A NONSTATIONARY METHOD OF MEASURING THE SORET COEFFICIENT IN A DIFFUSION COLUMN. III

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An improved form is given for a method previously described for measuring the Soret coefficient, and new values are presented.

We have previously [1] given a method of determining the Soret coefficient by a nonstationary technique applied to thermal-diffusion columns, which applies for the case where the concentration of one of the components is small and so the quadratic term in the transport equation can be linearized in the form $c(1-c) \approx c$; a complete solution has been given [10] for the transient state in a column having vessels at the ends, and asymptotic solutions for small times are also given there, which agreed well with the exact solution for $x \leq 1$. Figure 1 shows the asymptotic solutions in graphic form. The method of [1] involves approximating each of the curves in Fig. 1 throughout the range of variation in $\sqrt{x}$ by the linear relation

$$v = p - r\sqrt{x}, \tag{1}$$

and it has been applied for $r > 0$, i.e., when the concentration of the target components is elevated at the end of the column used in the sampling (positive end). In some of the experiments described below, we used the relationship of [10] for the case where the samples were taken from the negative end, which corresponds to $r < 0$; it has been shown [1] that the following relationships apply for small concentrations:

$$s\sqrt{D} = \sqrt{\frac{10}{7}} \cdot \frac{rh^2}{c_0 p^2 n} \cdot \frac{\delta}{\Delta T}\,; \quad \omega\sqrt{D} = \frac{1}{\sqrt{9!}}\,\frac{rh}{pn} \cdot \frac{g\beta\rho\delta^3\Delta T}{\eta L}\,, \tag{2}$$

$$\frac{r}{p^{3/2}} = \frac{n\sqrt{c_0}}{h^{3/2}}\sqrt{y_e\omega}. \tag{3}$$

We see from (2) and (3) that the quantities r/p^2, r/p, and $r/p^{3/2}$ are the decisive ones; in [1], the value of p was taken as constant for all the curves of Fig. 1, and although r varied for each of them, it was independent of $\sqrt{x}$, which introduced a certain amount of error into the calculation of the Soret coefficient from (2), since Fig. 1 shows that the slope of the tangent to the approximating curves varies quite appreciably with $\sqrt{x}$. For this reason, it was felt desirable to divide the entire significant range of $\sqrt{x}$ into several overlapping smaller ranges, for each of which the error introduced by the linear approximation in (1) will be small. Table 1 gives the results from this approximation, and in this connection it is necessary to examine the range of $\sqrt{x}$ used in any experiment. The appropriate estimate can be made if we write the expression for $\sqrt{x}$ in the expanded form

$$x = \frac{1}{9!}\left(\frac{g\rho^2\beta\delta^4\Delta TB}{\eta M}\right)^2 \frac{\tau}{D}\,. \tag{4}$$

If an experiment is performed with the column closed at both ends, all the quantities appearing in (4) are known apart from the mass M at the end of the column. The accumulated evidence indicates that x may be estimated by assuming that M = 0.1-0.2, after which the calculation is performed in the following sequence. We use (3) with a series of values for $y_e\omega$ to determine the corresponding values for $r/p^{3/2}$, and select from these the one that agrees with the data of Table 1. This operation is most conveniently performed graphically. From the result for $r/p^{3/2}$ we derive r/p^2 and r/p, with interpolation if necessary, and from (2) we calculate s and ω. Then from s we can calculate y_e from the formula

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TABLE 1. Data for Approximating (1)

Positive end

k	$y_e\omega_e$	$\sqrt{x}$=0,1—0,3					$\sqrt{x}$=0,2—0,4				
		p	r	$r/p^{3/2}$	r/p^2	r/p	p	r	$r/p^{3/2}$	r/p^2	r/p
4,5	0,25	0,984	0,56	0,573	0,578	0,569	0,968	0,5	0,524	0,534	0,516
2	0,66	0,978	0,52	0,538	0,542	0,5 1	0,964	0,46	0,486	0,495	0,477
1	2	0,976	0,453	0,468	0,475	0,464	0,952	0,36	0,388	0,397	0,378
0,8	3,33	0,972	0,376	0,393	0,398	0,387	0,946	0,28	0,304	0,312	0,296
0,666	6,02	0,966	0,266	0,280	0,284	0,275	0,935	0,15	0,166	0,171	0,16
0,125	8,0	0,962	0,20	0,212	0,216	0,208	0,935	0,095	0,105	0,109	0,101
k	$y_e\omega_e$	$\sqrt{x}$=0,3—0,5					$\sqrt{x}$=0,4—0,6				
4,5	0,25	0,946	0,43	0,468	0,48	0,454	0,92	0,383	0,43	0,45	0,415
2	0,66	0,942	0,396	0,432	0,446	0,421	0,916	0,343	0,39	0,408	0,374
1	2	0,924	0,278	0,313	0,326	0,301	0,896	0,22	0,26	0,274	0,245
0,8	3,33	0,916	0,196	0,224	0,234	0,214	0,891	0,14	0,166	0,176	0,157
0,666	6,02	0,914	0,092	0,105	0,110	0,101	0,898	0,053	0,0622	0,0656	0,059
0,125	8,0	0,918	0,046	0,052	0,0545	0,05	0,91	0,0283	0,0326	0,0342	0,0312
k	$y_e\omega_e$	$\sqrt{x}$=0,5—0,7					$\sqrt{x}$=0,6—0,8				
4,5	0,25	0,904	0,35	0,407	0,428	0,388	0,884	0,32	0,385	0,410	0,362
2	0,66	0,896	0,306	0,36	0,38	0,341	0,872	0,268	0,329	0,352	0,307
1	2	0,877	0,186	0,226	0,242	0,212	0,858	0,155	0,195	0,210	0,181
0,8	3,33	6,872	0,106	0,130	0,139	0,121	0,856	0,08	0,101	0,117	0,093
0,666	6,02	0,884	0,0286	0,0344	0,0366	0,0324	0,876	0,015	0,0183	0,0195	0,0171
0,125	8,0	0,904	0,0171	0,0199	0,0209	0,0189	0,9	0,01	0,0117	0,0123	0,0111
k	$y_e\omega_e$	$\sqrt{x}$=0,7—0,9					$\sqrt{x}$=0,8—1,0				
4,5	0,25	0,858	0,282	0,354	0,384	0,329	0,831	0,252	0,332	0,366	0,304
2	0,66	0,85	0,238	0,304	0,33	0,28	0,828	0,212	0,281	0,310	0,256
1	2	0,828	0,116	0,153	0,169	0,14	0,814	0,098	0,134	0,148	0,121
0,8	3,33	0,84	0,059	0,0766	0,0837	0,0702	0,824	0,04	0,054	0,059	0,048
0,666	6,02	0,872	0,012	0,0147	0,0158	0,0138	0,871	0,011	0,0135	0,0145	0,0126
0,125	8,0	0,902	0,007	0,0082	0,0086	0,0077	0,896	0,006	0,007	0,0075	0,0067

Negative end

k	$y_e\omega_e$	$\sqrt{x}$=0,1—0,3					$\sqrt{x}$=0,2—0,4				
		p	r	$r/p^{3/2}$	r/p^2	r/p	p	r	$r/p^{3/2}$	r/p^2	r/p
3,5	0,25	0,985	0,593	0,606	0,612	0,602	0,972	0,54	0,564	0,572	0,555
0	2	1,0	0,736	0,736	0,736	0,736	0,992	0,71	0,717	0,721	0,715
—0,2	3,33	1,006	0,85	0,842	0,841	0,844	1,006	0,836	0,830	0,826	0,832
—0,333	6,02	1,028	1,086	1,042	1,03	1,056	1,042	1,125	1,055	1,035	1,08
—0,375	8	1,038	1,246	1,182	1,16	1,20	1,052	1,30	1,20	1,17	1,23
k	$y_c\omega_c$	$\sqrt{x}$=0,3—0,5					$\sqrt{x}$=0,4—0,6				
3,5	0,25	0,955	0,49	0,524	0,536	0,514	0,936	0,45	0,496	0,512	0,482
0	2	0,982	0,682	0,70	0,706	0,694	0,966	0,646	0,678	0,690	0,668
—0,02	3,33	1,002	0,826	0,822	0,823	0,824	0,992	0,805	0,814	0,818	0,810
—0,333	6,02	1,026	1,08	1,04	1,025	1,052	0,991	1,008	1,020	1,024	1,016
—0,375	8	1,032	1,226	1,165	1,15	1,186	0,954	1,06	1,14	1,16	1,11
k	$y_e\omega_e$	$\sqrt{x}$=0,5—0,7					$\sqrt{x}$=0,6—0,8				
3,5	0,25	0,91	0,402	0,462	0,485	0,441	0,886	0,364	0,437	0,464	0,41
0	2	0,95	0,61	0,661	0,676	0,643	0,918	0,565	0,641	0,67	0,615
—0,2	3,33	0,962	0,748	0,793	0,81	0,778	0,918	0,677	0,77	0,802	0,739
—0,333	6,02	0,914	0,86	0,984	1,03	0,942	0,804	0,697	0,97	1,08	0,868
—0,375	8	0,826	0,837	1,11	1,22	1,01	0,692	0,631	1,096	1,32	0,912
k	$y_e\omega_e$	$\sqrt{x}$=0,7—0,9					$\sqrt{x}$=0,8—1,0				
3,5	0,25	0,868	0,34	0,42	0,451	0,391	0,846	0,312	0,4	0,435	0,368
0	2	0,882	0,518	0,626	0,665	0,587	0,85	0,478	0,61	0,664	0,563
—0,2	3,33	0,856	0,593	0,75	0,807	0,69	0,79	0,514	0,731	0,824	0,65
—0,333	6,02	0,701	0,561	0,957	1,14	0,80	0,634	0,477	0,946	1,19	0,754
—0,375	8	0,574	0,472	1,086	1,43	0,823	0,472	0,35	1,08	1,57	0,741

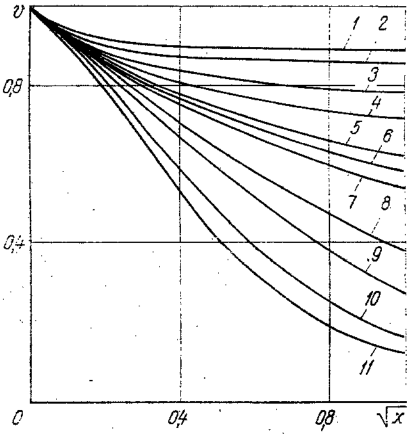

Fig. 1

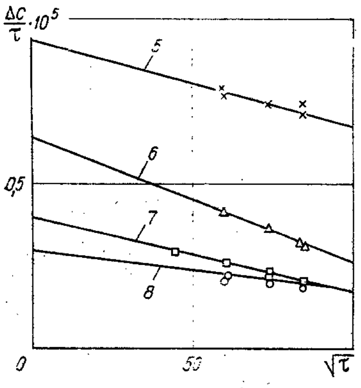

Fig. 2

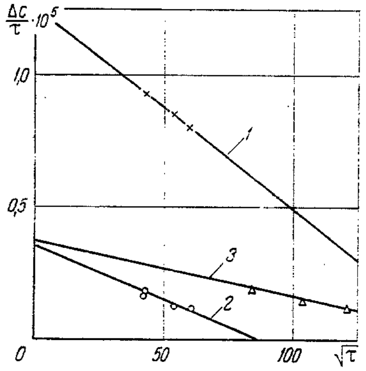

Fig. 3

Fig. 1. The relation of v to $\sqrt{x}$ for $y_e\omega_e$ of: 1) +8; 2) +6; 3) +10 / 3; 4) +2; 5) +2 / 3; 6) +0.25; 7) −0.25; 8) −2; 9) −10 / 3; 10) −6; 11) −8.

Fig. 2. Relation of $\Delta c / \tau$ (sec^{-1}) to $\sqrt{\tau}$ (sec$^{1/2}$) for mixtures 5–8 (Table 2).

Fig. 3. Relation of $\Delta c / \tau$ (sec^{-1}) to $\sqrt{\tau}$ (sec$^{1/2}$) for mixtures 1–3 (Table 4).

TABLE 2. Data on Binary Mixtures Used in Measuring the Soret Coefficient in a Thermal Diffusion Column at $\bar{T}$ = 308°K, ΔT = 30°C

No.	Mixture		c_0, molar fract.(mf)		$D\cdot 10^9$, m²/sec	$\beta\cdot 10^3$, deg^{-1}	$\eta\cdot 10^3$, N·sec / m²	$\rho\cdot 10^3$, kg/m³
	I	II	I	II				
1	CCl_4	C_6H_{14}	0,9612	0,0388	1,487 [2]	1,242	0,739	1,5557
2	CCl_4	C_6H_{12}	0,9648	0,0352	1,34 [2]	1,242	0,739	1,5557
3	CCl_4	C_6H_6	0,9578	0,0422	1,79 [2]	1,242	0,739	1,5557
4	CCl_4	C_6H_6	0,9767	0,0233	1,775 [2]	1,242	0,739	1,5557
5	n-C_7H_{16}	C_6H_6	0,908	0,092	3,56	1,29	0,338	0,6665
6	n-C_7H_{16}	C_6H_6	0,9646	0,0354	3,56	1,29	0,338	0,6665
7	C_6H_6	C_6H_{14}	0,978	0,022	2,1	1,28	0,503	0,8576
8	n-$C_{16}H_{34}$	n-C_7H_{16}	0,952	0,0482	0,76 [2]	0,804	2,232	0,7597

Note. 1. Diffusion coefficients of mixtures 5-7 calculated from formula of [3]. 2. Values of β, η, and ρ taken as for component I. 3. C_6H_{12} = cyclohexane.

$$y_e = 504\,\frac{s\eta\,DL}{\rho g\beta\delta^4}\,, \tag{5}$$

and also the product $y_e\omega$, which we compare with the result previously obtained for the chosen range in $\sqrt{x}$; if the two values do not agree, the calculation is repeated for another range in $\sqrt{x}$.

Measured values have been given [1] for the Soret coefficients for four mixtures: in each case the major substance was CCl_4, while the target components were C_6H_{14}, C_6H_{12}, and C_6H_6, which accumulate at the top of the column. Therefore, samples taken from the bottom of the column in [1] corresponded to the negative end, whereas the calculation was performed for the positive end, and for this reason the Soret coefficients for these mixtures were corrected in accordance with the method presented above. The first four lines in Table 3 give the resulting values for s.

In addition, we determined the Soret coefficients for several other binary mixtures: n-C_7H_{16}–C_6H_6, n-C_7H_{16}–n-$C_{16}H_{34}$, and C_6H_6–n-C_6H_{14}.

We use the apparatus and experimental technique of [1].

Table 2 gives the data on the mixtures and working temperatures.

Figure 2 gives the results; Table 3 gives the values resulting from processing the data (h, n, and ω), and also the results for s. Since the samples were always taken from the bottom of the column, the Soret coefficients for mixtures 5 and 6 were calculated by reference to the positive end, whereas those for 7 and 8 were calculated for the negative end, in accordance with the sense of variation in the concentration.

TABLE 3. Results for Soret Coefficients of Binary Mixtures

Mixture (Table 2)	$h\cdot10^5$, $\sec^{-1}$	$n\cdot10^7$, $\sec^{-3/2}$	ω from (6)	$s\cdot10^3$, $\deg^{-1}$	
				from (3)	cell tests
1	2,42	2,5	0,169	16,8	12,0 [7]
2	0,93	0,680	0,153	6,6	5,6 [8]
3	1,2	0,931	0,141	6,35	5,4 [9]
4	0,93	0,86	0,119	7,41	5,8 [9]
5	0,94	0,286	0,144	2,2	2,42 [4]
6	0,64	0,378	0,08	2,14	2,3 [4]
7	0,39	0,22	0,22	7,6	6,95 [6]
8	0,3	0,141	0,03	2,91	2,5 [5]

TABLE 4. Results for Soret Coefficients for $CCl_4-C_6H_{14}$ Sampled at Top and Bottom of Column (Nos. 1 and 2) and for $CCl_4-C_6H_6$ with the Top Joined to a Vessel (No. 3)

No.	Mixture	Impurity concentration in mixture		Δc	End	$h\cdot10^5$, $\sec^{-1}$	$n\cdot10^7$, $\sec^{-3/2}$	$S\cdot10^3$, $\deg^{-1}$
		impurity	mf					
1	$CCl_4-C_6H_{14}$	C_6H_{14}	0,0046	c_t-c_0	Positive	1,26	0,774	15,6
2	$CCl_4-C_6H_{14}$	C_6H_{14}	0,0046	c_0-c_b	Negative	0,35	0,4	15,4
3	$CCl_4-C_6H_6$	C_6H_6	0,02	c_0-c_b	Negative	0,37	0,214	6,9

Table 3 compares our values with published ones [4-9], which shows that in nearly all cases our results for s are higher than those determined in cells.

Two experiments were performed in order to check out the above method.

In the first case, samples were taken from both ends simultaneously. The column was of height 35 cm, diameter 22 mm, and, further, had $\delta = 0.25$ mm, $\Delta T = 40°C$, $\overline{T} = 318°C$; at each end there was a volume of 1.5 ml. The experiments were performed on a $CCl_4-C_6H_{14}$ mixture with an initial C_6H_{14} content of 0.0046 molar fraction. The samples were analyzed with an LKhM-7a chromatograph.

We calculated s for each end of the column separately by graphical processing (Fig. 3); sections 1 and 2 of Table 4 give the results, which show that the values from the two ends were virtually the same. In the second case, the upper end of the column was connected to a vessel in which a constant concentration c_0 was maintained. The samples were taken from the bottom. The column had L = 35 cm, diameter 30 mm, and $\delta = 0.25$ mm; the other conditions were $\Delta T = 40°C$, $\overline{T} = 318°C$ with a $CCl_4-C_6H_6$ mixture (0.02 molar fraction). Line 3 in Fig. 3 shows the results, while the calculated Soret coefficient (section 3 of Table 4) was $s = 6.9\cdot10^{-3}\ \deg^{-1}$. Section 4 of Table 3 relates to a column closed at both ends, for which this mixture gave $s = 7.41\cdot10^{-3}\ \deg^{-1}$. The somewhat higher s given in Table 3 for $CCl_4-C_6H_6$ and $CCl_4-C_6H_{14}$ mixtures, which are larger than those from the experiments of sections 1-3 of Table 4, arise because the latter experiments were performed at a temperature 10°C higher.

From this we may say that the result from (2) for the Soret coefficient is virtually the same for columns of various designs operated under various conditions no matter whether the samples are taken from the top or bottom of the column.

This provides additional evidence that the method is reliable.

NOTATION

c, concentration; τ, time; ρ, density; β, volume expansion coefficient; δ, gap width; $\Delta T = T_1 - T_2$; $\overline{T} = 1/2\,(T_1 - T_2)$; T_1, T_2, temperatures of hot and cold surfaces, respectively; B, gap perimeter; η, dynamic viscosity; D, diffusion coefficient; L, working height; $\omega = M/mL$; $m = \rho B\delta$; M, mass in volumes near ends; s, Soret coefficient; $v_e = [(c_e - c_0)/2c_0]\cdot[(2k-1)/x]$; $x = \Theta(k - 1/2)^2$; $k = 1/y_e\omega_e \pm 1/2$; $\Theta = H^2\tau/mK$; $H = sg\rho^2\beta\delta^3(\Delta T)^2B/6!\,\eta$; $K = g^2\rho^3\beta^2\delta^7(\Delta T)^2B/9!\,\eta^2D$; $y_e = HL/K$; r, slope in linear approximation of quadratic term $c(1-c)$. Indices: e, positive end; 0, initial value; b, bottom; t, top.

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THERMAL DIFFUSION IN A PACKED COLUMN

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UDC 533.735

A performance analysis is presented for packed thermal-diffusion columns; a method is given for determining the Soret coefficient for a packed column, and test results are presented.

A packed thermal-diffusion column is a form of gravitational Clausius–Dickel column in which the packing in the gap affects the convection and hence the separation.

In the first experiments on packed columns [1-3], it was found that the degree of separation is much larger than for the unpacked case with the same gap, and that the separation increases as the gap is reduced and the packing density increases. It was found that the time needed to attain the equilibrium state (a very important parameter) was very large and increased with the packing density.

The thermal diffusion in a packed column has been discussed theoretically [4], and recently this theory has been improved substantially [6], where it was stated that the hydrodynamic behavior in a packed column should be described by the infiltration equation

$$\mathbf{w} = -\frac{k}{\eta}(\operatorname{grad} p + \rho g), \tag{1}$$

where $\mathbf{w}$ is not the actual velocity in the pores, which is a distinction from the Navier–Stokes equation used in [4], but some effective velocity. In what follows, we retain the symbols and terminology used in [7]. The theory of gravitational thermal-diffusion columns presented there indicates that the coefficients in the transport equation are expressed in terms of the flux function $\varphi(x) = -\rho\int_0^x w_z dx$, which takes the following form on the basis of (1) in the sampling mode:

$$\Phi(x) = -\frac{\sigma x}{B\delta} - \frac{k\rho^2 g\beta\Delta T}{2\eta}x\left(\frac{x}{\delta} - 1\right). \tag{2}$$

From (2) we get the following expressions for the transport coefficients in a packed column by analogy with an unpacked one:

$$H = \frac{60k}{\delta^2}H^*\left(1 - \frac{\varkappa s\Delta T}{2}\right), \tag{3}$$

$$K_c = \frac{3024k^2}{\delta^4}\cdot\frac{D}{D_{\text{ef}}}K_c^*\left[1 - \frac{5}{6}\varkappa s\Delta T + \frac{5}{18}(\varkappa s\Delta T)^2\right], \tag{4}$$

$$K_\sigma = \frac{7!k^2}{2\delta^4}\cdot\frac{D}{D_{\text{ef}}}K_c^*\varkappa s\Delta T\left(1 - \frac{\varkappa s\Delta T}{2}\right), \tag{5}$$

$$K_d = \frac{D_{\text{ef}}}{D}K_d^*. \tag{6}$$

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