SURVEY

METHODS OF DETERMINING SORET COEFFICIENTS

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THEORY

A binary liquid mixture produces a flow in response to a temperature gradient even though there are no external forces, and this is described by the thermodynamics of irreversible processes [1] as follows:

$$\vec{j}_1 = -\rho D\,[\mathrm{grad}\, c_1 - s c_1 (1 - c_1)\, \mathrm{grad}\, T], \tag{1.1}$$

where s is the Soret coefficient, which can be expressed in terms of the heat of isothermal transport Q_i^*

$$s = (Q_2^* - Q_1^*) \Big/ T c_1 \frac{\partial \mu_1}{\partial c_1}, \tag{1.2}$$

where μ_1 is the chemical potential.

No means of measuring the Q_i^* can be indicated by the thermodynamics of irreversible processes, and so in modern theories of the liquid states one either uses model concepts on heat transport or else statistical mechanics.

It would seem that the first study based on model concepts used the kinetic theory with the assumption that diffusion involves an activation energy [2], where the following expression was given for the Soret coefficient in an isotopic mixture [3]:

$$s = \frac{q'_H - q''_H}{kT^2} = \frac{h\nu}{2kT^2}\left(\sqrt{\frac{M_1}{M_2}} - 1\right), \tag{1.3}$$

where q_H is the bond energy between the molecules, h is Planck's constant, k is Boltzmann's constant, and ν is molecular vibration frequency.

A point to be noted here is that part of the activation energy corresponding to hole formation may be neglected; it is stated [3] that although the use of (1.3) is restricted by the condition $h\nu > kT$, the equation agrees satisfactorily with Korsching's data for s in H_2O-D_2O mixtures.

Prigogine et al [4] drew analogous conclusions from

$$s = \frac{h\nu}{kT^2}\,\frac{\Delta M}{2M}\left\{\frac{3}{2} + \frac{\exp\left(\frac{h\nu}{kT}\right)\left(1 - \frac{h\nu}{kT}\right) - 1}{\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^2}\right\} \tag{1.4}$$

TABLE 1. Soret and Diffusion Coefficients [41] for Potassium Chloride Solution ($c_0 = 0.01826$)

Cell height δ, cm	Soret coefficient, $s \cdot 10^3\ \mathrm{deg}^{-1}$	Diffusion coefficient, $D \cdot 10^5\ \mathrm{cm}^2/\mathrm{sec}$
0,695	0,51	1,12
0,910	0,49	1,17
0,975	0,27	3,04
1,396	0,38	1,94

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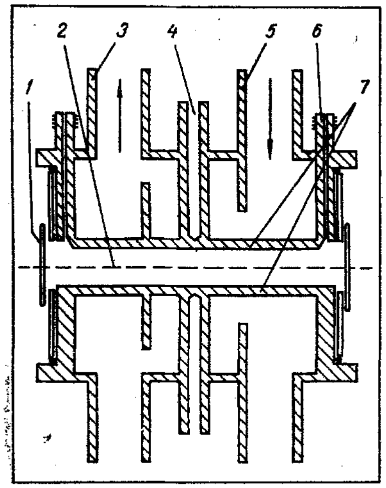

Fig. 1

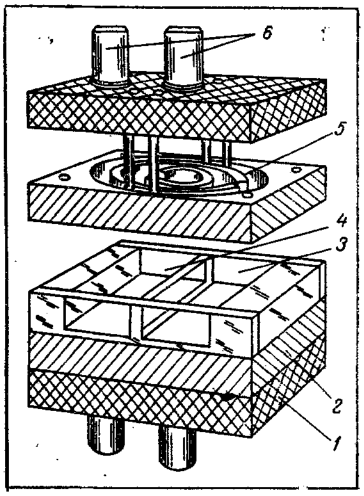

Fig. 2

Fig. 1. Tanner cell: 1) window; 2) working space; 3) water outlet; 4) thermometer sleeve; 5) water inlet; 6) filling channel; 7) silver body.

Fig. 2. Longworth cell: 1) bakelite plate; 2) silver plate; 3) solvent chamber; 4) solute chamber; 5) spiral water channel; 6) pipes.

which related to their results from experiments on the above isotopic mixture.

Until recently, (1.3) and (1.4) had not been checked on other isotopic mixtures.

Trevoy and Drickamer [30] used simple model concepts on thermal diffusion in liquids to show that the Soret coefficient for a binary mixture is

$$s = \frac{1}{T}(\chi_1 - \chi_2),$$

where χ_i is the probability of finding component i in the hot region, which can be expressed in terms of the mass m_i of the molecules and the cross section σ_i in the direction of motion as

$$\chi_i = \frac{k_i}{m_i \sigma_i}.$$

Measurements with mixtures of normal paraffins having from 7 to 18 carbon atoms showed that k_i is a constant, i.e., the formula can be used to derive the microscopic constants of mixtures from measured Soret coefficients. Subsequently, Drickamer abandoned this simplified model [9, 10].

Prigogine et al. [5] used the kinetic theory to derive the following formula for the Soret coefficient for a nonisotopic mixture:

$$s = \frac{q_A - q_B}{RT^2}, \tag{1.5}$$

in which q_A and q_B were, as in [3], a part of the activation energy needed to break the bonds between molecules.

We see from (1.2) that this becomes (1.5) for an ideal mixture if we equate the difference in the heats of transport to the difference in the bond energies; it has been shown [5] that (1.5) can be put in the form

$$s = \frac{2}{\zeta} \frac{(\sqrt{E_A} - \sqrt{E_B})(c_A\sqrt{E_A} + c_B\sqrt{E_B})}{RT^2}, \tag{1.6}$$

where E is the evaporation energy for a component and ζ is a coefficient of order 10^{-1}, which incorporates the fraction of the bond energy needed to produce a hole. We see from (1.6) that the sign of the coefficient is dependent on the energy of evaporation for each of the pure components, which is true only for molecules

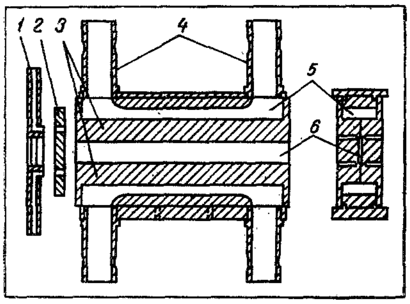

Fig. 3

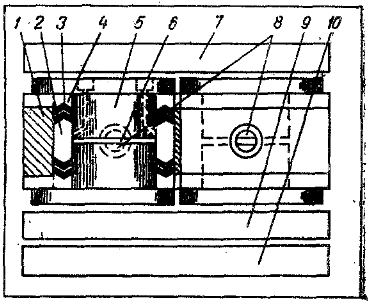

Fig. 4

Fig. 3. Korsching cell: 1) spring device; 2) window; 3) plates; 4) pipes; 5) water-circulation channel; 6) working volume.

Fig. 4. Tyrrell cell: 1) stainless-steel body; 2) PTFE ring; 3) sealing rings; 4) steel pressure ring; 5) heavy copper block; 6) working gap; 7) upper space; 8) windows; 9) pump; 10) lower space.

of identical shape [5]. If the molecules differ in shape, these workers suggested that the quantity determining the sign of the Soret coefficient should be taken as the difference of the ratios of the molar evaporation energy to the molar volume, i.e.,

$$s \sim \frac{E_A}{V_A} - \frac{E_B}{V_B}, \tag{1.6a}$$

with the positive sign corresponding to motion of the component of larger E/V to the cold region. Experiments with nine binary mixtures [5] confirmed (1.6a), although these were nearly ideal mixtures; if the properties deviate markedly from ideal, it has been found [6] for four mixtures containing alcohols that (1.6a) applies only up to a certain concentration, past which the sign of the Soret coefficient reverses.

These studies were continued by Thomaes [7], who confirmed the results of [5, 6] for six binary mixtures.

He also determined the ξ of (1.6) as 0.12 for cyclohexane + carbon tetrachloride.

The rule represented by (1.6a) was confirmed by Korsching [14] on five binary mixtures over a wide range of concentrations, and also for n-heptane mixed with benzene, which had been examined by Demichowicz–Pigoniowa et al [15]. However, exceptions were found even for regular solutions. For example, Guczi and Tyrrell [16] found for mixtures of carbon tetrachloride with benzene that the former moved towards the cold region, not the benzene, although the E/V for the latter is the higher. Story and Turner [17] observed a similar effect for mixtures of cyclohexane with benzene or carbon tetrachloride at low cyclohexane concentrations.

Nevertheless, rule (1.6a) due to Prigogine et al. is an extremely useful basis for semiempirical theories of binary mixtures in temperature gradients. Prigogine's rule covers more experimental data than does Brynza's [18] rule, which indicates that the denser component moves to the cold region.

Denbigh [8] applied the theory of regular binary solutions and assumed as a zeroth approximation that the total interaction energy of a molecule i with its nearest neighbors can be represented as the sum of pairwise potential energies W_{ij}, and he found that

$$s = -\frac{zNf}{2T}\,\frac{c_1(W_{11} - W_{12}) - c_2(W_{22} - W_{12})}{RT - zNc_1c_2(2W_{12} - W_{11} - W_{22})}, \tag{1.7}$$

where N is Avogadro's number, f is a numerical factor less than 1, and z is the coordination number.

It is clearly impossible to use (1.7) to calculate s directly, since quantities such as z and W_{ij} are unknown.

Alexander [11] applied nonequilibrium thermodynamics with model concepts from kinetic theory to derive the following expression for a mixture of nonelectrolytes:

$$s = -\frac{\omega_i\bar{Q}_1^* - \omega_2\bar{Q}_2^*}{TD_{12}}. \tag{1.8}$$

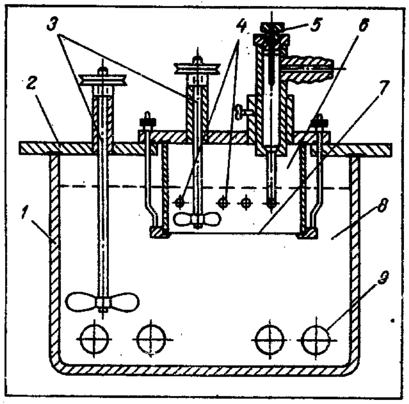

Fig. 5

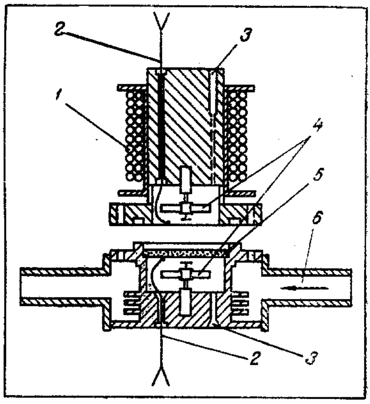

Fig. 6

Fig. 5. Riehl membrane cell: 1) body; 2) cover; 3) stirrers; 4) cooling coil; 5) thermometer sleeve; 6) upper space containing mixture; 7) membrane; 8) lower space containing mixture; 9) heating coil.

Fig. 6. Membrane cell: 1) electrical heater; 2) thermocouples; 3) holes for sampling; 4) magnetic stirrers; 5) porous diaphragm; 6) cold water inlet.

Here $\omega_i = D_i/RT$ is the molecular mobility, D_i is the self-diffusion coefficient, and $\overline{Q}_i^*$ is the kinetic heat of transport. Alexander [11] also gave a formula relating the Soret coefficient to the molecular mobilities of the ions and of the solvent, which correspond to the kinetic heats of transport, other quantities involved being the numbers of cations and anions produced by dissociation of the molecule and the molar concentration of these. Subsequently, Alexander [12] applied hydrodynamic theory to determine the molecular mobility.

It will be clear from the above that the kinetic theory cannot enable one to calculate the Soret coefficient, nor can the thermodynamics of irreversible processes, since one is forced to operate with quantities that have no analogs in the macroscopic characteristics of the mixture components.

Rutherford and Drickamer [9] attempted to relate the microscopic quantities determining the Soret coefficient to the macroscopic properties of the components; they transformed (1.7) to the form

$$s = \frac{(c_1\sqrt{H_1} + c_2\sqrt{H_2})(\sqrt{H_2} - \sqrt{H_1})}{2T\,[RT - c_1c_2(\sqrt{H_1} - \sqrt{H_2})^2]}, \tag{1.9}$$

in which

$$H_1 = -NzW_{11}; \quad H_2 = -NzW_{22},$$

with the H_i related to the macroscopic properties of the components on the hypothesis that there is an empirical relationship

$$H_i = T\left(\frac{\partial P}{\partial T}\right)_V \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]. \tag{1.10}$$

They also extended Denbigh's theory to binary mixtures in which the molecules of the components differ in size. They also tested their theory and made measurements up to pressures of 10,000 atm because (1.10) contains a combination of the coefficients of isothermal compression and bulk expansion, which are substantially dependent on pressure. In all they examined nine binary mixtures. The thermal-diffusion constant $\alpha = sT$ was calculated from (1.9) and (1.10); good agreement with experiment was obtained for two mixtures having molecules nearly the same in size: carbon disulfide + ethyl iodide and carbon disulfide + carbon tetrachloride. Rutherford, Saxton, Dougherty, and Drickamer [10, 97-99] also tested this theory on binary mixtures of haloethanes and other compounds with molecules of similar shape; they found fairly good agreement with experiment. The hypothesis due to Drickamer et al, which is expressed by (1.9), found indirect confirmation in a later paper by Bearman [21], in which techniques from statistical mechanics were used to show that there is a relationship between the Soret coefficient and the coefficients of isothermal compression and thermal expansion. Subsequently, Dougherty and Drickamer [49] showed that the

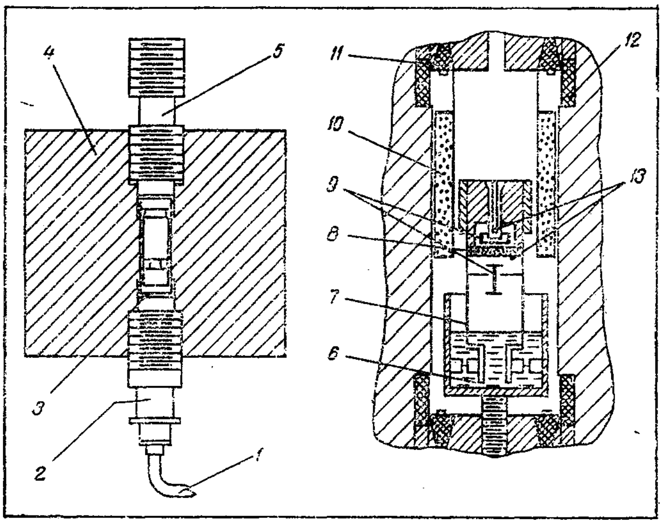

Fig. 7. High-pressure membrane cell: 1) power and thermocouple connections; 2) lower piston; 3) cell; 4) block; 5) upper piston; 6) mercury cup; 7) electric heater; 8) sintered-glass diaphragm; 9) stirrers; 10) solenoid; 11) lead seals; 12) sealing ring; 13) thermocouples.

energy transported by a molecule on passing from one state of equilibrium to another can be expressed in terms of half the activation energy for the viscosity $\Delta U_i/2V_i$, and they found the following expression for the Soret coefficient:

$$s = \frac{M_1V_2 + M_2V_1}{2MRT^2}\left(\frac{\Delta U_2}{V_2} - \frac{\Delta U_1}{kV_1}\right), \qquad (1.11)$$

where $M = c_1M_1 + c_2M_2$, V_i is the molar volume of component i, and k is a coefficient that incorporates the number of associated molecules; this formula was checked on 20 mixtures of carbon disulfide with various compounds, including alcohols, and the value of k for the latter was about 2.6. On the whole, there was satisfactory agreement between the calculated and measured values for the thermal-diffusion constant.

Story and Turner [17] tried to simplify (1.7) by eliminating the coordination number and replacing the difference $W_{ij} - W_{ij}$ by the partial heats of evaporation for the mixture; however, measurements on the mixtures $CCl_4 - C_6H_6$, $C_6H_{12} - C_6H_6$, and $CCl_4 - C_6H_6$ did not agree with the theory either as to the magnitude of the Soret coefficient or even as to the sign. Tichaček, Kmak, and Drickamer [13] extended the study of [49] and transformed the equations from the thermodynamics of irreversible processes to the laboratory coordinate system to get

$$s = \frac{\bar{V}_1\bar{V}_2}{TVc_1\frac{\partial\mu_1}{\partial c_1}}\left(\frac{Q_2^*}{\bar{V}_2} - \frac{Q_1^*}{\bar{V}_1}\right),$$

where $\bar{V}_i$ are the partial molar volumes and $V = c_1V_1 + c_2V_2$; further, they applied kinetic theory to find that

$$s = \frac{\bar{V}_1\bar{V}_2}{VRT^2}\left(\frac{q_2}{\bar{V}_2} - \frac{q_1}{\bar{V}_1}\right). \qquad (1.12)$$

Comparison of the two formulas shows that the heat of transport Q_i^* is identical with the energy of activation q_i for an ideal solution.

The Soret coefficient is determined by the difference of the $(q/\bar{V})_i$, which agrees with (1.6a) if we identify the activation energy with the latent heat of evaporation. However, Tichacek et al [13] followed [49] in relating the q_i to the enthalpies of activation for the viscosities of the pure components, which they confirmed on 12 binary mixtures, which in some cases gave satisfactory agreement with theory as to the sign and magnitude of the Soret coefficient. Mizushina and Ito [22] resembled [13] in transforming the equations of irreversible thermodynamics to the laboratory coordinate system and invoking kinetic theory, but

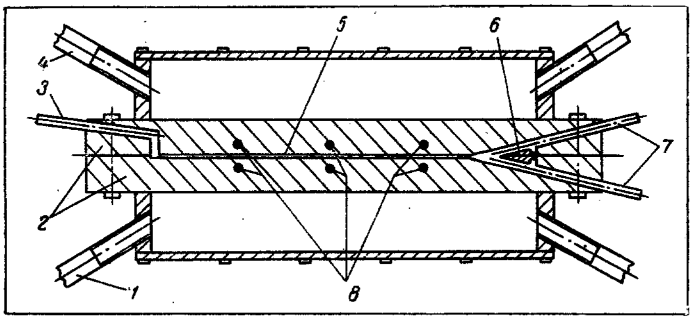

Fig. 8. Flow cell: 1) cold water inlet; 2) copper plates; 3) mixture inlet; 4) hot water inlet; 5) working gap; 6) flow divider; 7) sampling tubes; 8) thermocouple holes.

derived a different expression for the Soret coefficient, which included the coordination numbers and diffusion coefficients. It was found that the theory agrees with the trend in the Soret coefficient with temperature and concentration for mixtures of carbon tetrachloride with ethanol and methanol if the coordination number is chosen appropriately, which was shown by the Japanese workers themselves and by others; the value appropriate to the above experiments varied from 15 to 23. The weak point in this theory, as for others, is that it involves the coordination number as a parameter in calculating the Soret coefficient, and this quantity is indefinite, although this, of course, was recognized by the workers themselves. In that respect, one of the recent papers of this kind [23] has no advantages over other such studies.

The above researches, in fact, exhaust all the major studies on the derivation of the Soret coefficient from the thermodynamics of irreversible processes on the basis of model concepts from kinetic theory concerning the heats of transport. The latter lack rigor and are substantially dependent on the researcher's intuition. Kotousov's theory [29] is free from this deficiency, since he showed that the Soret coefficient in a condensed system can be determined within the framework of irreversible thermodynamics in terms of the excess thermodynamic functions: the free energy g, enthalpy h, and specific heat c_p, namely,

$$s = \frac{1}{KT} \frac{\partial^2 h}{\partial c_1^2} \left[n \frac{D_{12}}{\lambda} c_1 c_2 \left(c_p \frac{\Delta M}{M} + \frac{\partial c_p}{\partial c_1} \right) \frac{\partial^2 g}{\partial c_1^2} \right]^{-1}, \tag{1.13}$$

where D_{12} and λ are the thermal-diffusion coefficient and thermal conductivity, n is the molar density, and K is a coefficient varying from 0.5 to 1; however, (1.13) has not been checked by experiment on liquid mixtures.

A new stage in the theory of the Soret coefficient began in 1958, when the paper by Bearman, Kirkwood, and Fixman appeared [119]. In that study, the techniques of statistical mechanics were combined with Onsager's principle of detailed balancing. In that theory, α is the sum of the equilibrium part α_{11} and the nonequilibrium part α_{12}, which are defined as follows:

$$-\alpha_{11} c_1 \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T,P} = \frac{1}{2} \frac{\bar{V}_1 \bar{V}_2}{V} \left(\frac{\bar{L}_2}{\bar{V}_2} - \frac{\bar{L}_1}{\bar{V}_1} \right), \tag{1.14}$$

$$-\alpha_{12} c_1 \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T,P} = \frac{1}{2V} \frac{D_2 - D_1}{D_2 + D_1} \left[\bar{V}_1 \bar{V}_2 \left(\frac{L_1}{V_1} + \frac{L_2}{V_2} \right) \right.$$
$$\left. + 2c_1 (\bar{L}_1 \bar{V}_1 - L_1 V_1) + 2c_2 (\bar{L}_2 \bar{V}_2 - L_2 V_2) - \frac{3}{2} I_1 \right], \tag{1.15}$$

where $\bar{L}_i$ are the heats of evaporation of the components from the mixture, L_i are the same for the pure components, D_i are the self-diffusion coefficients, and I_1 is an integral that includes the microscopic parameters of the molecular interaction, including the radial distribution. The integral vanishes for a liquid whose molecules consist of hard spheres.

Bearman [21] did not employ irreversible thermodynamics but techniques from statistical mechanics to derive other expressions for α_{11} and α_{12}:

$$\alpha_{11} c_1 \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T,P} = \frac{1}{2} RT \frac{\bar{V}_1 - \bar{V}_2}{V} + \frac{\beta_2' \beta_1 - \beta_1' \beta_2}{\beta'} T \left(\frac{1}{2} RT - PV \right), \tag{1.16}$$

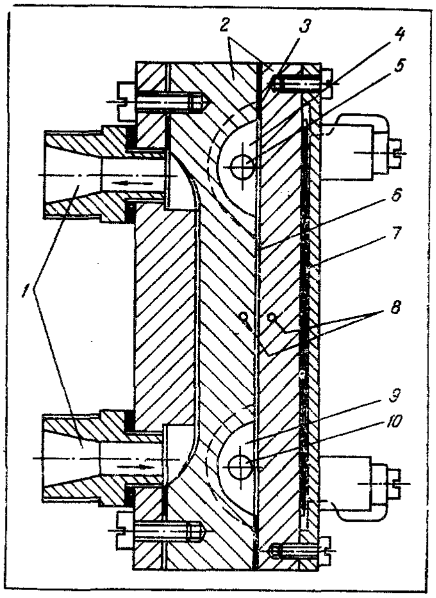

Fig. 9

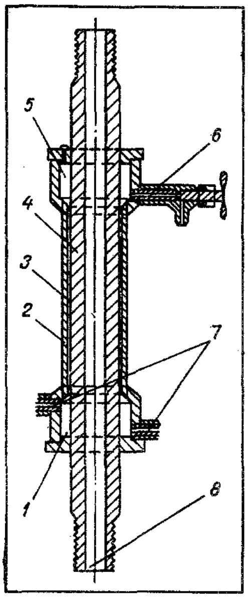

Fig. 10

Fig. 9. De Groot thermal-diffusion column: 1) water inlet and outlet; 2) plate; 3) insert; 4) upper space; 5) upper sampler; 6) working gap; 7) Nichrome heater; 8) thermocouple hole; 9) lower space; 10) lower sampler.

Fig. 10. Thermal-diffusion column: 1) lower space; 2) outer cylinder; 3) working gap; 4) internal cylinder; 5) upper space; 6) sampler; 7) recesses for lower samplers; 8) hot-water circulation channel.

$$\alpha_{12}c_1\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,P} = \frac{T}{V}\,\frac{D_2 - D_1}{D_2 + D_1}\left\{\frac{1}{2}R(\bar{V}_1 + \bar{V}_2) - \frac{\beta}{\beta'}\bar{V}_1\bar{V}_2\right.$$
$$\left. + \frac{\bar{V}_1\bar{V}_2}{V}\,\frac{\beta_2'\beta_1 - \beta_1'\beta_2}{\beta'}\left[\frac{1}{2}RT(c_2 - c_1) - P(c_2\bar{V}_2 - c_1\bar{V}_1)\right] + \frac{1}{3}I_2 + \frac{1}{6}I_3\right\}, \tag{1.17}$$

where β and β' are the thermal-expansion coefficient and isothermal compressibility of the solution, respectively, while β_i and β_i' are the same for the pure components, with the integrals I_2 and I_3 including the radial part of the distribution, with only the first of these becoming zero for a mixture whose molecules consist of hard spheres.

Bearman and Horne [24] tested (1.14)-(1.17) with a mixture of cyclohexane + carbon tetrachloride, for which they had previously [25] recorded measurements. It was found that the Bearman–Kirkwood–Fixman theory (BKF theory) agreed fairly well with experiment at medium concentrations, and the contributions from the equilibrium and nonequilibrium components were approximately the same. Bearman's theory [21] gave half the observed thermal-diffusion constant, with only a minor contribution from the equilibrium component. This major discrepancy between the two theories was ascribed [24] to the neglect of terms containing the integrals in calculations from (1.14)-(1.17), and while this is justified to some extent for the BKF theory, if the mixture is considered as consisting of hard spheres, for Bearman's theory it is permissible only for the integral I_2.

Story [17] tested both theories, using mixtures of carbon tetrachloride with benzene, cyclohexane with benzene, and cyclohexane with carbon tetrachloride, i.e., mixtures with molecules similar in shape and size. In all three cases there were marked discrepancies between the theories and measurements not only as regards the magnitude of the Soret coefficient, but even the sign. This gives interest to Shie's data [23], who compared her measurements on a mixture of n-hexane with n-heptane and values calculated from the BKF theory using only the equilibrium component defined by (1.14); the agreement was good. However, this result can hardly be said to support the theory, since there was no basis for neglecting the nonequilibrium component of the thermal-diffusion constant.

TABLE 2. Orders of Physical Characteristics of Mixtures Allowing (3.5), (3.6), and (3.8) to Be Used [45]

Characteristic	Order
Temperature T	300 °K
Density ρ	10^3 kg/m^3
Relative concentration coefficient of density $\frac{1}{\rho}\frac{\partial\rho}{\partial c}$	1
Thermal-expansion coefficient $\frac{1}{\rho}\frac{\partial\rho}{\partial T}$	10^{-3} deg^{-1}
Dynamic viscosity η	10^{-3} Nsec/m^2
Specific heat c_p	10^3 J/kg-deg
Transport heat Q^*	3 kJ/mol
Sedimentation constant S	$3\cdot10^{-8}$ m^2/N
Thermal-diffusion constant α	1,5
$\frac{1}{\alpha}\frac{\partial\alpha}{\partial c}$	1
$-\frac{1}{\alpha}\frac{\partial D}{\partial T}$	10^{-2} deg^{-1}
Diffusion coefficient D	10^{-9} m^2/sec
$\frac{1}{D}\frac{\partial D}{\partial c}$	1
$\frac{1}{D}\frac{\partial D}{\partial T}$	$2\cdot10^{-2}$ deg^{-1}
Thermal conductivity λ	0,1 W/m-deg
$\frac{1}{\lambda}\frac{\partial\lambda}{\partial c}$	1
$\frac{1}{\lambda}\frac{\partial\lambda}{\partial T}$	10^{-3} deg^{-1}

A further advance in applying the methods of statistical mechanics has been made by Zamskii (personal communication), in which the thermal-diffusion constant was derived in the following form for a multicomponent isotopic mixture:

$$\alpha_{ki} = \frac{1}{6}\left(\frac{\beta V_M}{\beta' R} - 1\right)\frac{\Delta M_{ki}}{M}, \tag{1.18}$$

where $M = M_k + M_i$; comparison of (1.18) with the available experimental evidence for bromine isotopes in bromobenzene [27] and chlorine isotopes in carbon tetrachloride [28] showed satisfactory agreement.

The following conclusions may be drawn from the history of theories of the Soret coefficient:

a) model concepts derived from kinetic theory sometimes serve to define the sign of the Soret coefficient and even the magnitude, and the same may be said for the thermodynamics of irreversible processes used in conjunction with the kinetic theory; however, in many cases these methods give values that diverge widely from experiment, so one cannot say that they fully reflect the interactions between molecules in binary mixtures;

b) Kotousov's theory requires extension to liquid mixtures, as well as experimental tests;

c) the methods of statistical mechanics lead to expressions that contain the microscopic parameters of the system, on which we have very scanty information; this applies particularly to the radial distributions. The results deserve acceptance only when they can be expressed with reasonable accuracy in terms of macroscopic quantities, as in the case of isotopic mixtures;

d) it is necessary to accumulate more experimental data on the Soret coefficient for mixtures with various molecular structures in order to test new theories and to determine some of the macroscopic and microscopic characteristics of such mixtures;

e) a purely empirical approach similar to that of [9, 19, 20] cannot be ruled out for a narrow class of mixtures, since it may be useful in applications of thermal diffusion, as well as in the technical separation of mixtures.

It is thus clear that the originators of the various theories have sought to demonstrate their applicability in calculations by comparing the results with measured Soret coefficients, and in this connection high accuracy is required in the measurements; this applies to all three factors that influence the reliability of the final results: a) the detailed design of the experiment, b) the method of calculation, and c) the method of measurement.

2. APPARATUS DESIGN

2.1. Convection-Free Cells. Ludwig [107] was the first to observe a concentration gradient produced by a temperature gradient; he kept one arm of a U-tube filled with a 9% solution of sodium sulfate at the melting point of ice, while the other was kept at the boiling point of water. Crystals of the solute were deposited in the cold arm within 2 days. Soret [108] studied this phenomenon 23 years later with an apparatus consisting of a vertical tube of height 30 cm and diameter 2 cm. The top end of the tube was kept at 80°C and the bottom at room temperature. Aqueous solutions of salts of lithium, sodium, potassium, and copper were used. In all cases the solute concentration increased towards the cold end, but even after 55 days it had not reached a steady value. Soret's experiments were repeated by Zhuravleva [95] with a solution of sodium chloride and gave the same results. De Groot [36] estimated the time needed to reach the steady state in Soret's experiment as 400 days. Times as large as this are quite unsuitable for research on thermal diffusion in liquids; moreover, it is inevitable that convection currents arise and mix the solution with a tube of such a height. For this reason, Wereide [109] designed a cell consisting of a glass cylinder of height only 15 mm, which was bounded at top and bottom by metal vessels kept at different temperatures.

The characteristic time in the diffusion process is defined

$$\tau_r = \frac{\delta^2}{\pi^2 D}, \tag{2.1}$$

and hence the sizes of the Soret and Wereide cells show that the latter cell should reach equilibrium in about 1 day. The actual value is about 2-3 days. The concentration change was monitored by sampling the upper and lower parts of the glass cylinder followed by measuring the refractive index. A similar design, but with a smaller height of 6.2 mm, was used in another study [54].

Tanner [35, 41] described an improved style of such a cell, which allowed scope for optical measurements; Fig. 1 shows the design which consists of a glass cylinder having two diametrically opposite windows to handle a beam and two silver blocks at the ends, in which a heat carrier is circulated at a high speed. The temperatures at the temperature-controlled surfaces were monitored by mercury thermometers placed in sleeves filled with glycerol. Tanner examined [41] the effects of the cell height on the values obtained for the Soret and diffusion coefficients for solutions of KCl, $BaCl_2$, and $Ba(OH)_2$; he concluded that the height of the cell had no effect on the results. However, we must note that the Soret and diffusion coefficients were calculated via (3.4), and we show below that this should reduce the Soret coefficients and increase the diffusion coefficient.

Table 1 indicates how the Soret and diffusion coefficients vary with the height of the cell.

It is clear from these data that the Soret coefficient tends to fall as the cell height increases, whereas the diffusion coefficient does the converse; this is clearly due to increased mixing by parasitic flows. This is confirmed by comparing Tanner's data with those of [50, 52, 105], which give higher values of the Soret coefficient for the same system.

Cells of similar design, i.e., with distances between the surfaces of 10-17 mm and volumes of 30-50 cm^3 or so, have been used in other studies [7, 26, 40], and in one case [26] it was considered that the cell showed convective mixing.

Two-chamber cells came into use when interferometry was applied; Figure 2 shows the cell used by Longworth [52], which consisted of a glass rectangular frame between two silver plates. The seals between the glass and silver, and also between the silver and bakelite, were provided by layers of a cementing compound of thickness 0.2 mm. The cell was divided in the middle into two parts, in one of which was the solution and in the other the solvent. Two-chamber cells of this type were also used in [16, 43, 105].

Measurements on solutions of polystyrene in toluene [43] showed that cells of heights 1.19, 2.05, and 4.04 mm gave identical values for the Soret coefficient; it is clear that in this case the high viscosity of the solution and the small temperature difference (0.5°C) prevented convection.

In 1955, Korsching [47] described another design of single-chamber cell of especially small volume, which was attained by reducing the dimension perpendicular to the optic axis to 0.3 mm while keeping the height about 10 mm. The cell length (which determines the deflection of the transmitted beams) was taken as 80 mm. Korsching considered that this change in dimensions should substantially reduce the scope for convection. The cell (Fig. 3) consisted of two iron-nickel plates, each of which had on one side a groove forming the working volume, while on the other side there were slots carrying liquid from a thermostat, which were closed by soldered covers bearing connecting pipes. The ends of the block were nickel-plated and polished, which gave surfaces to which the optical windows were pressed by springs. Mercury provided the seal between the window and the metal. Subsequently, Korsching [14] introduced some additional improvements, which were designed to eliminate convection: the thickness of the plate 3 tapered down to 0.04 mm in the direction of the liquid flow, in order to compensate the temperature nonuniformity arising from heat loss to the environment from the water flowing through the channels. Also, compensating heating was applied to the ends of the cell, and the mercury seal was replaced by indium foil [111].

Measurements have been made [39] on the performance of Tanner and Korsching cells with solutions of cane sugar; Korsching's cell gave a Soret coefficient three or four times larger than did Tanner's cell, so the former was considered as the better type. Higher values obtained with the Korsching cell were also confirmed by data on the separation of the mixtures $C_6H_{12}-CCl_4$ [7, 47] and $C_6H_6 + n-C_7H_{16}$ [14, 40].

Guczi and Tyrrell [16] sought to prevent convection currents and to reduce the equilibration time by reducing the distance between the thermostatic surfaces. They chose the cell dimensions to meet the specification $GrPr < 1700$; a similar criterion was used in [105], but unfortunately the specifications implied by this inequality were not actually realized in their cell. Guczi and Tyrrell used a two-chamber cell with a height in one chamber of 0.917 mm and 0.903 mm in the other. The cell consisted of two pairs of massive copper cylindrical blocks, which formed the upper and lower working surfaces of the chambers, while the side walls were made of PTFE cylinders bearing optical windows. The gap was set by standard hollow rods. Another style described by Farsang and Tyrrell [110] had the entire cell enclosed in a stainless-steel block instead of PTFE, the material previously used [16], and also had various other improvements (Fig. 4). The Soret coefficients obtained with this cell on a mixture of n-heptane with benzene [15] were even somewhat higher than those recorded by Korsching [14].

2.2. Membrane Cell. In 1943, Riehl [33] described a new design of cell, which he considered should prevent convective mixing and accelerate equilibration. Figure 5 shows this cell in the style used by Alexander [31]. The distinctive feature is the membrane that separates the two volumes.

Alexander tested the cell on aqueous solutions of lithium, sodium, potassium, and ammonium chlorides, and also potassium and zinc sulfates. He found that the result for the Soret coefficient was very much dependent on the size of the pores in the diaphragm, for which purpose he used various forms of cellophane and also filters with large pore sizes. The Soret coefficient decreased steadily as the pore radius increased, but was still twice the value found by Tanner [35] even in the case of the membrane with the largest pores (pore radius 0.03 μm). The reason for this is that the heat of transport is dependent on the pore size when this is small, and the effect is the most pronounced when the pore radius is comparable with the molecular size. This circumstance must be borne in mind with any membrane cell.

Saxton, Dougherty, and Drickamer [10] described another design of membrane cell (Fig. 6), in which the membrane itself consists of sintered glass (pore size 5-10 μm), while the mixing in the volumes was provided by magnetic stirrers. They found that there was a limiting stirring rate above which the convection currents began to penetrate into the membrane, which adversely affected the separation. However, no figure was given for this limit, and no other studies on this factor have been published.

A study has also been reported [10] of the effect from the mutual disposition of the two chambers in the cell; it was found that the results were unaffected if the cold chamber was above the hot one or vice versa. It is difficult to judge the performance of the cell of this type, since nothing has been published on the Soret coefficients for the mixtures used in [10] as measured by other techniques, in particular, in Korsching and Tyrrell cells. This applies also to all data on Soret coefficients from membrane cells, apart from [96], in which a value of $18 \cdot 10^{-3}$ deg^{-1} was obtained for a $C_6H_5-CCl_4$ mixture at a benzene concentration of 0.9, whereas Korsching found a value almost half this, $9.8 \cdot 10^{-3}$ deg^{-1}, for a benzene concentration of 0.95. This point appears extremely important, since if the results of [96] are reliable, they provide some confirmation of Kotousov's theoretical results [29]. On the other hand, there was no mixing in the chambers of the cell used by Rassoul and Bott [96], and no figures were given for the volumes of the chambers, so no definite conclusion can be drawn on this topic.

A cell of the type of [10] has been used also in other studies [32, 49, 98, 99]; the theory of [9] for thermal diffusion in liquids was tested with a cell designed to work under pressures up to 10,000 atm (Fig. 7). The cell consisted of two chambers separated by a diaphragm of porous glass of thickness 1 mm, and it was enclosed in a bomb of outside diameter 203.2 mm and internal diameter 22.2 mm. The bomb was immersed in a vessel maintained at a temperature of +17°C. The pressure on the mixture was provided by mercury in a cup. The volumes of the upper and lower chambers were unequal, being 0.15 and 1.1 cm^3, respectively. This cell was subsequently used in the research of [99]; unfortunately, the results obtained with these two cells are not comparable with the data obtained with Korsching or Tyrrell cells. Shie [23] recently described a new design of membrane cell, in which both chambers were of volume about 16 cm^3 and consisted of glass cylinders of outside diameter 30 mm. The two volumes were stirred by magnetic stirrers.

2.3. Flow Cell. In 1956, Thomaes [55] described a new method and appropriate type of cell for determining the Soret coefficient. The basic concept was that the mixture flows as a laminar layer between two horizontal plates having a separation of about 0.1 mm, across which there is a vertical temperature gradient, which produces a concentration gradient. The flow at the exit from the cell is split into two parts in the vertical direction, and each is assayed for the component concentrations. Turner et al [60, 59, 61] made a series of studies with a cell of this type; the original design of [60] was subsequently improved, and the new style [58] is shown in Fig. 8. The cell consists of two half-inch copper plates separated by PTFE inserts.

The plates are held together by bolts. The resulting flat channel was of width 5 cm and length 15 cm, and the flow at the exit was split by a stainless-steel knife edge into two parts.

The results obtained with $CCl_4-C_6H_6$ and with benzene–methanol mixtures [61] agreed well with Tyrrell's data [16, 112]. Nevertheless, one cannot assume that such cells have been shown to be reliable in view of a recent paper [63], in which it was shown that the flow rate has a very marked effect on the result for the Soret coefficient if the rate is less than some definite limit (in the experiments of [63], 4 cm^3/h for a gap of 0.2 mm, cell width 50 mm, and length 200 m).

2.4. Thermal-Diffusion Column. A thermal-diffusion column as an instrument was first used by Korsching [113] to determine Soret coefficients for $C_6H_6-C_6D_6$ mixtures in a cylindrical column of height 96 mm with a gap of 0.26 mm, which was also used by De Groot [114]; in the latter case, the Soret coefficient was determined for molar aqueous copper sulfate in a column of the style shown in Fig. 9. The column consisted of two copper plates: a hot one of thickness 9 mm and a cold one of thickness 11 mm. The heating was provided by a flat nichrome heater, while the cooling was by water flowing at 0.54 m^3/h, which was considered as providing a high heat-transfer factor and was sufficient to prevent the exit water temperature from rising by more than 1°. Vessels of volume about 18.2 cm^3 were placed at top and bottom of the column. The working height was 5.46 cm and the width 8 cm.

Soret coefficients have been measured for various binary mixtures in a column of this type [5-7]; a column of similar design, but with the electrical heating replaced by circulating hot water, has been used to determine the Soret coefficients for electrolyte solutions and in the separation of chlorine isotopes [11, 101]. A similar column has also been used with radiative heating of one of the copper plates [91], where the temperature difference along a surface did not exceed 0.5°C; the vessels were equal in volume (5.45 cm^3), while the gap was 0.2 mm. The results on the Soret coefficients for various solutions obtained with this column can be compared with other data only for ethanol–cyclohexane mixtures, where the data of [91] agree with those of [6].

Murin and Popov [89] followed Korsching in using a cylindrical column which was made of copper with a gap radius of 17 mm and a gap width of 0.45 mm in conjunction with a working length of 205 mm.

Wider sleeves at the top and bottom of the column produced volumes of 6.7 cm^3; the heating was provided by an electrical spiral and the cooling by flowing water.

There are two major features that (if neglected) might discredit the thermal-diffusion column as a means of measuring Soret coefficients. Firstly, the gap geometry should be as nearly ideal as possible within existing manufacturing techniques, since geometrical nonuniformities produce parasitic convection [65, 84, 115, 116]. For this reason, planar columns, which have very marked gap nonuniformity, are very undesirable [75]. Secondly, the same consequences should be eliminated by avoiding temperature asymmetry which can arise from uneven heating or cooling, which is most likely when the heating is provided by electrical means as in [89, 114]. For the same reasons, glass columns are also unsuitable, and these also make it difficult to measure the temperatures at the two surfaces. A packed column has been used to determine the thermal-diffusion constant for bromine isotopes in bromobenzene [27], but there has been little progress in the theory of such columns, and further research is needed to determine their use in the measurement of Soret coefficients. Trevoy and Drickamer [30] appear to have used the above considerations in making a cylindrical metal column (Fig. 10). This had two vessels equal in volume with sampling devices. The inner cylinder was made with a tolerance of 5 μm, while the inner surface of the outer cylinder had a tolerance of 13 μm. The internal cylinder, internal diameter 1.7 mm, had hot water circulating with a speed of 1.5 m/sec ($Re = 15,000$). The cooling was provided by a thermostat enclosing the column. The working height was 101.6 mm. The method of cooling was unsatisfactory, since the heat-transfer rate on immersing a column in a large thermostat is quite low, while there is a considerable chance of an uneven temperature distribution around the parameter. All the same, the results for the Soret coefficient for an equimolar mixture of n-heptane with benzene ($4.02 \cdot 10^{-3}$ deg^{-1}) were fairly close to those obtained by Demichowicz–Pigoniowa [102] ($4.6 \cdot 10^{-3}$ deg^{-1}) and also agreed closely with Korsching's value ($3.9 \cdot 10^{-3}$ deg^{-1}).

A further advance in the design of thermal gravitational columns suitable for determining Soret coefficients was provided by Horne and Bearman [75], who improved the design of [30] by providing vigorous cooling of the outer cylinder in a circulation jacket (flow rate 1.8 m^3/h) and a high flow rate in the inner cylinder (flow rate 1.6 m^3/h). The tolerances in cylinder manufacture were reduced, being 0.1 μm for the outside diameter of the internal cylinder and 1μm for the internal diameter of the outside cylinder.

The results agreed exactly with those of [59] for cyclohexane–carbon tetrachloride mixtures at all concentrations.

A similar result was obtained by Stanford and Beyrlein [117] with a column closed at both ends manufactured with tolerances of 2.5-7.5 μm. However, even close tolerances on the two cylinders do not necessarily guarantee successful operation.

Bott and Romero [93] found that the relative eccentricity affects the separation in the thermal diffusion column; their column was 101.6 cm high, and closed at both ends; it was made extremely carefully, and the mean deviations of the working diameter of the two cylinders from the nominal value were, respectively, 0.5 and 0.8 μm.

However, if the axes of the working surfaces do not coincide, the eccentricity varies with the height; the column was operated [93] at various points with high heat-transfer rates at the hot and cold surfaces (water flow rates of 3.6 m^3/h), and it was found that the eccentricity has a substantial effect on the results, from which it was concluded that a thermal-diffusion column is unsuitable for determining Soret coefficients.

However, it has been shown [85] that the last conclusion is a consequence of using the formulas given in [83], which are unsuitable for a column closed at both ends. Appropriate recalculation [85] showed that the values obtained by Bott and Romero for the Soret coefficient were close to those obtained in the best cells even with an eccentricity of 7 μm.

Another column closed at both ends [94] differed from that of [93] in the method of centering the inner cylinder with respect to the outer one; this has been used to measure Soret coefficients [86] for various mixtures, and the results agreed satisfactorily with data from cells.

We can thus say definitely that some pessimistic views [74, 93] are unjustified, and a cylindrical vertical thermal-diffusion column can be used as an instrument for measuring Soret coefficients.

Von Halle [90] described a new variety of thermal-diffusion column, namely a horizontal one, whose main advantage was seen as being that the flows within the column are not dependent on the rate of withdrawal of the enriched products (in contrast to a Clausius–Dickel column), a further advantage being that the flows in opposite directions do not interact hydrodynamically, which rules out mixing. This is provided by separating the flows with a permeable membrane, the countercurrent motion being forced (provided by a pump). This column is to be considered as an industrial application of thermal diffusion for mixture separation rather than an instrument, but Von Halle showed that his column of length 2.3 mm (gap between the 0.4 mm cellophane membrane at the bottom of each channel of 0.89 mm) could be used to determine Soret coefficients for aqueous ethanol. However, his results differed substantially from published data for certain concentration ranges, and this goes with the complexity of manufacture for such columns for use under laboratory conditions and difficulties in selecting the membrane to make this design unsuitable as an instrument for measuring Soret coefficients.

We thus conclude as follows:

1) the most reliable Soret coefficients are those measured in convection-free cells as described by Korsching [14, 47] and Tyrrell [16, 110];

2) the Thomaes flow cell can give reliable results if appropriately calibrated, but some results obtained with this instrument [63] still remain unexplained;

3) membrane cells have not yet been properly examined, and the large discrepancies between the results from them and those from Korsching or Tyrrell cells oblige one to view them with reserve;

4) cylindrical thermal-diffusion columns of appropriate design are fully justified as instruments for measuring Soret coefficients.

3. METHODS OF CALCULATING SORET COEFFICIENTS

3.1. Convection-Free Cells. The following assumptions are made in the mathematical description of separation in a cell with a vertical temperature gradient:

1. There are no convection currents.
2. The two thermostatic surfaces have ideal geometry.
3. The mixture at the start is uniform in composition throughout the cell.
4. The steady-state temperature distribution is set up instantaneously.
5. The Soret and diffusion coefficients are independent of temperature and concentration, as is the density.

In the steady state, the flux defined (1.1) is zero, and so we have the following simple formula for the Soret coefficient:

$$s = \frac{\ln q}{\Delta T} \approx \frac{\Delta c}{c_s (1 - c_l)\, \Delta T}, \tag{3.1}$$

where

$$q = [c/(1-c)]_l / [c/(1-c)]_s, \tag{3.2}$$

and the subscripts l and s correspond to the larger and smaller values of $c(l-c)$ at the cell boundaries.

Tanner [35] employed a method based on (3.1) in his first study on Soret coefficients, and this equation has been used in [7, 15, 16, 47], in all studies made on membrane cells [9, 10, 23, 31-33], and also in packed cells [34].

It is permissible to use (3.1) to calculate Soret coefficients from data for membrane cells only if the volumes on the two sides of the membrane are equal, as was the case in [23]. This follows from the results of [44]. If the volumes are unequal, the steady state is not defined by (3.1) but will also be dependent on the hot and cold volumes.

For this reason, the Soret coefficients of [9, 10, 31-33] cannot be considered as reliable.

A disadvantage of the steady-state method is the considerable length of time needed, so the nonstationary method proposed by De Groot in his dissertation [36] provides a very considerably shorter measurement time.

The transient process is described by

$$\rho \frac{\partial c}{\partial \tau} = -\operatorname{div} \vec{j}_1, \tag{3.3}$$

where $\vec{j}_1$ is the flux defined by (1.1), and the solution to (3.3) should provide that this flux is zero at the surfaces bounding the cell.

Equation (3.3) is nonlinear, and De Groot solved it for the case $c \ll 1$ on the assumption that the density is temperature-independent; his solution gives the concentration difference between the surfaces at large times as

$$c_e - c_i = c_0 s\Delta T(1 - e^{-\tau/\tau_r}), \tag{3.4}$$

where the relaxation time is $\tau_r = \delta^2/\pi^2 D$.

Bierlein [37] solved (3.3) under the same boundary conditions but incorporating the temperature dependence of the density, with the working concentration range extended by linearizing the nonlinear term by putting $c(1-c) \approx c_0(1-c_0) + b(c-c_0)$; the solution was obtained as a series, and Bierlein found that if $0 < \Delta T < 20$ deg, $0 < \beta < 2 \cdot 10^{-3}$ deg^{-1}, $0 < s < 10^{-2}$ deg^{-1}, $-1 < b < 1$ the quantities incorporating the thermal expansion of the liquid can be neglected, and if one takes only the first term in the series (as De Groot did), then

$$c_e - c_i = s\Delta T c_0(1 - c_0)\left(1 - \frac{8}{\pi^2} e^{-\tau/\tau_r}\right). \tag{3.5}$$

Equation (3.5) becomes (3.4) for c small, except that in (3.5) there is a preexponential factor less than 1; this discrepancy is due to an error made by De Groot, which has been discussed in detail by Tyrrell [38].

Bierlein obtained the following result for any point $\xi = x/\delta$ for large times:

$$c = c_0\left[1 + s\Delta T(1 - c_0)\left(\frac{1}{2} - \xi\right) - \frac{4}{\pi^2} s\Delta T(1 - c_0)\cos \pi\xi e^{-\tau/\tau_r}\right]. \tag{3.6}$$

This expression was then used to find the concentration gradient, which was used in processing the optical measurements.

Subsequently, Bierlein [40] found that (3.5) is applicable only for $\tau/\tau_r > 0.5$, and he gave a graphical method of determining the Soret coefficient from (3.6). It would appear that Japanese workers [39] arrived at similar recommendations independently.

The above difference between (3.4) and (3.5) is important, since the Soret coefficient derived from (3.4) should be about 20% lower. For this reason, Tanner's data [41], which were derived from (3.4) without allowance for the substantial restriction on τ/τ_r, cannot be considered reliable, and this applies also to [50].

Bierlein's method has been used in particular in [14, 42, 43, 51, 52] to determine Soret and diffusion coefficients; Mizushina and Ito [44] solved (3.3) with Bierlein's formulation, but with a series of Gaussian functions.

These solutions were used [44] in three approximate methods of determining the Soret and diffusion coefficients simultaneously; measurements with glucose solutions showed that these methods give results for the diffusion coefficient that differ considerably, so the assertion [44] that the methods are suitable is subject to some doubt.

Mizushina and Ito [44] also determined the concentration gradient at the middle of the cell for small times ($D_T/\delta^2 < 0.1$), which is required (see above) in calculating the Soret coefficient when optical methods are used to measure the concentration:

$$\left(\frac{\partial c}{\partial \xi}\right)_{\xi=\frac{1}{2}} = 2c_0(1 - c_0)s\Delta T \operatorname{erfc}(1/4\sqrt{D\tau/\delta^2}). \tag{3.7}$$

The same result was obtained previously by Agar [69] for small c.

The literature bears no indication that (3.7) has been used. Bobrova and Rabinovich [53] derived Bierlein's solution to (3.3) but neglecting the temperature dependence of the density. They truncated the series at the first term and described a method of determining the Soret and diffusion coefficients via measurements made over two time intervals differing by a factor 2. This method was used in [54]. They also showed that the separation in the cell is not symmetrical, although the asymmetry is small.

At the beginning of Sec. 3 we have formulated the assumptions usually made in analytical discussion of separation in cells; Bierlein estimated the error arising from assuming ρ = constant when the density actually varies with temperature, and this error is much less than the error of measurement under ordinary experimental conditions.

Horne and Anderson [45] used a rigorous formulation in a detailed discussion of the effects of assumptions 4 and 5; this involved solving the equation of continuity, the Navier–Stokes equation, and the energy equation on the basis of expressions for the heat and mass fluxes. The temperature and concentration coefficients were incorporated for the density, specific heat, thermal conductivity, diffusion coefficient, and thermal-diffusion coefficient. Also, the time needed to attain the steady temperature distribution was defined on the basis of a simple exponential temperature curve for the plates bounding the working volume, as in [48]. They concluded [45] from an analysis of the very complex expression that the error would not exceed 0.1% if the mixture had parameters of the order of those given in Table 2, and that the following formula can be used for the Soret coefficient for $\tau/\tau_r > 1/2$ and $\Delta T < 25°C$:

$$c|_{\xi'=+\xi'} - c|_{\xi'=-\xi'} = c_0(1-c_0)\,s\Delta T\left[\xi' - \frac{8}{\pi^2}(1+\Gamma)\sin\frac{\pi\xi'}{2}\exp\left(-\frac{\tau}{\tau_r}\right)\right], \tag{3.8}$$

where the differences from (3.6) are that $\xi' = 2x/\delta$ and the origin lies at the midsection of the cell. It is simple to derive (3.8) without the $(1+\Gamma)$ factor from (3.6), since the latter incorporates the time needed to reach the steady temperature distribution, with $\Gamma = \pi^2/8(\gamma/\tau_r)$, where γ is the measured relaxation time for the temperature distribution. This time was 46 sec in the experiments of [46].

The contribution introduced by Γ into the second term in the right in (3.8) for a cell whose plates have a separation of about 1 cm should not exceed about 0.1%, but it may be several per cent and must be allowed for if the cell is of the type used by Tyrrell [16].

Horne and Anderson's study thus gives a complete theoretical basis for the conditions for using (3.5)-(3.8).

3.2. Flow Cell. The following assumptions are made in calculating the concentration distribution in such a cell;

1. The flow is laminar.
2. The laminar velocity distribution is established instantaneously at $x = 0$.
3. The upper and lower plates are ideally isothermal.
4. The side walls have no effect on the velocity distribution.
5. The thermal conductivity, viscosity, diffusion coefficient, and Soret coefficients are constants.
6. Diffusion along the flow direction may be neglected.

Subject to these assumptions, the differential equation for the separation in the steady state, div $\vec{j}_1 = 0$ with

$$j_{1x} = -\rho D\frac{\partial c}{\partial x} + \rho c w_y, \tag{3.9}$$

$$j_{1y} = -\rho D\left[\frac{\partial c}{\partial y} - sc(1-c)\frac{\Delta T}{\delta}\right]$$

for c small takes the form

$$\frac{\partial^2 c}{\partial y^2} + s\frac{\Delta T}{\delta}\frac{\partial c}{\partial y} - \frac{w_y}{D}\frac{\partial c}{\partial x} = 0, \tag{3.10}$$

where $w_y = (\Delta P/2\eta L)(y^2 - y\delta)$, L is the cell length, and ΔP is the pressure difference between the ends.

The solution to (3.10) should meet the condition that the fluxes of (3.9) are zero at the surfaces of the cell.

The main interest attaches to conditions under which there is maximal separation between the upper and lower halves of the flow at the exit.

Thomaes [55] first solved (3.10) and found that the maximum separation is obtained if

$$\frac{xD}{\delta^2\bar{w}}\left[\pi^2 + \left(\frac{s\Delta T}{2}\right)^2\right] \geqslant 5, \tag{3.11}$$

where x is the longitudinal coordinate and $\bar{w}$ is the mean flow speed. He also gave a formula for the Soret coefficient for an arbitrary initial component concentration:

$$s = \frac{8}{3}\,\frac{\Delta\bar{c}_\infty}{\Delta T c_0(1-c_0)}, \tag{3.12}$$

in which $\Delta\bar{c}_\infty$ is the maximum difference in the mean concentrations in the halves.

Equation (3.12) has been used [57] to determine the Soret coefficient for a mixture of n-hexane with nitrobenzene near the critical point; Thomaes also examined the effects of displacing the knife edge on the error of the result and found that even an appreciable displacement from the middle position had very little effect.

Butler and Turner [56] showed that for $\Delta T < 20°C$ the second term in (3.10) may be neglected, although they incorporated the effects of thermal expansion. The solution to (3.10) was obtained by computer. Three approximations were obtained for $F(Dx/\delta^2\bar{w})$, which defined $\Delta\bar{c}_x/\Delta\bar{c}_\infty$, for various ranges in $Dx/\delta^2\bar{w}$; in particular, for $(Dx/\delta^2\bar{w}) > 0.035$ they found

$$\frac{\Delta\bar{c}_x}{\Delta\bar{c}_\infty} = 1 - 1.045 \exp\left(-13.66 \frac{Dx}{\delta^2\bar{w}}\right). \tag{3.13}$$

Klapisz and Chanu [62] used a different mathematical technique to solve (3.10) and derived the ratio c/c_m as a function of the dimensionless transverse and longitudinal coordinates together with the parameter $s\Delta T$ subject to the condition $c \ll 1$, where c_m is the mean concentration at any point. However, they made no recommendations on how the calculation should be performed.

3.3. Thermal-Diffusion Column. Jones, Furry, and Onsager [64, 65] and independently Debye [66] developed the theory of gravitational thermal-diffusion columns of Clausius–Dickel type, in which the following assumptions were made:

1. The two working surfaces are ideally isothermal and there is a temperature gradient only perpendicular to the convective flow.
2. The flow in the gap between the working surfaces is laminar.
3. The effects of temperature and concentration on the density, thermal conductivity, viscosity, and diffusion and Soret coefficients can be neglected.

The theory then gives the following equations for the transport of the desired component towards the positive end of the column:

$$j = Hc(1-c) - K\frac{\partial c}{\partial z} + \sigma c. \tag{3.14}$$

In the steady state, we get from (3.14) for a column closed at both ends in the absence of sampling that

$$s = \frac{\rho g \beta \delta^4}{504 \eta D L \ln q^*}, \tag{3.15}$$

where

$$q^* = \frac{c_e(1-c_i)}{c_i(1-c_e)} \tag{3.16}$$

is the degree of separation in the steady state. De Groot [70] pointed out that the variation of density with concentration can have a substantial effect on separation in a thermal-diffusion column. This essentially correct observation served as basis for explaining various anomalies observed in the operation of thermal-diffusion columns [5, 6], and for many years the effect was considered as a major factor in the separation [38, 71-74], until Korchinsky and Emery [118] performed a numerical solution of the equation for convective diffusion containing a term incorporating the horizontal component of the velocity arising from the density variation over the cross section and height of the column.

This solution indicated that the density effect could be neglected in the steady state, while its effect was small for gaps $\delta > 0.25$ mm even in the transient state; the effect was also negligible when the concentration of one of the components was small.

Horne and Bearman [77] drew the same conclusion from estimates of the effect in the separation of a mixture of carbon tetrachloride with cyclohexane, where the effect was around 1%.

They also made a very careful study of the effects of temperature and concentration on all the transport coefficients [25, 76], and found that the effects could usually be neglected in the steady state under the condition $0.28 < \Delta T < 56.8°C$, which agreed with Emery's results [78], which were based on a theoretical study of the effects of the temperature dependence of the viscosity; it was found that the temperature dependence of the viscosity could have a substantial effect on the separation in the thermal-diffusion column only for extremely viscous liquids such as glycerol.

Measurements of the Soret coefficient have been based on (3.15) in various studies [4, 27, 30, 75, 79, 87]; however, nonstationary methods were used well as the stationary one, which were based on the solution to

$$m\frac{\partial c}{\partial \tau} = -\operatorname{div} j, \tag{3.17}$$

where j is the flux defined by (3.14).

The solutions to (3.14) will vary with the formulation of the boundary conditions; if the column is closed at both ends, the conditions are taken as that the fluxes are zero (for $\sigma = 0$) at both ends. Bardin [68] and Debye [66] solved this problem with different forms of approximation for the nonlinear term $c(1-c)$; Majumdar [81] and Von Halle [82] derived the exact solution, while Ruppel and Coull [83] derived a modified form of the solution applicable for small times, and the latter was used by Romero and Bott [93] to determine the Soret coefficient in the form

$$s = \frac{(c_e - c_i)\delta}{4c_0(1-c_0)\Delta T}\sqrt{\frac{10}{7}\,\frac{\pi}{D\tau}}\ . \tag{3.18}$$

The value found [93] from (3.18) for an equimolar mixture of n-pentane with benzene was much less than the value found in convection-free cells.

We shall not deal in more detail with the result of [66, 68, 81, 82, 83], nor with solutions derived for the case where one end of the column is joined to a large vessel and the other is closed [80, 84], since an actual thermal-diffusion column operating in the nonstationary state can never be considered as closed at both ends or at one end, i.e., the mathematical formulation of the boundary conditions for (3.17) cannot contain a specification that the fluxes at the ends are zero. Rabinovich [85] emphasized this point, which was confirmed by the above study [93], and also by Rabinovich's own experiments [86, 92]. The basis of [85, 86] was the view that at the ends of the column there are always volumes arising from the turn through 180° in the direction of the convection current. The mathematical formulation of the boundary conditions should incorporate these volumes, and a column that is usually called closed at both ends then has boundary conditions in the following form for the case, for example, where $c(1-c) \approx \text{const} = \psi$:

$$\begin{aligned} y_e\omega_i \left.\frac{\partial c}{\partial \theta}\right|_{y=0} &= \left.\frac{\partial c}{\partial y}\right|_{y=0} - \psi, \\ y_e\omega_e \left.\frac{\partial c}{\partial \theta}\right|_{y=y_e} &= \left.\frac{\partial c}{\partial y}\right|_{y=y_e} + \psi. \end{aligned} \tag{3.19}$$

The solution to (3.17) subject to (3.19) gave the following expression for the Soret coefficient:

$$s = 1.17\frac{h^2\delta}{n\Delta T}, \tag{3.20}$$

where h and n are the intercepts on the ordinate and the slope of the straight line in $(\Delta c/\tau) - \sqrt{\tau}$ coordinates.

An analogous formula has been derived [86] for c small.

An approximate solution to (3.17) subject to the conditions of (3.19) is possible if one assumes that the separation is quasistationary, provided that ω is reasonably large. De Groot has shown [70] for this case that there is a simple linear relationship between the concentrations at the ends and the run time for small times and equal volumes in the two vessels for various forms of approximation for the nonlinear $c(1-c)$ term, and this takes the following form for the case $c(1-c) \approx \text{const} \approx \psi$, for example

$$\begin{aligned} \frac{c_e}{c_0} - 1 &= \frac{\psi}{c_0}\,\frac{\rho g\beta s\delta^3(\Delta T)^2 B}{6!\,V\eta}\,\tau, \\ 1 - \frac{c_i}{c_0} &= \frac{\psi}{c_0}\,\frac{\rho g s\beta\delta^3(\Delta T)^2 B}{6!\,V\eta}\,\tau. \end{aligned} \tag{3.21}$$

Then a curve for the concentration as a function of time may be drawn up, and the tangent at the point $\tau = 0$ gives the Soret coefficient. This method was used in [5, 6, 11, 87, 91]; unfortunately, it has been pointed out [5, 38] that the method involves an uncertainty arising from constructing the tangent at zero. Murin [88] also obtained a quasistationary approximation for the transient in a column having volumes at the end, which differed from De Groot's solution in that the volumes of the vessels were not equal. Later, Murin and Popov [89] used a formula analogous to (3.21) to determine Soret coefficients for various electrolyte solutions, but not by constructing the tangent at zero; instead, they used concentration measurements at some point in time.

A formula of the type of (3.21) is acceptable if the run time is substantially less than the characteristic time; this condition was observed in [5, 6, 11], but in Tyrrell's view [38] it was not met in the experiments of Murin and Popov [89].

Von Halle [90], who developed the theory of horizontal thermal-diffusion columns with two flows moving in opposite directions and separated by a permeable membrane, derived the following formula for the Soret coefficient:

$$s = \frac{1}{55}\,\frac{2R+\delta}{R+\delta}\left(\frac{\psi_0}{s_0}\right)s_0, \tag{3.22}$$

in which R is the channel depth, δ is the membrane thickness, s_0 is the reduced length of the separating stage, and (ψ_0/s_0) is found by calculation from the measurements.

The results obtained in this way for the Soret coefficients of ethanol–water mixtures agree satisfactorily with results given by others.

4. MEASUREMENT METHODS

Measurements designed to give the Soret coefficients from the above formulas involve determining the following: a) the geometrical dimensions of the apparatus, b) the temperature conditions, and c) the concentration changes at set points.

Although at first sight it would appear that the geometrical parameters are the simplest to determine, the task is in fact fairly complex, especially for parameters such as the working height of a cell or the working gap in a thermal-diffusion column. Any variation in these quantities in the apparatus will result in a temperature nonuniformity, and as a consequence will produce parasitic flows. Unfortunately, little attention has been given to this aspect in measurements. The first direct measurements of geometrical variations in a thermal gravitational column are those of [93], which were followed by those of [94]. It seems that nothing has been published on this aspect for cells. The error of measurement for the distance between the thermostatic surfaces is equally important. This is especially so [75] in determining the Soret coefficient from separation data for a thermal-diffusion column operating in the steady state on the basis of (3.15), since the result is directly proportional to the fourth power of the gap. For this reason Prigogine [4] stated that the error may attain ±40% in determining the Soret coefficient for H_2O-D_2O mixtures, since the error in measuring the gap may be ±10%.

The nonstationary method is free from this disadvantage [85, 86], in which the Soret coefficient is proportional only to the first power of the gap.

Formulas (3.11) and (3.13) imply that it is important to measure precisely the distance between surfaces also for flow cells, particularly since the gaps in such cells are very small (about 0.1 mm). Other geometrical characteristics are the deviation from vertical or horizontal positions. Korsching [14] made measurements on these deviations using a level indicator to set the cell with an error of 0.1 mm/m; however, such measurements by themselves cannot determine whether this level of accuracy is sufficient to suppress convection currents. Here considerable interest attaches to measurements made by Nachtigall and Meyerhoff [43], who found that the Soret coefficients remained unaltered when the cell was tilted by up to 0.8 mm/m. This means that Longworth's quoted setting accuracy (5') could have resulted in convection currents, with a corresponding reduction in the Soret coefficient, since this tilt is almost twice the limit indicated by Nachtigall and Meyerhoff.

As regards thermal-diffusion columns, we have only the data of Horne and Bearman, who found that the error in the concentration difference did not exceed $3 \cdot 10^{-5}$ when the cylindrical column deviated from vertical by 2°, i.e., the effect was negligible. It has been shown [44] that the volumes of the chambers in a membrane cell are important; the values for the volumes are quoted in certain papers [9, 23, 31], but they were not used in the calculations, which, as we have seen above, is justified only when the two volumes are equal, and this condition was not met in [9, 31].

The temperatures at the thermostatic surfaces of cells have usually been measured with thermocouples, but in earlier studies [107-109] the measured temperatures were those of the hot and cold liquid flows, which were provided by thermostatic systems, which naturally resulted in errors due to neglect of the thermal resistance of the walls. Unfortunately, this error persisted in a much later study [95]. Tanner's method [35, 41] is somewhat better, in which a mercury thermometer was immersed in a recess in the plate, which was filled with glycerol. However, here there is still a small temperature difference within the body of the plate. A similar deficiency occurs in Thomaes' method [7], in which platinum resistance thermometers were used instead of mercury thermometers, which recorded the temperature difference by connection in a bridge circuit.

An important point for a membrane cell is to measure the temperatures directly at the membrane surfaces, which is technically difficult if thermocouples are used, since the membranes are made of glass.

In [96], for example, the authors restricted themselves to stating that the thermocouples were placed near the surfaces of the membrane, while in [23] the temperatures were measured with thermistors. On the other hand, Alexander [31] has shown that the temperature difference between the surfaces of a membrane may be as much as 10-20% of the overall temperature difference between the two chambers, and that substantial errors can arise in calculating the Soret coefficient if the temperature is measured at a point characterized by the indefinite concept of "near." More reliable results have been obtained by cementing the thermocouples to the membrane [9, 10, 97-99].

Another major aspect of measurements on Soret coefficients is the concentration shift; if the device is a membrane cell, flow cell, or thermal–gravitational column, the concentration is measured during the experiment by taking samples for analysis by some traditional method. The usual instruments are precision refractometers or interferometers, which naturally require preliminary calibration. However, other instruments have been used: for density measurement with H_2O-D_2O mixtures in the column [4], a pycnometer in separating hydrogen isotopes in benzene [113], chlorine isotopes in trichloroethylene, and bromine isotopes in bromobenzene [27, 101], or else a mass spectrometer [92] in separating bromine isotopes in brominated n-hydrocarbons. Evaporation has also been used [91] to measure the concentration of a solid solute. The radioisotopes Co^{60}, S^{35}, I^{131}, Pb^{212} have also been used [89] to determine Soret coefficients for dilute aqueous electrolyte solutions. The same method has been used with a binary mixture of n-heptane and n-hexadecane [23], the first being labeled with C^{14} and the second with tritium. The concentrations were expressed as count rates when the radioactive labels were employed.

Assays on dilute electrolyte solutions have also been based on the electrical conductivity [11, 31], and interference from electrolysis has been eliminated by using an audiofrequency oscillator and a vacuum-tube voltmeter.

It is undesirable to sample the working space directly in a convection-free cell [54], since this can substantially distort the results. This disadvantage is absent in the optical method, which was first used by Tanner in 1927 [35] to measure thermal diffusion in liquids, and which had first been suggested by Wiener [100] for measuring diffusion coefficients. The basis is that a light beam passing through the medium, which contains a vertical density gradient arising from temperature and concentration gradients, is deflected in the direction of increasing refractive index. This deflection γ is measured, and a correction is applied for the temperature gradient, which gives the following expression [37, 39, 40]:

$$\gamma - \gamma_0 = \frac{fL}{\delta} \cdot \frac{\partial n}{\partial c} \cdot \frac{\partial c}{\partial \xi}, \tag{4.1}$$

where γ_0 is the beam deflection caused by the temperature gradient, f is the distance from the cell to the screen, L is the cell length along the beam path, and δ is the cell height.

We substitute for $dc/d\xi$ for (3.6) to get

$$\gamma - \gamma_0 = c_0 (1 - c_0) s\Delta T \frac{fL}{\delta} \frac{\partial n}{\partial c} \left(1 - \frac{4}{\pi} \sin \pi\xi e^{-\frac{\tau}{\tau_r}} \right). \tag{4.2}$$

The concentration gradient is least in the central section of the cell, so the beam should pass through this section, which corresponds to $\xi = 1/2$. The value of γ_0 is found from a measurement at the start, while the value of dn/dc, which is taken as constant during the experiment, is found from preliminary measurements of the refractive index as a function of concentration, as in the case of benzene + n-heptane [102]. We see from (4.2) that the optical method does not require the absolute concentration to be measured in order to calculate the Soret coefficient.

This method has been used in various styles in several studies [14, 35, 30, 40, 41, 42, 47].

From 1956 onwards, interferometery has been used in such measurements [50]; Longworth [52, 103] improved the technique and applied it for the first time in measuring thermal diffusion in a two-chamber cell, which had the advantage that it eliminated any possible temperature fluctuations. This method has been used in the various modifications described in [38, 104] in several researches [16, 105, 106].

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