

THE VALIDITY OF THE HOFFMAN AND EMERY
EQUATION IN THERMAL DIFFUSION

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ABSTRACT

The most widely used equation in thermal diffusion is discussed in what concerns its range of validity. It is shown that when the separation curves are non-symmetrical with respect to the initial composition the error involved in the Hoffman and Emery equation when using a value of $t=0.3 t_r$ for the lower limit of the time, may be significantly larger than those predicted by their original authors. Experimental cases described in the literature are discussed on the light of previous analysis.

INTRODUCTION

Thermal diffusion techniques have been increasingly used not only to separate difficult mixtures but also as a means of testing kinetic theories of the liquid state⁽¹⁾. In many instances, though, discrepancies have been observed between the experimental results and the established phenomenological theories of the columns, leading sometimes to the introduction of "correction factors" into the phenomenological equations involved. Of these, one of the most widely used is the so-called Hoffman and Emery equation which relates the degree of separation between the two ends of the column to the physical variables affecting the process, including the time. Hoffman and Emery⁽²⁾ claim that the usual simplified form of their equation may be used with an error less than 1% for separation times greater than $0.3 t_r$, where t_r is a relaxation time that measures the rate of approach of equilibrium, or, roughly, the time required for the degree of separation to attain 70% of its steady-state value. This

lower limit of the time - $0.3 t_r$ - has, however, been questioned by Pinheiro⁽³⁾ who showed that the criteria to estimate this lower limit should also take into account the value of the parameter λ - the "separation potential" of the system. Otherwise, the error introduced in the simplified form of the Hoffman and Emery equation for $t=0.3 t_r$ could be much larger than 1%. Pinheiro discussed only symmetrical separations of equimolar mixtures. Yet, the vast majority of separations are non-symmetrical and non-equimolar, i.e., the value of $c_T - c_O$ is different from $c_O - c_B$ and $c_O \neq 0.5$ (the subscripts mean, respectively: - T = top, B = bottom O= feed compositions) which would apparently reinforce Pinheiro's comments. The present paper is, then, an attempt to shed further light into the subject by considering firstly different kinds of theoretical cases and discussing, finally, experimental situations reported in the literature.

THE HOFFMAN AND EMERY EQUATION

Derivation

In a batch thermogravitational column, the concentration profile along the column length as a function of the time is given by the following equation⁽⁴⁾

$$\mu \frac{\partial c}{\partial t} = -H(1-2c) \frac{\partial c}{\partial z} + K \frac{\partial^2 c}{\partial z^2} \quad (1)$$

with

$$\mu = \rho_M (2\omega) B \quad (2)$$

$$H = \frac{\alpha \beta \rho_M g B (\Delta T)^2 (2\omega)^3}{6! < T > \mu} \quad (3)$$

$$K = K_c + K_d \quad (4)$$

$$K_c = \frac{\beta^2 \rho_M g^2 B (\Delta T)^2 (2\omega)^7}{9! D \mu^2} \quad (5)$$

$$K_d = (2\omega) \rho_M D B \quad (6)$$

(see Nomenclature for physical meaning of the variables)

Equation (1) was linearized by Majundar⁽⁵⁾ who firstly introduced the dimensionless variables

$$Z = \frac{H z}{K} \quad (7)$$

$$\theta = \frac{H^2 t}{\mu K} \quad (8)$$

so that equation (1) becomes

$$\frac{\partial c}{\partial \theta} = - (1 - 2c) \frac{\partial c}{\partial Z} + \frac{\partial^2 c}{\partial Z^2} \quad (9)$$

and afterwards used the transformation

$$c(Z, \theta) = \frac{1}{2} + \frac{1}{\psi} \frac{\partial \psi}{\partial Z} \quad (10)$$

where

$$\psi = \psi(Z, \theta) \quad (11)$$

to obtain the following equation linearized in ψ :

$$\frac{\partial \psi}{\partial \theta} = \frac{\partial^2 \psi}{\partial Z^2} \quad (12)$$

Majundar integrated equation (10) using the Laplace Transform to get:

$$\begin{aligned} \psi(Z, \theta) = & \frac{e^{\theta/4} (e^{c_0 \lambda} - 1) e^{Z/2} + (e^\lambda - e^{c_0 \lambda}) e^{-Z/2}}{e^\lambda - 1} \\ & + \sum_{n=1}^{\infty} \frac{2 \frac{n \pi}{\lambda} (\frac{1}{4} - b_0^2) 1 - (-1)^n e^{-b_0 \lambda}}{(\frac{1}{4} + \frac{n^2 \pi^2}{\lambda^2}) (b_0^2 + \frac{n^2 \pi^2}{\lambda^2})} \\ & (\exp - \frac{n^2 \pi^2}{\lambda^2} \theta) \cdot \sin \frac{n \pi}{\lambda} \dots (13) \end{aligned}$$

where λ is the adimensional length of the column (for $Z = L$) and

$$b_0 = \frac{1}{2} - c_0 \quad (14)$$

Now, to determine the degree of separation Δ , i.e., the difference between the concentration at the top (c_T) and bottom (c_B) of the column, one evaluates $\partial \psi / \partial Z$ from equation (13) substitutes this value into equation (10) and obtains c_B for $Z=0$ and c_T for $Z=\lambda$.

In doing so, the degree of separation is obtained in terms of a sum of two terms, one of which involves a infinite series, as :-

$$\begin{aligned} \Delta = c_T - c_B = & (e^{c_0 \lambda} - 1)(e^\lambda - e^{c_0 \lambda}) + \\ & + (-1)^n e^{b_0 \lambda} - 1 \cdot \frac{2 \pi^2}{\lambda^3} (\frac{1}{4} - b_0^2) \cdot \\ & \sum_{n=1}^{\infty} \frac{1 - (-1)^n e^{-b_0 \lambda} n^2}{(\frac{1}{4} + \frac{n^2 \pi^2}{\lambda^2}) (b_0^2 + \frac{n^2 \pi^2}{\lambda^2})} \cdot \\ & \exp(-\frac{\frac{1}{4} + \frac{n^2 \pi^2}{\lambda^2}}{\frac{1}{4} + \frac{n^2 \pi^2}{\lambda^2}} \frac{t}{t_r}) \quad (15) \end{aligned}$$

where

$$t_r = \frac{\mu K}{H^2 (\frac{1}{4} + \frac{\pi^2}{\lambda^2})} \quad (16)$$

is the relaxation time.

Hoffman and Emery claim that for times greater than $0.3 t_r$ all the terms of the infinite series in equation (15) can be neglected with an error less than 1%. This rapid convergence enables the simplification of equation (15) to

$$\Delta = \Delta_{\infty} (1 - k_3 e^{-t/t_r}) \quad (17)$$

where Δ_{∞} is the steady-state degree of separation:

$$\Delta_{\infty} = \frac{(e^{c_o \lambda} - 1) (e^{\lambda} - e^{c_o \lambda})}{e^{c_o \lambda} (e^{\lambda} - 1)} \quad (18)$$

and k_3 is a coefficient given by

$$k_3 = \frac{2 c_o (1 - c_o) \pi^2 (1 + c_o^{-b_o \lambda}) (e^{\lambda} - 1) (e^{c_o \lambda} + e^{\lambda/2})}{\lambda^3 (b_o^2 + \frac{\pi^2}{\lambda^2}) (-\frac{1}{4} + \frac{\pi^2}{\lambda^2}) (e^{c_o \lambda} - 1) (e^{\lambda} - e^{c_o \lambda})}$$

$$\approx \frac{8}{\pi^2} \quad (19)$$

Equation (17) is the so-called Hoffman and Emery equation.

Validity

In obtaining equation (17), Hoffman and Emery introduced the limitation of $t > 0.3 t_r$ so that, and with an error less than 1% as claimed, a simplified form for the degree of separation could be attained. Hoffman and Emery have based their criterium on the analysis of the two most important factors concerning the convergence of the infinite series in equation (15) :- n and t/t_r . The other parameters involved, b_o and λ were neglected in the analysis.

In what concerns b_o , it may be easily seen that, in fact, its value is of no importance for the series convergence. Yet, for λ the same is not true since it affects remarkably the relative magnitude of the terms of the series.

To define new criteria for the lower limit of validity of the Hoffman and Emery equation it is necessary to analyse further the infinite series involved in equation (15). In doing so it may be noti-

ced that

- Regardless of the value of c_o , the even terms are positive and the odd terms are negative. Thus, the series may be thought as composed of two sub-series, one being positive (n even) and the other negative (n odd).
- Both sub-series are rapidly convergent with n
- The absolute values of the negative sub-series are much larger than those involved in the positive sub-series and therefore the convergence of the series may be studied with relation solely to the odd terms

In neglecting all the terms beyond the first, an error is implicitly introduced, which may be defined as

$$\epsilon (\%) = \frac{\sum_{n=2}^{\infty} f(n)}{\sum_{n=1}^{\infty} f(n)} \times 100 \quad (20)$$

where $f(n)$ goes for the argument of the infinite series.

Representing the i^{th} -term of the series as $f_i(n)$ and noting that for n -even and $n > 3$ the terms become negligible as compared to the first term, equation (20) becomes

$$\epsilon (\%) = \frac{f_3(n)}{f_1(n) + f_3(n)} \times 100 \quad (21)$$

But, since $f_1(n) \gg f_3(n)$ one may simply write

$$\epsilon (\%) = \frac{f_3(n)}{f_1(n)} \times 100 \quad (22)$$

ϵ is therefore a measure of the error involved in neglecting all the terms of the series beyond the first. From equation (15) it is seen that its value will depend strongly on t/t_r and λ .

Now, the influence of λ may be analysed in two different ways, either

a) Making $\epsilon = 1\%$ and evaluating t/t_r vs. λ

or

b) Making $t/t_r = 0.3$ and evaluating ϵ vs. λ

In this work an attempt is made to tackle both approaches since both are of interest:- Case b) to give an idea of the errors possibly committed in the past and case a) to provide some guide-lines for the future.

SYMMETRICAL SEPARATIONS

Symmetrical separations occur when the separation attained in the upper half of the thermogravitational column equals the separation in the lower half, i.e.,

$$c_T - c_o = c_o - c_B = \frac{\Delta}{2} \quad (23)$$

Symmetrical separations have been reported for several hydrocarbon mixtures⁽⁶⁾ for which the dependence of Δ on the composition is a parabola. For symmetrical separations the value of λ associated with a certain degree of separation may be obtained theoretically either through equation (18) or more accurately using its definition⁽⁴⁾

$$\lambda = \ln \frac{c_T (1-c_B)}{c_B (1-c_T)} \quad (24)$$

where the subscript ∞ indicates a steady-state condition, i.e., $\Delta_\infty = C_T - C_{B\infty}$

The results obtained using equation (24) are shown in Fig 1 for several values of the initial composition c_o .

(Note that the curves obtained for c_o are exactly the same as obtained for $1-c_o$)

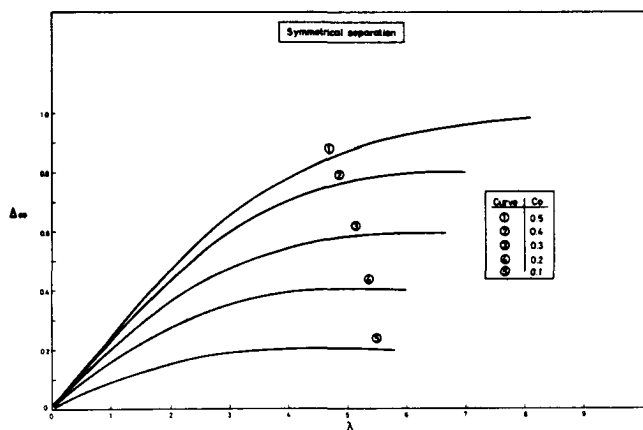


FIGURE 1 - The relationship between Δ_∞ and λ for various values of feed composition in symmetrical separations.

It is seen that regardless of the values of c_o or Δ_∞ involved the values of λ may vary from zero to infinite, although in practice they remain relatively small.

In fact, equation (24) clearly shows that λ only reaches high values if one of the extreme compositions (c_T or c_B) approaches either zero or unity.

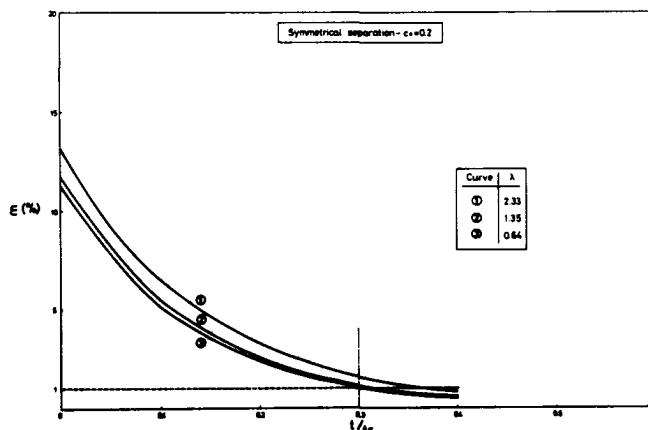


FIGURE 2 - ϵ vs. t/t_r for different values of λ for $c_o = 0.2$ and symmetrical separation

Thus if, for instance, $c_B \sim 0$, then $c_T \sim 2 c_o$ and equation (24) becomes

$$\lambda = \ln \frac{2 c_o / (1-2 c_o)}{c_B} \quad (25)$$

clearly showing that when c_B approaches zero, λ approaches infinite.

One may also conclude that when $c_o = 0.5$ equation (24) simplifies to

$$\lambda = 2 \ln \frac{c_T}{c_B} \quad (26)$$

It is now possible for different values of the initial composition c_o , to evaluate

a) ϵ vs. λ for $t/t_r = 0.3$

and

b) t/t_r vs. λ for $\epsilon = 1\%$

$$c_T - c_O \neq c_O - c_B$$

are, by far, the most common case in practice, though in many instances the "degree of asymmetry" (7) is small.

Theoretical discussion

For non-symmetrical separations it is virtually impossible to use equation (24) to evaluate the value of λ associated with a given value of Δ_∞ mainly because there are several pairs of values (c_T, c_B) that may satisfy the condition $\Delta_\infty = c_T - c_B$.

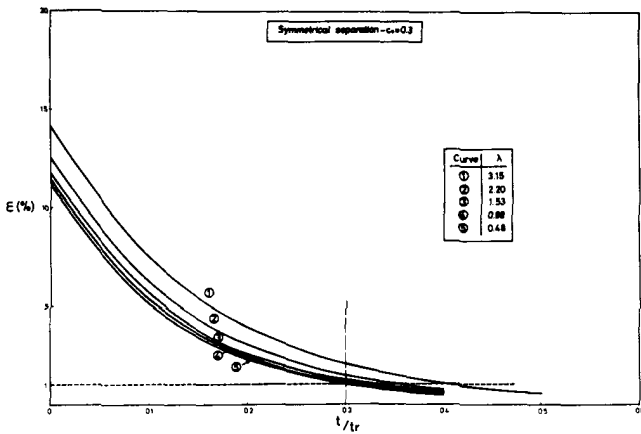


FIGURE 3 - ϵ vs. t/t_r for different values of λ for $c_0 = 0.3$ and symmetrical separation

The results obtained are presented graphically in Figs. 2 to 4 where it may be seen that in the vast majority of cases (for which λ is not large, i. e. $\lambda < 5$ say), the error ϵ although larger than 1%, is comparatively small and most probably smaller than the usual experimental error.

One may then conclude, that the Hoffman and Emery equation represents fairly accurately the symmetrical separations.

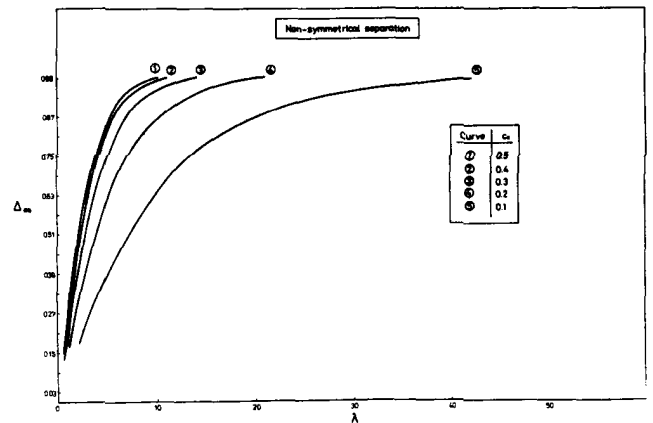


FIGURE 5 - The relationship between Δ_∞ and λ for various values of feed composition in non-symmetrical separations

To overcome this difficulty one may use equation (18) to determine the dependence of λ on Δ_∞ for various values of c_0 . The consequent results are shown in Fig. 5, where it may be noticed that (contrary to what happened with the symmetrical situation) the values of λ may reach relatively high values, even though the end compositions may be far from zero or unity.

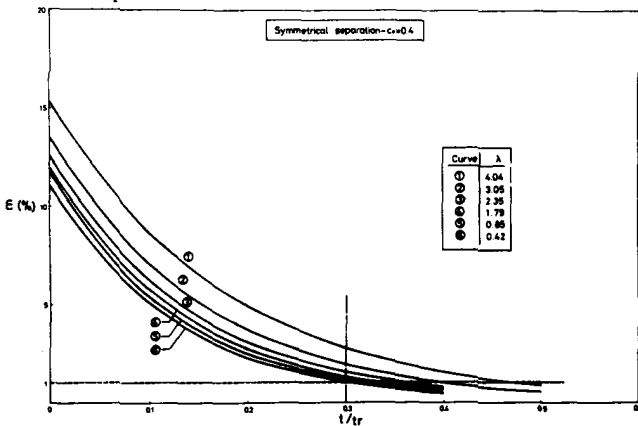


FIGURE 4 - ϵ vs. t/t_r for different values of λ for $c_0 = 0.4$ and symmetrical separation

NON - SYMMETRICAL SEPARATIONS

Non-symmetrical separations, i.e., when

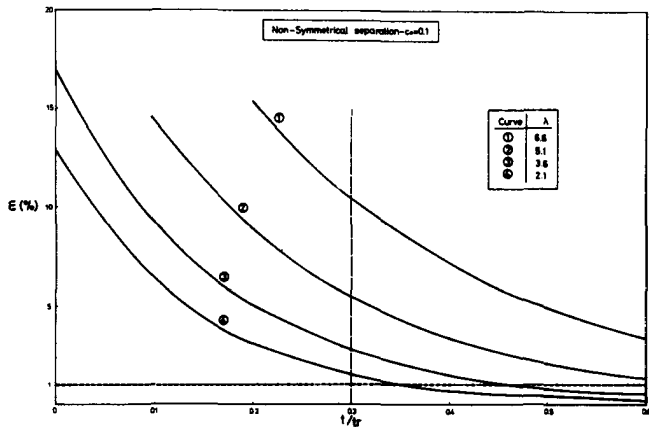


FIGURE 6 - ϵ vs. t/t_r for different values of λ for $c_0 = 0.1$ and non-symmetrical separation

Not surprisingly the curves of ϵ vs. t/t_r for different values of λ and c_0 (Figs. 6 to 10) show a quite distinct behavior. In fact, for $t/t_r = 0.3$ the corresponding values of ϵ are larger than 1% even for moderate values of λ (or, which is the same, $\epsilon = 1\%$ only for t/t_r greater than 0.3).

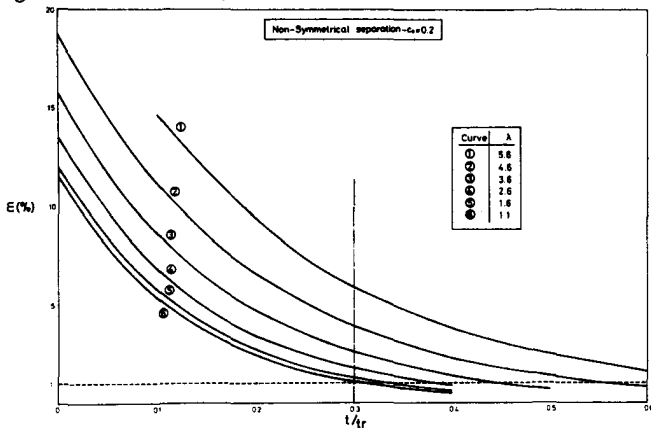


FIGURE 7 - ϵ vs. t/t_r for different values of λ for $c_0 = 0.2$ and non-symmetrical separation

Experimental cases

It is interesting to analyse the range of values of λ and c_0 that have been involved in experimental separations reported in the literature in order to estimate (with the help of Figs. 5 to

10) the implicit values of ϵ involved in such cases.

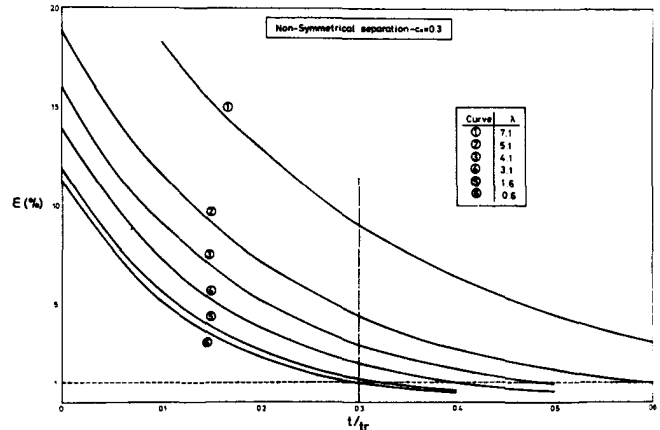


FIGURE 8 - ϵ vs. t/t_r for different values of λ for $c_0 = 0.3$ and non-symmetrical separation

A summary of this analysis is presented in Table 1 where one may clearly note that the values of ϵ for $t/t_r = 0.3$ is, in some instances, of the order of 10% or more. This may explain some of the discrepancies that have been reported when attempting to the experimental results to the Hoffman and Emery equation.

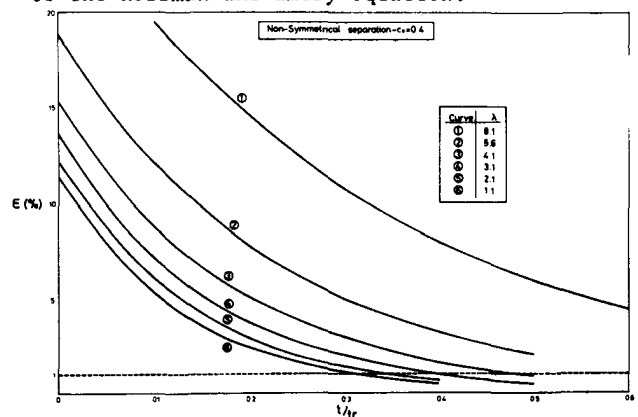


FIGURE 9 - ϵ vs. t/t_r for different values of λ for $c_0 = 0.4$ and non-symmetrical separation

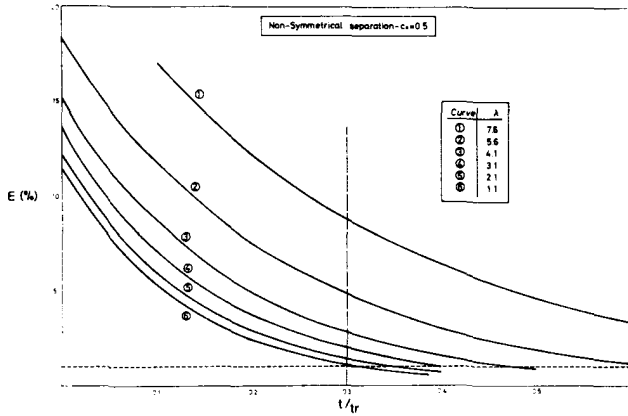


FIGURE 10 - ϵ vs. t/t_r for different values of λ for $c_o = 0.5$ and non-symmetrical separation

CONCLUSIONS

The use of the Hoffman and Emery equation to correlate the experimental separation vs. time curve involves an error of the order of 1% for $t/t_r = 0.3$ when the separation is symmetrical. For non-symmetrical separations, the error involved for $t/t_r = 0.3$ is generally quarter than 1%, its value increasing with the value of λ and with the "degree of assymetry" of the curve relating the evolution of c_T and c_B with the time. It is therefore strongly recomended that for values of λ greater than about 4-5 an inspection of the lower limit of time is carried out before using the Hoffman and Emery equation to correlate the experimental data.

NOTATION

- $b_o = 1/2 - c_o$
- B column dimension in the horizontal non-thermogravitational direction
- c molar fraction of the reference component
- c_o feed composition
- c_T top composition
- c_B botton composition
- D ordinary diffusion coefficient
- g accelaration of gravity

- H thermogravitational transport coefficient
- k_3 coefficient defined by eq. (19)
- K transport coefficient associated with the parasitic remixing
- K_C transport coefficient associated with the convective remixing
- K_d transport coefficient associated with the ordinary back-diffusion
- L column length
- t time
- t_r relaxation time
- T absolute temperature
- ΔT temperature difference between the column walls
- $\langle T \rangle$ average absolute temperature

Greek Letters

- α thermal diffusion factor
- β temperature coefficient of density
- Δ degree of separation = $C_T - C_B$
- Δ_∞ equilibrium degree of separation
- ϵ truncation error defined by eq. (20)
- λ dimensionless length = $504 \times D \xi L / \beta g \Delta T Q \omega$ ⁴
- μ number of moles per unit of column length
- ζ viscosity
- ω one-half of the distance between the hot and cold walls
- ρ_M molar concentration of the solution

T A B L E I

Mixture	Ref ^{ce}	c _o	λ	$\epsilon \leq 1\%$ t/t _r	t/t _r = 0.3 $\epsilon \%$
n-dodecane/ carbon tetrachloride	(8)	0.4846	7.65	0.98	9.02
n-heptane/cetane	(9)	0.6659	2.31	0.36	1.52
n-octane/decane	(9)	0.5459	1.37	0.32	1.17
iso-octane/n-octane	(9)	0.4961	0.73	0.31	1.05
n-heptane/triptane	(9)	0.4977	5.14	0.59	4.10
n-hexane/carbon tetrachloride	(8)	0.6599	13.74	2.95	39.14
n-heptane/carbon tetrachloride	(8)	0.6346	12.28	2.31	28.30
n-octane/carbon tetrachloride	(8)	0.6133	8.25	1.13	11.34
cumene/cetene	(10)	0.324	0.63	0.31	1.04
cumene/cetene	(10)	0.324	0.89	0.31	1.08
cumene/cetene	(10)	0.324	1.09	0.31	1.11
cumene/cetene	(10)	0.324	1.17	0.32	1.13
cumene/cetene	(10)	0.324	1.20	0.32	1.14
cumene/cetene	(10)	0.317	0.77	0.31	1.06
cumene/cetene	(10)	0.317	1.11	0.31	1.12
cumene/cetene	(10)	0.317	1.85	0.34	1.33
cumene/cetene	(10)	0.317	2.32	0.36	1.53
cumene/cetene	(10)	0.317	2.41	0.37	1.58
cumene/cetene	(10)	0.317	3.14	0.41	2.04
cumene/cetene	(10)	0.317	3.30	0.42	2.17
benzene/n-heptane	(8)	0.484	5.71	0.67	5.01
toluene/n-hexane	(8)	0.5268	4.60	0.53	3.38
o-xylene/n-hexane	(8)	0.5816	5.33	0.62	4.45
benzene/carbon tetrachloride	(8)	0.6638	9.36	1.43	16.44
benzene/carbon tetrachloride	(9)	0.5211	6.09	0.72	5.67
benzyl alcohol/ethylenediol	(9)	0.7035	1.20	0.32	1.14
cumene/methyl-naphtalene	(9)	0.5028	1.46	0.32	1.19
Folvne/chlorobenzene	(9)	0.4974	1.11	0.31	1.11
β -methylnaphtalene/ α -methyl- naphtalene	(9)	0.4936	0.52	0.30	1.03
cetane/benzene	(9)	0.7670	1.48	0.33	1.22
cetane/toluene	(9)	0.7332	0.61	0.31	1.04

T A B L E I (Cont.)

Mixture	Ref ^{ce}	c _o	λ	ε ≤ 1% t/t _r	t/t _r = 0.3 ε %
cetane/m-xylene	(9)	0.7043	0.73	0.31	1.06
n-heptane/benzene	(9)	0.6228	6.42	0.78	6.64
n-heptane/methylcyclohexane	(9)	0.5349	5.16	0.59	4.14
cyclohexane/carbon tetrachlo ride	(9)	0.6471	7.96	1.08	10.95
cyclohexane/n-hexane	(8)	0.4759	7.95	1.04	9.78

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