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THERMAL DIFFUSION IN A PACKED COLUMN

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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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Here an asterisk denotes the corresponding quantity for an unpacked column with the same gap but operated without sampling. Since the process is operated in a porous medium, the ordinary diffusion coefficient has to be replaced by the effective diffusion coefficient D_{ef} in the porous medium, although the exact relationship to the ordinary diffusion coefficient has not been established [9]. The relationship most commonly employed is that given by Satterfield and Sherwood [10]:

$$D_{ef} = \frac{\varepsilon}{\xi} D. \tag{7}$$

If the porous medium is a powder, the factor ξ varies in the range 1.5–2, whereas for a porous medium with very small pores, such as a catalyst, the factor exceeds 2. We see from (3) and (4) that H is dependent only on one characteristic of the packing, namely, the permeability, while K_c is dependent on the porosity and the previous factor via D_{ef}. It would appear that in [6] an error was made in the diffusion equation on incorporating the velocity effect, and therefore H differs by a factor ε from (3), while K_c differs by a factor ε^2 from (4). In what follows, we assume that the samples are so small that the quantities in the brackets in (3) and (4) are equal to 1, while K_σ may be neglected. Since the optimum gap in an unpacked column is about 0.25 mm, while that for a packed column is usually larger by an order of magnitude, it is of interest to compare the performance of the two types; the performance is defined in terms of parameters such as the separation factor, productivity, time to attain a given concentration, and effects of parasitic convection.

The following expression can be given for the logarithm of the degree of separation in a packed column without sampling:

$$\ln q \equiv y_e = \frac{5\delta^2}{252} \cdot \frac{D_{ef}}{D} \cdot \frac{k}{k^2 + 120\varphi^2} y_e^*, \tag{8}$$

where

$$\varphi = \frac{\eta D}{\rho\beta g\delta\Delta T} \cdot \frac{D_{ef}}{D}. \tag{9}$$

Then (8) has its maximum value at

$$k_{\max} = \sqrt{120}\,\varphi.$$

To estimate $k_{\max}$ we use the values for the quantities characteristic of liquids: $\eta = 10^{-3}$ N · sec / m^2, $D = 10^{-9}$ m^2/sec, $\beta = 10^{-3}$ deg^{-1}, $\rho = 10^3$ kg / m^3, $\Delta T = 50°C$, $\delta = 2.5 \cdot 10^{-3}$ m, while the effective diffusion coefficient for a packing consisting of glass balls was taken as $D_{ef} = 0.25D$. Substitution of these values into the expression for $k_{\max}$ gives $k_{\max} \approx 2 \cdot 10^{-12}$ m^2, and if $k \geq 10k_{\max}$; as is usually the case in practice, then (8) can be put with an error of 1% as

$$y_e = \frac{5\delta^2}{252k} \cdot \frac{D_{ef}}{D} y_e^*. \tag{10}$$

We substitute into (10) the dimensionless length of a column having the optimal gap from the formula $y_e^* = (\delta^0/\delta)^4 y_e^0$, where the superscript zero denotes the parameters for an unpacked column, and then we write the condition for the degree of separation for the packed column to be the same as that for the unpacked one, $y_e = y_e^0$, which corresponds to a permeability of

$$k = \frac{5\delta^2}{252} \cdot \frac{D_{ef}}{D} \left(\frac{\delta^0}{\delta}\right)^4. \tag{11}$$

If we substitute the above values into (11), we get $k = 3 \cdot 10^{-12}$ m^2, and this can be attained with a packing consisting of spheres of diameter 80–100 μ. Therefore, a packed column can give a degree of separation larger than that for an unpacked column with the optimum gap if the permeability and gap in the packed column are small. If the two columns are to have identical output, $\sigma = \sigma^0$, not only must the separation factors be equal, but also the dimensionless sample sizes $\varkappa = \varkappa^0$ must be equal [7], which implies that $H = H^0$.

However, since we have

$$H = \frac{60k}{\delta^2} \left(\frac{\delta}{\delta^0}\right)^3 \left(\frac{B}{B^0}\right) H^0, \tag{12}$$

the latter condition gives

$$k = \frac{\delta^2}{60} \left(\frac{\delta^0}{\delta}\right)^3 \left(\frac{B^0}{B}\right), \tag{13}$$

which in conjunction with (11) gives

$$\left(\frac{B^0}{B}\right)\left(\frac{\delta}{\delta^0}\right) = \frac{25}{21} \cdot \frac{D_{ef}}{D}. \tag{14}$$

We see from (14) that a packed column should have a perimeter larger by 20-30 times than an unpacked one in order to provide the same output.

The transient response is defined by parameters y_e and θ [7]; if y_e and y_e^0 are the same, identical concentrations will be attained after equal dimensionless times θ and θ^0.

However, we have

$$\theta = \frac{25}{21\varepsilon} \cdot \frac{D_{ef}}{D}\left(\frac{\delta^0}{\delta}\right)^2 \frac{\tau}{\tau^0}\,\theta^0, \tag{15}$$

so for the ratio of the times in these columns we have

$$\tau/\tau^0 \approx (\delta/\delta^0)^2. \tag{16}$$

We now compare the effects of parasitic convection in packed and unpacked columns without sampling on the basis of [7, 8]; the parasitic convection is very much dependent on $\varkappa_n y_e$, and if we compare columns with identical separation factors, the effect from parasitic convection will be dependent on the relation between the dimensionless values for the resulting parasitic flows.

It has been shown [7] that the parasitic sampling factor in an unpacked column is

$$\varkappa_n^0 = \frac{\sigma_n}{H^0} = 15\,\frac{(\delta T)^0}{s(\Delta T)^2}, \tag{17}$$

and the mean speed of the parasitic flow is

$$\bar{w}_n^0 = 4\bar{w}^0\,\frac{(\delta T)^0}{\Delta T}. \tag{18}$$

From (2) we have for a packed column that

$$\bar{w} = \frac{2}{\delta}\int_{\frac{\delta}{2}}^{\delta} w_z\,dx = \frac{g\beta\rho\Delta T k}{4\eta}, \tag{19}$$

while for the parasitic sampling we have by analogy with (17) and (18) that

$$\varkappa_n = 6\,\frac{\delta T}{s(\Delta T)^2}. \tag{20}$$

With an accuracy sufficient for practical purposes we can assume that

$$(\delta T) = \frac{\Delta}{\delta}\,\Delta T. \tag{21}$$

Then for given identical eccentricities and temperature differences for the two columns, the ratio of the parasitic sample values will be

$$\frac{\varkappa_n}{\varkappa_n^0} = 0.4\,\frac{\delta^0}{\delta}. \tag{22}$$

Therefore, the parasitic-sampling factor for a packed column is larger by a factor 10-25 than that for an unpacked one, and so parasitic convection should be virtually absent in a packed column.

This comparison indicates that the absence of parasitic convection is a major advantage of a packed column; if the parasitic convection in an unpacked column is appreciable, this reduces the advantage as regards the other parameters, and a packed column may be extremely useful in certain instances. For example, one expects that the separation of isotopic mixtures in a packed column would be better, since the parasitic convection in an unpacked column is particularly important when the thermal-diffusion constant is small [7].

Tests have been performed [5, 11-13] on the Emery – Lorenz theory [4]; qualitative agreement was found, although none of the experiments were carried through to the steady state, in which the concentration changes would have been large. On the other hand, the parameters of the mixtures, and, in particular, the Soret

TABLE 1. Column Characteristics and Working Temperatures

Column	$r\cdot10^3$, m	$\delta\cdot10^3$, m	M_e, g	L, m	$d\cdot10^6$, m	k, m^2	$\overline{T}$, °K	ΔT, °C
1	15,010	2,52	33,5	0,33	230—300	$4,7\cdot10^{-11}$	313	50
2	15,015	2,03	18,5	0,33	80—120	$5,35\cdot10^{-12}$	313	50

TABLE 2. Characteristics of Benzene—CCl_4 Mixture at $\overline{T}$ = 313°K*

C_0 (wt. fract. of; CCl_4)	$D\cdot10^9$, m^2/sec	$\eta\cdot10^3$, N·sec/m^2	$\beta\cdot10^3$, deg^{-1}	$\rho\cdot10^{-3}$, kg/m^3
0,33	2,32	0,541	1,19	1,008

*Diffusion-coefficient data from [19]; the viscosity, density, and volume expansion coefficient were measured in our laboratory.

coefficients, were substantially dependent on the concentrations, and so substantial errors would result from averaging them over large concentration ranges. In [11], the theory was tested in the sampling mode, and it was pointed out that quantitative agreement between theory and experiment would not be obtained in the absence of sampling. We have performed quantitative tests on this theory by the nonstationary method, which is of considerable advantage with packed columns on account of the very much reduced time required.

The tests were done with two cylindrical columns, with a constant concentration maintained at one end, which was equal to the initial value, while at the other end there was a volume containing a mass of liquid M_e. The concentration change in this volume at small times has been given previously [18]:

$$\Delta c = \frac{Hc(1-c)}{M_e}\tau\left(1 - \frac{4}{3\sqrt{\pi}}\cdot\frac{\sqrt{mK}}{M_e}\sqrt{\tau} + \ldots\right). \tag{23}$$

A plot in $(\Delta c/\tau) - \sqrt{\tau}$ coordinates gives the straight line

$$\frac{\Delta c}{\tau} = h - n\sqrt{\tau}, \tag{24}$$

where

$$h = \frac{Hc(1-c)}{M_e};\quad n = \frac{4}{3\sqrt{\pi}}\cdot\frac{Hc(1-c)\sqrt{mK}}{M_e^2}. \tag{25}$$

With (3) and (4) we get from (25) that

$$\sqrt{\frac{15\pi D_{\text{ef}}}{32\varepsilon}} = \frac{h^2}{n}\cdot\frac{\delta}{\Delta T c s(1-c)}. \tag{26}$$

An advantage of this method is that one can determine the Soret coefficient independently from the ordinate h, as (25) shows; the effective diffusion coefficient can be determined from (26) by means of the Soret coefficient already calculated.

Table 1 gives the characteristics of the column and also the working temperature.

The working part of the column was formed by a layer of packing of height 33 cm, above and below which there were free volumes formed by the dead spaces in the column and the sealing elements. The top of the column was linked by a thermal siphon to a vessel having 20 times the volume of the column, which maintained a constant concentration at that end. The vessel had a bellows for transmitting the pressure from a compressed-air cylinder. The bottom of the column also had a thermal siphon linked to a small vessel, from which the samples were taken. A pressure of 1 atm was applied to the working gap in order to facilitate the sampling, which was performed through special sampling devices. The inner cylinder in the column was heated, while the outer one was cooled by water supplied from a thermostatic system. The surface temperatures were monitored by 12 thermocouples on the cold surface and one on the hot surface. The temperature nonuniformity was judged from the readings of the couples on the cold surface; a vertical difference was found, which did not exceed 1°C in column No. 1 or 1.5°C in column No. 2.

A benzene—carbon tetrachloride mixture was used, whose Soret coefficient has previously been determined with cells [14-17], while the other characteristics are given in Table 2. The analyses were performed

TABLE 3. Separation of a Benzene–CCl_4 Mixture in a Packed Column at $\overline{T}$ = 313°K and C_0 = 0.33 by Weight

Column No.	h, sec^{-1}	n, $sec^{-3/2}$	$S \cdot 10^3$, deg^{-1}			D_{ef}/D
			[17] at $\overline{T}$=313°K	[15, 16] at $\overline{T}$=298°K	our res.	
1	$2,2 \cdot 10^{-6}$	$3,8 \cdot 10^{-9}$	4,72	6,7–7,05	7,15±0,32	0,188±0,016
2	$3,74 \cdot 10^{-7}$	10^{-10}			7,26±0,4	0,167±0,018

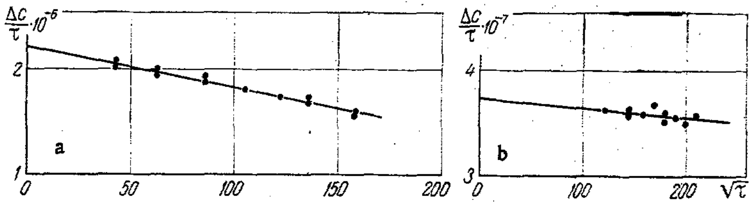

Fig. 1. Relation of $\Delta c / \tau$ (sec^{-1}) to $\sqrt{\tau}$ ($sec^{1/2}$) for columns: a) No. 1; b) No. 2.

with an ITR-1 interferometer using a calibration curve previously constructed. The error of measurement for the difference in refractive index was $\pm 6 \cdot 10^{-6}$, which corresponded to a concentration change of 0.01%.

The dissolved gas was removed from the mixture before filling the column; preliminary tests had shown that this ensured reproducibility.

The permeability of the packing was measured directly on the column by a classical technique under isothermal conditions.

Parts a and b of Fig. 1, and also Table 3, show the results; the Soret coefficient and the effective diffusion coefficient were calculated from (25) and (26), with correction for the longitudinal diffusion in the case of column No. 2.

The main contribution to the errors in determining the Soret coefficients, which were, respectively, 4.5 and 5.5% for the first and second columns, arose from the error in measuring the mass M_e at the ends. The values of the Soret coefficient calculated by this method for the packed column were somewhat higher than those found with cells [14-17], which is ascribed to the minor effect of the parasitic convection, in accordance with the above.

There is entirely satisfactory agreement for the Soret coefficient and effective-diffusion coefficient as obtained from columns differing in gap and packing permeability, and so a packed column has an advantage over cells as a means of determining the Soret coefficient, and this should be particularly pronounced for mixtures with low separation factors.

NOTATION

c, concentration; $H^* = sg\rho^2\beta\delta^3(\Delta T)^2B/6!\eta$; $K_c^* = g^2\beta^2\rho^3\delta^7(\Delta T)^2B/9!\eta^2D$; $K_d^* = \rho B\delta D$; $y_e^* = H^*L/K^*$; $\theta = H^2\tau/mK$, $\varkappa = \sigma/H^*$; τ, time; ρ, density; β, volume expansion coefficient; ΔT, temperature difference between hot and cold surfaces; B, gap perimeter; η, viscosity; D, diffusion coefficient; D_{ef}, effective diffusion coefficient; z, vertical coordinate; x, horizontal coordinate; k, permeability; ε, porosity; ξ, corrugation factor; M_e, mass at positive column end; L, column height; s, Soret coefficient; r, radius of separating slit; δ, gap width; Δ, eccentricity; $m = \rho B\delta\varepsilon$; σ, sample; w, effective velocity; (δT), temperature nonuniformity; d, ball diameter. Indices: *, unpacked column; 0, unpacked column with optimum gap δ^0; p, parasitic convection.

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SOLUTION OF BOUNDARY-VALUE PROBLEMS OF HEAT CONDUCTION FOR CYLINDRICAL REGIONS WITH NONCIRCULAR BOUNDARIES

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UDC 536.24

We employ the principle of superposition to obtain the solution of stationary heat-conduction problems for cylindrical regions with a noncircular boundary.

We consider the problem of the stationary temperature distribution in an infinite cylinder with a noncircular contour

$$\rho = f(\theta), \tag{1}$$

where ρ, θ, and z are cylindrical coordinates (the z axis coincides with the axis of the cylinder). We assume the cylinder contour to be convex and smooth [the derivative $f'(\theta)$ is continuous]. The known surface temperature is constant along the contour; along a generator of the cylinder it varies as cos nz.

Thus, we solve the following three-dimensional boundary-value problem of the theory of heat conduction: Find a function $u(\rho, \theta, z)$ satisfying Laplace's equation

$$\Delta u = 0 \tag{2}$$

and the boundary condition

$$u|_{\rho=f(\theta)} = \cos nz \quad (n = 1, 2, \ldots). \tag{3}$$

To obtain such a solution we use the principle of superposition (see [1]). In the space of the coordinates x, y, and z we select a new system of coordinates X, Y, and z, which depends on the parameter λ and is defined by the expressions

$$\begin{cases} X = x\cos\lambda + y\sin\lambda, \\ Y = -x\sin\lambda + y\cos\lambda, \\ z = z. \end{cases} \tag{4}$$

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