1210. *A Modified Type of Thermal-diffusion Cell, and its Application to the Measurement of Soret Coefficients for Solutions of Carbon Tetrachloride in Benzene*

By L. Guczi and H. J. V. Tyrrell

The principles underlying the design of a satisfactory cell for the direct study of the Soret effect are discussed, and an improved cell, suitable for use with most non-aqueous mixtures, is described. It has been used, in conjunction with a phase-contrast schlieren technique of measuring refractive-index gradients, to study thermal diffusion in some solutions of carbon tetrachloride in benzene at a mean temperature of 25°. The results confirm that carbon tetrachloride migrates to the cold wall, the average Soret coefficient (σ) for an equimolar solution being $6{\cdot}40 \times 10^{-3}$ deg.$^{-1}$, a figure based on 49 separate values obtained in four independent experiments (standard deviation $= 0{\cdot}08 \times 10^{-3}$ deg.$^{-1}$). The coefficient varies only slightly with concentration down to $N_{(\mathrm{CCl_4})} = 0{\cdot}2$, though some preliminary measurements at lower mole fractions suggest that σ may rise rapidly as the system becomes richer in benzene.

The partial de-mixing of a binary solution under the influence of a thermal gradient (thermal diffusion, Soret effect) is important for gaseous mixtures, both technically, as in isotope separations, and as a tool in the study of intermolecular forces. Its technical importance for the separation of liquid mixtures is less certain, and its use for the study of the liquid state is restricted by theoretical and practical problems. Most of the experimental data available, especially on mixtures of non-electrolytes, are at best semi-quantitative, and further advances in this field can only be achieved if improved experimental techniques become available. This Paper discusses some of the problems which must be overcome, and describes apparatus and techniques which have been applied successfully to the measurement of Soret coefficients in mixtures of benzene with carbon tetrachloride.

The Soret coefficient, σ, is defined as:

$$\sigma = -(m)^{-1}(dm/\mathrm{d}T)_{\mathrm{stat.}} = (N_1N_2)^{-1}(\mathrm{d}N_2/\mathrm{d}T)_{\mathrm{stat.}} \qquad (1)$$

where N_1 and N_2 are, respectively, the molar fraction of solvent and solute, and m is the molality of the solute. The concentration changes are those which occur in a layer of solution in the absence of convective transport, and the suffix " stat." indicates that the differential coefficients in equation (1) are measured in this condition. In principle, the simplest method of obtaining σ is to apply a known temperature gradient across a horizontal layer of the solution, and to measure the concentration gradient when the steady state has been attained, using a method of analysis which does not disturb the solution. Since σ is usually less than 10^{-2} deg.$^{-1}$, the observed concentration changes are small, and measurement of refractive-index changes within the liquid layer is the most generally applicable technique of analysis at present available. Experimentally, therefore, this direct method of obtaining σ requires (a) a cell in which a convection-free layer of the solution can be maintained subject to a temperature gradient of known magnitude, and (b) a suitable technique for studying the refractive-index changes along the applied temperature gradient.

Other methods for measuring σ are available [1] and are currently being developed [2,3] but these will not be discussed here.

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[1] H. J. V. Tyrrell, " Diffusion and Heat Flow in Liquids," Butterworths, London, 1961.

[2] F. H. Horne and R. J. Bearman, *J. Chem. Phys.*, 1962, **37**, 2842, 2857.

[3] J. C. R. Turner, *Chem. Eng. Sci.*, 1962, **17**, 95; and personal communication.

CELL DESIGN

Conventionally, a pure Soret-effect cell consists of two horizontal metal plates separated by vertical walls of low thermal conductivity. The liquid layer lying between the horizontal plates may be up to 10 mm. thick, and if refractive-index changes are to be followed the non-conducting cell walls must incorporate optical windows at opposite ends of a diameter. To minimise convection within the liquid layer, the upper surface is heated with respect to the lower one. If the liquid layer is a cm. thick, and the diffusion coefficient for the system is D, the rate at which the steady-state concentration gradient is developed depends [1] on a characteristic time $\theta = a^2/\pi^2 D$; if $a = 1$ cm. and $D = 10^{-5}$ cm.^{2} sec.$^{-1}$, θ is approximately 3 hr., and the steady state will be substantially attained in about 5θ, or 15 hr. Experimental studies [4] on a cylindrical cell (diameter 7·6 cm.) of this type showed that the temperature gradient produced across a layer of liquid 1 cm. thick was never linear, the departure from linearity being greatest for liquids of low thermal conductivity. Furthermore, it became clear that convective re-mixing processes were always likely to mask the separation due to thermal diffusion when non-aqueous solutions were being studied. Both the existence of non-uniform temperature gradients in the solution, and the onset of convection, are associated with heat losses through the walls, and the inevitable difference in thermal properties between these walls and the liquid filling the cell.

In an infinitely extended liquid film bounded by two rigid horizontal surfaces, and heated from below, convection will not occur if the dimensionless product of the Grashof ($N_{Gr.}$) and Prandtl ($N_{Pr.}$) numbers, defined as

$$N_{Gr.}N_{Pr.} = ga^3\Delta T(\rho\beta/\eta K)$$

is less than 1700.[5] Here, g is the acceleration due to gravity, ρ is the density, β the coefficient of thermal expanion, η the viscosity, and K the thermal diffusivity of the liquid in the film. ΔT is the temperature interval across it. At a vertical wall, convection sets in at a lower value of this product, and it is convection arising at such surfaces which we wish to inhibit in any practical design of thermal diffusion cell. The problem is essentially that encountered in steady-state methods of measuring the thermal conductivity of liquids,[6] and a logical procedure would be to design a cell such that $N_{Gr.}N_{Pr.}$ is small, and to apply the temperature gradient in such a direction that the liquid film is heated from the top downwards. The thickness of the film, a, is of great importance. Table 1 shows values of the ratio $\rho\beta/\eta K$ for a few liquids, and also the value of a corresponding to $N_{Gr.}N_{Pr.} = 1000$, when the temperature gradient across the film ($\Delta T/a$) is 10 deg. cm.$^{-1}$, a gradient comparable with that normally used in measurements of the Soret coefficient. It can be seen that if solvents such as carbon tetrachloride or benzene are to be studied, a should be less than 1 mm. to ensure that the product $N_{Gr.}N_{Pr.}$ is near this (arbitrary) limit of 1000. The experimental findings [4] that convective re-mixing was more serious in non-aqueous than in aqueous solutions can also be understood from the values of $\rho\beta/\eta K$ in this Table.

TABLE 1

Factors affecting the onset of convection in heated fluids. ($a_{crit.}$ is the critical cell height at which $N_{Gr.}N_{Pr.} = 1000$ for a temperature gradient of 10° cm.$^{-1}$)

Substance	$\rho\beta/\eta K$ (sec.^{2} cm.$^{-4}$ deg.$^{-1}$)	$a_{crit.}$ (mm.)
Carbon tetrachloride	$2{\cdot}52 \times 10^3$	0·797
Benzene	$1{\cdot}55 \times 10^3$	0·902
Methanol	$1{\cdot}52 \times 10^3$	0·910
Water	$0{\cdot}157 \times 10^3$	1·60

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[4] H. J. V. Tyrrell, J. G. Firth, and M. Kennedy, *J.*, 1961, 3432; H. J. V. Tyrrell, J. G. Firth, and M. Zaman, *J.*, 1965, 3613.

[5] S. Chandrasekhar, " Hydrodynamic and Hydromagnetic Stability," Oxford University Press, 1961, p. 43.

[6] *E.g.*, E. McLaughlin, *Chem. Rev.*, 1964, **64**, 389.

Concentration changes in such a thin film can best be measured by measuring the refractive-index gradient produced in the film when a temperature field is applied to it. Several methods of doing this are available, though diffraction effects in a cell with such a small plate separation are not entirely absent, and very careful alignment of the cell along the optic axis is essential. The magnitude of the optical effect produced by the passage of light through the cell depends on optical constants of the apparatus, including the cell length, and upon the refractive-index gradient produced both by the temperature gradient and by the concentration gradient within the cell. With non-aqueous solvents, the temperature effect can easily be an order of magnitude greater than the concentration effect, the measured optical effect being the sum of the two. It is therefore essential to be able to calculate accurately the contribution of the temperature gradient to the total measured effect. With the optical system described below, a change of 10^{-3} °c across a film of benzene 0·9 mm. thick caused a lateral displacement of the schlieren image of approximately 10 μ; the contribution of the concentration gradient, produced in the cell by the temperature field, to the total image displacement was, in some cases, no more than 20 times this. The temperature-control system used[7] permitted a variation of 0·003° in the temperature difference between the upper and lower parts of the cell. To minimise the effect of even this small variation, the same temperature gradient was applied simultaneously to a pair of " identical " cells, one containing the solution and the other the pure solvent. The deflection of the schlieren image observed for the solvent cell gave the temperature gradient across this cell, and, after correcting for unavoidable small differences between the two cells, the temperature gradient across the solution cell, and its contribution to the total observed image displacement for this cell, could be calculated with the minimum error possible. The plate separation in each cell must be uniform, measurable, and constant over long periods, and the materials of which the cells are made must not react with, or selectively adsorb, any component of the solutions to be examined in it. Such selective adsorption could produce concentration changes as large as, or larger than, those produced by thermal diffusion. This last consideration immediately eliminates many of the elastomers normally used for making liquid-tight seals.

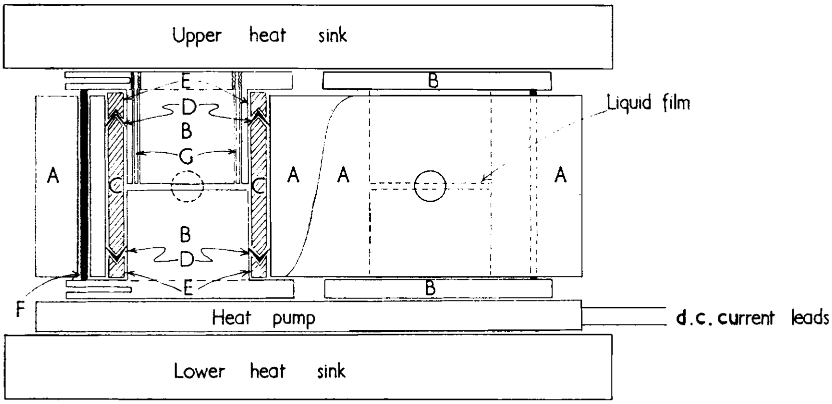

FIGURE 1. Details of twin cell, and of its relation to the heat sinks (not to scale)

A, Outer case, Polythene; B, cylindrical copper blocks forming upper and lower boundaries to the cells; C, PTFE cylinder forming cell walls (diameter 3·49 cm.); D, Chevron rings; E, PTFE spacing rings; F, stainless steel spacing rods; G, filling holes and plugs

These considerations led to the cell design shown in Figure 1. The main body A of the twin cell was made from a block of high-density Polythene, which acted as a thermal

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[7] L. Guczi and H. J. V. Tyrrell, *J. Sci. Instr.*, 1964, **41**, 468.

insulator and as a mechanical support for the actual cells. The cells consisted of two pairs of solid cylindrical copper blocks B. Each of these formed the upper and lower boundary surfaces of one cell, the vertical walls of which were formed by a polytetrafluorethylene (PTFE) cylinder C. The blocks B fitted snugly into C, but the liquid-tight seal between B and C was achieved by using Chevron PTFE rings, D. Moderate pressure in the vertical direction, applied through the PTFE spacing rings E, distorted D sufficiently for a satisfactory seal to be made.* The pressure was applied by screws passing through the flanges of the copper blocks B into steel inserts in A (not shown in Figure 1). The spacing between the upper and lower cell surfaces, and their parallelism, was mainly controlled by stainless steel spacer rods F (made from tube, with closed domed ends to minimise heat conduction), three to each cell, which passed through over-size holes in A and were in contact with the flanges on B. Circular section optical windows were inserted in holes drilled into C at opposite ends of a diameter, and cemented into place with cold-setting Araldite resin. In order to ensure a satisfactory bond between the glass and the PTFE of which C is made, C was given a preliminary etch.† The windows were placed almost flush with the inner surface of the cylinder C, and were recessed from the outer surface. When the cell was assembled, these cylinders were slipped into the main body A, so that the windows were opposite holes of similar size in the latter. The upper plate of each cell carried two filling holes, set well away from the optical path. They were closed as shown (Figure 1) by well-fitting plugs carrying a screw thread at the upper end.

TEMPERATURE MEASUREMENT AND CONTROL

The general arrangement is shown in Figure 1. The cells rested on the semiconductor sandwich, comprising the heat pump, which, in turn, lay on the lower heat sink. A similar heat sink was placed on top of the cells. Water from a thermostat at 25°c flowed by gravity through the upper heat sink into the lower one, and thence to a pump which returned it to the thermostat. Radial holes drilled into the flanges of the four cell-blocks carried the sensors for controlling and measuring the temperature difference between the upper and lower plates of each cell. A pair of reasonably well-matched thermistors (approximately 1800 ohms, Gulton 32CB1), in conjunction with the regulating circuit for the heat pump which has already been described,[7] were used to control this temperature difference. One was placed in the upper plate and the other in the lower plate of one of the twin cells. The temperature difference between the plates of each cell was measured by five-junction copper–constantan thermocouples, and the temperature of the upper plate of one of the cells relative to ice was similarly measured. These temperature readings were used to provide a check upon the performance of the system, and to show that the cells were in an isothermal condition at the beginning and end of each experiment. The whole assembly was heavily insulated to minimise unwanted temperature inequalities.

OPTICAL SYSTEM

The phase-contrast method of displaying refractive-index gradients developed by Wiedemann [8] was used.‡ A collimated light beam from a sodium source passed through the medium in which the refractive-index gradient exists, and was then focussed on a glass phase-plate, half of which was coated with a magnesium fluoride layer, one half-wavelength thick. The linear boundary between these two zones was inclined at an

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* This type of sealing ring is supplied by James Walker, Woking, Surrey.

† This etching process consisted of treatment for a few seconds in a solution of sodium in liquid ammonia, followed by quenching in water. It was carried out for us by de Havilland Aircraft Co., Stevenage.

‡ Apparatus manufactured by Strübin and Co., Basle.

[8] E. Wiedemann, *Helv. Chim. Acta*, 1958, **40**, 2074.

angle ϕ to the vertical. A combination of a spherical lens and a cylindrical lens with its neutral axis horizontal gave an image in the focal plane of a 35 mm. camera (Praktina II A), which, in the horizontal plane, was an extended image of the cell. The upper and lower boundaries of the cell appeared as the upper and lower limits of the horizontal illuminated area [cf. Figure 2(c)]. Across this area ran a fine shadow line (arising from the boundary on the phase plate), which was vertical when the collimated beam had passed through a uniform refractive-index gradient. If this uniform gradient changed, the whole shadow line was displaced horizontally by a distance proportional to the change in the gradient and to tan ϕ. If the refractive-index gradient varied from one horizontal plane to another in the cell, the horizontal displacement of any point on the shadow line depended upon its distance from the cell boundaries, and the image was no longer vertical but bent. The advantage of this system is that the refractive-index gradient across the whole cell can be displayed simultaneously, and any deviations from uniformity can be easily seen. The sensitivity increases with ϕ, as does the width of the shadow line. In the present work ϕ was normally 35°.

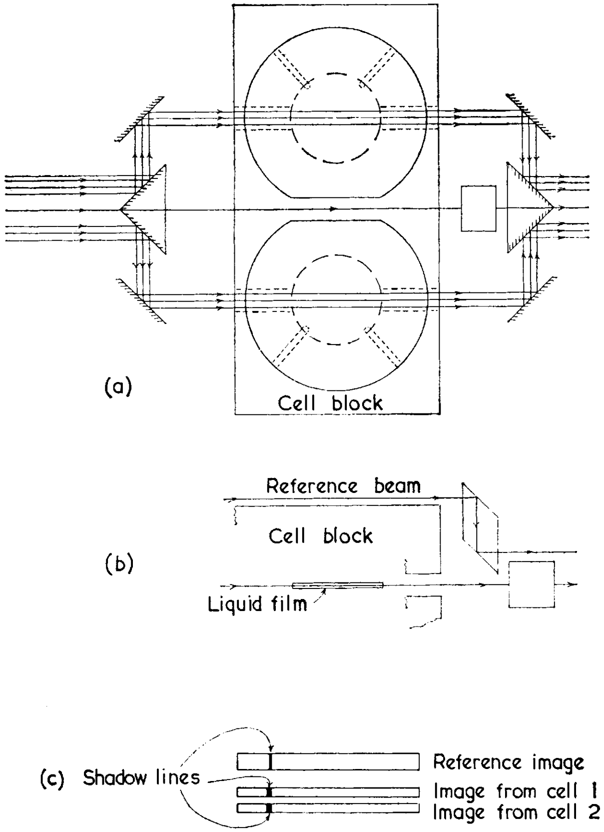

FIGURE 2. Optical details

(a) Plan view of method of illuminating the cells. (b) Side view showing displacement of reference beam by a rhomb. (c) Images as seen in camera

Owing to the unavoidable separation between the optical paths through each cell, the unmodified collimated beam could not be used directly to illuminate them. Figures 2(a) and (b) shows the beam-splitter and recombination system used to overcome this problem. The reference beam, which passed through air, gave an image in the camera plane with a shadow line which did not move and was used as a reference with respect to which line-displacements in the other images were measured. The beam-splitter was adjusted to give uniformly illuminated horizontal images of the two cells which lay one above the other as shown in Figure 2(c). The rhomb, which brought the reference image close to the cell images, was introduced to facilitate the measurement of the line-displacements. This was done with a photoelectric microscope patterned on that described by Bennett and Koehler.[9]

EXPERIMENTAL TECHNIQUE

After adjusting the optical system, the magnification factor in the horizontal plane was determined. In the absence of a refractive-index gradient in the collimated beam, a sharp slit-image was formed on the phase plate at the optical axis. A uniform refractive-index gradient displaced this sharp image upward or downward, and the shadow line in the final image plane then moved horizontally. If this horizontal displacement is Y, for a vertical displacement y, then

$$Y = \gamma y \tan \phi, \qquad (2)$$

where γ is an optical magnification factor. This was found by measuring the displacement, Y, of the reference image when the phase plate was displaced by known amounts (y) in a vertical direction. This was done for several values of ϕ, and $Y/\tan \phi$ plotted against y. A straight line with a slope $\gamma = 0{\cdot}984$ was obtained, and this figure was used in all subsequent experiments. When a similar experiment was carried out with the isothermal cells filled with the same liquid also in the beam-path, it was found that the horizontal displacements of the three shadow lines (one from the reference beam and two from the cells) for a given displacement of the phase plate, were not quite the same. These differences arose from slight differences in the alignment of the two cells with respect to the light beams passing through them, and they increased approximately linearly with the total reference image displacement. Empirical correction plots of the observed difference against the total displacement of the shadow line in the reference beam were constructed for each cell beam and used to correct the measured shadow-line displacements before applying equation (2) (with $\gamma = 0{\cdot}984$). These correction factors remained valid until it became necessary to strip and reassemble the cell; they were then remeasured.

The cell system was put together as follows. The heat pump was placed on the lower heat sink, and its upper surface levelled using a clinometer sensitive to 30 seconds of arc. The empty assembled cell was placed on this, and the screws in the flanges of the upper cell plates adjusted slightly until the upper surfaces were level and in the same horizontal plane. Since both upper and lower surfaces of the cell blocks were made to be parallel within close limits, this adjustment ensured that the upper and lower boundary surfaces of the cells were also horizontal. The separation between these surfaces was then measured at the cell windows by means of a travelling microscope; these quantities were needed in the subsequent calculations. The cell was then filled, the closures were inserted, and the upper heat sink was placed in position. All contact surfaces were greased to improve heat transfer, the whole assembly was insulated, the regulator set to give isothermal conditions, and the cell left until these were attained. Preliminary experiments showed that it was necessary to leave the system for several hours before the temperature differences across each cell, as recorded by the thermocouples, were close to zero, and fluctuated approximately in phase within the limit of 0·002—0·003° set by the regulator. The images were then photographed at intervals of a few minutes during a period of 1 hr.; from the observed shadow lines, it was possible to find whether (i) the (nominally zero) temperature gradients in the liquid films were uniform, (ii) the positions of the shadow lines from the two cells with respect to the shadow line in the reference image varied in phase. Non-uniform gradients in the cell were shown by distorted images of the shadow line and normally indicated that vapour bubbles had not been completely eliminated from the cell. Such distortions could be detected visually in the camera viewfinder and remedied by refilling the cell. The heat-pump regulator was then set to cool the lower plates of the cell by about 0·5°, and the images were recorded when temperature equilibrium had again been attained (40—60 min.). The temperature interval was successively increased in steps of 0·1°, and the images were recorded as before. The highest temperature difference used was approximately 0·9°, which corresponded to a temperature gradient of about 10 deg. cm.^{-1}. The cells were then returned to the isothermal condition, and the images again recorded so as to provide a

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[9] J. M. Bennett and W. F. Koehler, *J. Opt. Soc. Amer.*, 1959, **49**, 466.

check on the zero position. The complete programme was a lengthy one, and was controlled automatically from a taped programme of instructions.[10]

The system was first tested by filling both cells with the same liquid, and calculating, from the shadow-line displacements and the plate separations in each cell, the effective temperature interval across them for each setting of the regulator. Some results for benzene and for carbon tetrachloride are shown in Table 2. These show that the temperature intervals across the two cells varied in phase to a high degree of accuracy. The amounts of heat flux through the two cells in these experiments were clearly not the same, since, if this had been the case, $\Delta T_1/\Delta T_2$ would have been equal to a_1/a_2. It is an accidental coincidence that, when both cells were filled with the same liquid, the observed ratio was close to a_2/a_1, and this small discrepancy must have arisen from some difference in the thermal contact resistances for the two cells. An experiment with carbon tetrachloride in cell 1 and benzene in cell 2 was also carried out (Table 2). Carbon tetrachloride has the lower thermal conductivity, and, for this reason, the temperature interval across the cell containing it was higher in cell 1 than in cell 2, although the cell separation in cell 1 was slightly less. This effect could also be seen from the thermocouple readings taken in these experiments. When the same liquid was in both cells the temperature difference recorded across both by the thermocouples was the same within a few thousandths of a degree. When the cells were filled with dissimilar liquids, the thermocouple across the cell with the liquid of lower thermal conductivity gave a reading about 2% higher than did the other. These observations confirm the validity of the experimental techniques used. They also showed that the change in the temperature interval across the cell as the thermal conductivity of the cell contents was changed made it necessary to apply a correction to the measured temperature interval across the cell containing the solvent before the temperature interval across the " twin " cell containing the solution under test could be estimated. This was done with sufficient accuracy simply by interpolating between the known ratio when the cells were filled with the same pure solvent, and that when they were filled with the different solvents, at the point corresponding to the composition of the solution under test. The ratios shown in Table 2 were checked periodically, and found to alter only when the cell had been stripped down and reassembled. Since successive experiments were carried out without disturbing the cell, except when it was essential to do so, corrections found as described could be safely applied to a series of separate runs.

TABLE 2

Comparison of effective temperature intervals (ΔT_1,ΔT_2) across the two components of the twin cell. a_1 = experimental plate separation in cell 1, a_2 that in cell 2 (mm.)

Cell No. 1, Benzene Cell No. 2, Benzene			Cell No. 1, CCl_4 Cell No. 2, CCl_4			Cell No. 1, CCl_4 Cell No. 2, Benzene		
a_1	a_2	a_2/a_1	a_1	a_2	a_2/a_1	a_1	a_2	a_2/a_1
0·917	0·903	0·985	0·917	0·903	0·985	0·917	0·903	0·985
ΔT_1	ΔT_2	$\Delta T_1/\Delta T_2$	ΔT_1	ΔT_2	$\Delta T_1/\Delta T$	ΔT_1	ΔT_2	$\Delta T_1/\Delta T_2$
0·342°	0·344°	0·996	0·345°	0·351°	0·987	0·364°	0·351°	1·039
0·348	0·351	0·993	0·354	0·359	0·986	0·368	0·355	1·036
0·458	0·465	0·994	0·357	0·362	0·987	0·481	0·465	1·035
0·463	0·466	0·994	0·474	0·481	0·986	0·486	0·469	1·037
0·463	0·466	0·995	0·474	0·481	0·985	0·484	0·468	1·034
0·571	0·575	0·994	0·475	0·483	0·984	0·603	0·584	1·032
0·575	0·579	0·993	0·588	0·597	0·985	0·613	0·594	1·032
0·682	0·689	0·990	0·590	0·599	0·985	0·732	0·709	1·033
0·683	0·690	0·990	0·592	0·600	0·987	0·735	0·711	1·034
0·683	0·691	0·990	0·703	0·712	0·988	0·734	0·711	1·032
0·793	0·801	0·989	0·705	0·714	0·986	0·850	0·821	1·034
0·796	0·804	0·990	0·708	0·716	0·988	0·852	0·825	1·033
0·796	0·805	0·990	0·820	0·829	0·989	0·979	0·947	1·034
0·905	0·912	0·992	0·824	0·833	0·989	0·980	0·949	1·033
0·906	0·914	0·991	0·824	0·833	0·989	0·980	0·947	1·035
0·906	0·913	0·991						
Mean $\Delta T_1/\Delta T_2$ = 0·991			Mean $\Delta T_1/\Delta T_2$ = 0·987			Mean $\Delta T_1/\Delta T_2$ = 1·034		

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[10] P. F. Cole, R. Dickenson, L. Guczi, D. Hill, and H. J. V. Tyrrell, *J. Sci. Instr.*, 1965, **42**, 650.

THERMAL DIFFUSION IN SOME BENZENE–CARBON TETRACHLORIDE MIXTURES

This system was chosen for study because some earlier experiments in this laboratory with a less elaborate apparatus had been interpreted as showing that carbon tetrachloride migrated to the hot wall.[11] This, while not in agreement with earlier experimental data appeared to confirm expectations, based on simple theoretical models.[12,13] It was clearly important to verify this point. Furthermore, the system is not a particularly favourable one experimentally since the refractive indices of the pure components do not differ much, and its examination represented a stringent test of the cell and of the experimental techniques employed.

Analytical grade carbon tetrachloride and benzene were used. Before use, the carbon tetrachloride was refluxed over mercury, washed with 5% sodium hydroxide solution and water, and dried over phosphorus pentoxide. After drying, it was distilled through a long vacuum-jacketed column filled with Fenske helices, and the product stored in the dark. The benzene was washed successively with sulphuric acid, water, 5% sodium hydroxide, and water, dried over phosphorus pentoxide, and distilled through the same column.

The variation of refractive index (n) with mole fraction (N) for the sodium D-line (the source used in the phase-contrast optical equipment used in the diffusion experiments) was studied at 25° with a Hilger Rayleigh refractometer. A solution of known composition was made up, together with a set whose composition differed from this by small known amounts. The fringe-shift measured for each of these against the original solution was plotted against the mole fraction difference, ΔN, between the two solutions. Over the small range of concentration used, the fringe shift was a linear function of ΔN, and $(\partial n/\partial N)_{25}$ could thereby be obtained. The usual problems associated with the identification of the zero-order fringe with a white-light source were not serious, since estimates of the total fringe shift to within one fringe could normally be made using published data.[14] If this estimate happened to be inadequate, inspection of the graph of fringe-shift against ΔN revealed the error. Compositions in the neighbourhood of $N(\mathrm{CCl_4}) = 0{\cdot}1$, $0{\cdot}5$, and $0{\cdot}9$ were examined, and $(\partial n/\partial N)_{25}$ found to be a linear function of N. It was not therefore necessary to examine intermediate compositions. Results are shown in Table 3(a).

Accurate measurements of $(\partial n/\partial T)_N$ can easily be made with the Rayleigh refractometer provided that this quantity is known for one substance. If similar liquids are placed in the two sides of the refractometer, the normal fringe pattern for a monochromatic source is seen, however large the refractive index difference may be. If the fringe pattern is brought into coincidence with the reference fringe pattern at a given temperature, a fringe-shift occurs as the temperature is changed. When the temperature change is small enough, the fringe-shift is less than 1, and is therefore known unequivocally. By a series of small stepwise temperature changes, a shift of several fringes can be accurately determined. The observed shift contains a small component characteristic of the effect of the temperature change upon the instrument, but this can easily be measured and allowed for. The total shift, which should not be less than about five fringes, depends on the length of the refractometer cell used, and upon the integral:

$$\int_{T_1}^{T_2} [(\partial n/\partial T)_a - (\partial n/\partial T)_b]\mathrm{d}T$$

where the suffixes a and b refer to the solutions used. If the difference between these differential coefficients is independent of T, then $(T_1 - T_2)$ can be large. Otherwise, the required sensitivity must be obtained by increasing the cell length. In the present work,

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[11] H. J. V. Tyrrell and J. G. Firth, *Proc. Chem. Soc.*, 1961, 201.

[12] I. Prigogine, L. de Brouckère, and R. Amand, *Physica*, 1950, **16**, 577, 581.

[13] K. G. Denbigh, *Trans. Faraday Soc.*, 1952, **48**, 1.

[14] J. Timmermanns, " Physico-Chemical Constants of Binary Mixtures," vol. 1, Interscience, London, 1959.

stoppered cells either 1 or 4 cm. long were used. To avoid evaporation, mercury seals were placed round the stoppers. The stoppers themselves were hollow, and open at the top, and inside one of them was sealed the end of a five-junction copper–constantan thermocouple. This couple was used to measure the temperature of the cell at a point as close to the liquid contents as possible. With a Cambridge vernier potentiometer, temperatures were measured to better than 0·001°. The temperature of the cell was controlled by placing it in a double-walled container through which water from a thermostat was passed; the lid of the container was also thermostatted in this way. The whole instrument, apart from the eyepiece and entrance slit, was contained in an air thermostat.

Water was taken as the ultimate standard, and, from Tilton and Taylor's work,[15] $(\partial n/\partial T)$ for this substance in the range 25—26° was taken as $-1{\cdot}050 \times 10^{-4}$ deg.$^{-1}$. The difference $[(\partial n/\partial T)(\mathrm{CCl_4}) - (\partial n/\partial T)(\mathrm{water})]$ was found to be $-4{\cdot}67_7 \times 10^{-4}$ deg.$^{-1}$ between 25° and 25·7°. The differences between $(\partial n/\partial T)_N$ for carbon tetrachloride and benzene, and between the former and several solutions of benzene in carbon tetrachloride, were also determined; for these combinations, the temperature could be changed over 10° without the plot of fringe-shift againt T deviating noticeably from linearity. The results are shown in Table 3(b). It is worth noting that $(\partial n/\partial T)_N$ is not a linear function of composition when this is expressed in mole fractions.

In the preparation and handling of these volatile solutions, care was taken to avoid evaporation losses, the techniques adopted being broadly similar to those described by Horne and Bearman.[2]

The most favourable solution for thermal-diffusion studies is the equimolar mixture of carbon tetrachloride and benzene, with either benzene or carbon tetrachloride as the reference liquid. Since their optical and thermal properties are different, agreement between Soret coefficients derived from independent experiments with these two reference substances would be a good indication of their reliability. Results obtained are shown in Table 4. Table 4(*a*) shows Soret coefficients calculated from successive observations in one experiment, for temperature intervals ranging from 0·47° to 0·93°, and it can be seen that they show a substantially random scatter about the mean. The value of σ depends mainly upon the difference between the deflections observed from images formed by light passing through the two cells. For the first observation recorded in Table 4(a) this was the difference between slit-image deflections of 7·150 and 6·426 mm.; the corresponding deflections recorded in the camera plane were somewhat smaller because the phase-plate angle in this experiment was 35°. A reasonable estimate of the error in the difference would be 5—7 μ, or about 1% for this smallest temperature interval. For the highest temperature interval, the difference in the slit-image deflection was almost double, but the absolute error remained the same. Table 4(*b*) demonstrates the degree of reproducibility in independent experiments, and the fact that the mean Soret coefficient is independent of the reference substance. Run 26 was carried out some months after the others listed, to check that new correction factors measured after the cell had been

TABLE 3

(*a*) $(\partial n/\partial N)_{25}$ for benzene–carbon tetrachloride mixtures

Molar fraction of carbon tetrachloride	0·10	0·50	0·90
$(\partial n/\partial N)_{25} \times 10^2$	3·75	3·95	4·15

(*b*) $(\partial n/\partial T)_N$ for benzene–carbon tetrachloride mixtures (Δ is the difference between this quantity and that for the reference substance, carbon tetrachloride)

Molar fraction of $\mathrm{CCl_4}$	1·00	0·90	0·50	0·43	0·00
$10^4\Delta$	—	$-0{\cdot}101$	$-0{\cdot}399$	$-0{\cdot}432$	$-0{\cdot}487$
$(\partial n/\partial T)_N \times 10^4$ (deg.$^{-1}$)	$-5{\cdot}727$	$-5{\cdot}828$	$-6{\cdot}126$	$-6{\cdot}159$	$-6{\cdot}214$

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[15] L. W. Tilton and J. K. Taylor, *J. Res. Nat. Bur. Stand.*, 1938, **20**, 419.

TABLE 4

Study of equimolar mixture of benzene and carbon tetrachloride at 25° (benzene concentrates at the hot wall)

(*a*) Effect of size of temperature interval on calculated Soret coefficient (CCl_4 as reference; run 9)

ΔT	0·471	0·471	0·582	0·585	0·586	0·697	0·699
$10^3\sigma$ (deg.$^{-1}$)	6·36	6·44	6·48	6·39	6·43	6·40	6·47
ΔT	0·700	0·810	0·813	0·813	0·922	0·925	0·926
$10^3\sigma$ (deg.$^{-1}$)	6·45	6·47	6·52	6·52	6·40	6·45	6·41

(*b*) Summary of data from all runs

Run	Reference	Mean Soret coefficient (deg.$^{-1}$ × 10^3)	No. of observations	Standard deviation (deg.$^{-1}$ × 10^3)
7	Benzene	6·36	11	0·11
8	Benzene	6·46	12	0·09
9	CCl_4	6·44	14	0·05
26	Benzene	6·33	12	0·04

Grand mean, $\bar{\sigma} = 6{\cdot}40 \times 10^{-3}$ deg.$^{-1}$. Standard deviation (49 readings) $= 0{\cdot}08 \times 10^{-3}$ deg.$^{-1}$.

stripped and reassembled were valid; it can be seen that the agreement with the earlier experiments was good.

A number of other solutions in the benzene-rich range were examined in less detail, and the results are shown in Figure 3. In all cases the benzene migrated to the hot wall of the cell, and the Soret coefficients obtained did not vary much for compositions between $N(CCl_4) = 0{\cdot}2$ and $0{\cdot}5$, though the shallow minimum shown by the curve as drawn seems to be real. Preliminary results at still lower concentrations (not shown) suggest that the Soret coefficient rises rapidly as the carbon tetrachloride concentration decreases. If true, this would be consistent with the single value of $9{\cdot}7 \times 10^{-3}$ deg.$^{-1}$ reported for $N(CCl_4) = 0{\cdot}054$ by Korsching[16] from experiments at a mean temperature of 33° in a cell consisting of a narrow vertical slit (" Spalt-Apparat "). A recent experiment on a solution,

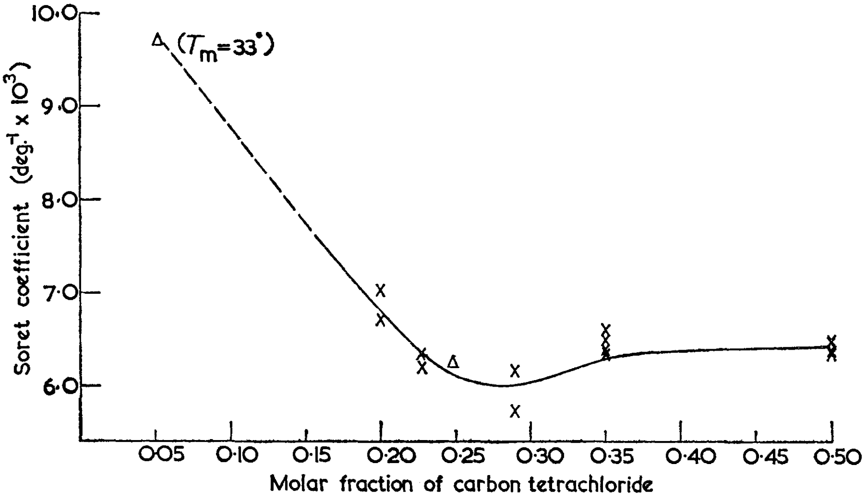

FIGURE 3. Soret coefficients of solutions of carbon tetrachloride in benzene. The curve, as shown, is no more than tentative

× Present work. △ Korsching (refs. 16 and 17)

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

$N(CCl_4) = 0{\cdot}247$, using an improved form of this cell, gave the value $6{\cdot}13 \times 10^{-3}$ deg.$^{-1}$ (mean temperature 33·5°).[17] This is shown in Figure 3, and is clearly in excellent agreement with the present results. Tichachek, Kmak, and Drickamer,[18] using a stirred diaphragm cell technique (mean temperature 40°), examined this system at $N(CCl_4) =$ 0·2, 0·5, 0·8, and obtained the following values for σ: 4·76, 4·56, $4{\cdot}38 \times 10^{-3}$ deg.$^{-1}$. These are lower than our present values but show a similar variation with concentration. These workers also examined mixtures of cyclohexane and carbon tetrachloride, and their results for this system are similarly lower than more recent ones obtained by other authors.[2,3]

DISCUSSION

It is clear from this work that, in a mixture of benzene and carbon tetrachloride, carbon tetrachloride migrates towards the cold wall, and that an earlier suggestion [11] that it migrated in the opposite direction was in error. It has been suggested on theoretical grounds that, in a binary solution, the component with the higher heat of vaporisation per unit volume, should migrate to the cold wall. Usually this component is the one with the higher molecular weight but in the benzene–carbon tetrachloride system the benzene has the higher heat of vaporisation per unit volume. There is now no doubt that, for this system, this suggestion, based on the work of Prigogine *et al.*[12] and of Denbigh,[13] does not hold. Although some thermodynamic properties of this system are characteristic of a " regular " solution, evidence from several sources shows that there are significant specific interactions between the components,[19] and such interactions were excluded from the theoretical development. They would be expected to affect the thermal diffusion behaviour.

The primary aim of the experiments reported here was to test the basic design of the cell. Both from the observed uniformity of the refractive-index gradient across the cell, and from the reproducibility of the calculated Soret coefficients found from the extensive work on equimolar mixtures, errors due to convection or preferential adsorption of one component seem to have been eliminated. Large temperature gradients, and hence a high sensitivity, were obtained for small temperature intervals. Since the physical properties, including the Soret coefficient, of a solution may change quite rapidly with temperature, this is a desirable characteristic of the method. The main disadvantage which arises from the use of a small plate-separation, lies in the necessity for very careful control of temperature fluctuations within the system. Also, since the thermal equilibrium in the cell of large heat capacity takes longer to establish than does the steady-state diffusion equilibrium in the liquid layer, it is not possible to check that the rate at which this is attained is in accord with the phenomenological theory. To some extent, this is compensated for by applying different temperature intervals across the cells and calculating Soret coefficients from each of them; any drift in the calculated values showed that the experiment was, for some reason, unsatisfactory. In this work, the cell heights used were about 0·9 mm., and the shadow line was consequently broadened by diffraction to some extent, but this purely optical effect did not give rise to serious problems. It would be fair to claim that the results obtained, even on this somewhat unfavourable system, are satisfactory, and that the method described represents one way in which the thermal-diffusion behaviour of non-aqueous solutions can be studied in a meaningful quantitative manner.

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[17] H. Korsching, personal communication.

[18] L. J. Tichachek, W. S. Kmak, and H. G. Drickamer, *J. Phys. Chem.*, 1956, **60**, 660.

[19] *E.g.*, M. L. McGlashan, *Ann. Reports*, 1962, **59**, 75.