

TRANSIENT-STATE SORLET-COEFFICIENT
 DETERMINATION FOR A THERMAL-
 DIFFUSION COLUMN. IV

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Another method is given for approximating a solution previously obtained for small times, and a comparison is made with experiment.

An asymptotic solution has been derived [1,2] for the transient response in a thermal diffusion column having volumes at the ends:

$$v = \frac{1}{\pm 2k + 1} - \frac{\pm 2k(\pm 2k - 1)}{(\pm 2k + 1)^2 x} \left[1 - \exp\left(\frac{\pm 2k + 1}{\pm 2k - 1} x\right) \operatorname{erfc}\left(\frac{\pm 2k}{\pm 2k - 1} \sqrt{x}\right) \right] + \frac{\pm 2k - 1}{\pm 2k + 1} \left[\frac{1}{\pm 2k - 1} + \frac{4k^2 + 1}{2(\pm 2k + 1)x} \right] \operatorname{erf}\left(\frac{\sqrt{x}}{\pm 2k - 1}\right) + \frac{\pm 2k - 1}{(\pm 2k + 1)\sqrt{\pi x}} \exp\left[-\frac{x}{(\pm 2k - 1)^2}\right], \quad (1)$$

where the plus sign relates to the end of the column at which the concentration of the target component increases for $c_0 < 0.5$, while the minus sign relates to the other end; the signs are interchanged if $c_0 > 0.5$.

An approximation has been given [2,3] for the solution to (1) in the form

$$v = p_1 - r_1 \sqrt{x}, \quad (2)$$

which, however, has the disadvantage that, although it describes (1) closely, it approximates the derivative with a rather large error, and the derivative is an important quantity in calculating the Soret coefficient from measurements in terms of $\Delta c/\tau$ versus $\tau^{1/2}$. This disadvantage has [4] been overcome to a certain extent by splitting up the entire range of variation in x into a series of small ranges; however, then the Soret coefficient has to be derived by successive approximations, which makes the procedure more laborious.

For this reason, we have derived another approximation for the v defined by (1), which describes the function closely, and also the derivative. It is difficult to meet both of these conditions with a fairly simple function over a wide range in x , but there is no particular need to do this, since even x up to 0.16 correspond to time intervals sufficient for performing an experiment.

We have found that the following function satisfies both the above conditions:

$$\frac{v}{\sqrt{x}} = p + \frac{r}{\sqrt{x}}, \quad (3)$$

i.e., v/\sqrt{x} is a linear function of $1/\sqrt{x}$.

From (3) we get the derivative $d(v/\sqrt{x})/d(1/\sqrt{x})$ as a constant equal to r .

On the other hand,

$$r = \frac{d(v/\sqrt{x})}{d(1/\sqrt{x})} = v - \sqrt{x} \frac{dv}{d\sqrt{x}}, \quad (4)$$

and from (1) we have

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TABLE 1. Relation of r to Dimensionless Time x

$y_e^* \omega$	x				
	0.0025	0.01	0.04	0.10	0.16
2	0,998	0,990	0,973	0,956	0,893
0	1,0	0,999	0,984	0,954	0,948
-2	1,0	0,999	0,998	0,991	0,982

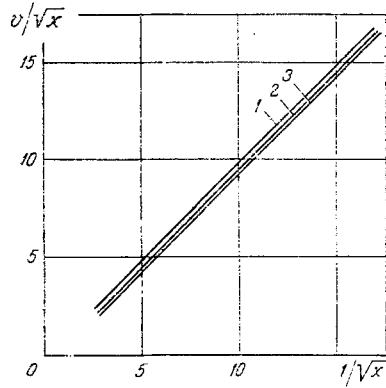


Fig. 1. Relation of v/\sqrt{x} to $1/\sqrt{x}$ for $y_e^* \omega$ of: 1) $-10/3$; 2) 0; 3) 8.

$$\frac{dv}{d\sqrt{x}} = \frac{\pm 2k - 1}{(\pm 2k + 1)^2 x^{3/2}} \left[\pm 4k - (4k^2 + 1) \operatorname{erf} \left(\frac{\sqrt{x}}{\pm 2k - 1} \right) - \left[\frac{\pm 2k - 1}{(\pm 2k + 1)x} - 1 \right] \right] \times \frac{\pm 4k}{(\pm 2k + 1)\sqrt{x}} \exp \left(\frac{\pm 2k + 1}{\pm 2k - 1} x \right) \operatorname{erfc} \left(\frac{\pm 2k}{\pm 2k - 1} \sqrt{x} \right) - \frac{2(\pm 2k - 1)}{(\pm 2k + 1)\sqrt{\pi x}} \exp \left(-\frac{x}{(\pm 2k - 1)^2} \right) \quad (5)$$

If we substitute (5) into (4), the right side of (4) should be approximately constant for a given k for all values $x \leq 0.16$; Table 1 gives calculations for three values of $y_e^* \omega$, which show that the best approximation to the condition $r \approx \text{const}$ is attained in the range $y_e^* \omega \leq 0$, which means that the experiment should be arranged to meet this condition. For instance, if $c_0 < 0.5$ and the target component accumulates at the bottom of the column, then the samples for analysis should be taken from the upper part, and vice versa if $c_0 > 0.5$. We use the relationship established by Prigogine [5], which indicates that usually the component that accumulates in the cold region is the one with the larger value of the solubility parameter $\sqrt{E_1/V_1} - \sqrt{E_2/V_2}$, where E and V are, respectively, the energy of evaporation and the molar volume for each of the pure components; then one can determine before starting the experiment which end of the column is to be sampled.

Table 1 shows that r differs little from 1 for various x and $y_e^* \omega$, and with an error not exceeding 4% we can assume it as constant for $r = 0.98$; Fig. 1 shows this more clearly, being constructed in terms of v/\sqrt{x} and $1/\sqrt{x}$ as coordinates from calculations based on (1). It is clear that, within the error of the graphical construction, (3) is closely described by straight lines with the same slope of 0.985 for the range $-3.33 < y_e^* \omega < +8$; as regards the parameter p in (3), the latter is closely approximated by the following linear relation for the same range in $y_e^* \omega$:

$$p = -0.5575 + 0.0229 y_e^* \omega. \quad (6)$$

We substitute for v and x in (3) and use the expressions for y_e , ω , and θ together with the following notation:

$$\frac{pH}{M^2} c_0(1 - c_0)\sqrt{mK} = h, \quad \frac{rc_0(1 - c_0)H}{M} = n \quad (7)$$

to get instead of (3) that

$$\frac{\Delta c}{\tau^{3/2}} = h + \frac{n}{\sqrt{\tau}}. \quad (8)$$

Then the measurements may be processed with $\Delta c/\tau^{3/2}$ and $1/\sqrt{\tau}$ as coordinates, and the points corresponding to the concentration shift after a certain time should lie on a straight line of slope n that meets the ordinate axis with an intercept h.

TABLE 2. Temperatures and Concentration Change for CCl_4 at the Bottom of a Column for a CCl_4 -Cyclohexane Mixture ($c_0 = 64.8$ wt. %)

Run No.	Time, sec	$\Delta c \cdot 10^2$	$T_1, ^\circ\text{K}$	$T_2, ^\circ\text{K}$	$\Delta T, ^\circ\text{C}$	$\tau^{-1/2} \cdot 10^2, \text{sec}^{-1/2}$	$\tau^{-3/2} \cdot 10^7, \text{sec}^{-3/2}$
1	900	1,00	308,3	296,0	12,3	3,33	3,69
2	1800	1,88	311,3	298,8	12,5	2,36	2,47
3	2700	2,69	308,8	296,2	12,6	1,93	1,94
4	3600	3,45	308,5	296,7	11,8	1,66	1,58
5	5400	4,84	308,5	296,0	12,5	1,36	1,22
6	7440	6,20	310,0	298,6	11,4	1,16	0,967
Mean			309,2	297,0	12,2		

TABLE 3. Mean Values for $s \cdot 10^3$ Reported for Equimolar CCl_4 -Cyclohexane

Our tests $t=30^\circ\text{C}$	[6], 25°C	[7], 25°C	[8]	[13]
5,53	5,18	5,9	5,22	5,6

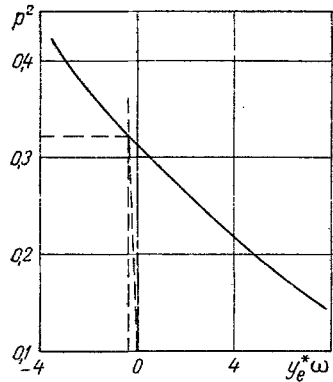


Fig. 2. Relation of p^2 to $y_e^* \omega$.

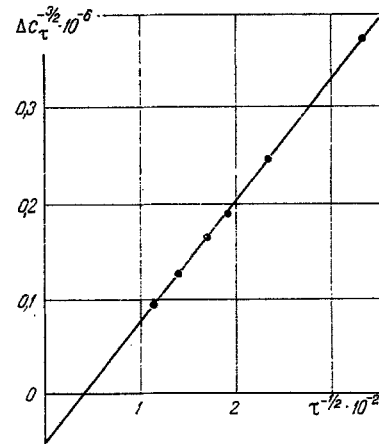


Fig. 3. Results from processing data of Table 2.

From (7) we have

$$\frac{h}{n^2} = \frac{p \sqrt{mK}}{c_0 (1 - c_0) r^2 H}; \quad \frac{H}{\sqrt{mK}} = \frac{pn^2}{c_0 (1 - c_0) hr^2} \quad (9)$$

We substitute for H, K, and m to get the following expression for the Soret coefficient:

$$s \sqrt{D} = \sqrt{\frac{10}{7}} \cdot \frac{pn^2}{hr^2} \cdot \frac{\delta}{c_0 (1 - c_0) \Delta T} \quad (10)$$

On the other hand, we have from (7) that

$$\frac{h}{n} = \frac{p}{r} \cdot \frac{1}{\omega \sqrt{D}} \cdot \frac{g \rho \beta \delta \Delta T}{\sqrt{9!} \eta L},$$

whence

$$\omega \sqrt{D} = \frac{pn}{hr} \cdot \frac{g \rho \beta \delta \Delta T}{\sqrt{9!} \eta L} \quad (11)$$

The quantity p appearing in (10) and (11) is not known when the experiment is being formulated, since (6) shows that it is dependent on the unknown parameter $y_e^* \omega$.

The latter, however, can be put in the following form if we replace y_e by its value and ω by the value given by (11):

$$y_e^* \omega = \frac{504}{\sqrt{9!}} \cdot \frac{bpn}{hr} \cdot \frac{\Delta T}{\delta} s \sqrt{D}$$

or, if we use (10), by

$$y_e^* \omega = \frac{b}{c_0(1-c_0)} \cdot \frac{p^2 n^3}{h^2 r^3},$$

whence we have

$$p^2 = c_0(1-c_0) \frac{h^2}{b} \left(\frac{r}{n}\right)^3 y_e^* \omega. \quad (12)$$

Formula (12) thus relates p to $y_e^* \omega$ for the detailed conditions of the experiment defined by h and n .

If we eliminate $y_e^* \omega$ from (6) and (12), we get the result for p ; however, a graphical method of determining p is more convenient, and (6) is shown as $p^2 = f(y_e^* \omega)$ in Fig. 2 for this purpose.

We use the measurements to calculate the coefficient to $y_e^* \omega$ in (12) and draw a straight line with this slope through the origin to meet the curve $p^2 = f(y_e^* \omega)$, which gives the desired value of p^2 . Note that p and r may be positive or negative, the sign being dependent on the concentration change at the end of the column used for sampling. If $\Delta c > 0$, then p is always negative, and $r > 0$; if, on the other hand, $\Delta c < 0$, then p is positive, but $r < 0$. The above method was tested with a mixture of carbon tetrachloride and cyclohexane containing 64.8% of the first by weight. This mixture was chosen for the following reasons: first, it had been studied in detail on several occasions in a cell free from convection [6], in a flow cell [7], and in the steady state of a thermal gravitational column [8-10,13]. The results obtained in these ways differ little one from the other and thus can serve to test our method; secondly, extensive evidence is available on the diffusion coefficient at a variety of temperatures [12] for this mixture, and this is necessary in calculating the Soret coefficient from (10).

A cylindrical column as described in [11] has a working height $L = 35$ cm; the outer and inner cylinders were made with a tolerance of $\pm 5 \mu\text{m}$, while the mean gap was measured at $\delta = 0.263$ mm. The surface temperatures of the outer and inner cylinders were measured with copper-constantan thermocouples, which were calibrated after insertion in the body of the cylinder. The emf was measured with a PP-63 potentiometer. The upper end of the column was joined to a large vessel (250 cm³) by a thermal siphon, which maintained a constant concentration at that end, which was equal to the initial value. In the lower part of the inner cylinder there was a recess of a volume of 0.6 cm³. The heating and cooling were provided by U-10 thermostats.

The method of performing the experiments has been described [2] and differed from the latter only in certain details associated with the presence of the vessel at the end. After a preset time, a 1-cm³ sample was taken from the column for analysis with an ITR-1 interferometer, whereupon the run was terminated, the contents were removed, a fresh filling was supplied, and a fresh run was begun. The coefficient of variation for the concentration measurement for this mixture was $\pm 0.012\%$.

Table 2 gives the results, which show that the mean temperature difference was $\Delta T = 12.12^\circ\text{C}$ and the mean temperature in the gap was $\bar{T} = 303.1^\circ\text{C}$.

Columns 7 and 8 have been used to construct Fig. 3, which gives $h = -4.8 \cdot 10^{-8} \text{ sec}^{-3/2}$ and $n = 1.26 \cdot 10^{-5} \text{ sec}^{-1/2}$; the slope in the linear approximation $c(1-c) = a + bc$ for the concentration shift was $b = -0.296$ in these experiments, i. e., $y_e^* \omega < 0$, and then (12) gives

$$p^2 = -0.85 y_e^* \omega. \quad (13)$$

The relationship of (13) is shown by the broken straight line in Fig. 2, which meets the curve at a point corresponding to $p^2 = 0.318$ and $y_e^* \omega = -0.38$; as $\Delta c > 0$ here, we have $p = -0.564$.

These results give, with (10) and $c_0 = 0.648$, that $s\sqrt{D} = 2.16 \cdot 10^{-7} \text{ deg} \cdot \text{m} \cdot \text{sec}^{-1/2}$.

The diffusion coefficient was derived from the following formula [12]:

$$D \cdot 10^9 (\text{m}^2/\text{sec}) = 1.481 - 0.187 X + 0.024(t - 25) + 0.0024 X(t - 25),$$

in which X is the molar concentration of carbon tetrachloride, which in our case was 0.502.

We substitute this value for X with $t = 30^\circ\text{C}$ to get $D = 1.514 \cdot 10^{-9} \text{ m}^2/\text{sec}$, and also $s = 5.53 \cdot 10^{-3} \text{ deg}^{-1}$; Table 3 compares this result with those given by others. The mean result from the last four columns is $s = 5.47 \cdot 10^{-3} \text{ deg}^{-1}$, and our value differs from this by 1%.

We then determine $\omega\sqrt{D}$ from (11) on the basis that [12] $\rho = 1.158 \cdot 10^3 \text{ kg/m}^3$, $\eta = 0.856 \cdot 10^{-3} \text{ N} \cdot \text{sec/m}^2$, $\beta = 1.223 \cdot 10^{-3} \text{ deg}^{-1}$ for this mixture; then $\omega\sqrt{D} = 2.58 \cdot 10^{-6} \text{ m} \cdot \text{sec}^{-1/2}$, and the above value for the diffusion coefficient gives $\omega = 0.0648$. The definition (see the section "Notation") indicates that ω is the ratio of the volume at the end of the column to the volume of the working part of the column, and the latter is 8.67 cm^3 on the basis of the known geometry ($L = 0.35 \text{ m}$, $\delta = 2.63 \cdot 10^{-4} \text{ m}$, $B = 9.42 \cdot 10^{-2} \text{ m}$); consequently, the volume at the lower end of the column was $8.67 \cdot 0.0648 = 0.56 \text{ cm}^3$, which agrees closely with the volume of the recess there.

The next stage in testing the results given in Table 3 is to determine $y_e^1 \omega$ and compare it with the value given by the graphical construction in Fig. 2; as $y_e^1 \omega = by_e \omega_e$, we calculate that $y_e = 19$ and get that $y_e^1 \omega = -0.365$, which is also extremely close to the value $y_e^* \omega = -0.38$ found from Fig. 2.

It remains to establish in what range in x our experiments were performed; substitution of the known values for the quantities gives $x = 4.58 \cdot 10^{-5}$, where τ is in sec. Table 2 then gives that four of the runs were in the range $x \leq 0.16$, and then Table 1 indicates that this provides reasonably high accuracy in approximating the slope in (3). Note that runs 5 and 6 of Table 2 lie outside this restricted range in x , but the results still fit very closely to the straight line in Fig. 1, which indicates that the range of permissible values of x might almost be doubled within the accuracy of graphical construction.

NOTATION

c , concentration; $\theta = H^2 \tau / mK$; $m = \rho B \delta$; $H = sg \rho^2 \beta \delta^3 (\Delta T)^2 B / 6!$; η ; $K = g^2 \rho^3 \beta^2 \delta^7 (\Delta T)^2 B / 9!$; $\eta^2 D$; τ , time; ρ , density; β , volumetric expansion coefficient; δ , size of gap; $\Delta T = T_1 - T_2$; $T = \frac{1}{2} (T_1 + T_2)$; T_1, T_2 , temperatures of hot and cold surfaces; B , perimeter of gap; η , dynamic viscosity; D , diffusion coefficient; $y = Hz/K$; z , vertical coordinate; $y_e = HL/K$; L , working height; $\omega = M/mL$; M , mass of mixture in volumes at ends; s , Soret coefficient;

$$v = \frac{b(c - c_0)}{c_0(1 - c_0)} \cdot \frac{\pm 2k - 1}{2x},$$

$$k = \frac{1}{y_e^* \omega_e} + \frac{1}{2}, \quad y_e^* = by_e, \quad x = \left(k - \frac{1}{2}\right)^2 \theta^*.$$

$\theta^* = b^2 \theta$. Indices: e , positive end of the column; 0 , initial value.

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