Non-steady-state density effects in liquid thermal diffusion columns

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Abstract. The Furry, Jones and Onsager column theory is reformulated to determine the effect of the buoyancy-driven convection induced by the density composition dependence on the separation of a binary liquid mixture (the 'forgotten effect'). The transport equation is obtained in terms of correction factors depending on the separation parameter and to be applied to the standard column coefficients. From this equation, the column transient operation is carefully analysed. It is found that, contrary to what happens at the steady state, the forgotten effect greatly affects the approach to equilibrium. The excellent agreement obtained between the theory developed and the experimental data opens up the possibility of determining accurate values of ordinary and thermal diffusion coefficients of liquid mixtures from column separation measurements.

1. Introduction

The thermal diffusion (TD) factor, α, is a kinetic quantity that has been widely used in the past to study the interaction between molecular species. TD factors are very sensitive even to minor changes in the interaction features. An expressive example is the gas phase separation of isobaric species of isotopically substituted methane molecules [1], where TD factor is mainly dominated by rotational effects. In addition, the well established Chapman–Enskog kinetic formulation had shown the way to relate the measured TD data to the intermolecular potential functions between species in gas phase mathematically [2, 3]. For this reason, work on TD properties of dilute gas mixtures was strongly directed towards the study of the microscopic features of the pairs interactions [4–6]. Simultaneously, a notable improvement in the understanding of the experimental techniques was obtained [7, 8].

However, a similar route was not generally practicable in the case of the liquid mixture, and most of the work in the field has been done in relation to more phenomenological aspects or as simple improvements of a material-science separation tool [8, 9]. Recently, advances in the experimental techniques and new directions of work have renewed interest in thermal diffusion as a powerful source of phenomenological information. Recently contributions on the diffusion properties of macromolecules [10], TD-induced buoyancy-driven instabilities [11], diffusion properties in the vicinity of the critical points of liquid mixtures [12, 13], isotopic thermal diffusion in liquid mixture [14],

etc have been reported. In this connection, Bonner and Sundelöf [15] have suggested that important mass fluxes can be generated in living matter by thermal gradients, in conditions of incipient phase separation, where the Fickian diffusion currents are suppressed.

Some remarks about the ways of acquiring experimental data on diffusion coefficients are now pertinent. In the first place, the elementary non-convective TD unit provides the quantity D_T/D, i.e., the ratio of the thermal and Fickian diffusion coefficients. Moreover, the time evolution of the separation suffices to determine D. Some recent improvements in the optical measurements of the separation in the elemental TD cell make this method an attractive way of determining both quantities [11, 12].

On the other hand, it is widely known that the Clusius–Dickel tube produces greater separations than the non-convective units, although its characteristic operation times are also correspondingly higher. An elementary theoretical description of the separation in the column predicts that the steady Rayleigh separation factor [16] is proportional to the pure TD coefficient [17], D_T, and that the Fickian coefficient, D, completely determines the time evolution of the Rayleigh factor [18, 19]. So, the two Onsager phenomenological coefficients can be extracted, in two independent ways, from the separation data measured.

The above results hold for the ideal case, i.e., when the composition dependence of the mixture density is ignored. If this dependence is allowed for, the column operation deviates from the ideal behaviour (the 'forgotten effect'). At steady-state, departures from the ideal are small and increase with the ratio D_T/D. This result is now well established, both theoretically [20, 21] and experimentally [22], at least for mixtures with not very high separation parameters [20]. However, the non-steady-state operation shows most apparent deviations from the ideal. Separation rates are higher than the ideal at the early stages of the process, but the final consequence of the forgotten effect is always to increase the time needed to achieve the steady-state condition. As we shall show, this time also increases with D_T/D.

Contrary to that which is stated above for the steady state operation, a theory giving the time evolution of the separation in the non-ideal case has not yet been achieved, and to do so for mixtures with positive separation parameters is the aim of the present paper. Furthermore, we shall present preliminary experimental work performed in order to check the theoretical predictions.

The results here presented point out that density effects must be carefully allowed for so as to describe correctly the overall operation of thermogravitational units. Moreover, they also suggest that the use of this technique in the measurement of diffusion properties of liquid mixtures in states close to its critical lines would seem to be a very attractive route. As is well known, the high intrinsic sensitivity of D_T for the detection of even small changes in the molecular interaction fields caused by long-range-order contributions, is sufficiently amplified by the countercurrent convection mechanisms. In addition, a high extra enhancement of the column amplification factor is to be induced by the large forgotten contributions to be expected near the critical region. So it would seem plausible to expect very high separations in the critical region or, alternatively, to obtain notable improvements in the threshold of the experimental detection of small long-range effects, when experimental conditions are not too close to the critical ones. In any case, it seems necessary to put more experimental and theoretical effort into this field until reliable D_T and D values can be confidently reckoned from separation data measured in the vicinity of the critical states.

2. The transport equation equilibrium

We shall consider a binary liquid mixture in a closed thermogravitational column of length L, breadth b and annular gap width $2w$. The column walls are placed at $x = \pm w$ and are kept at temperatures T_1 and T_2, with $T_1 > T_2$.

In order to determine the influence on separation of the extra buoyancy effects induced by the horizontal variation of fluid density with composition, the so-called *forgotten effect*, we shall follow the basic assumptions of the standard Furry, Jones and Onsager (FJO) column theory [23]. Furthermore, under the usual measurement conditions of thermal diffusion factors in a gravitational column, the cylindrical aspects of the apparatus can be ignored and the Boussinesq assumptions are applicable.

We shall take the density in the buoyancy term of the hydrodynamic equation as a linear function of temperature, T, and the mass-fraction of the less dense component, c

$$\rho = \bar{\rho}[1 - \beta(T - \bar{T}) - \gamma(c - \bar{c})] \tag{1}$$

where β and γ are, respectively, the coefficients of thermal expansion and density variation with composition, and the barred quantities are to be taken at the reference state.

Finally, we shall assume the product $c\,(1 - c)$ to be constant along the column. As is shown in [24], the variation of this quantity does not affect the resulting separation factor between the column ends when the overall separations are small.

In the FJO formulation referred to, the relevant quantity for calculating the separation is the transport of one component through a column cross section. For the lighter component, the transport, q, is defined as

$$q = b \int_{-w}^{+w} \rho v c \, \mathrm{d}x \tag{2}$$

where v is the velocity of the convective-flow field. A working equation for q can be derived by integrating the continuity equation with respect to x

$$v(\partial c/\partial z) = D(\partial/\partial x)\{(\partial c/\partial x) - [\alpha c(1 - c)/\bar{T}]\,(\mathrm{d}T/\mathrm{d}x)\} \tag{2a}$$

where z is the vertical coordinate, D, the ordinary diffusion coefficient and α the thermal diffusion factor. On operating, one obtains the well known equation FJO

$$q = Hc(1 - c) - K\partial_z c \tag{3}$$

where H and K are the column transport coefficients given by

$$H = \alpha \frac{\Delta T}{\bar{T}} \frac{b}{2w} \int_{-w}^{+w} g(x) \, \mathrm{d}x \qquad K = \frac{b}{D} \int_{-w}^{+w} g^2(x) \, \mathrm{d}x \tag{4}$$

with $\Delta T = T_1 - T_2$ and $g(x)$, the flow function being defined as

$$g(x) = -\int_{-w}^{x} v \, \mathrm{d}x. \tag{5}$$

The FJO formulation assumes that convective flow is induced by the horizontal thermal gradient. The additional contribution induced from the horizontal composition

gradient can be included in the theory by introducing equation (1) into the hydrodynamic equation

$$\eta(\mathrm{d}^2v/\mathrm{d}x^2) = \mathrm{d}p/\mathrm{d}z + \rho g \tag{5a}$$

where η is the viscosity, g the gravitational acceleration and p the pressure. Differentiating this equation with respect to x and taking into account equations (1) and (2a), in terms of the non-dimensional variables:

$$x^* = x/w \qquad v^* = (v/w^2)(2\eta/\rho\beta g\Delta T) \tag{6}$$

one obtains for the flow pattern the equation

$$\mathrm{d}^4g^*/\mathrm{d}x^{*4} = (1 + S) - Rg^* \tag{7}$$

where g^* is the non-dimensional $g(x)$ function, and S and R are, respectively, the separation parameter and the Rayleigh number based on the vertical composition gradient

$$S = \alpha c(1 - c)\gamma/\beta\bar{T} \qquad R = \rho\gamma\delta gw^4/\eta D. \tag{8}$$

Here δ stands for $\partial_z c$. In the following, the separation parameter is considered to be a known constant through the column operation and R, being proportional to $\partial_z c$, will be used as the local measure of the separation. Both non-dimensional groups are the quantities relevant to the description of the separation process.

Equation (7) must be solved to the boundary conditions

$$g^*(1) = g^*(-1) = g_x^*(1) = g_x^*(-1) = 0 \tag{9}$$

which express mass-flow cancellation through a column cross section and zero velocity at the walls. In the absence of density composition effects, $\gamma = 0$ and, consequently, $S = R = 0$. In this situation, (7) and (9) agree with the FJO equations for the g^* function.

Inserting the solution of (7) and (9) in (4), the column-transport coefficients can be written in terms of forgotten correction factors to be applied to the standard FJO coefficients H_0 and K_0:

$$H = H_0 h(R, S) \qquad K = K_0 k(R, S) \tag{10}$$

with

$$H_0 = \frac{b(2w)^3}{6!}\frac{\alpha\rho^2\beta g(\Delta T)^2}{\eta\bar{T}} \qquad K_0 = \frac{b(2w)^7}{9!}\frac{\rho^3\beta^2 g^2(\Delta T)^2}{\eta^2 D} \tag{11}$$

and

$$h = (1 + S)\alpha_1(R) \qquad k = (1 + S)^2\alpha_2(R) \tag{12}$$

where

$$\alpha_1 = \frac{6!}{2^6\mu^4}\left[1 - \frac{1}{\mu}\frac{\cosh(2\mu) - \cos(2\mu)}{\sinh(2\mu) + \sin(2\mu)}\right] \tag{13}$$

$$\alpha_2 = \frac{9!}{2^{13}\mu^8}\left[2 + \frac{2\sinh(2\mu)\sin(2\mu)}{[\sinh(2\mu) + \sin(2\mu)]^2} - \frac{5}{2\mu}\frac{\cosh(2\mu) - \cos(2\mu)}{\sinh(2\mu) + \sin(2\mu)}\right] \qquad \mu = (R/4)^{1/4}. \tag{14}$$

The correction factors h and k reduce to unity for the ideal FJO case ($S = R = 0$).

Simple approximate expressions for h and k can be derived by expanding the functions α_1 and α_2 in a Taylor series about $R = 0$. One obtains

$$\alpha_1 = 1 - r + (1 + \lambda_1)r^2 - (1 + \lambda_2)r^3 + \ldots$$
$$\alpha_2 = 1 - 2(1 + \lambda_1)r + 3(1 + \lambda_2)r^2 + \ldots$$

(15)

with $r = 2R/63$ and $\lambda_1 = 19/(4 \cdot 55 \cdot 13)$ and $\lambda_2 = 2879/(11 \cdot 13 \cdot 63 \cdot 5)$. Neglecting the comparatively small terms in λ_1 and λ_2, the resulting series are, respectively, the expansions of $(1 + r)^{-1}$ and $(1 + r)^{-2}$. Thus, from (12) we have for h and k the simple expressions

$$h = (1 + S)/(1 + r) \qquad k = (1 + S)^2/(1 + r)^2.$$

(16)

These approximations prove to be accurate to within more than 1% for $r \leqslant \frac{1}{2}$ (i.e., $R \leqslant 63/4$). Thus, they can be used (see below), for $0 \leqslant S \leqslant \frac{1}{2}$.

At the early stages of the separation process one can expect large gradients of $\partial_z c$, and consequently of R. But at times close to the standby state, $\partial_z c$ tends towards to a constant value in all parts of the tube. In this way R loses its local character and can be used as an appropriate measure of the steady-state separation (for transient states see (28) below). By expressing the fact that q cancels out at the final equilibrium state, we get from (3), 10) and (12), a transcendental equation giving the stationary Rayleigh number, R_∞, as a function of S

$$R_\infty = (63S/2)(h_\infty/k_\infty)$$

(17)

where $h_\infty = h(R_\infty)$ and $k_\infty = k(R_\infty)$. In the ideal case, $h_\infty = k_\infty = 1$, and (17) yields $R_\infty/S = 63/2$. Note that, although R_∞ and S are both zero in this case, the quotient R_∞/S remains finite.

Insertion of the approximations (16) into (17) leads to the same result as above for R_∞/S. Further, by retaining the linear term in $\lambda_1 r$ in the expansion of α_2 in (15), we obtain from (17) the approximation for R_∞

$$R_\infty = (63S/2)(1 + 2\lambda_1 S).$$

(18)

Taking into account the expressions defining R and S, (18) reads

$$l_\infty = 504L/[g\bar{T}(2w)^4](\alpha\eta D/\rho\beta)(1 + 2\lambda_1 S)$$

(19)

where l_∞ is the natural logarithm of the steady Rayleigh separation factor. Equation (19) coincides with the expression previously reported in the literature [18, 19]. Numerical calculations from (17) show that the approximation (18) enables one to obtain R_∞ values within an accuracy of better than about 1% for $0 \leqslant S \leqslant 2$. All this indicates that the influence of density effects in the steady state is small, even for S values of higher than those found in standard TD practice.

3. The approach to equilibrium

The partial differential equation (PDE) that gives the time evolution of the separation process is derived from a mass balance applied to cross-sectional overall transport. Following FJO, we have

$$\mu\partial_t c = -\partial_z q$$

(20)

where t is the time and μ is the mass of fluid per unit length of column. Taking into account (3) and (10), and introducing the non-dimensional variables

$$\zeta = z/L \qquad \tau = (K_0/\mu L^2)t$$

equation (20) reads

$$\partial c/\partial \tau = D^*(\partial^2 c/\partial \zeta^2) \tag{21}$$

where

$$D^* = k(1 + 2S)/(1 + S) + R\,dk/dR. \tag{22}$$

Boundary conditions for the problem merely state the q cancellation at both closed-column ends. Thus, in terms of R, we have

$$R = R_\infty \qquad \text{at} \qquad \zeta = 0 \qquad \text{and} \qquad \zeta = 1. \tag{23}$$

Finally, the uniform state of non-segregation furnishes the initial condition

$$c = c_0 \qquad \text{at} \qquad \tau = 0. \tag{24}$$

It is convenient to rewrite the differential problem in terms of the new function w defined through

$$R = R_\infty(1 - w). \tag{25}$$

Differentiating (21) with respect to ζ and accounting for the proportionality between R and $\partial_\zeta c$, one obtains

$$\partial w/\partial \tau = (\partial/\partial \zeta)D^*(\partial w/\partial \zeta) \tag{26}$$

and the conditions (23) and (24) read

$$
\begin{aligned}
w &= 0 \qquad \text{at} \qquad \zeta = 0 \qquad \text{and} \qquad \zeta = 1 \\
w &= 1 \qquad \text{at} \qquad \tau = 0.
\end{aligned}
\tag{27}
$$

The function w is related to the natural logarithm of the measured non-steady-state Rayleigh separation factor, $l(\tau)$, through

$$l(\tau) = l_\infty(1 - \Omega) \qquad \Omega = \int_0^1 w\,d\zeta. \tag{28}$$

The differential problem, (26)–(27), is formally analogous to a standard desorption problem [25], D^* being the effective diffusion coefficient. Some qualitative information about the time evolution of the desorption process can be gained from the examination of the $S \leqslant 1/2$ case. Using (16) and (22), the coefficient D^* becomes

$$D^* = (1 + S)[1 + S(1 + w)]/[1 + S(1 - w)]^2. \tag{29}$$

In the ideal case $(S = R = 0)$, $D^* = 1$. In the real case, $w \simeq 1$ at short times and, according to (29), $D^* \simeq (1 + S)(1 + 2S)$, i.e. $D^* > 1$. Then the time rate of the desorption process is higher than in the ideal case. On the other hand, $D^* \simeq (1 + S)^{-1}$ for long times, and thus the desorption rate is lower than in the ideal case. The separation process behaves in the same way: the separation rate for $S \neq 0$ is higher than in the ideal case at the initial stages of the process, but there is a slowing down at times close to the final
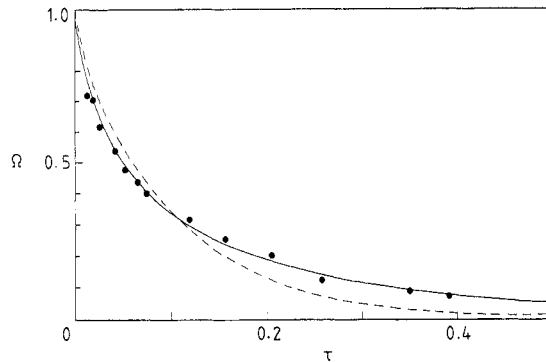
Figure 1. Dependence of Ω, equation (28), against the non-dimensional time τ for $S = 0$ (———) and $S = 1.3$ (——); ● experimental results for the carbon tetrachloride-$n$hexane mixture at 28% molar fraction of carbon tetrachloride.

equilibrium state. (Figure 1 displays the numerical results obtained for Ω against τ for $S = 0$ and $S = 1.3$, that show the differences between ideal and actual behaviour.)

At the final stages of the separation process, $D^* = D_\infty^*$ (where D_∞^* is D^* at $w = 0$). But the time evolution with a constant D^* coefficient corresponds to an exponential decay with a characteristic relaxation time

$$\tau_r = 1/\pi^2 D_\infty^* . \tag{30}$$

For small values of S, in dimensional variables, one obtains from (29) the simple result

$$t_r = (t_r)_0(1 + S) \tag{31}$$

where

$$(t_r)_0 = \mu L^2/\pi^2 K_0$$

is the characteristic time of the ideal process, when the forgotten contribution is absent. The approximation (31) gives a first indication of the strong influence of the density effects on the non-equilibrium states. In this respect, as $(t_r)_0$ is proportional to D, the use of the ideal formulation eventually to determine ordinary diffusion coefficients from transient separation data, produces high errors even for mixtures with small values of S. Numerical calculation confirms this fact. Moreover, it can also be concluded that the use of numerical solutions of the PDE problem is necessary: some approximate solutions of the desorption problem in the literature [25] show strong deviations from the numerical ones and thus they cannot be confidently used to describe the entire time-evolution process.

In order to check the validity of the theory developed, we shall in the next section advance some preliminary non-steady-state experimental results.

4. Experimental results and conclusions

The liquid thermal-diffusion column used in this work is a conventional stainless-steel concentric-tube type closed at both ends, which has been described in detail in earlier
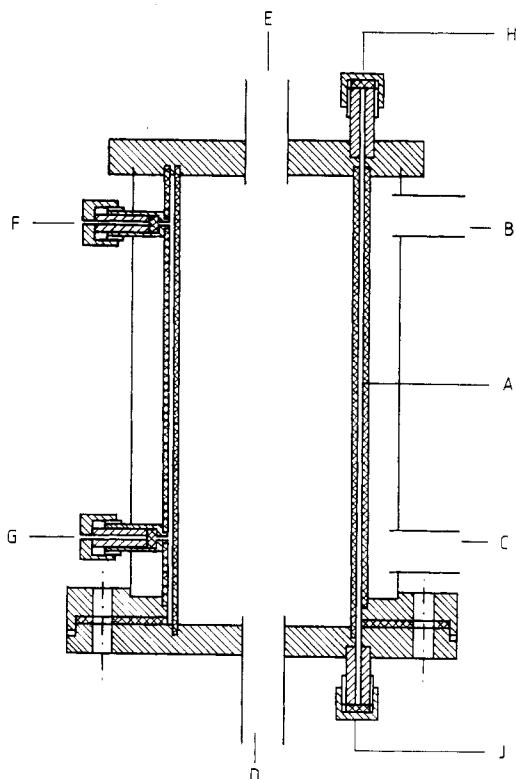
Figure 2. A schematic drawing of the liquid thermal diffusion column. A, working space; B, C, connections to circulating cooling water; D, E, outlet and inlet hot water; F, G, sampling ports; H, J, filling and draining connections.

publications [22]. The total length of the column is $L = 0.9$ m, and the distance between the sampling ports at either end is 0.791 m. The annular gap size is 0.95 mm. Figure 2 represents a diagram of the column showing the working space. The temperature of the walls was kept constant using two circulating ($15\,l\,min^{-1}$) thermostatically controlled baths. The temperature difference across the annulus is considered to be the temperature difference between the two water baths, corrected for the conductivity of the stainless-steel walls ($\Delta T = 4$ K). The mean temperature under our experimental conditions is the arithmetic mean between the hot and cold temperatures, $\bar{T} = 311$ K. Determination of mass concentration was carried out with a Zeiss refractometer. A Pulfrich-type refractometer (with a nominal accuracy of 5×10^{-6}) was used in some experimental runs, when more precise determinations were required. The experimental procedure and the preparation and manipulation of the liquid mixture have been described elsewhere [22].

In the present work, the separation factor was measured as a function of time for a carbon tetrachloride-$n$hexane mixture (molar fraction of carbon tetrachloride = 28.0%). This system was chosen because it presents a large separation parameter ($S = 1.3$), mainly due to the large difference in the densities of the two components.

Figure 1 displays the experimental results obtained for the quantity $\Omega = 1 - l(\tau)/l_x$ as a function of the non-dimensional time τ. The time scale factor required for real-time conversion was determined from the thermophysical properties of the mixture. The density and the density coefficients were calculated from experimental density data of the pure components [26], assuming an ideal mixture. The viscosity was measured by us in a Ubbelhode viscometer at the working temperature ($\eta = 3.23 \times 10^{-3}$ P) and the ordinary diffusion coefficient was estimated from the data of Bidlak and Anderson [27]

at 298 K, extrapolated to 311 K using the Wilke correlation [28]. The result obtained was $D = 3.6 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$.

Figure 1 also displays the theoretical solution for Ω of (26)–(28) against the non-dimensional time, τ, for $S = 1.3$. The thermal diffusion factor, needed to calculate S, was extracted from the measured equilibrium separation data, according to the procedure in [22] ($\alpha = 3.1$). As can be seen, the agreement between theory and experiment is highly satisfactory. Conversely, the experimental data, which have been used to reconstruct both ordinary and non-Fickian diffusion coefficients, reproduce the starting values to within an uncertainty of 1%.

From the foregoing, we can conclude that the non-steady state-theory accounting for the forgotten effect and presented in this work correctly describes the transient behaviour of a liquid thermogravitational column. This conclusion opens up the possibility of determining ordinary diffusion coefficients and thermal diffusion factors from the separation runs, even for moderately high values of the separation parameter.

The situation for higher values of S merit some additional comments. In the first place, the present theory is *a priori* restricted to the case of low separations. This limitation prevents the use, in principle, of the solution of the PDE derived to interpret experiments with mixtures in states close to their critical lines, where one can expect high values of S and hence large separations. It seems clear that a more refined theory for high values of S must be developed. In any case, it can be concluded that the present work gives a good explanation of the current status in the field of standard TD practice. More effort, both theoretical and experimental in this field, would seem necessary. In this respect, we are now undertaking experiments with different mixtures, some of them close to the critical conditions.

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