DETERMINATION OF THE SORET COEFFICIENT IN A THERMODIFFUSION COLUMN BY THE TRANSIENT METHOD. I

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A method of determining the Soret coefficient for binary mixtures is proposed and suggestions are made on how to use thermodiffusion columns for this purpose.

The Soret coefficient is a phenomenological quantity which characterizes the rate of thermodiffusion in liquids. A compilation of test data pertaining to this coefficient for various binary mixtures seems important on two counts. First of all, such data may provide a valuable tool to researchers engaged in developing the theory of the liquid state and, secondly, they provide a basis for evaluating the practical advantages of the thermodiffusion process in partition technology.

At the present time the Soret coefficient is determined in cells, various forms of which have been described in [1]. An outstanding feature of these devices is that they operate on the principle of measuring the elemental thermodiffusion effect in liquids. Disregarding for the time being some other drawbacks of this method, we will point out one of them: the small changes of concentration in these cells and, therefore, the imprecision of measurements. This aspect is largely manifested in mixtures where one of the components appears in very small quantities. In this case the difference between the concentrations at the active cell surfaces under steady-state conditions is

$$c_e - c_i = c_i s\Delta T.$$

It is evident from this relation that, when concentrations are of the order of 10^{-4} or lower, a change in concentration lies within the sensitivity range of modern instruments such as the laser interferometer which the authors of [2] have used.

These difficulties become magnified further in the case of isotope mixtures. In this regard a thermodiffusion column is preferable to a cell, inasmuch as the high multiplication of the elemental effect in the former can yield large changes in concentration. However, the use of a column as an instrument for measuring the Soret coefficient has made it necessary to develop a theory of the partition process occurring in such a column and such a theory has, indeed been developed by Jones and Ferry in their well known work [3]. This theory is built on the premise that the components of a mixture do not differ with respect to such physical properties as density, viscosity, and volume expansivity, which happens to be most nearly the case in an isotope mixture. If these physical properties of the components differ significantly, however, then assuming them constant along the column height will inevitably lead to erroneous results. Nevertheless, if the process is continued for only a limited time within which the change in concentration remains small and, consequently, the physical properties of the mixture will not vary much along the column height, then the use of such a column as an instrument for determining the Soret coefficient becomes proper and worthwhile.

Apparently, the feasibility of such an application for thermodiffusion columns was first indicated by Ruppel and Coull in [4]. For short time intervals and $c \ll 1$ Debye [5] has established a direct proportionality between the difference of concentrations at the ends of a column, when both ends are closed, and the square root of the time, von Halle [6] then used his method of linearizing the appropriate nonlinear differential

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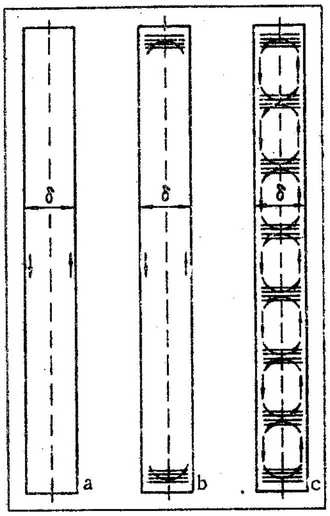

Fig. 1. Schematic diagram representing the hydrodynamics in a liquid-type thermodiffusion column with both ends closed.

equation, while the authors of [4] later used the Majumdar method [7] of linearization in deriving an analogous formula for any concentration c:

$$c_e - c_i = 4c_0(1-c_0)\sqrt{\frac{\theta}{\pi}}, \tag{1}$$

differing from that in [5] by the factor $(1-c_0)$.

The idea originated in [4] was subsequently tried out by Bott and Romero [8] in a rather highly sophisticated experiment. As the test substance they used an equimolar n-heptane–benzene mixture. Although these authors claim a close agreement with formula (1), an examination of the graphs presented in their report indicates that the straight lines in $\Delta c-\sqrt{\tau}$ coordinates do not pass through the origin of coordinates and that the value for the thermodiffusion constant here ($\alpha = 0.82$) is equal to almost half the value obtained by the authors of [9] for the same mixture in a cell.

This offset of such a straight line from the origin of coordinates was noted in many tests with various binary mixtures. In many tests which Bukhtilova and this author have performed with various binary mixtures the straight line was also offset from the origin of coordinates, in agreement with formula (1) requiring that $\Delta c = 0$ at $\theta = 0$.

It could have been hypothesized that such an offset is a consequence of the mixing due to parasitic convection. A review of the test data in [8] indicates, however, that the straight lines corresponding to larger column eccentricities (tests Nos. 19 and 20) and thus also to the highest rate of parasitic convection intersect the axis of abscissas closer to the origin of coordinates than the straight line in test No. 18 with a smaller column eccentricity. This leads us to conclude that the said offset may hardly be attributed to parasitic convection.

In connection with this, it is appropriate to quote Jones and Ferry [3, p. 66] pertaining to relation (1): "in practice this relation is violated at small values of θ, since the space at a column end where the convection stream reverses constitutes a sort of small reservoir."

On the strength of this statement, one may propose another model of the process, other than the conventional physical model, based on the existence of small regions at the column ends (Fig. 1). The conventional flow pattern assumed in a column closed at both ends is shown in Fig. 1a, where the existence of any such region has been disregarded. In reality, however, a 180° reversal of the stream generates a region (shaded area in Fig. 1b) where there occurs no transverse molecular thermodiffusive transfer corresponding to an elemental partition effect, i.e., which is equivalent to a region of mixing.

It is to be noted here that utterly insufficient research has been done so far on the hydrodynamics in vertical gaps, especially in liquid-type thermodiffusion columns. Apparently, the idealized model on the basis of the flow pattern in Fig. 1b is inaccurate. Mikheev [15] has noted that in narrow gaps between vertical surfaces there form closed loops along the gap height, their number depending on the gap width, on the temperature difference, and on the kind of liquid. The model in Fig. 1b must then be replaced by the model in Fig. 1c, where the entire column seems to comprise a series of columns with interstitial spaces between them. This pattern, however, can be reduced to the pattern in Fig. 1b with several times larger end regions.

On the basis of such a physical model, the description of the transfer process in a column with both ends closed must, at least along the initial segment of the kinetic curve, take into account the existence of reservoirs at the ends, i.e., the boundary conditions must be stipulated without assuming a zero flux at the column ends.

As is well known, the following differential equation

$$\frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial y^2} - \frac{\partial\,[c(1-c)]}{\partial y} \tag{2}$$

describes the thermodiffusion process in a column. We will further consider the case where $c(1-c) = \psi$, with the quantity ψ almost constant. This case corresponds exactly to the conditions in the Bott–Romero experiment.

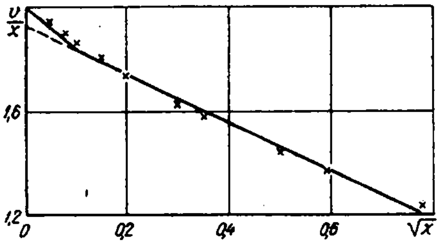

Fig. 2. Linear approximation to formula (14).

Instead of (2) we have then

$$\frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial y^2}. \tag{3}$$

According to [1], the boundary conditions with said regions formed at the column ends are stipulated as follows:

$$y_e\omega_i \frac{\partial c}{\partial \theta}\bigg|_{y=0} = \frac{\partial c}{\partial y}\bigg|_{y=0} - \psi, \tag{4}$$

$$y_e\omega_e \frac{\partial c}{\partial \theta}\bigg|_{y=y_e} = -\frac{\partial c}{\partial y}\bigg|_{y=y_e} + \psi,$$

$$c|_{\theta=0} = c_0. \tag{6}$$

Under conditions (4) and (5), the solution to Eq. (3) in Laplace–Carson transforms is

$$\bar{c}_e - c_0 = \frac{\psi}{\sqrt{p}} \frac{\operatorname{ch}\sqrt{p}\,y_e + y_e\omega_i\sqrt{p}\operatorname{sh}\sqrt{p}\,y_e - 1}{(1 + y_e^2\omega_i\omega_e p)\operatorname{sh}\sqrt{p}\,y_e + y_e(\omega_e + \omega_i)\sqrt{p}\operatorname{ch}\sqrt{p}\,y_e}, \tag{7}$$

$$\bar{c}_i - c_0 = \frac{\psi}{\sqrt{p}} \frac{1 - \operatorname{ch}\sqrt{p}\,y_e - y_e\omega_e\sqrt{p}\operatorname{sh}\sqrt{p}\,y_e}{(1 + y_e^2\omega_i\omega_e p)\operatorname{sh}\sqrt{p}\,y_e + y_e(\omega_e + \omega_i)\sqrt{p}\operatorname{ch}\sqrt{p}\,y_e}. \tag{8}$$

In a column closed at both ends the volumes of the two end regions must be equal, in dimensionless terms, $\omega_e = \omega_i = \omega$.

Under this condition, (7) and (8) yield

$$\bar{c}_e - \bar{c}_i \equiv \Delta c = 2\psi \frac{\operatorname{ch}\sqrt{p}\,y_e + y_e\omega\sqrt{p}\operatorname{sh}\sqrt{p}\,y_e - 1}{(1 + y_c^2\omega^2 p)\sqrt{p}\operatorname{sh}\sqrt{p}y_c + 2y_e\omega p\operatorname{ch}\sqrt{p}\,y_e}. \tag{9}$$

An inverse transformation yields

$$v = \frac{1}{\omega}\left\{1 - 4\sum_{n=1}^{\infty} \frac{(1 + \omega\mu_n \sin\mu_n - \cos\mu_n)\exp(-\mu_n^2\omega^2 x)}{\mu_n\left[(1 + \mu_n^2\omega^2 + 2\mu_n^2\omega)\sin\mu_n + \mu_n(\mu_n^2\omega^2 - 1)\cos\mu_n\right]}\right\}, \tag{10}$$

where

$$v = \frac{\Delta c}{\psi y_e\omega}, \quad x = \theta/(y_e\omega)^2; \tag{11}$$

and μ_n are the roots of the characteristic equation

$$\operatorname{tg}\mu_n = \frac{2\omega\mu_n}{\omega^2\mu_n^2 - 1}. \tag{12}$$

For short time intervals or large dimensionless lengths y_e the hyperbolic sine and cosine may be assumed equal. In that case we have instead of (9)

$$\Delta\bar{c} = \frac{2\psi}{p}\left[\frac{1}{y_e\omega} - \frac{1}{(y_c\omega)^2} \cdot \frac{1}{\sqrt{p} + (1/y_e\omega)}\right], \tag{13}$$

and an inverse transformation, with the notation in (11), yields

$$v = 2\left(e^x \operatorname{erfc}\sqrt{x} + 2\sqrt{\frac{x}{\pi}} - 1\right). \tag{14}$$

A comparison between the results obtained according to formulas (10) and (14) indicates that solution (14) is valid for $x < 1$ (when $\omega < 0.1$).

When the left-hand side of (14) is divided by x, it appears that the right-hand side can be approximated as follows:

$$\frac{v}{x} = a - b\sqrt{x}. \tag{15}$$

The graph in Fig. 2, where the values of v/x have been calculated according to formula (14), confirms within a 1.5% accuracy that v/x is a linear function of $\sqrt{x}$. Substituting in (15) for v and x their values from (11) and using the expressions for θ, y_e, and ω, we may rewrite formula (15) as

$$\frac{\Delta c}{\tau} = h - n\sqrt{\tau}, \tag{16}$$

TABLE 1. Difference in Concentration (mol. fract.) as a Function of Time (sec), in the Bott–Romero Experiment [8]

Test No.							
17		18		19		20	
$\tau \cdot 10^{-3}$	Δc	$\tau \cdot 10^{-3}$	Δc	$\tau \cdot 10^{-3}$	Δc	$\tau \cdot 10^{-3}$	Δc
3,6	0,110	4,2	0,100	3,6	0,073	5,1	0,136
8,1	0,206	8,1	0,170	8,1	0,116	8,7	0,158
10,8	0,225	14,4	0,233	15,0	0,182	15,0	0,209
16,2	0,333	22,5	0,306	20,4	0,199	18,0	0,233
25,2	0,397	30,0	0,400	28,2	0,243	21,0	0,252
				39,0	0,314	24,6	0,262
						28,2	0,291
						30,0	0,310

where

$$h = \psi a \frac{H}{M}, \quad n = \psi b \frac{H}{M^2} \sqrt{mK}. \tag{17}$$

It is evident from (16) that the test points in $(\Delta c/\tau) - \sqrt{\tau}$ coordinates fit on a straight line with the slope n and the intercept h on the axis of ordinates. Both these parameters are determined graphically and experimentally. With the aid of (17), we can easily find

$$\frac{h^2}{n} = \psi \frac{a^2}{b} \frac{H}{\sqrt{mK}}, \quad \frac{h}{n} = \frac{a}{b} \frac{M}{\sqrt{mK}} = \frac{a}{b} \omega L \sqrt{\frac{m}{K}}, \tag{18}$$

from where

$$s\sqrt{D} = \sqrt{\frac{10}{7} \frac{bh^2}{\psi n a^2} \frac{\delta}{\Delta T}}, \quad \omega \sqrt{D} = \frac{1}{\sqrt{9!}} \frac{bh}{an} \frac{g\rho\beta\delta^3 \Delta T}{\eta L}. \tag{19}$$

The quantities a and b in (15) are found from Fig. 2, their values being different for different ranges of the variable x: $a = 2$ and $b = 1.504$ for $0 < x < 0.01$, but $a = 1.92$ and $b = 0.915$ for $x > 0.01$.

The values of a and b within the first range of x can also be obtained analytically, if in (14) $e^x \approx 1 + x$ and $\operatorname{erf}\sqrt{x} \approx 2(x^{1/2} - (x^{3/2}/3))/\sqrt{\pi}$.

Then, discarding the term with $x^{5/2}$, we obtain

$$\frac{v}{x} = 2\left(1 - \frac{4}{3\sqrt{\pi}} x^{1/2}\right), \tag{20}$$

i.e., the result in [6]. According to the formula derived here, $b = 8/3\sqrt{\pi} = 1.504$.

In (11) we now substitute for θ, y_e, and ω their values. Then

$$x = mK\tau/M^2,$$

which together with (18) yields

$$\tau = \left(\frac{bh}{an}\right)^2 x.$$

In the second approximation range $(b/a)^2 = 0.227$. This range, as has been shown here, corresponds to $x > 0.01$. Consequently, the test points in $(\Delta c/\tau) - \sqrt{\tau}$ coordinates will fit a straight line for a time τ

$$\tau > 6.45 \cdot 10^{-3} \left(\frac{h}{n}\right)^2. \tag{21}$$

In test No. 18 in [8], for instance, $h/n = 2.55 \cdot 10^2$ (see Table 2) and for time intervals longer than 450 sec there must exist a linear relation (16).

With the inequality sign in (21) reversed, the range of time is defined where formula (20) applies.

It is evident from (19) that, in order to determine the Soret coefficient as well as in order to use formula (1), one must know the diffusivity at some mean temperature in the column which, in the absence of test data, can be calculated.

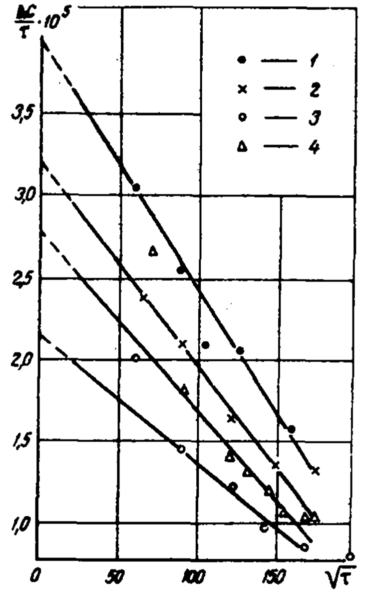

Fig. 3. Evaluation of the test data in [8] according to formula (16): 1) test No. 17, 2) test No. 18, 3) test No. 19, 4) test No. 20; ordinates $\Delta c/\tau$, sec^{-1}; abscissas $\sqrt{\tau}$, sec$^{1/2}$.

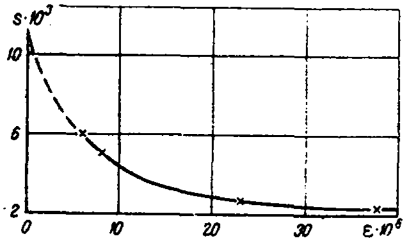

Fig. 4. Values of the Soret coefficient (s, °C^{-1}) for an equimolar n-heptane–benzene mixture, based on measurements in a thermodiffusion column with various amounts of eccentricity (ε, m).

It is noteworthy that the first formula in (19) does not contain the dimensionless volume ω explicitly but, as (18) indicates, in terms of parameters n and h determined experimentally.

These formulas were used for calculating the Soret coefficient from test data given in [8] and shown here graphically in Figs. 2 and 4. From those graphical data, this author has set up Table 1 and, on this basis, plotted the graphs in Fig. 3 in $(\Delta c/\tau)-\sqrt{\tau}$ coordinates.

It is evident that most test points lie on straight lines, within an entirely satisfactory accuracy. Exceptions are the last points in tests No. 18, 19, 20 falling beyond the linear approximation to Eq. (14) and the first points in tests No. 19, 20, the values of Δc for which are apparently too high.

Since in [8] were given data on the mean temperature difference throughout the test time, with a gap width $2.65\cdot 10^{-4}$ m, hence the values of n and h found from Fig. 3 will easily yield the Soret coefficient according to the first expression in (19), this expression becoming now

$$s = 6{,}37\frac{h^2}{n\Delta T}. \qquad (22)$$

The results are shown in Table 2 along with the values based on data in [8] and calculated according to formula (1) (last line in Table 2). A comparison between these and other values indicates that formula (1) yields distinctly lower values for the Soret coefficient. In Table 3 are shown test data pertaining to the Soret coefficient obtained by cell measurements by other authors, as of this author's writing. According to Tables 2 and 3, the more reliable values obtained by column measurements are higher than such values obtained by cell measurements.

These facts merit special attention. In this author's view, these facts indicate that in cells widely used for measuring the Soret coefficient there always occurs parasitic convection due to inevitable temperature nonuniformities. The latter may be a consequence of the difficulties in establishing a uniform distance between the thermostaticized surfaces and in making these surfaces ideally isothermal, also a consequence of a not exactly horizontal position of the cell. The effect of surface anisothermality on the hydrodynamics in cells was studied in [12], for instance.

Thus, there is no doubt that parasitic convection occurs in any cell with a free volume (without membranes) described in the technical literature. This explains the wide scatter of test points obtained under apparently, at first glance, the same conditions by various authors, and even a mere comparison between values for the Soret coefficient in Table 3 as well as a comparison with its values for a methanol–benzene mixture obtained by various authors and shown in [14] will convincingly support this conclusion.

As we well know, columns are also not free of this deficiency. The cylindrical shape of the apparatus, however, ensures that it can be set up with high precision, which together with a well designed construction and heating–cooling process makes it feasible to reduce the effect of parasitic convection.

TABLE 2. Data for Calculating the Soret Coefficient in an Equimolar n-Heptane – Benzene Mixture

Parameter	Test No.			
	17	18	19	20
$\varepsilon \cdot 10^6$, m	5,6	7,7	37,1	22,9
ΔT, °C	10,8	10,4	14,2	15,6
$n \cdot 10^7$, $\sec^{-3/2}$	1,54	1,265	0,808	1,10
$h \cdot 10^5$, $\sec^{-1}$	3,95	3,22	2,17	2,78
$s\sqrt{D} \cdot 10^7$, $m \cdot {}^\circ C^{-1} \cdot \sec^{-1/2}$ according to [19]	4,58	3,92	2,03	2,23
$s \cdot 10^3$, $^\circ C^{-1}$	6,0	5,01	2,61	2,88
$s \cdot 10^3$, $^\circ C^{-1}$ according to data in [8]	2,73	2,63	1,2	1,2

Notes. 1) The Soret coefficient was calculated on the basic of the diffusivity at 25°C according to data in [13]: $D = 2.47 \cdot 10^{-9}$ m^2/sec · 2) in [8] were given values of the thermodiffusion constant. Conversion to the Soret coefficient was made on the basis of temperature T = 300°K.

The data in Table 2 indicate that the test value for the Soret coefficient increases with smaller column eccentricity, until at $\varepsilon \approx 6\ \mu$ it appreciably exceeds the values obtained in earlier studies for an n-heptane – benzene mixture. The relation is shown graphically in Fig. 4. An extrapolation of the curve here till intersection with the axis of ordinates will yield the hypothetical value of the Soret coefficient for the given mixture at zero column eccentricity.

Values for the Soret coefficient obtained in cells must be considered too low, therefore, and this agrees with the results of L. S. Kotousov's* irreversible-thermodynamics analysis of thermodiffusion in liquids, according to which the values of the Soret coefficient must be much higher than those known at the present time.

In view of all this, there arises the question as to what is the true value of the Soret coefficient and as to whether the more reliable values in Table 2 approach the maximum possible value. Unfortunately, the theory which has been presented here cannot provide an answer.

The values according to formulas (19) approach the true values, as the column used for measurements becomes more nearly perfect.

The quantity ω, which characterizes the size of the end regions, offers some indication as to how nearly perfect a column with both ends closed can be. The second formula in (19) yields $\omega \approx 0.07$ for tests No. 17, 18 and $\omega \approx 0.11$ for tests No. 19, 20 with a larger eccentricity. As the eccentricity increases, so does the parasitic convection. Thus, the value of ω appears to be some effective value which includes the actual volume as well as some fictitious volume equivalent to the mixing region due to parasitic convection.

Further research ought to be directed toward designing an apparatus where interference by parasitic convection is minimized. Nevertheless, the analysis presented here does already indicate that a thermodiffusion column is a better instrument than a conventional cell for measuring the Soret coefficient. The last statement applies particularly to isotope mixtures where one component appears in very small amounts.

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*Private Communication.

TABLE 3. Data on the Value of the Soret Coefficient for an Equimolar n-Heptane – Benzene Mixture, Obtained by Various Authors

Authors	$\bar{T}$, °K	$s \cdot 10^3$, $^\circ C^{-1}$
D.J. Trevoy and H.G. Drickamer [10]	296,1	4,02
J.A. Bierlein, C.R. Finch, and H.E. Bowers [11]	298	1,49*
J. Demichowicz-Pigoniowa, M. Mitchell, and H.J.V. Tyrell [9]	298	4,58—5,02

* Interpolation obtained.

NOTATION

c	is the concentration;
$\theta = H^2\tau/mK$;	
$H = sg\rho\beta\delta^3(\Delta T)^2B/6!\eta$;	
$K = g^2\rho^3\beta^2\delta^7(\Delta T)^2B/9!\eta^2D$;	
$m = \rho B\delta$;	
τ	is the time;
ρ	is the density;
β	is the volume expansivity;
δ	is the gas width;
$\Delta T = T_1 - T_2$;	
$\overline{T} = (T_1 + T_2)/2$;	
T_1, T_2	are the temperature of the hot and cold surfaces;
B	is the gap perimeter;
η	is the dynamic viscosity;
D	is the diffusivity;
$y = Hz/K$;	
z	is the vertical coordinate;
$y_e = HL/K$;	
L	is the active height of the column;
$\omega = M/mL$;	
M	is the mass of the partitioned mixture filling the end spaces of the column;
ε	is the column eccentricity;
s	is the Soret coefficient;
n	is the slope of the correlation line.

Subscripts

e	denotes the positive end;
i	denotes the negative end of the column.

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