·10	4·45	5·05	4·35	4·95	4·36	5·20	4·35
5·02	4·34	5·16	4·42	5·00	4·33	—	—
Mean	4·39	Mean	4·37	Mean	4·37	Mean	4·35

Table 3 shows results obtained with a cell, only 2 mm. in height, in which the steady state was reached in about 20 minutes. It was not possible to use measurements made during the approach to this state principally because the " warming-up " period can no longer be ignored and method (3) is the only practicable one. The deflection at zero time was calculated from the known temperature coefficient of refractive index of the solution derived from measurements in the 10 mm. cell, and the temperature interval from the thermocouple readings corrected for the slight (~1%) temperature loss in the discs described in an earlier section. Obviously, with a cell of this limited height, the accuracy with which ξ_1 could be determined is low, and the relative importance of the finite width of the beam greater than before; neither of these factors, however, should affect the measurement of the infinite time displacement. The results labelled " whole cell " were obtained by omitting the double slit immediately before the cell. The temperature was kept at 25° at the plane explored except in the case of the " whole cell " measurements where this temperature was maintained at the cell centre. There is little difference between the average value of σ for each group of experiments and the mean of the 19 results is $4{\cdot}37 \times 10^{-3}$ deg.$^{-1}$ with a standard deviation of the mean of $0{\cdot}01 \times 10^{-3}$ deg.$^{-1}$, a value substantially identical with that obtained on the 10 mm. cell from the second group of experiments recorded in Table 1 for methods (3) and (4). Longsworth's careful study [25] of the same system with a temperature interval of about 10° and a temperature at the cell centre of 25° gave $\sigma = 4{\cdot}27 \times 10^{-3}$ deg.$^{-1}$, which is significantly lower than our values derived from measurements in the steady state, and slightly less than that found by calculation from results obtained during the approach to this state. However, in spite of these differences it is encouraging that two such different methods should give such similar results. The low standard deviation of the mean of the Soret coefficients tabulated in Table 3 arises partly from the large number of observations which the small characteristic time of the 2 mm. cell makes possible. This fact, the satisfactory agreement with the much more laborious experiments carried out in the 10 mm. cell, the smaller risk of convection currents in a cell with a large area : height ratio, and the greater potential sensitivity, make the combination of the optical beam-displacement method with a cell only 2 mm. in height particularly useful.

TABLE 4. *Soret coefficients for more dilute solutions of silver nitrate calculated (method* 3) *from results obtained from the modified Tanner cell* ($a = 2$ mm.) ($\xi_1 = 0{\cdot}5$, *T at* $\xi = 0{\cdot}5$ *maintained at* 25°. *Temperature gradient* 15° cm.$^{-1}$).

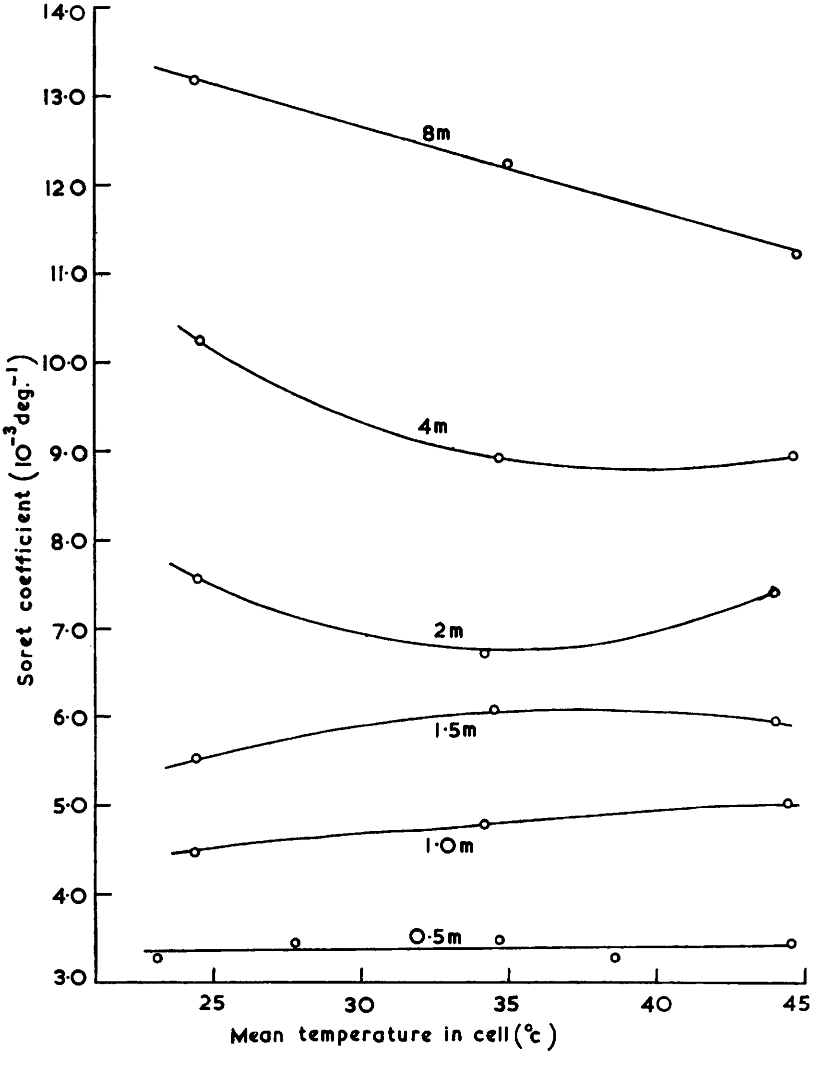
Concn. (molality)	$\sigma \times 10^3$ (deg.$^{-1}$) This work	$\sigma \times 10^3$ (deg.$^{-1}$) Longsworth
0·1	3·38	2·84
	3·06 (3·17)	
	3·06	
0·2	3·11 (3·06)	2·89
	3·01	
0·5	3·13 (3·14)	3·23
	3·16	

The sensitivity of the apparatus in its present form with the 2 mm. cell can be seen from Table 4 in which results on more dilute solutions of silver nitrate are tabulated and compared with those obtained by Longsworth [25] by the integral-fringe method. The agreement can be considered good, though the accuracy with which the coefficient for the 0·1m-solution could be found was inevitably not very high because of the small proportion of the total beam displacement due to the concentration changes.

Before the necessity for a full analysis of the experimental results was entirely realised, a number of experiments, in which the beam entered at $\xi_1 = \frac{1}{3}$ and the temperature was maintained at the desired value in this plane, were carried out for a wide range of silver nitrate concentrations at several temperatures. While these will not be as accurate as the mean values derived from the results in Tables 2, 3, and 5, their general trend is worth recording here. In Fig. 5 data obtained on the unmodified Tanner cell at 25°, 35°, and 45° are shown for 1—8m-solutions. At the lowest concentrations the Soret coefficient increases with temperature, as is usual for electrolyte solutions, but, at higher concentrations this trend is reversed, a phenomenon which does not seem to have been observed before for an electrolyte solution. Fig. 6 shows the variation of σ with molality at 25°, the data from Tables 2 and 3 being included at the low molality end for comparison. The increase in σ with molality at higher concentrations is characteristic, and there are distinct signs of the minimum which has been observed for a number of electrolyte solutions (cf. ref. 12, chapter 10). When the activity coefficient term $[1 + (\partial \ln \gamma_{\pm}/\partial \ln m)_{T,\,P}]$ is included and the sum of the ionic entropies of transfer is calculated, the results are rather more striking (Fig. 7). There is a clear minimum at about 0·5m and a steep rise thereafter up to 2m. Above this concentration it falls off slightly to the highest concentration studied. The initial fall in the entropy of transfer with increasing concentration observed for all electrolytes studied in sufficiently dilute solution has been explained by Agar,[4] but a detailed explanation of the changes at higher concentrations is not at present possible. In any event this would be complicated for silver nitrate solutions by the ion association which occurs.

Conclusions.—(1) The available solutions of the diffusion equation for a pure Soret effect cell, when expressed in an easily usable form, give reasonably satisfactory representations of optical beam-displacement measurements on m-silver nitrate. They are not, however, completely satisfactory for this purpose, since Soret coefficients calculated from measurements in the early stages of the experiment vary significantly with the position of the exploring beam in the cell and with the magnitude of the temperature gradient. Similar coefficients calculated from steady-state measurements alone varied much less.

FIG. 5. *Variation of the Soret coefficient of aqueous silver nitrate solutions with mean cell temperature.* (*Unmodified Tanner cell, a* = 10 mm.)



(2) Mean values of such coefficients, obtained from experiments on m-silver nitrate in which the cell was explored at planes disposed approximately symmetrically above and below the centre, and calculated from the rate of attainment of the steady-state

equilibrium, were slightly lower ($4 \cdot 31 \times 10^{-3}$ deg.$^{-1}$) than the similar mean coefficients calculated from steady-state data. Almost identical values ($4 \cdot 38$, $4 \cdot 37 \times 10^{-3}$ deg.$^{-1}$) for these coefficients were obtained from experiments on cells having $a = 10$ mm. and 2 mm. respectively. All these values are slightly higher than that obtained ($4 \cdot 27 \times 10^{-3}$ deg.$^{-1}$) for the same system at the same mean temperature (25°) by Longsworth who used an integral-fringe method.

(3) It has been shown that accurate measurements can be made rapidly on a cell with a plate separation of 2 mm., the results being identical with those obtained, with much greater labour, on a cell with the more usual separation of 10 mm. In addition, the sensitivity of the beam-displacement method then matches that of the integral-fringe arrangements without the use of large temperature intervals.

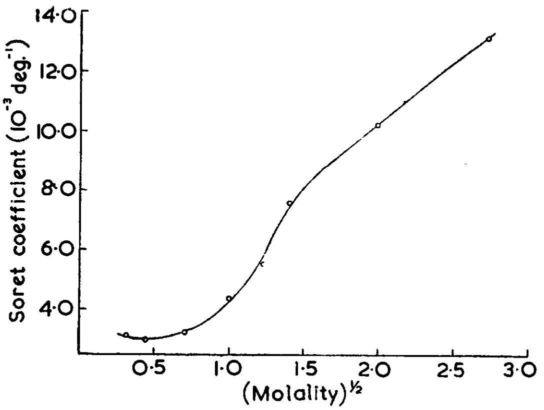


FIG. 6. *Variation of the Soret coefficient of aqueous silver nitrate with molality at a mean cell temperature of* 25°.

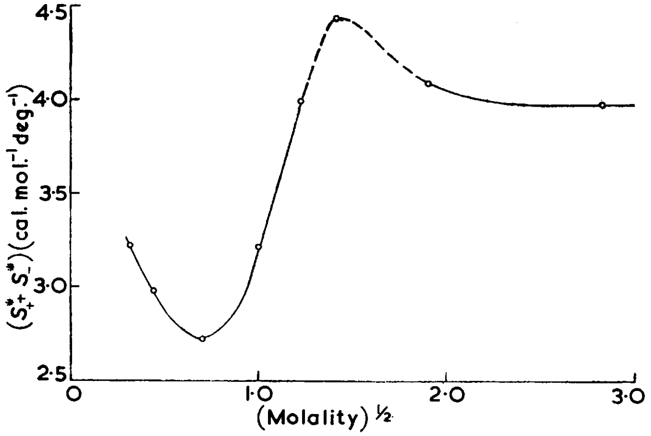


FIG. 7. ($S_+^* + S_-^*$) *for aqueous* 0·1—8m-*silver nitrate at* 25°.

(4) Approximate results obtained for silver nitrate solutions up to 8 molal have shown the interesting variations in σ and ($S^*_+ + S^*_-$) for this system with changes in concentration and mean temperature, though these are at present not explicable in terms of the structure of the solution.

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