Non-steady separation factor in a closed thermal diffusion column†

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Abstract. From the Majumdar solution a simple analytical expression is obtained for the non-steady separation factor of a binary isotopic mixture in a thermal diffusion column closed at both ends. The result represents the exact solution very well (better than 1 % for $\ln \bar{Q} \leqslant 2$), it is independent of the initial concentration and allows the value of the magnitude $\gamma = H^2/\mu(K_c + K_d)$ to be easily obtained from experiment.

The proposed formulation qualitatively interprets the principal characteristics of the experimental results of separation of ^{36}Ar–^{40}Ar at four temperatures. The influence of the non-active volumes present in the column is analysed and, by means of numerical calculus, an empirical expression is presented which gives a very good account of their influence on the determination of γ

1. Introduction

The transient behaviour of a closed thermal diffusion column is completely characterized by the value of the steady separation factor and the magnitude $H^2/\mu(K_c + K_d)$ where μ represents the mass of gas per unit column length and H, K_c, K_d are the transport coefficients used by Jones and Furry (1946) in their theory of these separation units.

To obtain the value of γ from experiment (Brun *et al* 1971) it is necessary to apply a formulation which adequately describes the transient behaviour of a closed column. This is obtained for the case of binary mixtures from the solution of a nonlinear partial differential equation. If restrictive hypotheses are put forward on the concentrations of the components of the mixture, it is possible to linearize the differential equation; the bibliography includes references to a number of solutions obtained by this procedure (Debye 1939, Bardeen 1940, Powers 1962). An exact procedure for linearizing the equation also exists due to Majumdar (1951), which allows solutions adequate to all the conditions of the initial concentration to be obtained. Finally, numerical solutions of the equation through finite differences methods have been laid out by the authors (Madariaga *et al* 1970).

These two procedures are inconvenient as the magnitude γ appears implicitly in the formulation. Also, because of the difficulty in handling Majumdar's analytical solutions, it is not clear how the transient operation of a thermal diffusion column depends on γ. These are the aspects which will be investigated in this paper.

2. The non-steady separation factor

The Majumdar solution gives the concentration distribution along the column as a function of time by means of the dimensionless variables

$$x = \frac{Hz}{K} \qquad t = \frac{H^2\tau}{\mu K}$$

where z is the longitudinal coordinate of the column and τ the time. For $z = L$, with L the length of the column, x represents the logarithm of the equilibrium separation factor $\bar{Q}$. In what follows, for simplicity we shall call $l = \ln \bar{Q}$ and $l(t) = \ln Q(t)$, $Q(t)$ being the non-steady separation factor.

By particularizing the result of Majumdar at the ends $x = 0$ and $x = 1$ of the column, the following expressions are obtained for the concentration of the light isotope in them:

$$c(l, t) = c_t + \exp(\sigma l) \sum_{n=1}^{\infty} (-1)^n A_n \exp[(-q_n^2 + \tfrac{1}{4})t]$$

$$c(0, t) = c_b + \sum_{n=1}^{\infty} A_n \exp[(-q_n^2 + \tfrac{1}{4})t] \tag{1}$$

where

$$A_n = 2q_n^2(\tfrac{1}{4} - \sigma^2)[1 - (-1)^n \exp(-\sigma l)]/l(q_n^2 + \tfrac{1}{4})(\sigma^2 + q_n^2)$$

$$q_n = n\pi/l \qquad \sigma = \tfrac{1}{2} - c_0,$$

c_t and c_b being the concentrations at the top and bottom ends of the column in the steady state and c_0 the initial concentration.

For the case in which l is small compared with unity these expressions are notably simplified. In this approximation the even-nth terms of the summations in (1) are small compared to the odd-nth ones. Besides,

$$q_n^2 \gg \tfrac{1}{4} > \sigma^2$$

and it is therefore possible to write (1) in the form:

$$c(l, t) = c_t - A \sum_{k=0}^{\infty} \exp(-q_k^2 t)q_k^{-2}$$

$$c(0, t) = c_b + A \sum_{k=0}^{\infty} \exp(-q_k^2 t)q_k^{-2} \tag{2}$$

with

$$A = \frac{4c_0(1 - c_0)}{l} \qquad q_k = \frac{(2k + 1)\pi}{l}.$$

Furthermore, if $l \ll 1$ we obtain from the first-order terms of the expansion of $c/(1 - c)$ about $c_0/(1 - c_0)$ the following expression for $l(t)$:

$$l(t) = \frac{c(l, t) - c(0, t)}{c_0(1 - c_0)}.$$

By substituting the values of $c(l, t)$ and $c(0, t)$ given by (2) in the above relationship, it follows that

$$l(t) = l - \frac{8}{l} \sum_{k=0}^{\infty} \exp(-q_k^2 t) q_k^{-2}. \tag{3}$$

This equation is valid for $l \ll 1$ with no restriction on c_0. In accordance with it, the non-steady separation factor results are independent of the initial concentration. This confirms previous experimental results (Madariaga *et al* 1970).

3. Study of the solution

We shall analyse the validity range of the solution (3) by comparing the relative differences that it presents with respect to the Majumdar solution. In figure 1 the results obtained for values of the initial concentration of $c_0 = 0.50$, 0.30 and 0.01 are shown graphically. As the differences between the $l(t)$ values cancel for zero time and for infinite time, the relative differences have been estimated for the value of t at which they are maximum. This value coincides approximately with the relaxation time corresponding to the first exponential term of the series (3), q_0^{-2}.
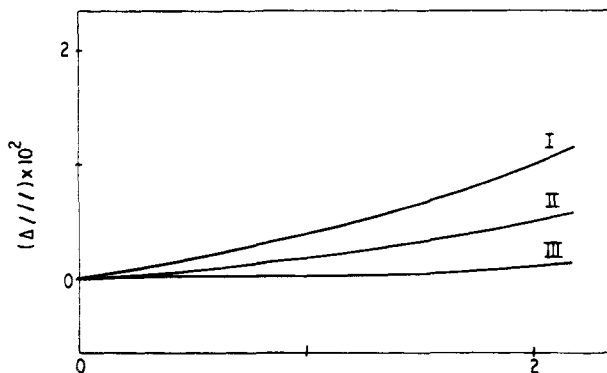

Figure 1. Maximum relative differences, estimated at $t = l^2/\pi^2$, between the separation factors of the approximation (3) and those obtained from the Majumdar solution. The curves (I), (II) and (III) correspond to $c_0 = 0.50$, 0.30 and 0.01 respectively.

The results obtained make evident the excellent form in which (3) represents the Majumdar solution. The differences between both are less that 0.5% for $l < 1$ and the approximation (3) can be used confidently for values as high as $l = 2$ with errors no greater than 1%. It must be remembered that these values of l are higher than those which represent in practice the columns of the multi-stage separation installations. That is, the approximation (3) seems to be able to cover all cases in usual practice with thermal diffusion columns.

As it is to be expected, all the solutions proposed by other authors through the linearization of the equation of approach to equilibrium by imposing restrictions on the values of c_0, lead, in the limit $l \ll 1$, to the same result (3) for $l(t)$. It clearly shows that the nonlinear terms of the equation are irrelevant as far as the separation factor is

concerned. It follows from the above discussion that it must be true even for considerable values of l.

As the range of validity of the solution (3) has already been established, it is possible to obtain from it a simpler expression. In effect, for values of t such as $\pi^2 t/l^2 > \frac{1}{3}$, a single term of the series (3) can be safely taken. These values of t correspond to values of $l(t) > l/3$. In this range the separation factor is given by

$$l(t) = l - \frac{8l}{\pi^2} \exp(-\pi^2 t/l^2)$$ (4)

and indicates a simple exponential increase with a relaxation time τ_r:

$$\tau_r = \frac{l^2}{\pi^2 \gamma}$$

which allows the value of γ to be obtained very simply from the experimental data.

4. Comparison with experiment

In obtaining the approximate expressions (3) and (4), at no time has the existence of non-active volumes at the ends of the column been taken into account. As these exist to a greater or lesser extent as an inevitable consequence of the construction, it is practically impossible, as a result, to have available adequate experimental data for comparison with theoretical results. To verify the general characteristics of the formulations obtained we shall, however, make use of the results obtained by Brun (1973) for the separation of the isotopic mixture ^{36}Ar–^{40}Ar. In table 1 the reduced separation factors obtained by Brun are shown at different times and for hot-wire temperatures $T_2 = 500$, 620, 750 and 1000 K. The cold-wall temperature was fixed at 301 K and in each case the data correspond to the optimum pressure. The characteristics of the column used in the experiments are given in the caption to table 1. The experimental arrangement and equilibrium data have been published elsewhere (Yarza *et al* 1970).

Figure 2 shows these experimental results in the plot of $-\ln(l - l(\tau)/l)$ against time and, as (4) predicts, it corresponds in fact to a lineal relationship. In table 1 are included the reduced values of γ ($\gamma_{0\,approx}$) deduced from the slope of each straight line adjusted by least squares. In the same table are also indicated the reduced values of γ ($\gamma_{0\,exact}$) calculated by Brun (1973) by means of the numerical solution of the differential equation of approach to equilibrium, with the boundary conditions corresponding to the existence of non-active volumes at the ends of the column.

Figure 2 provides evidence that the experimental data follow a behaviour qualitatively analogous to that predicted by (4). As it was to be expected, important quantitative differences exist due to the real existence of non-active spaces. For example, the straight lines of figure 2 present a common value for their coordinate at the origin, as predicted by (4), but this value differs from the expected theoretical one.

The values of γ obtained from (4) also differ from those calculated with the numerical solution. As shown in table 1 the relative differences $\Delta\gamma/\gamma_{approx}$ take the same values in all the operations, ie they are independent of l. Therefore, it seems adequate to interpret quantitatively these differences as functions of the ratios of the volumes of non-active spaces to the volume V of the column, $v_1/V, v_2/V$.

Table 1. The reduced logarithm of the separation factor at different times for $^{36}Ar-^{40}Ar$ The ln Q_0 and γ_0 are the reduced values of ln Q and γ. The length of the column used is 1018 cm; the active volume $V = 1345\,cm^3$; the non-active volumes are $v_1/V = 0.04$ at the top and $v_2/V = 0.1$ at the bottom.

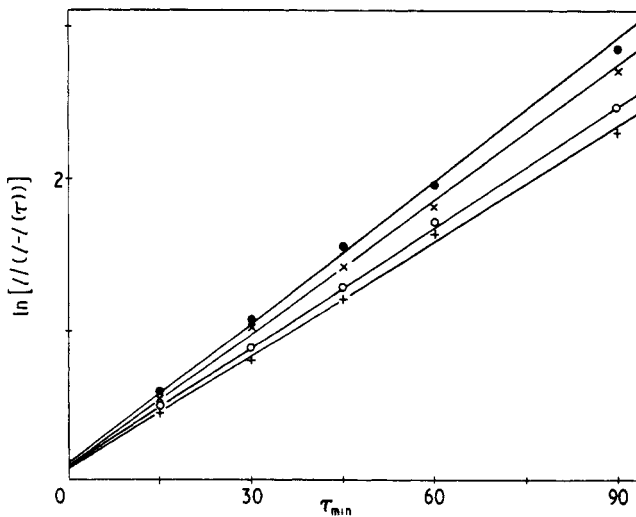| T_2 (K)	τ (min)	ln Q_0	$\gamma_{0\,approx}$ $(10^5\,s^{-1})$	$\gamma_{0\,exact}$ $(10^5\,s^{-1})$	$\Delta\gamma/\gamma_{approx}$
500	15	3.2			
	30	4.95			
	45	6.24			
	60	7.16			
	90	8.00			
	∞	8.88	335	425	0.27
600	15	5.67			
	30	8.50			
	45	10.5			
	60	11.9			
	90	13.3			
	∞	14.5	939	1211	0.29
750	15	8.2			
	30	12.9			
	45	15.2			
	60	16.8			
	90	18.7			
	∞	20.0	1931	2471	0.28
1000	15	13.0			
	30	19.6			
	45	23.6			
	60	25.8			
	90	28.3			
	∞	30.0	4590	5875	0.28

Figure 2. Adjustment of experimental results of $^{36}Ar-^{40}Ar$ by means of expression (4). Temperature of the hot wire: + $T_2 = 500K$; ○ $T_2 = 620\,K$; × $T_2 = 750\,K$; ● $T_2 = 1000\,K$.

The result, $\gamma_{approx} < \gamma_{exact}$, agrees with the physics of the problem. The existence of non-active volumes in a column effectively delays the equilibrium time of it, since its transport mechanics are characteristic of the active part and the time required to reach equilibrium is longer than in the ideal case. On treating the real process with a formulation that does not include those volumes, values of γ smaller than the real ones should be obtained, as indeed is the case.

Moreover, Mendia (1970) has pointed out that, when experimental data are dealt with using the numerical solution, for different values of the non-active spaces the corresponding values obtained for γ are given by

$$\frac{\Delta\gamma}{\gamma_{approx}} = 2\frac{\Delta v}{V}, \qquad \Delta v = v_1 + v_2.$$

The values of table 1 are in agreement with this relation, despite the high value of the non-active volume of our installation.

This result suggests that the relaxation time of a column with non-active spaces should be of the form

$$\tau_r = \frac{l^2}{\pi^2\gamma}\left(1 + 2\frac{\Delta v}{V}\right).$$

With this correction our formulation may be used reliably to obtain correct values of γ from experiment.

Acknowledgments

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