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Correction to the Furry–Jones–Onsager Theory of the Thermal-Diffusion Column

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ABSTRACT

The famous theory of the thermal diffusion column derived by Furry, Jones, and Onsager is based on the implicit premise that the mass of a component in a binary mixture is given by the product between the mass of the whole mixture and the molar concentration of that component. The premise is strictly correct only if $m_2/m_1 = 1$, where m_1 and m_2 are the molecular masses of the two components. Here a corrected theory is derived, which is valid for any value of the ratio m_2/m_1. Comparison of the original and corrected theory shows that for the case of a column operated at total reflux, the two theories give identical results. However, for productive operations the original Furry–Jones–Onsager theory can produce deviated data. The magnitude of the deviation depends on the ratio m_2/m_1. It is: a) null for $m_2/m_1 = 1$, b) small for heavy isotopes (up to 0.86% for a ${}^{235}UF_6$–${}^{238}UF_6$ mixture), c) significant for light isotopes

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(up to 33% for a ^{3}He–^{4}He mixture), and d) very high for $m_2/m_1 \gg 1$ (absurd results are obtained for $m_2/m_1 = 10$).

Key Words: Thermal-diffusion column; Isotope separation; Helium 3.

INTRODUCTION

The separation column by thermal-diffusion (TD) was discovered in 1938 by Clusius and Dickel.[1] Soon after that, Furry, Jones, and Onsager (FJO)[2–4] derived their famous theory of the TD column. From then until now many publications have been dedicated to this subject (see the bibliography[5] and the monograph[6] by Văsaru et al.,) and the literature cited in later articles.[7–14]) The TD column has been used to separate the components from a mixture [especially isotope separation[6]] and to determine the thermal diffusion coefficient (Soret effect).[6,14] As a separation process, the TD column has a low thermodynamic efficiency; still it has certain advantages and is preferred in many applications.[7–10] For example the TD column is used for production of noble gas and oxygen isotopes.

In a previous paper[15] I developed an overall axiomatic theory of the separation column and, as an application, I derived an independent theory of the TD column. Recently I observed that there is a discrepancy between my results and those of FJO. A careful analysis revealed that the discrepancy is due to a premise that is implicitly used in the FJO theory. It is assumed that: *the mass of a component in a binary mixture is given by the product between the mass of the whole mixture and the molar concentration of that component*. This is strictly correct only if $m_2/m_1 = 1$, where m_1 and m_2 are the molecular masses of the two components. This FJO premise cannot be considered as a simplifying assumption because it is not necessary and not used for the derivation of the theory.

In this paper a corrected theory is rebuilt that is valid for any value of the ratio m_2/m_1. With few exceptions, the FJO derivation procedure is followed. A comparison between the corrected and original theory is done, and the effects of the FJO premise in several applications are evaluated.

REBUILDING THE CORRECTED THEORY

Bulk Velocity and Flux

A series of notations introduced in Refs.[2–4] have been used in the TD literature. Here I use a good part of them, but introduce additional ones, as they are necessary in the corrected theory and discussion. In addition, I mark with an asterisk the symbols that represent expressions affected by the FJO premise. The symbols without asterisk are used in the corrected theory.

Consider a binary mixture and let $\boldsymbol{v}_i$ denote the local mean velocity of the ith species with respect to stationary coordinate axes ($i = 1$ is for the lighter component). The local molar average velocity is defined as $\boldsymbol{v} = c_1\boldsymbol{v}_1 + c_2\boldsymbol{v}_2$, where c_i is the mole fraction of species i. Similarly, the local mass average velocity is defined as $\boldsymbol{v}_m = w_1\boldsymbol{v}_1 + w_2\boldsymbol{v}_2$, where w_i is the mass fraction of species i.

The mass flux of species i with respect to stationary coordinate axes is defined by:

$$\boldsymbol{J}_i = m_i n_i \boldsymbol{v}_i = m_i n c_i \boldsymbol{v}_i \tag{1}$$

where m_i is the molecular mass of species i ($m_1 \leq m_2$), n_i is the molar density of species i, and $n = n_1 + n_2$ is the total molar density.

The equation of diffusion may be written as:

$$c_1(\boldsymbol{v}_1 - \boldsymbol{v}) = -D(\nabla c_1 - \alpha c_1 c_2 \nabla \ln T) \tag{2}$$

In this equation, $\boldsymbol{v}_1 - \boldsymbol{v}$ is the diffusion velocity of species 1 with respect to $\boldsymbol{v}$, D is the binary diffusion coefficient, and α is the thermal diffusion constant.

The form of the diffusion equation depends on the definition of D and α. These coefficients may be defined in numerous ways.[16] Fortunately, a unique definition is used in the TD literature and in important reference books with more general subjects.[17,18] I have adopted the same definition in writing Eq. (2).

From Eqs. (1) and (2), and by algebraic manipulation, the mass flux of species 1 can be written in the forms:

$$\boldsymbol{J}_1 = m_1 n c_1 \boldsymbol{v} - m_1 n D(\nabla c_1 - \alpha c_1 c_2 \nabla \ln T) \tag{3a}$$

$$= \rho w_1 \boldsymbol{v}_m - \rho D(\nabla w_1 - \alpha w_1 w_2 \nabla \ln T) \tag{3b}$$

$$= m_1 n c_1 \boldsymbol{v}_m - \frac{n^2 m_1 m_2}{\rho} D(\nabla c_1 - \alpha c_1 c_2 \nabla \ln T) \tag{3c}$$

where $\rho = m_1 n_1 + m_2 n_2$ is the mass density. In Eq. (3a) $\boldsymbol{J}_1$ is expressed in *molecular–molecular* terms: the *molecular* average velocity $\boldsymbol{v}$ is used for bulk velocity and *mole* fraction c_1 for concentration. In Eq. (3b) $\boldsymbol{J}_1$ is expressed in *mass–mass* terms: the *mass* average velocity $\boldsymbol{v}_m$ is used for bulk velocity and the *mass* fraction w_1 for concentration. In Eq. (3c) $\boldsymbol{J}_1$ is expressed in hybrid *mass-molecular* terms: $\boldsymbol{v}_m$ is used for bulk velocity and c_1 for concentration.

In the FJO theory the equation for flux of species 1 is [Eq. (10) in Ref.[2]]:

$$\boldsymbol{J}_1^* = \rho[\boldsymbol{v}c_1 + D(-\nabla c_1 + \alpha c_1 c_2 \nabla \ln T)] \tag{3a*}$$

This is a *molecular–molecular* variant of the flux and should be compared with Eq. (3a). The essential difference should be noted: The flux $\boldsymbol{J}_1$ contains the convective term $m_1 n\boldsymbol{v}c_1$ in which $m_1 nc_1$ represents the mass density of species 1. The corresponding term in $\boldsymbol{J}_1^*$ is $\rho\boldsymbol{v}c_1$ in which, according to the curious FJO premise, ρc_1 stands for mass density of species 1. The densities $m_1 nc_1$ and ρc_1 coincide only if $m_1 = m_2$.

The FJO theory was developed for the stationary state of the TD column for which the fluxes satisfy the conditions:

$$\nabla \boldsymbol{J}_i = 0 \tag{4}$$

From Eqs. (3a) and (3a*) one obtains the relation between the correct and wrong fluxes:

$$\boldsymbol{J}_1^* = \left[\frac{m_2}{m_1} + \left(1 - \frac{m_2}{m_1}\right)c_1\right]\boldsymbol{J}_1 \tag{5}$$

From Eqs. (4) and (5) it follows:

$$\nabla \boldsymbol{J}_1^* = (1 - m_2/m_1)(\nabla c_1)\boldsymbol{J}_1$$

One can see that if $m_2 \neq m_1$, then generally $\nabla \boldsymbol{J}_1^* \neq 0$. However, the FJO theory was derived supposing that $\nabla \boldsymbol{J}_1^* = 0$.

Corrected Cylindrical Case

A cylindrical TD column consists of an annular space between two vertical, coaxial, right-circular cylindrical walls. The inner wall, of radius r_2, is of temperature T_2; the outer wall, of radius r_1, is at temperature T_1; $r_2 < r_1$ and usually $T_1 < T_2$. Let r be the radial ($r_2 < r < r_1$) and z the longitudinal coordinate.

The FJO theory is derived in molecular–molecular terms: the bulk velocity is described by the molecular average velocity $\boldsymbol{v}$ and the flux is given by Eq. (3a).

A main assumption of the FJO theory is that the thermal diffusion constant α is small. This condition is well fulfilled as, according to the Chapman–Enskog treatment,[17] thermal diffusion is a second-order phenomenon, in contradiction to diffusion, which is a first-order phenomenon.

Another assumption is that the velocity $\boldsymbol{v}$ is entirely in the vertical direction and independent of z, that is:

$$\boldsymbol{v} = \boldsymbol{v}(r), \quad v_r = 0, \quad v_z = v \tag{6}$$

This condition is well fulfilled at least for the mixture of ideal gases.

The two assumptions induce the mathematical simplifications that are made in what follows.

When the temperature gradient is determined by thermal conduction alone, the temperature field is described by:

$$2\pi Q_1 = 2\pi r\lambda(-dT/dr) \tag{7a}$$

$$Q_1 \log(r_1/r_2) = \int_{T_1}^{T_2} \lambda dT \tag{7b}$$

$$(\partial/\partial r) = -(Q_1/r\lambda)(\partial/\partial T) \tag{7c}$$

In these equations $2\pi Q_1$ is the radial heat flow per unit length of column, λ is the thermal conductivity, and T is the temperature.

Taking into account Eq. (6), the hydrodynamic equation in cylindrical coordinates is[3]:

$$r^{-1}(\partial/\partial r)r\eta(\partial v/\partial r) = (dp/dz) + \rho g \tag{8}$$

where η is the viscosity, p is the pressure, and g is the acceleration of gravity. Substitution from Eq. (7c) gives:

$$(Q_1^2/\lambda r^2)(d/dT)(\eta/\lambda)(dv/dT) = (dp/dz) + \rho g \tag{9}$$

with the boundary conditions:

$$v(T_1) = v(T_2) = 0 \tag{10}$$

Equations (7)–(10) are the very equations (106)–(109) of Ref.[3]. The difference begins now, with the expression for the mass flux of species 1: instead of the FJO flux $\boldsymbol{J}_1^*$ given by Eq. (3a*), the correct flux $\boldsymbol{J}_1$ given by Eq. (3a) is used.

The argument in Ref.[2], Eqs. (12)–(26), or in Ref.[3], Eqs. (112)–(126) is approximatively followed below.

The flux $\boldsymbol{J}_1$ has the components:

$$J_{1z} = m_1 n\left(c_1 v - D\frac{\partial c_1}{\partial z}\right) \tag{11a}$$

$$J_{1r} = -m_1 n\left(\frac{\partial c_1}{\partial r} - \alpha c_1 c_2 \frac{\partial(\ln T)}{\partial r}\right) \tag{11b}$$

Because the walls are impenetrable, the flux component J_{1r} satisfies the conditions:

$$J_{1r}(T_2, z) = J_{1r}(T_1, z) = 0 \tag{12}$$

Substituting the flux Eq. (3a) in Eq. (4) and taking into account Eq. (7c) one obtains:

$$\frac{\partial}{\partial r}\left[\frac{nD}{\lambda}\left(\frac{\partial c_1}{\partial T} - \frac{\alpha c_1 c_2}{T}\right)\right] = \frac{\lambda n r^2}{Q_1^2}\left(v\frac{\partial c_1}{\partial z} - \frac{\partial^2 c_1}{\partial z^2}\right) \tag{13}$$

The term containing $(\partial^2 c_1/\partial z^2)$ is of second order and may be neglected.[15] Then, the following equation is used:

$$\frac{\partial}{\partial T}\left[\frac{nD}{\lambda}\left(\frac{\partial c_1}{\partial T} - \frac{\alpha c_1 c_2}{T}\right)\right] = \frac{\lambda n r^2 v}{Q_1^2}\frac{\partial c_1}{\partial z} \tag{14}$$

As in Ref.[2], the function $G(z, T)$ is introduced, which, in our case, is defined by:

$$\frac{\partial c_1}{\partial z} G(z, T) = \frac{\lambda Q_1^3}{m_1 n D} r J_{1r} \tag{15a}$$

$$= Q_1^4\left(\frac{\partial c_1}{\partial T} - \frac{\alpha c_1 c_2}{T}\right) \tag{15b}$$

Then Eq. (14) can be written:

$$\frac{\partial}{\partial T}\left[\frac{nD}{\lambda}\frac{\partial c_1}{\partial z} G(z, T)\right] = Q_1^2 \lambda n r^2 v \frac{\partial c_1}{\partial z} \tag{16}$$

As in Ref.[2], the assumption $(\partial^2 c_1/\partial z \partial T) = 0$ is made, that is $(\partial c_1/\partial z)$ does not depend on T. This assumption has two important consequences: G is a function of T only and the total molar transport through the column is zero.

Taking into account Eq. (11a), the mass transport of species 1 through the column is:

$$\tilde{\tau}_1 = 2\pi\int_{r_2}^{r_1} J_{1r} r\,dr = \frac{2\pi}{Q_1}\int_{T_1}^{T_2} \lambda J_{1z} r^2\,dT \tag{17a}$$

$$= \frac{2\pi m_1}{Q_1}\int_{T_1}^{T_2} \lambda n r^2 c_1 v\,dT - \frac{2\pi m_1}{Q_1}\int_{T_1}^{T_2} \lambda n r^2 D \frac{\partial c_1}{\partial z}\,dT \tag{17b}$$

Equation (4) implies that $\tilde{\tau}_1$ does not depend on z; thus the derivation of Eq. (17b) gives:

$$\frac{d\tilde{\tau}_1}{dz} = \frac{\partial c_1}{\partial z}\frac{2\pi m_1}{Q_1}\int_{T_1}^{T_2} \lambda n v r^2\, dT = \frac{\partial c_1}{\partial z} m_1 \hat{\tau} = 0 \tag{18}$$

where the term containing $(\partial^2 c_1/\partial z^2)$ was neglected as it is of second order and:

$$\hat{\tau} = 2\pi\int_{r_2}^{r_1} nvrdr = \frac{2\pi}{Q_1}\int_{T_1}^{T_2} \lambda n v r^2\, dT$$

is the total molar transport through the column. Since $(\partial c_1/\partial z)$ is not identically zero, the total molar transport must vanish at $\hat{\tau} = 0$. (The contradiction should be noted: in the original FJO theory the total *mass* transport must vanish.)

Equations (19)–(22) are derived in the same manner as the corresponding Eqs. (15)–(18) of Ref.[2].

By Eqs. (15a) and (12), we have:

$$G(z, T_1) = G(z, T_2) = 0 \tag{19}$$

The factor $(\partial c_1/\partial z)$ on each side of Eq. (16) cancels, and since the only remaining quantity that can be a function of z is $G(z, T)$, one finds, on integrating Eq. (16) that $(nD/\lambda)G$ can depend on z only through an additive function of z. Then since Eq. (19) holds identically in z, we have:

$$G(z, T) = G(T)$$

Concealing $\partial c_1/\partial z$ in Eq. (16), and solving for v, one obtains:

$$v(T) = \frac{1}{\lambda n Q_1^2 r^2}\frac{d}{dT}\left(\frac{nD}{\lambda}G(T)\right) \tag{21}$$

Then from Eqs. (21), (16), and (10):

$$G'(T_1) = G'(T_2) = 0 \tag{22}$$

If Eq. (21) is substituted in Eq. (9), followed by differentiation with respect to T, the differential equation for $G(T)$ is obtained:

$$\frac{d}{dT}\frac{1}{\lambda r^2}\frac{d}{dT}\frac{\eta}{\lambda}\frac{d}{dT}\frac{1}{\lambda n r^2}\frac{d}{dT}\left(\frac{nD}{\lambda}G(T)\right) = g\frac{d\rho}{dT} \tag{23}$$

This equation, with the boundary conditions Eq. (19) and Eq. (22), completely determines the function $G(T)$. Using this function one can obtain an expression for the mass transport of species one $\tilde{\tau}_1$.

By substituting v, given by Eq. (21), in Eq. (17b) and partial integration, one obtains:

$$\tilde{\tau}_1 = -\frac{2\pi m_1}{Q_1^3}\int_{T_1}^{T_2}\frac{nD}{\lambda}G\frac{\partial c_1}{\partial T}\,dT - \frac{2\pi m_1}{Q_1}\int_{T_1}^{T_2}\lambda n r^2 D\frac{\partial c_1}{\partial z}\,dT \tag{24}$$

Solving Eq. (15b) for $\partial c_1/\partial T$, and substituting it in Eq. (24):

$$\tilde{\tau}_1 = -\left(\frac{2\pi m_1}{Q_1^3}\int_{T_1}^{T_2}\frac{\alpha n D}{\lambda T}G\,dT\right)c_1c_2 - \left(\frac{2\pi m_1}{Q_1^7}\int_{T_1}^{T_2}\frac{nD}{\lambda}G^2\,dT\right) \times\frac{dc_1}{dz} - \left(\frac{2\pi m_1}{Q_1}\int_{T_1}^{T_2}\lambda n r^2 D\,dT\right)\frac{dc_1}{dz} \tag{25}$$

Remember that the mass transport given by Eq. (25) was obtained for the case when the total molar transport is zero, $\hat{\tau} = 0$. By the arguments presented in Ref.[2], in the general case when a small total transport through the column exists, that is $\hat{\tau} \neq 0$, the mass transport of species one is obtained by simply adding to Eq. (25) a supplementary term:

$$\tau_1 = \tilde{\tau}_1 + m_1\hat{\tau}c_1 \tag{26}$$

In conclusion, the mass transport of species one through the TD column is given by:

$$\tau_1 = m_1\hat{\tau}c_1 + Hc_1(1 - c_1) - (K_c + K_d)\frac{dc_1}{dz} \tag{27a}$$

where

$$H = -\frac{2\pi m_1}{Q_1^3}\int_{T_1}^{T_2}\frac{\alpha n D}{\lambda T}G\,dT \tag{27b}$$

$$K_c = \frac{2\pi m_1}{Q_1^7}\int_{T_1}^{T_2}\frac{nD}{\lambda}G^2\,dT \tag{27c}$$

$$K_d = \frac{2\pi m_1}{Q_1}\int_{T_1}^{T_2}\lambda n r^2 D\,dT \tag{27d}$$

and $G = G(T)$ is the solution of:

$$\frac{d}{dT}\frac{1}{\lambda r^2}\frac{d}{dT}\frac{\eta}{\lambda}\frac{d}{dT}\frac{1}{\lambda n r^2}\frac{d}{dT}\left(\frac{nD}{\lambda}G(T)\right) = g\frac{d\rho}{dT} \tag{27e}$$

which satisfies the boundary conditions:

$$G(T_1) = G(T_2) = G'(T_1) = G'(T_2) = 0 \tag{27f}$$

Equations (27a–f) represent the essential result of the column theory.

For comparison, the corresponding result in the FJO theory is reproduced here:

$$\tau_1^* = \sigma^* c_1 + H^* c_1(1 - c_1) - (K_c^* + K_d^*)\frac{dc_1}{dz} \tag{27a*}$$

where σ^* stands for total mass transport through the column and:

$$H^* = -\frac{2\pi}{Q_1^3}\int_{T_1}^{T_2}\frac{\alpha\rho D}{\lambda T}G^*\,dT \tag{27b*}$$

$$K_c^* = \frac{2\pi}{Q_1^7}\int_{T_1}^{T_2}\frac{\rho D}{\lambda}G^{*2}\,dT \tag{27c*}$$

$$K_d^* = \frac{2\pi}{Q_1}\int_{T_1}^{T_2}\lambda\rho r^2 D\,dT \tag{27d*}$$

and $G^* = G^*(T)$ is the solution of:

$$\frac{d}{dT}\frac{1}{\lambda r^2}\frac{d}{dT}\frac{\eta}{\lambda}\frac{d}{dT}\frac{1}{\lambda\rho r^2}\frac{d}{dT}\left(\frac{\rho D}{\lambda}G^*(T)\right) = g\frac{d\rho}{dT} \tag{27e*}$$

which satisfies the boundary conditions:

$$G^*(T_1) = G^*(T_2) = G^{*\prime}(T_1) = G^{*\prime}(T_2) = 0 \tag{27f*}$$

Corrected Plane Case

The cylindrical case contains at its limit the plane case. Let $\bar{r}$ be the mean radius of the annular space $\bar{r} = (r_1 + r_2)/2$. When $(r_1 - r_2)/\bar{r}$ is very small, the cylindrical column is equivalent to a plane column of width $B = 2\pi\bar{r}$, the distance between the cold and hot plane walls being $r_1 - r_2$. In Eq. (27e), the variable r tends to a constant value and the substitution $r = B/2\pi$ can be made. The constant B will disappear by the substitution $G = (B/2\pi)^4 G_0$.

In addition, for the plane case the use of the heat flux $Q = -\lambda \nabla T$ is appropriate, so that the substitution $Q_1 = rQ = (B/2\pi)Q$ is made in Eqs. (27b–d). Finally, for the plane case, mass transport of species one through the TD column is given by the same Eq. (27a), but the coefficients H, K_c, and K_d are given by the expressions:

$$H = -\frac{Bm_1}{Q^3}\int_{T_1}^{T_2} \frac{\alpha nD}{\lambda T} G_0 \, dT \tag{27b$'$}$$

$$K_c = \frac{Bm_1}{Q^7}\int_{T_1}^{T_2} \frac{nD}{\lambda} G_0^2 \, dT \tag{27c$'$}$$

$$K_d = \frac{Bm_1}{Q}\int_{T_1}^{T_2} \lambda nD \, dT \tag{27d$'$}$$

and $G_0 = G_0(T)$ is the solution of:

$$\frac{d}{dT}\frac{1}{\lambda}\frac{d}{dT}\frac{\eta}{\lambda}\frac{d}{dT}\frac{1}{\lambda n}\frac{d}{dT}\left(\frac{nD}{\lambda} G_0(T)\right) = g\frac{d\rho}{dT} \tag{27e$'$}$$

which satisfies the boundary conditions:

$$G_0(T_1) = G_0(T_2) = G_0'(T_1) = G_0'(T_2) = 0 \tag{27f$'$}$$

COMPARISON BETWEEN THE CORRECTED AND THE ORIGINAL FJO THEORY

It is sufficient to consider the cylindrical case only, as it contains at its limit the plane case too.

One has to compare Eqs. (27a–f) with Eqs. (27a*–f*). For this purpose, the asterisked symbols are expressed in terms of non-asterisked ones.

The density of the mixture can be expressed as:

$$\rho = knm_1 \tag{28}$$

where:

$$k = 1 + (m_2/m_1 - 1)(1 - c_1) \tag{29}$$

Insert ρ given by Eq. (28) in Eqs. (27b*–f*) and consider k is independent of T, which is possible because c_1 varies only slightly in the radial direction. The so obtained relations compared with Eqs. (27b–f) lead to:

$$G^* = G \tag{30}$$

$$H^* = kH \quad K_c^* = kK_c \quad K_d^* = kK_d \tag{31}$$

The situation of the symbols σ^* and τ_1^* is more complicated. If one analyzes the derivation of the FJO theory one finds that strictly speaking these quantities have no physical meaning. They are not conservative quantities (that is, σ^* and τ_1^* vary along the column) because in derivation the non-conservative flux $\boldsymbol{J}_1^*$ was used.

In applications, it has been considered that σ^* stands for the real total mass transport through the column. Still the first term in Eq. (27a$*$), $\sigma^* c_1$, is again incorrect; it contains the false FJO premise: a *total mass* transport σ^* is multiplied by *molar concentration* c_1. Compare this with the corresponding correct term $m_1 \hat{\tau} c_1$ in Eq. (27a), where the mole transport of species one $\hat{\tau} c_1$ is multiplied by molecular mass of that species m_1.

Similarly, in applications, τ_1^* is considered as the real total mass transport of species one. When at the end of a column the concentrated material is extracted at the rate σ^* and concentration c_{1f}, it is considered that $\tau_1^* = c_{1f}\sigma^*$. This relation contains again the false FJO premise. (See for example Eq. 223 in Ref.[4].)

MAGNITUDE OF ERROR PRODUCED BY THE FJO THEORY IN APPLICATIONS

Operation at Total Reflux

For simplicity reasons, the total reflux operation has been preferred for the experimental study of the TD column and the determination of the thermal diffusion coefficient α.

In applications, Furry–Jones–Onsager, and the authors that have followed, have considered that σ^* represents the actual total mass transport through the column and τ_1^* represents the actual mass transports of species one through the column. In this interpretation the relations:

$$(\sigma^*)_{\text{total reflux}} = 0 \tag{32}$$

$$(\tau_1^*)_{\text{total reflux}} = 0 \tag{33}$$

are satisfied. Thus, the transport Eq. (27a*) reduces to:

$$0 = H^* c_1(1 - c_1) - (K_c^* + K_d^*)\frac{dc_1}{dz} \tag{34}$$

Taking into account the relations shown in Eq. (31), Eq. (34) can be written:

$$0 = Hc_1(1 - c_1) - (K_c + K_d)\frac{dc_1}{dz} \tag{34'}$$

Exactly this equation, Eq. (34′), is obtained if the correct transport Eq. (27a) is written for total reflux. This is an extraordinary coincidence, which means that the errors in the original FJO theory are not visible when the TD column is operated at total reflux.

In conclusion: *All published data obtained by using FJO theory are correct if the TD column was operated at total reflux.*

Ideal Cascade

A column operated at total reflux does not produce separative work. To produce separative work, a column may be operated in many ways. A representative case is when the column is an element in an ideal cascade, in which case the separative power of the column is maximal.

In an ideal cascade, a unit length of a TD column produces in a unit time a separative work given by[20]:

$$W = \frac{H^2}{4(K_c + K_d)} \tag{35}$$

This equation is written for the correct transport Eq. (27a). The corresponding equation for the transport Eq. (27a*) is:

$$W^* = \frac{H^{*2}}{4(K_c^* + K_d^*)} \tag{36}$$

Using here the relations of Eqs. (31) and (29), one obtains the ratio between incorrect and correct separation power:

$$W^*/W = 1 + (m_2/m_1 - 1)(1 - c_1) \tag{37}$$

This formula may be used as a criterion for the applicability of the original FJO theory to the productive separation problems. Let us consider a few typical examples.

a) In the very particular case when $m_2/m_1 = 1$ then $W^*/W = 1$, which means that in this case the original FJO theory leads to correct results.

b) For heavy isotope separation, m_2/m_1 is very near to one. Suppose one has to separate isotopic molecules $^{235}UF_6$ and $^{238}UF_6$ for which $m_1 = 349$ and $m_2 = 352$. Equation (37) gives:

$$W^*/W = 1 + 0.0086(1 - c_1)$$

It means that the use of the original FJO theory introduces errors that are not greater than 0.86%. Such errors are acceptable in practice.

c) For light isotope separation the ratio m_2/m_1 differs significantly from one. For helium isotope separation $m_1 = 3$ and $m_2 = 4$. Equation (37) gives:

$$W^*/W = 1 + 0.33(1 - c_1)$$

Hence in this case the use of the original FJO theory introduces errors of up to 33%. This error level is not acceptable in practice.

d) Finally, suppose now that the molecular masses are very different, say $m_2/m_1 = 10$. Then

$$W^*/W = 1 + 9(1 - c_1)$$

Hence W^* can be ten times greater then W. The original FJO theory leads to absurd results in such cases.

RUTHERFORD VARIANT

Rutherford[19] derived a variant of the FJO theory in which he used mass quantities instead of molar quantities: mass concentration w_i instead of molar concentration c_i and the mass average velocity $\boldsymbol{v}_m$ instead of molar average velocity $\boldsymbol{v}$. Also, he used the correct flux expression, Eq. (3b). In such an approach the assumption in Eq. (6) is substituted by:

$$\boldsymbol{v}_m = \boldsymbol{v}_m(r), \quad v_{mr} = 0, \quad v_{mz} = v_m \tag{38}$$

The difference between Eqs. (6) and (38) represents the basic difference between Rutherford variant and the corrected theory derived in this article. For this reason the two assumptions should be examined closely.

From Eqs. (3a and c) one obtains:

$$\boldsymbol{v}_m - \boldsymbol{v} = \frac{(m_2 - m_1)nD}{\rho}(\nabla c_1 - \alpha c_1 c_2 \nabla \ln T) \tag{39}$$

By projecting this equation onto the radial direction one obtains that $v_{mr} - v_r$ is generally different of zero, that is, the conditions of Eqs. (6) and (38) cannot be generally fulfilled at the same time. Then the question arises: Which assumption is better fulfilled by a real system? It seems difficult to give a general, rigorous answer. Still, for two particular categories of mixtures one can answer as follows:

a) The first category consists of mixtures that have the property that n does not depend on composition (on c_1). A mixture of perfect gases has this property. Thus, if c_1 varies along the column, then $\partial n/\partial z = 0$. When the velocity field, Eq. (6), is substituted in the equation of number conservation $\nabla(n\boldsymbol{v}) = 0$, it is found that this equation is automatically satisfied.

On the contrary, for this category, density generally varies along the column $\partial \rho/\partial z = n(m_1 - m_2)\partial c_1/\partial z$. Thus, if the velocity field in Eq. (38) is inserted in the equation of mass conservation $\nabla(\rho \boldsymbol{v}_m) = 0$ one obtains:

$$\boldsymbol{v}_m n(m_1 - m_2)\partial c_1/\partial z = 0$$

This equation can not be satisfied if $m_1 \neq m_2$. Consequently, the following proposition holds:

If the number density n does not depend on composition (on c_1*) and* $m_1 \neq m_2$ *then Eq. (6) can be satisfied and Eq. (38) cannot be satisfied.*

b) The second category consists of mixtures which have the property that ρ does not depend on composition (on c_1). Some liquid mixtures have this property. In a similar way one demonstrates the proposition:

If the mass density ρ *does not depend on composition (on* c_1*) and* $m_1 \neq m_2$ *then Eq. (6) cannot be satisfied and Eq. (38) can be satisfied.*

One can conclude that the corrected theory derived here should be preferred at least for gas mixtures, where the total molar density does not depend on composition.

CONCLUSION

a) The essential and corrected result of the theory is Eq. (27a) for the transport of one mixture component through the column. The coefficients H, K_c, and K_d in Eq. (27a) are given by the relations (27b–f) for the cylindrical case and by the relations (27b′–f′) for the plane case.

b) For several molecular models and several practical conditions, working expressions or numerical values of the coefficients H, K_c, and K_d have been published.[6] They have been established using the original FJO theory. To obtain the corrected coefficients, the literature coefficients should be marked with an asterisk (H^*, K_c^*, K_d^*) for distinction. Then the correct coefficients are obtained with formulas: $H = H^*/k$, $K_c = K_c^*/k$, and $K_d = K_d^*/k$, where k is given by Eq. (29). The correct coefficients will then be used in the transport Eq. (27a).

c) The error magnitude produced by the FJO theory is zero for columns operated at total reflux. However, in the case of productive columns the errors can become severe if the ratio m_2/m_1 is far from unity.

d) The corrected theory derived here is applicable for any value of the ratio of molecular masses m_2/m_1. Nowhere in the derivation was it necessary to suppose that $(m_2 - m_1)/m_1$ is small.

e) Rutherford[19] derived a variant of the FJO theory using mass quantities. As it is argued in the preceding section, the corrected theory derived here should be preferred at least for gas mixtures where the total molar density does not depend on composition.

NOMENCLATURE

c_i	mole fraction of species i (1)
D	coefficient of ordinary diffusion ($m^2 \cdot s^{-1}$)
g	acceleration of gravity ($m \cdot s^2$)
G	function, cf. Eq. (15a)
H	Transport coefficient, cf. Eq. (27a) ($kg \cdot s^{-1}$)
$\boldsymbol{J}_1$	Mass flux due to molecules of species 1 ($kg \cdot m^{-2} \cdot s^{-2}$)
$\boldsymbol{J}_{1r}$	Radial component of $\boldsymbol{J}_1$($kg \cdot m^{-2} \cdot s^{-2}$)
$\boldsymbol{J}_{1z}$	longitudinal component of $\boldsymbol{J}_1$($kg \cdot m^{-2} \cdot s^{-2}$)
k	coefficient, cf. Eq. (29)
K_c, K_d	transport coefficients, cf. Eq. (27a) ($kg \cdot m \cdot s^{-1}$)
Q	heat flux ($W \cdot m^{-2}$)
$2\pi Q_1$	conductive heat flow per unit length of column ($W \cdot m^{-1}$)
m_i	molar mass of species i ($kg \cdot mol^{-1}$)
n	total molar density ($mol \cdot m^{-3}$)
n_i	molar density of species i ($mol \cdot m^{-3}$)
p	pressure (Pa)
r	radial coordinate (m)

r_1	radius of outer cylinder (m)
r_2	radius of inner cylinder (m)
T	temperature (°K)
T_1	temperature of outer cylindrical wall (°K)
T_2	temperature of inner cylindrical wall (°K)
$\boldsymbol{v}$	molecular average velocity of all species ($\mathrm{m \cdot s^{-1}}$)
$\boldsymbol{v}_i$	molecular average velocity of species i ($\mathrm{m \cdot s^{-1}}$)
$\boldsymbol{v}_m$	mass average velocity of all species ($\mathrm{m \cdot s^{-1}}$)
w_i	mass fraction of species i[1]
W	maximal separative work per unit column length, per unit time, cf. Eq. (35) ($\mathrm{kg \cdot m^{-1} \cdot s^{-1}}$)
Subscript	
$i = 1, 2,$	molecular species, i = 1 is for the lighter component ($m_1 \leq m_2$)
Superscript	
*	asterisked symbols stand for expressions affected by FJO premise
Greek letters	
α	thermal diffusion constant (1)
η	viscosity (Pa·s)
λ	thermal conductivity ($\mathrm{W \cdot m^{-1} \cdot K^{-2}}$)
ρ	density ($\mathrm{kg \cdot m^{-3}}$)
σ	total mass transport through column ($\mathrm{kg \cdot s^{-1}}$)
$\hat{\tau}$	total molar transport through column ($\mathrm{mol \cdot s^{-1}}$)
τ_1	mass transport of species 1 through column ($\mathrm{kg \cdot s^{-1}}$)
$\hat{\tau}_1$	mass transport of species 1 through column when $\hat{\tau} = 0$ ($\mathrm{kg \cdot s^{-1}}$)

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