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Theory and Performance of Thermal-Diffusion Column

S. C. SAXENA* AND S. RAMAN

Chemical Engineering Division, Atomic Energy Establishment, Trombay, Bombay, India

I. INTRODUCTION

SOON after the introduction of the thermal-diffusion column by Clusius and Dickel,[1] some elementary theories were advanced by a number of workers.[2–7] All these theories were developed on the one basic assumption that the column consists of two plane parallel walls, one hot and the other cold. Furry and Jones[8] gave the theory for the realistic cylindrical columns as more or less an extension from the plane case.[4] The assumptions involved in this derivation are: (1) The temperature distribution in the column is determined by conduction only. (2) The convective flow is viscous and is entirely in the vertical direction so that the velocity is constant along the entire length of the column. (3) The dependence of the coefficient of viscosity (η), thermal conductivity (λ), diffusion (D), and density (ρ) on the composition of the isotopic mixture is neglected. (4) The time variation of the concentration of a particular species at each point in the tube is assumed to be negligible; this implies that either a stationary or a quasi-stationary condition exists in the column. (5) The quantities (λ/T), (η/λ), ($\rho D/\lambda$), and (ρT) are assumed to be independent of temperature and pressure, where T is the temperature in °K. (6) In tabulating the column-shape factors, the temperature variation of the thermal-diffusion factor (α_T) is neglected.

These tabulations are applicable for those columns which conform to the category of either "the extreme cylindrical case," or "the nearly plane case" of Furry and Jones.[8] Assumption (1) holds fairly well in practice, except near both ends of the column. As the Reynolds number for the column under actual operating conditions is much smaller than the values at which turbulence starts, one can reasonably assume the convective flow to be lamellar. The transport coefficients and the density are substantially independent of composition if the fractional difference of the molecular weight is small.

In a column, the stationary condition exists only at the final steady state; during the approach to equilibrium, an essentially stationary condition is realized if column ends are connected to sufficiently large, end reservoirs. Following Bardeen,[7] we show here that the contribution of this assumption for the cylindrical columns is negligible. Assumption (5) is rigorously valid only for monatomic gases interacting according to the Maxwellian model. It is now well established[9] that even the simple inert gases do not follow this interaction potential, although the general inverse-power model is capable of effectively representing the interaction in the limited temperature range. We develop in this paper a general theory of the cylindrical columns filled with gases which follow the inverse-power potential. Srivastava[10] gave the theory for molecules which interact according to the rigid-sphere model. This latter work, therefore, presents the treatment for molecules which constitute the other extreme end; the real gases lie in between these two extremes. Unfortunately, Srivastava's paper[10] contains some algebraic- and numerical-computational errors which have led to certain wrong conclusions, and these are discussed in this paper. As pointed out by Furry and Jones,[8] their calculations can be readily extended to include any chosen, simple, temperature dependence of α_T. This was actually performed by Srivastava and Srivastava[11] and by Srivastava.[12] They found an improved agreement with the experimental data when α_T was considered as temperature-dependent. This has been further investigated in this paper with a view to the analysis of the consequences of assumption (6).

A critical summary of the column theory along with its limitations and an interpretation of some experimental data are discussed at length by Jones and Furry[13] in their excellent review article. Since the publication of their work,[13] several groups have contributed experimental data on thermal-diffusion columns, and the transport theory has also advanced to such an extent that some of the above-mentioned assumptions can be reliably understood and satisfactorily accounted for, so that a proper evaluation of the predicted and

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* Present address: Department of Physics, Rajasthan University, Jaipur, India.

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actual performance of a column is possible. This is the purpose of the present work and is found essential as thermal-diffusion columns are still considered as the best means to separate some isotopes to meet certain particular requirements. Recently, McInteer and Reisfeld[14] have calculated the column constants assuming a more realistic Lennard-Jones (12–6) potential. These results are also applicable only to nonatomic gases and involve assumptions (1) through (4), mentioned above. Results obtained according to this work have also been considered and are discussed here.

II. DEVELOPMENT OF THEORY

Let us consider a thermal-diffusion column which has concentric cylinders as the hot and cold surfaces. The outer surface is of radius r_1 and maintained at a temperature T_1, while the inner one is of radius r_2 and at temperature T_2, such that $r_1>r_2$ and $T_1<T_2$. The annular gap is filled with the gaseous isotopic mixture to be separated. The hydrodynamical equation in cylindrical co-ordinates is[8]

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\eta\frac{\partial v}{\partial r}\right)=\frac{dp}{dZ}+\rho g, \tag{1}$$

where r and z are the variable cylindrical co-ordinates, the convection velocity v is parallel to Z axis, p is the pressure of the gas, and g the acceleration due to gravity. The boundary conditions for Eq. (1) are

$$v(T_1)=v(T_2)=0. \tag{2}$$

The equation for the flux of species 1 is[4]

$$\mathbf{J}_1=\rho[\mathbf{v}C_1+D(-\operatorname{grad}C_1+\alpha_T C_1C_2\operatorname{grad}\ln T)]. \tag{3}$$

Here, C stands for the molar concentration and the subscripts 1 and 2 refer to the molecular species. We have for the equation of continuity of the gas[7]

$$\partial(\rho C_1)/\partial t+\operatorname{div}\mathbf{J}_1=0, \tag{4}$$

where t refers to time. Substituting for $\mathbf{J}_1$ from Eq. (3) in (4) we get

$$\begin{aligned}\partial(\rho C_1)/\partial t=-\operatorname{div}[\rho C_1\mathbf{v}-\rho D\operatorname{grad}C_1\\+\rho D\alpha_T C_1C_2\operatorname{grad}\ln T].\end{aligned} \tag{5}$$

Equation (5) is to be solved with the following two boundary conditions:

$$\text{(i)}\quad\int_{r_2}^{r_1} r\rho v dr=0, \tag{6}$$

since there is no net flow of the gas, and

$$\text{(ii)}\quad \rho C_1 v_{1r}=-\rho D\frac{\partial C_1}{\partial r}+\frac{\rho D\alpha_T C_1C_2}{T}\frac{\partial T}{\partial r}=0, \tag{7}$$

at $r=r_1$ and $r=r_2$, since the flux J_{1r} vanishes at the walls. Equation (5) in conjunction with Eqs. (6) and (7) simplifies to

$$\int_{r_2}^{r_1} r\rho v\frac{\partial C_1}{\partial Z}dr=-\int_{r_2}^{r_1} r\rho\left(\frac{\partial}{\partial t}-D\frac{\partial^2}{\partial Z^2}\right)C_1 dr. \tag{8}$$

Let us define a new function[15]

$$G(r)=\int_{r_2}^{r}\rho v r dr. \tag{9}$$

In terms of this new function, the boundary conditions given by Eq. (2) become

$$G(r_1)=G'(r_1)=G(r_2)=G'(r_2)=0. \tag{10}$$

Here, primes represent differentiation with respect to r. Integrating Eq. (5) with respect to r and rearranging, we get

$$\begin{aligned}r\rho D\frac{\partial C_1}{\partial r}=r\rho D\frac{\alpha_T C_1C_2}{T}\frac{\partial T}{\partial r}+\int_{r_2}^{r}\Bigg[r'\rho'v'\frac{\partial C_1}{\partial Z}\\+r'\rho'\frac{\partial C_1}{\partial t}-r'\rho'D'\frac{\partial^2 C_1}{\partial Z^2}\Bigg]dr'.\end{aligned} \tag{11}$$

The prime indicates that the various quantities in the integrand are functions of r'. Equation (11), on differentiation with respect to Z, yields

$$\begin{aligned}\frac{\partial^2 C_1}{\partial Z\partial r}=\frac{\alpha_T}{T}\frac{\partial T}{\partial r}\frac{\partial}{\partial Z}(C_1C_2)+\frac{1}{r\rho D}\int_{r_2}^{r}\Bigg[r'\rho'v'\frac{\partial^2 C_1}{\partial Z^2}\\+r'\rho'\frac{\partial^2 C_1}{\partial Z\partial t}-r'\rho'D'\frac{\partial^3 C_1}{\partial Z^3}\Bigg]dr'.\end{aligned} \tag{12}$$

In terms of the function $G(r)$, Eq. (12) becomes

$$\begin{aligned}\frac{\partial^2 C_1}{\partial Z\partial r}=\frac{\alpha_T}{T}\frac{\partial T}{\partial r}\frac{\partial}{\partial Z}(C_1C_2)+\frac{1}{r\rho D}\Bigg\{G(r)\frac{\partial^2 C_1}{\partial Z^2}\\+\int_{r_2}^{r} r'\rho'\left(\frac{\partial}{\partial t}-D'\frac{\partial^2}{\partial Z^2}\right)\frac{\partial C_1}{\partial Z}dr'\Bigg\}.\end{aligned} \tag{13}$$

Also, we have

$$\begin{aligned}-\int_{r_2}^{r_1} r\rho v\frac{\partial C_1}{\partial Z}dr=-\int_{r_2}^{r_1}\frac{\partial C_1}{\partial Z}d\{G(r)\}\\=\int_{r_2}^{r_1} G(r)\frac{\partial^2 C_1}{\partial Z\partial r}dr.\end{aligned} \tag{14}$$

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[15] It is related to $G(T)$ of Furry and Jones,[8] such that

$$G(T)=[G(T)]_{F.J.}\frac{\rho D}{\lambda Q^3}.$$

Substituting for $\partial^2 C_1/\partial Z\partial r$ from Eq. (13), Eq. (14) becomes equal to

$$\left[\int_{r_2}^{r_1} \frac{\alpha_T G(r)}{T}\frac{\partial T}{\partial r}dr\right]\frac{\partial}{\partial Z}(C_1C_2)+\frac{\partial^2 C_1}{\partial Z^2}\int_{r_2}^{r_1}\frac{[G(r)]^2}{r\rho D}dr$$
$$+\left[\int_{r_2}^{r_1} r\rho\left(\frac{\partial}{\partial t}-D\frac{\partial^2}{\partial Z^2}\right)\left\{\int_{r_2}^{r}\frac{G(r')}{r'\rho' D'}dr'\right\}\frac{\partial C_1}{\partial Z}dr\right]. \quad (15)$$

Let us put

$$I(r)=\int_{r_2}^{r}\frac{G(r')}{r'\rho' D'}dr'. \quad (16)$$

Combining Eq. (8) with Eqs. (15) and (16), and after some rearrangement, we get

$$2\pi\int_{r_2}^{r_1} r\rho\frac{\partial}{\partial t}\left[1-I(r)\frac{\partial}{\partial Z}\right]C_1 dr$$
$$=-\frac{\partial}{\partial Z}\left[HC_1C_2-K_c\frac{\partial C_1}{\partial Z}-K_d\frac{\partial C_1}{\partial Z}+K_d'\frac{\partial^2 C_1}{\partial Z^2}\right], \quad (17)$$
$$=-\frac{\partial \tau_1}{\partial Z}, \quad (18)$$

where

$$H=-2\pi\int_{r_2}^{r_1}\frac{\alpha_T G(r)}{T}\frac{\partial T}{\partial r}dr, \quad (19)$$

$$K_c=2\pi\int_{r_2}^{r_1}\frac{[G(r)]^2}{r\rho D}dr, \quad (20)$$

$$K_d=2\pi\int_{r_2}^{r_1} r\rho D dr \quad (21)$$

$$K_d'=2\pi\int_{r_2}^{r_1} r\rho D I(r) dr, \quad (22)$$

and τ_1 the transport of species 1 is given by

$$\tau_1=HC_1C_2-(K_c+K_d)\frac{\partial C_1}{\partial Z}+K_d'\frac{\partial^2 C_1}{\partial Z^2}. \quad (23)$$

Further, because of the assumption (1), the equations giving the temperature field in the column are[8]

$$2\pi Q=2\pi r\lambda(-dT/dr),$$
$$Q\ln(r_1/r_2)=\int_{T_1}^{T_2}\lambda dT, \quad (24)$$
$$(\partial/\partial r)=-(Q/r\lambda)(\partial/\partial T).$$

Here, $2\pi Q$ is the heat flow by conduction per unit length of the cylinders in cal/cm sec. Equation (9) in conjunction with Eq. (24) gives for the convection velocity

$$v(T)=\frac{Q}{\lambda\rho r^2}\frac{d}{dT}G(T). \quad (25)$$

Substitution of Eqs. (24) and (25) in Eq. (1), and subsequent differentiation with respect to T, leads to the required differential equation for $G(T)$ as follows:

$$Q^3\frac{d}{dT}\frac{1}{\lambda r^2}\frac{d}{dT}\frac{\eta}{\lambda}\frac{d}{dT}\left(\frac{1}{\lambda\rho r^2}\frac{dG}{dT}\right)=g\frac{d\rho}{dT}, \quad (26)$$

with the boundary conditions

$$G(T_1)=G'(T_1)=G(T_2)=G'(T_2)=0. \quad (27)$$

In order to solve Eq. (26), a knowledge of the temperature dependence of the transport coefficients and density is essential. An analytic solution of Eq. (26) is possible if λ, η, and D are assumed to vary with temperature according to that given by the inverse-power model, viz., proportional to some power of T, and further restrict overselves only to the monatomic gases. The quantities

$$\frac{\lambda}{T^n},\quad \frac{\eta}{T^n},\quad \frac{\eta}{\lambda},\quad \frac{\rho D}{\lambda},\quad \text{and}\quad \rho T \quad (28)$$

are then assumed to be temperature independent. The exponent n is related to the force index ν of the inverse-power model by the relation

$$\nu=(2n+3)/(2n-1). \quad (28a)$$

Integrating Eq. (24), we get

$$(n+1)\ln r=-(\lambda/QT^n)T^{n+1}+\text{const}. \quad (29)$$

We now introduce the dimensionless variable t and the dimensionless parameters t_1 and t_2 defined by

$$t=(\lambda/QT^n)^{1/(n+1)}T,$$

and

$$t_i=(\lambda/QT^n)^{1/(n+1)}T_i,\quad (i=1,2). \quad (30)$$

The quantities t_1 and t_2 are determined from

$$t_2/t_1=T_2/T_1, \quad (31)$$

$$t_2^{n+1}-t_1^{n+1}=(n+1)\ln(r_1/r_2). \quad (32)$$

For the sake of brevity, we rewrite Eq. (29) as

$$r^{n+1}=r_0^{n+1}\exp(-t^{n+1}). \quad (33)$$

In analogy with Furry and Jones,[8] we introduce a master function γ which is related to G as

$$G(T)=-\left(\frac{QT^n}{\lambda}\right)^{3/(n+1)}\left[\frac{g\lambda_1{}^3\rho_1{}^2}{\eta_1 Q^3 t_1{}^{2n-2}}\right]r_0{}^4\gamma(t). \quad (34)$$

In terms of the master function, the differential equation (26) takes the form

$$\frac{d}{dt}t^{-n}\exp\left(\frac{2t^{n+1}}{n+1}\right)\frac{d^2}{dt^2}t^{1-n}\exp\left(\frac{2t^{n+1}}{n+1}\right)\frac{d\gamma}{dt}=t^{-2},\tag{35}$$

with the boundary conditions

$$\gamma(t_1)=\gamma(t_2)=\gamma'(t_1)=\gamma'(t_2)=0.\tag{36}$$

Equations (19)–(22) now reduce to

$$\begin{aligned}H&=-2\pi\int_{T_1}^{T_2}\frac{\alpha_T G(T)}{T}dT\\&=2\pi\left[\frac{g\rho_1{}^2t_1{}^{2+n}}{\eta_1}\right]r_1{}^4\exp\left(\frac{4t_1{}^{n+1}}{n+1}\right)\int_{t_1}^{t_2}\frac{\alpha_T\gamma}{t}dt.\end{aligned}\tag{37}$$

$$\begin{aligned}K_c&=2\pi\int_{T_1}^{T_2}\frac{[G(T)]^2}{\rho D}\frac{\lambda}{Q}dT\\&=2\pi\left[\frac{g^2\rho_1{}^3}{\eta_1{}^2D_1}t_1{}^{4+3n}\right]r_1{}^8\exp\left(\frac{8t_1{}^{n+1}}{n+1}\right)\int_{t_1}^{t_2}\gamma^2dt.\end{aligned}\tag{38}$$

$$\begin{aligned}K_d&=\frac{2\pi}{Q}\int_{T_1}^{T_2}\lambda\rho Dr^2dT\\&=2\pi\rho_1D_1r_1{}^2t_1{}^{-n}\exp\left(\frac{2t_1{}^{n+1}}{n+1}\right)\int_{t_1}^{t_2}t^{2n}\\&\qquad\times\exp\left(-\frac{2t^{n+1}}{n+1}\right)dt.\end{aligned}\tag{39}$$

$$\begin{aligned}K_d'&=\frac{2\pi}{Q^2}\int_{T_1}^{T_2}\lambda^2r^2\left\{\int_T^{T_2}G(T')dT'\right\}dT\\&=-2\pi\left[\frac{g\rho_1{}^2t_1{}^{2+n}}{\eta_1}\right]r_1{}^6\exp\left(\frac{6t_1{}^{n+1}}{n+1}\right)\\&\qquad\times\int_{t_1}^{t_2}t^{2n}\left\{\int_t^{t_2}\gamma(t')dt'\right\}\exp\left(-\frac{2t^{n+1}}{n+1}\right)dt.\end{aligned}\tag{40}$$

Alternatively, these four column constants can be put in terms of the dimensionless "shape factors" h, k_c, k_d, and k_d' for convenience of numerical computation. These expressions are

$$H=\frac{2\pi g}{6!}\left\{\frac{\alpha_T\rho^2}{\eta}\right\}_1r_1{}^4h,\tag{41}$$

$$K_c=\frac{2\pi g^2}{9!}\left\{\frac{\rho^3}{\eta^2D}\right\}_1r_1{}^8k_c,\tag{42}$$

$$K_d=2\pi\{\rho D\}_1r_1{}^2k_d,\tag{43}$$

$$K_d'=-2\pi g\{\rho^2/\eta\}_1r_1{}^6k_d',\tag{44}$$

where

$$h=6!t_1{}^{2+n}\exp\left(\frac{4t_1{}^{n+1}}{n+1}\right)\int_{t_1}^{t_2}\frac{\alpha_T}{\alpha_{T_1}}\frac{\gamma}{t}dt,\tag{45}$$

$$k_c=9!t_1{}^{4+3n}\exp\left(\frac{8t_1{}^{n+1}}{n+1}\right)\int_{t_1}^{t_2}\gamma^2dt,\tag{46}$$

$$k_d=t_1{}^{-n}\exp\left(\frac{2t_1{}^{n+1}}{n+1}\right)\int_{t_1}^{t_2}t^{2n}\exp\left(-\frac{2t^{n+1}}{n+1}\right)dt,\tag{47}$$

$$\begin{aligned}k_d'&=t_1{}^{n+2}\exp\left(\frac{6t_1{}^{n+1}}{n+1}\right)\int_{t_1}^{t_2}t^{2n}\left\{\int_t^{t_2}\gamma(t')dt'\right\}\\&\qquad\times\exp\left(-\frac{2t^{n+1}}{n+1}\right)dt.\end{aligned}\tag{48}$$

In Eqs. (41) to (44), the quantities within the curly brackets are to be evaluated at the lower temperature T_1. α_{T_1} is the value of α_T at the temperature T_1. In the expressions for H, K_c, K_d, and K_d', all quantities appearing outside the integrals are temperature independent because of Eq. (28), and, therefore, may be evaluated at any temperature. As, in the hot-wire type of thermal-diffusion columns, most of the gas is at temperature T_1, the evaluation at T_1 seems a more reasonable choice.[8]

A knowledge of the master function γ is essential for the calculation of h, k_c, and k_d'. γ is to be determined from the solution of the differential equation (35) with the boundary conditions of Eq. (36). Equation (35) can be solved in somewhat the same way adopted by Furry and Jones.[8] Let y be the particular integral of Eq. (35) and u, v, w, l, the four linearly independent integrals of the homogeneous equation

$$\frac{d}{dt}t^{-n}\exp\left(\frac{2t^{n+1}}{n+1}\right)\frac{d^2}{dt^2}t^{1-n}\exp\left(\frac{2t^{n+1}}{n+1}\right)\frac{dZ}{dt}=0.\tag{49}$$

Then, γ is given by

$$\gamma=y+Au+Bv+Cw+D.\tag{50}$$

Applying the boundary conditions Eq. (36), the four constants A, B, C, and D, of Eq. (50) can be determined. Finally, we get

$$\gamma=\epsilon/\delta,\tag{51}$$

where

$$\epsilon=\begin{vmatrix}y&u&v&w&1\\y_1&u_1&v_1&w_1&1\\y_2&u_2&v_2&w_2&1\\y_1'&u_1'&v_1'&w_1'&0\\y_2'&u_2'&v_2'&w_2'&0\end{vmatrix},\tag{52}$$

and δ is the cofactor of y in ϵ. Here, the prime means differentiation with respect to t, and subscripts 1, 2 indicate that the functions are evaluated at t_1 and t_2, respectively. y, u, v, and w are given by the following equations:

$$y=\tfrac{1}{2}ef-g;\quad u=d;\quad v=f,\quad w=e. \tag{53}$$

Here, e, f, g, and d are defined as

$$\begin{aligned} e&=\exp\left(-\frac{2t^{n+1}}{n+1}\right),\quad e_i=\exp\left(-\frac{2t_i^{n+1}}{n+1}\right),\quad (i=1,2),\\ f&=\int^t x^{n+1}\exp\left(-\frac{2x^{n+1}}{n+1}\right)dx,\\ g&=\int^t x^{n-1}\exp\left(-\frac{4x^{n+1}}{n+1}\right)dx,\\ d&=2\int^t x^{n-1}\exp\left(-\frac{2x^{n+1}}{n+1}\right)\left\{\int^x \mathrm{epx}\left(-\frac{2y^{n+1}}{n+1}\right)dy\right\}dx. \end{aligned} \tag{53a}$$

In the above integrals, the lower limits are not specified, but are to be the same in any formulation. Let us also define

$$\begin{aligned} f_{0t}&=\int_0^t x^{n+1}\exp\left(-\frac{2x^{n+1}}{n+1}\right)dx\\ f_{t\infty}&=\int_t^\infty x^{n-1}\exp\left(-\frac{2x^{n+1}}{n+1}\right)dx,\\ f_{it}&=\int_{t_i}^t x^{n-1}\exp\left(-\frac{2x^{n+1}}{n+1}\right)dx,\quad (i=1,2),\\ f_{ij}&=\int_{t_i}^{t_j} x^{n-1}\exp\left(-\frac{2x^{n+1}}{n+1}\right)dx,\quad (i,j=1,2). \end{aligned} \tag{54}$$

The quantities g_{0t}, $g_{t\infty}$, etc., d_{0t}, $d_{t\infty}$, etc., have similar meanings. Equation (51) holds irrespective of the choice for the lower limit of the integrals. If t_2 is taken as the lower limit of the integrals, we get

$$\gamma=g_{t2}-\tfrac{1}{2}(e+e_2)f_{t2}-Ad_{t2}+C_2(2t_2f_{t2}+e_2-e), \tag{55}$$

where

$$A=\frac{2f_{12}(e_1t_1-e_2t_1-t_1t_2f_{12})-\frac{1}{2}(e_1-e_2)^2-2g_{12}(t_2-t_1)}{2\{d_{12}(t_1-t_2)-k_{12}(e_1-e_2-2t_2f_{12})\}}, \tag{55a}$$

and

$$C_2=\frac{k_{12}(2e_1f_{12}-4g_{12})+d_{12}(e_1-e_2-2t_1f_{12})+2e_2k_{12}f_{12}}{4\{d_{12}(t_1-t_2)-k_{12}(e_1-e_2-2t_2f_{12})\}}. \tag{55b}$$

Here, k stands for the integral

$$k=\int^t \exp\left(-\frac{2x^{n+1}}{n+1}\right)dx, \tag{55c}$$

with the nomenclature for the specification of the limits as in Eq. (54). If t_1 is assumed as the lower limit, then,

$$\gamma=\tfrac{1}{2}(e+e_1)f_{1t}-Ad_{1t}+C_1(e_1-e-2t_1f_{1t})-g_{1t}, \tag{56}$$

where A is as defined in the foregoing, while

$$C_1=\frac{k_{12}(2e_2f_{12}-4g_{12})+d_{12}(e_2-e_1+2t_2f_{12})+2e_1k_{12}f_{12}}{4\{d_{12}(t_1-t_2)-k_{12}(e_1-e_2-2t_2f_{12})\}}. \tag{56a}$$

k_d can be readily obtained from Eq. (47) by direct integration. The final result is

$$k_d=\tfrac{1}{2}-\tfrac{1}{2}\left(\frac{t_2}{t_1}\right)^n\exp\left\{\frac{2}{n+1}(t_1^{n+1}-t_2^{n+1})\right\}+\tfrac{1}{2}nt_1^{-n}f_{12}\exp\left(\frac{2t_1^{n+1}}{n+1}\right). \tag{57}$$

Thus, we find that the transport Eq. (23) derived here differs from that of Furry and Jones[8] in the inclusion of an additional term containing K_d'. Also, the expressions derived here for H, K_c, K_d, and K_d' are general and reduce to those of Furry and Jones[8] for $n=1$, and those of Srivastava[10] for $n=(1/2)$. However, the expression for γ assumed by Srivastava[10] is wrong, as he takes f^2 to be one of the solutions of Eq. (49) with $n=\frac{1}{2}$, which is incorrect. For this reason, all the numerical results of Srivastava[10] are in error and hence are not used in this paper. We are publishing the revised tables for the shape factors in a separate paper.[16] Bardeen[7] investigated the contribution of K_d' for the plane case with $n=1$ and found that the fractional error involved because of the neglect of this term is less than 1%. In the present case, it can be estimated as follows:

We define a quantity ϵ, the measure of the error involved in the neglect of the additional term

$$K_d'(\partial^2C_1/\partial Z^2)$$

appearing in Eq. (23) as

$$\begin{aligned} \epsilon&=\frac{1}{C_1}\frac{\partial C_1}{\partial Z}\frac{K_d'}{K_d},\\ &\simeq\left\{\frac{H}{K_c+K_d}\right\}\frac{g\rho_1}{\eta_1D_1}r_1^4t_1^{2n+2}\exp\left(\frac{4t_1^{n+1}}{n+1}\right)\\ &\quad\times\left[\frac{\displaystyle\int_{t_1}^{t_2}t^{2n}\left\{\int_t^{t_2}\gamma(t')dt'\right\}\exp\left(-\frac{2t^{n+1}}{n+1}\right)dt}{\displaystyle\int_{t_1}^{t_2}t^{2n}\exp\left(-\frac{2t^{n+1}}{n+1}\right)dt}\right]. \end{aligned} \tag{58}$$

In order to estimate the value of ϵ, it is essential to

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[16] S. Raman and S. C. Saxena, (to be published).

assign a numerical value to n. We consider here its two extreme possible values, viz., $n=\frac{1}{2}$ and 1, in conjunction with the experimental data of Simon[17] for argon with $T_2=1500°\text{K}$. The factor within the curly brackets was given the maximum, observed value. The integrals were evaluated by direct, numerical integrations. For $n=1$, the γ values of Furry and Jones[8] were used, whereas the other quantities in Eq. (58) were given appropriate values. This gave ϵ as 0.018. For $n=\frac{1}{2}$, a similar procedure was adopted except the γ values of Raman and Saxena[16] were used. This gave ϵ as 0.0065. Thus, we find that the neglect of this term causes only an error of approximately 1% and, consequently, we neglect the last term of the transport equation (23) in the rest of our discussions.

Since, in most of the hot-wire columns, $r_1 \gg r_2$, Furry and Jones[8] further simplified the expression for γ and hence of h and k_c using this assumption. They designate this as the extreme, cylindrical case. The master function for this case is given by

$$\gamma \simeq \frac{\gamma_\infty-(\gamma''/t_2)}{1-(\delta''/t_2)}, \tag{59}$$

where

$$\begin{aligned}\gamma_\infty=(g_{t\infty}-\tfrac{1}{2}ef_{t\infty})+d_{t\infty}(g_{1\infty}-e_1f_{1\infty}+t_1f_{1\infty}{}^2)/\Delta \\ +f_{t\infty}[k_{1\infty}(e_1f_{1\infty}-2g_{1\infty}) \\ +d_{1\infty}\{(e_1/2)-t_1f_{1\infty}\}]/\Delta,\end{aligned} \tag{60}$$

$$\begin{aligned}\gamma''=\delta''(g_{t\infty}-\tfrac{1}{2}ef_{t\infty})+d_{t\infty}[t_1g_{1\infty}-(e_1{}^2/4)]\Delta \\ +e[2k_{1\infty}(e_1f_{1\infty}-2g_{1\infty})+d_{1\infty}(e_1-2t_1f_{1\infty})]/4\Delta,\end{aligned} \tag{61}$$

$$\Delta=2k_{1\infty}f_{1\infty}-d_{1\infty}, \tag{62}$$

and

$$\delta''=(e_1k_{1\infty}-t_1d_{1\infty})/\Delta. \tag{62a}$$

Various d, e, f, g, and k functions occurring in Eqs. (60) to (62a) can be readily obtained from Eqs. (53a) and (55c). The two subscripts assigned to these functions merely represent the lower and upper limits of the integrals, [Eq. (54)]. For the extreme, cylindrical case, the simplified expressions for h and k_c are

$$h=6!t_1{}^{2+n}\exp\left(\frac{4t_1{}^{n+1}}{n+1}\right)\frac{h_0-(h_0''/t_2)}{1-(\delta''/t_2)}, \tag{63}$$

$$k_c=9!t_1{}^{4+3n}\exp\left(\frac{8t_1{}^{n+1}}{n+1}\right)\frac{k_\infty-(2k_1''/t_2)+(k_2''/t_2{}^2)}{\{1-(\delta''/t_2)\}^2}, \tag{64}$$

where

$$h_0=\int_{t_1}^{\infty}\frac{\alpha_T}{\alpha_{T_1}}\left(\frac{\gamma_\infty}{t}\right)dt;\quad h_0''=\int_{t_1}^{\infty}\frac{\alpha_T}{\alpha_{T_1}}\left(\frac{\gamma''}{t}\right)dt, \tag{65}$$

and

$$k_\infty=\int_{t_1}^{\infty}\gamma_\infty{}^2dt;\quad k_1''=\int_{t_1}^{\infty}\gamma_\infty\gamma''dt;\quad k_2''=\int_{t_1}^{\infty}\gamma''^2dt. \tag{66}$$

In the above expression for h[Eqs. (63) and (65)], α_T can be assigned any type of temperature dependence. If α_T is assumed to vary as $A-(B/T)$, we now get

$$\begin{aligned}h_0\alpha_{T_1}&=A\int_{t_1}^{\infty}\left(\frac{\gamma_\infty}{t}\right)dt-\left(\frac{Bt_1}{T_1}\right)\int_{t_1}^{\infty}\left(\frac{\gamma_\infty}{t^2}\right)dt,\\ &=Ah_\infty-\left(\frac{Bt_1}{T_1}\right)h_{\infty B},\end{aligned} \tag{67}$$

$$\begin{aligned}h_0''\alpha_{T_1}&=A\int_{t_1}^{\infty}\left(\frac{\gamma''}{t}\right)dt-\left(\frac{Bt_1}{T_1}\right)\int_{t_1}^{\infty}\left(\frac{\gamma''}{t^2}\right)dt,\\ &=Ah''-(Bt_1/T_1)h_B''.\end{aligned} \tag{68}$$

Here

$$\begin{aligned}h_\infty&=\int_{t_1}^{\infty}\left(\frac{\gamma_\infty}{t}\right)dt, & h_{\infty B}&=\int_{t_1}^{\infty}\left(\frac{\gamma_\infty}{t^2}\right)dt,\\ h''&=\int_{t_1}^{\infty}\left(\frac{\gamma''}{t}\right)dt; & h_B''&=\int_{t_1}^{\infty}\left(\frac{\gamma''}{t^2}\right)dt.\end{aligned} \tag{69}$$

III. COMPARISON OF THEORY AND EXPERIMENT

For comparing the results of theory developed in Sec. II with the measured, isotope separation in a thermal-diffusion column, one has to make use of the transport equation. Neglecting the K_d' term in Eq. (23), it can be shown that for discontinuous operation ($\tau=0$) at the steady state ($\tau_1=\tau_2=0$)

$$q=e^{2AL}, \tag{70}$$

where q is the equilibrium-separation factor and is the ratio of (c_1/c_2) at the top end of the column to that at the bottom end, L is the length of the column, τ is the total transport of the gas through the column, and

$$2A=H/(K_c+K_d). \tag{71}$$

Owing to the practical difficulties involved in the construction of ideal columns, certain asymmetries very often result. These are caused either by the nonverticality and nonconstancy of the annular gap or lack of uniformity in the temperatures of the two surfaces. Consequently, the vertical lamellar flow of the gas in the column becomes disturbed, which has been assumed in deriving the theory. The flow of gas becomes somewhat turbulent and causes parasitic remixing and, hence, reduction in separation.[18] As shown by Jones and Furry[13] in detail, the effect of this is to add an additional term $K_p(\partial C_1/\partial Z)$ in the transport equation. Equation (71), therefore, becomes

$$2A=H/(K_c+K_d+K_p). \tag{72}$$

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[17] R. Simon, Phys. Rev. **69**, 596 (1946); J. W. Corbertt and W. W. Watson, *ibid.* **101**, 519 (1956); J. Donaldson and W. W. Watson, *ibid.* **82**, 909 (1951).

[18] S. C. Saxena and W. W. Watson, Phys. Fluids **3**, 105 (1960).

TABLE I. Values for various gases, of η, D, α_T, ρ, n, and m.

Gas	T °K	$10^6\,\eta$ gm/cm sec	$10^2\,D^a$ cm^2/sec	$10^3\,\alpha_T$	$10^5\,\rho^a$ gm/cc	n and m
He	288	194.7	154.8	59.0	16.94	0.6567
	300	200.0	165.8	59.0	16.27	0.6567
Ne	298	316.1	50.9	26.5	82.54	0.63
	358	356.7	69.2	27.2	68.71	0.63
Ar (normal)	288	219.5	17.1	16.2	169.0	0.72
	293	222.5	17.6	16.5	166.2	0.72
Ar (9.7% Ar^{36})	288	218.5	17.1	16.2	167.7	0.72
	358	259.9	25.3	20.0	134.9	0.72
Kr	298	265.9	9.64	167.3[b]	342.8	0.83
	358	295.5	13.6	232.0[b]	285.3	0.83
H_2	293	89.82	139.8	172	8.65	0.676, 0.818
O_2	293	204.6	20.22	12.69	133.1	0.686, 0.911
CH_4	300	111.0	22.4	8.15	65.19	0.787, 1.36

[a] Values refer to 1 atm pressure.

[b] Reduced, thermal-duffusion factor $=\alpha_T\left(\frac{M_1+M_2}{M_1-M_2}\right)$.

The theoretical expressions of H, K_c, and K_d indicate that these quantities are proportional to P^2, P^4, and P^0, respectively, where P is the pressure. K_p will depend on P in the same way as K_c. Hence, the separation factor will have the following pressure dependence:

$$\ln q=\frac{a/P^2}{(1+K_p/K_c)+b/P^4}, \tag{73}$$

where a and b are constants given by

$$a=(HLP^2/K_c), \quad b=(K_dP^4/K_c). \tag{74}$$

We have put the theory in a form such that it can be directly compared with the experimental data. If the isotopic separation is measured either as a function of pressure in a column keeping the temperatures of the hot and cold walls constant, or at a single pressure as a function of the hot-wall temperature, Eqs. (73) and (74) are to be used. One very interesting and crucial test of the theory lies in its success in the prediction of the observed pressure dependence of the separation factor. The constants a and b depend on the intermolecular forces, column dimensions, and the temperatures of the two surfaces. As it is hard to construct columns which are completely free from any type of parasitic-remixing effect, and also as extensive tabulations of H, K_c, and K_d are not available for a potential which is adequate for most of the common gases used, it would be interesting to test the qualitative form of the pressure dependence of q given by theory. We have analyzed the available experimental, column data of various groups of workers on a number of isotopic mixtures; He, Ne, Ar, Kr, Xe, CH_4, H_2, and O_2. In the theoretical calculations of q, a knowledge of η, D, α_T, and ρ is necessary. η, D, and α_T were computed at the relevant temperature according to the Lennard-Jones (L-J) (12–6) potential[9] using the theoretical formulas,[9] and are recorded in Table I. ρ values, also listed in Table I, were evaluated according to the perfect-gas equation. Values of n obtained from viscosity and thermal-conductivity data in the case of monatomic gases, and of n and m obtained from viscosity and thermal-conductivity data, respectively, for polyatomic gases are also recorded in Table I. The constants a and b of Eq. (73) (neglecting the K_p/K_c term) have been determined in each case from the experimental data by the least-squares method. These constants are also computed from theory, assuming the intermolecular potential of L-J (12–6) type and inverse-power potential with $n=1$ and $\frac{1}{2}$. These theoretical values of a and b are recorded in Table II. Throughout our calculations we have used the tabulated shape factors of McInteer and Reisfeld[19] for L-J (12–6) potential, of Furry and Jones,[8] and of Raman and Saxena[16] for the inverse-power potential with $n=1$ and $\frac{1}{2}$, respectively. To facilitate a direct, numerical comparison of theory and experiment, we equate the experimental value of a to its theoretical value, and the values of $b'=(b_{\text{exptl}}a_{\text{theoret}}/a_{\text{exptl}})$ so obtained are tabulated in Table II. For a good agreement, b' values should be equal to b values. Also shown in this table are values of K_p/K_c equal to $(a_{\text{theoret}/\text{exptl}})-1$, which give the idea of the magnitude of parasitic remixing, if we assume the validity of theory.

To check the adequacy of theory, theoretical- and experimental-separation factors have been plotted as a function of pressure wherever possible for a number of gases. A consistent notation is used in designating the various curves. Thus, curve a in all cases represents a least-square fit through the experimental points according to Eq. (73) when the (K_p/K_c) term is dropped. Curves b and d are according to the inverse-power model with $n=1$ and $\frac{1}{2}$, respectively, and assuming α_T to be temperature-independent. b' and d' correspond to b and d when α_T is assigned a temperature dependence of the form $A-(B/T)$. The constants A and B are determined by the least-square method, assuming the theoretical tabulated values[20] according to the L-J (12–6) potential. Curve c represents in all cases the theoretical plot according to L-J (12–6) potential. We now discuss the results for individual gases in detail.

A. Monatomic Gases

Helium

For helium isotopes, McInteer, Aldrich, and Nier[21] determined H for a hot-wire column at two pressures

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[19] B. B. McInteer and M. J. Reisfeld, Los Alamos Scientific Laboratory Report, LAMS-2517 (1961); see also J. Chem. Phys. **34**, 1844 (1961).

[20] S. C. Saxena and E. A. Mason, J. Chem. Phys. **28**, 623 (1958).

[21] B. B. McInteer, L. T. Aldrich, and A. O. Nier, Phys. Rev. **74**, 946 (1948).

TABLE II. Theoretical values[a] of a and b of Eq. (74); values[a] of $b'=b_{\text{exptl}}a_{\text{theoret}}/a_{\text{exptl}}$ and $K_p/K_c=(a_{\text{theoret}}a_{\text{exptl}})-1$.

	Inverse-power model and $n=1$				Inverse-power model and $n=\frac{1}{2}$				Lennard-Jones (12–6) Model			
Gas	a_{theoret}	b_{theoret}	b'	K_p/K_c	a_{theoret}	b_{theoret}	b'	K_p/K_c	a_{theoret}	b_{theoret}	b'	K_p/K_c
He Bowring B.	0.294	38	47	−0.141	···	···	···	···	0.297	30.6	47.6	−0.131
Ne $T_1=298$°K	0.0525	7.153	4.38	5.69	0.0259	2.49	2.16	2.30	0.0459	5.34	5.34	4.84
Ne $T_1=358$°K	0.0992	24.24	15.43	4.01	0.0489	8.44	7.61	1.47	0.0859	18.00	13.35	3.33
Ar Simon, $T_2=1100$°K	0.0014	0.0086	0.0059	0.23	0.00055	0.0021	0.0024	−0.507	0.0013	0.0043	0.0056	0.178
Ar Simon, $T_2=1500$°K	0.0032	0.026	0.024	−0.094	0.0013	0.0044	0.0100	−0.626	0.0025	0.0082	0.0192	−0.285
Ar (normal) *M* and *W* $T_1=288$°K	0.0036	0.092	0.076	0.57	0.0018	0.0321	0.0375	−0.226	0.0040	0.078	0.083	0.713
Ar (9.7% Ar^{36}) *M* and *W* $T_1=288$°K	0.0037	0.094	0.079	1.344	0.0018	0.0326	0.0391	0.159	0.0040	0.079	0.086	1.56
Ar (9.7% Ar^{36}) *M* and *W* $T_1=358$°K	0.0099	0.448	0.472	1.525	0.0049	0.156	0.2324	0.243	0.0101	0.368	0.482	1.58
Kr $T_1=298$°K	0.0064	0.0105	0.0097	0.993	0.0031	0.0037	0.0048	−0.019	0.0088	0.0095	0.0135	1.77
Kr $T_1=358$°K	0.0166	0.0374	0.0681	0.425	0.0082	0.0130	0.0335	−0.298	0.0203	0.0324	0.0832	0.742
H_2	0.240	4.94	4.88	7.67	0.0931	1.27	1.89	2.36	0.161	2.25	3.23	4.80
O_2	0.0135	0.440	0.728	1.82	···	···	···	···	0.0132	0.433	0.714	1.77
CH_4	1.81	0.163	0.170	0.35	···	···	···	···	2.51	0.140	0.236	0.87

[a] Units of a_{theort} are $(\text{atm})^2$, b_{theort} and b' in $(\text{atm})^4$.

and also for a concentric-tube column at one pressure, keeping the other factors constant. Their results are shown in Table II, and H values for the hot-wire column are found to follow the theoretically predicted, pressure dependence. In Table III are also listed the theoretically calculated values according to the L-J (12–6) potential and inverse-power potential for $n=1$ and $\frac{1}{2}$. For the concentric-tube column, the value for $n=1$ is calculated according to the nearly plane-case theory of Furry and Jones.[8] Our calculated H values completely agree with the previous calculations[14] for $n=1$. For the L-J (12–6) potential calculated values obtained according to the revised tabulations for the shape factors[19] are in reasonable agreement with the reported values of McInteer and Reisfeld[14] for the hot-wire column only, but differ by about 8.5% for the concentric-tube column. The agreement between theory and experiment is quite poor for the hot-wire column, the experimental values being too high. For helium, the attractive force is weak,[9] and the assumption of a purely inverse, power potential is adequate. In fact, viscosity measurements in the range 4° to 1100°K yield[22] $n=0.6567$, and, accordingly, if the theoretical value of H is corrected for this n, the disagreement with the experimental value is approximately 30%. The agreement of the calculated L-J (12–6) values with the experimental values is also poor, though it is partly expected as helium molecules are much softer[9] than represented by this potential. The source of this discrepancy also could not be traced in the possibility

TABLE III. Experimental and calculated values[a] of H, K_c, K_d, and $2A$ for helium.

	McInteer *et al.*			Bowring	
	Hot wire	Column	Conc. tube column	Column A	Column B
Pressure (atm)	7.8	9.7	7.8	1	1
H (exptl)	16.5	24.8	257	0.432	7.78
H ($n=1$)	9.5	14.8	267	0.657	10.02
H ($n=\frac{1}{2}$)	12.5	19.3	···	0.792	···
H (L-J, 12–6)	12.1	18.8	282	0.784	11.93
K_c (exptl)	···	···	···	0.0032	0.26
K_c ($n=1$)	0.443	1.06	129	0.0026	0.394
K_c ($n=\frac{1}{2}$)	1.382	3.31	···	0.0065	···
K_c (L-J, 12–6)	0.940	2.24	134	0.0050	0.463
K_d (exptl)	···	···	···	1.90	15.0
K_d ($n=1$)	1.70	1.70	26.7	3.34	14.8
K_d ($n=\frac{1}{2}$)	1.25	1.25	···	2.36	···
K_d (L-J, 12–6)	1.36	1.36	26.1	2.53	14.2
$2A$ (exptl)	0.043	···	0.017	0.0028[b]	0.0060[c]
$2A$ ($n=1$)	0.051	0.062	0.020	0.0023	0.0076
$2A$ ($n=\frac{1}{2}$)	0.055	0.032	···	0.0039	···
$2A$ (L-J, 12–6)	0.061	0.060	0.020	0.0036	0.0094

[a] Units of H are litres STP/day, K_c and K_d in cc STP/cm sec, $2A$ in cm^{-1}.
[b] Extrapolated value.
[c] Interpolated value.

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[22] J. Kestin and W. Leidenfrost, Physica **25**, 537 (1959).

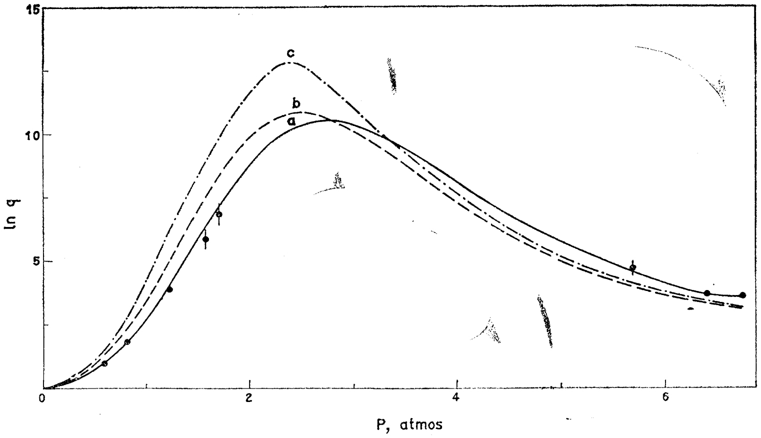

FIG. 1. Comparison of theoretical and experimental-separation factors as a function of pressure for He. ●—Experimental points, Bowring's *B* column.

of a parasitic-remixing effect, Table II. In all these calculations, an $\alpha_T=0.059$ was assumed, following McInteer *et al.*[23] This value has been confirmed by the recent measurements of van der Valk and de Vries.[24] They found $\alpha_T=0.062$ in the approximate temperature range 300–500°K. Consequently, the lack of this disagreement cannot be attributed to the α_T value or to its variation with temperature. The reduction in the value of the exponent 12 will tend to decrease the value of H and may, thereby, further worsen the agreement between theory and experiment. Also listed in Table III are the experimental and calculated $2A$ values, and these also show the same type of disagreement as found in the case of H values. It may be noted in connection with an earlier conclusion of Srivastava[10] that the experimental H values of McInteer *et al.* for the hot-wire column lie in between the two theoretical values corresponding to $n=1$ and $\frac{1}{2}$ is wrong. He was led to this because of the interchange of the theoretical values of H for $n=1$ with the experimental values. Our theoretical H values for $n=\frac{1}{2}$, are greater than the corresponding values for $n=1$, whereas Srivastava[10] found them to be smaller.

Bowring[25] has investigated the pressure dependence

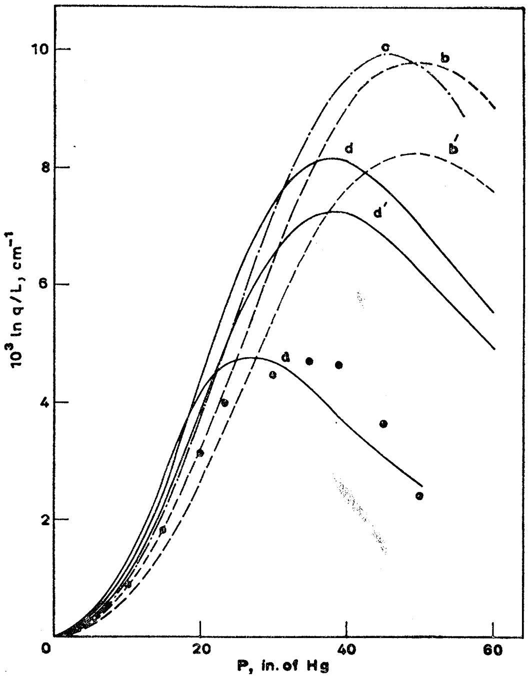

FIG. 2. Comparison of theoretical- and experimental-$(\ln q)/L$ plots as a function of pressure for Ne. ●—Experimental points, Moran and Watson, $T_1=298$°K.

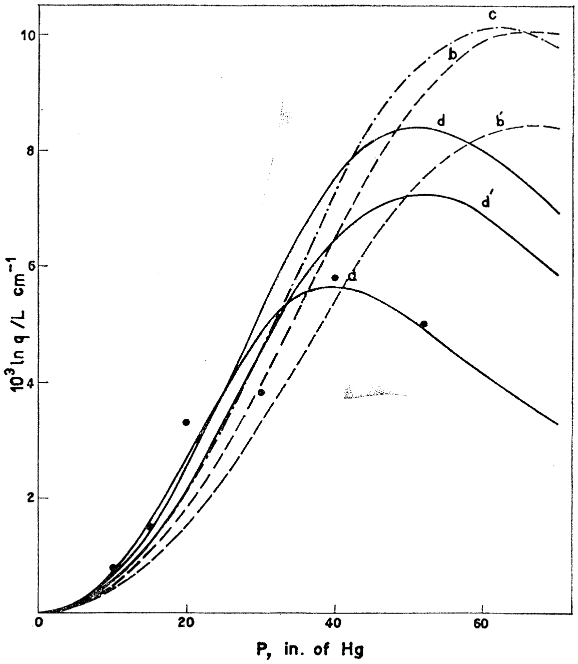

FIG. 3. Comparison of theoretical- and experimental-$(\ln q)/L$ plots as a function of pressure for Ne. ●—Experimental points, Moran and Watson, $T_1=358$°K.

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[23] B. B. McInteer, L. T. Aldrich, and A. O. Nier, Phys. Rev. **72**, 510 (1947).

[24] F. van der Valk and A. E. de Vries, J. Chem. Phys. 34, 345 (1961).

[25] R. W. Bowring, Great Britain Atomic Energy Research Establishment, Harwell Report, AERE-GP/R-2058, Part I (1957).

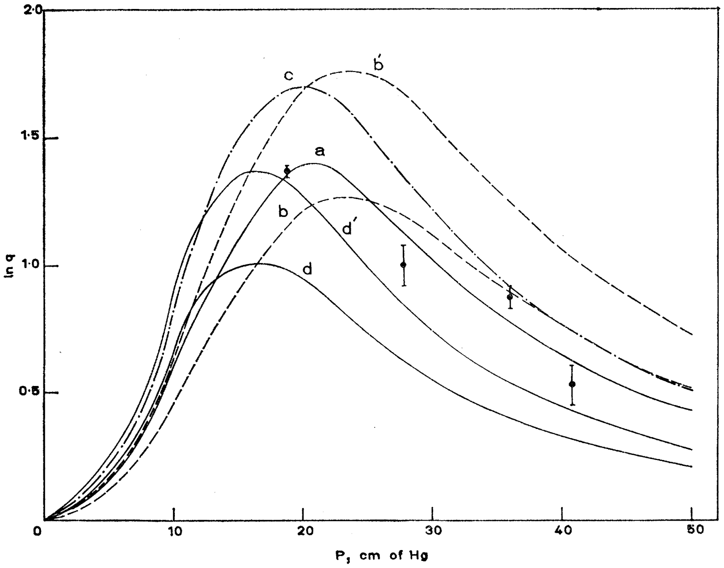

FIG. 4. Comparison of theoretical- and experimental-separation factors as a function of pressure for Ar. ●—Experimental points, Simon, $T_2=1100$°K.

of the separation factor for this gas using a hot-wire column (Column A) and a concentric-tube column (Column B). His experimental results for column A have been considered by us in another paper,[16] while those of Colum B are plotted in Fig. 1. In Table III are tabulated the experimental and theoretical values of H, K_c, K_d, and $2A$ for both columns. From Fig. 1, we find that the experimental data follow the qualitative form of the pressure dependence given by theory; the quantitative agreement is also quite satisfactory. Somewhat similar conclusions were also drawn in connection with the data on Column A by Raman and Saxena.[16] It is interesting to note that, unlike the McInteer *et al.* data[21] for the hot-wire column, here the experimental q values are mostly lower than the calculated values. From Table III, we also find that the agreement between the theoretical and the experimental H, K_c, K_d, and $2A$ values is poor. Our calculated H values differ considerably from those of McInteer and Reisfeld,[14] and we feel that there is some computational error in their reported values. Thus, we find that the two sets of data for He show discrepancies of opposite nature when compared with theory. This result is rather surprising, for helium accords well to the assumptions of theory. The parasitic remixing cannot improve or explain the disagreement. Some other column experiments also have been performed[26] with this gas, but the data are not suitable for quantitative interpretation. Further precise column measurements will be extremely useful to resolve this discrepancy.

Neon and Argon

Several workers[18,27,28] have used thermal-diffusion columns either to enrich the neon isotopes or to measure

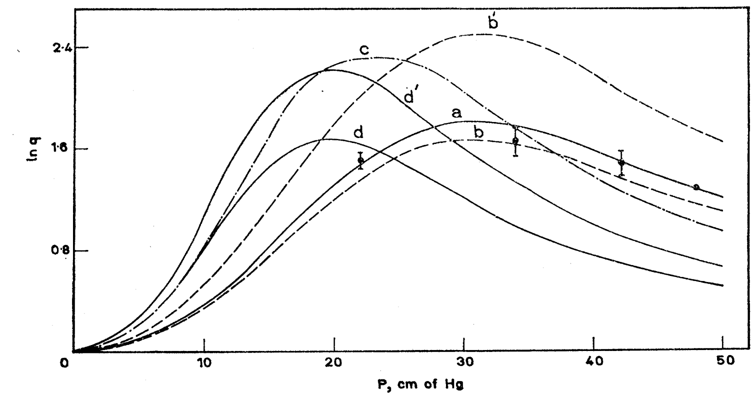

FIG. 5. Comparison of theoretical- and experimental-ln$q$ values as a function of pressure for Ar. ●—Experimental points, Simon, $T_2=1500$°K.

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[26] A. Andrew and W. R. Smythe, Phys. Rev. **74**, 496 (1948); O. F. Schuette, A. Zucker, and W. W. Watson, Rev. Sci. Instr. **21**, 1016 (1950).

[27] T. I. Moran and W. W. Watson, Phys. Rev. **111**, 380 (1958).

[28] W. W. Watson, L. Onsager, and A. Zucker, Rev. Sci. Instr. **20**, 924 (1949); G. Dickel and K. Clusius, Z. physik. Chem. **B48**, 50 (1940); K. Clusius and M. Huber, Experimentia **6**, 262 (1950).

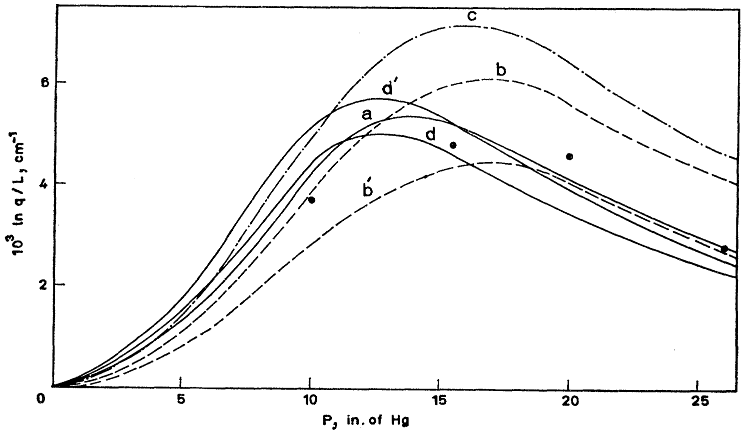

FIG. 6. Comparison of theoretical- and experimental-(ln$q$)/L values as a function of pressure for Ar. (Normal). ●—Experimental points, Moran and Watson, $T_1=288$°K.

the separation factor under different conditions with a view to determining the most efficient operation of the column. Moran and Watson[27] determined the separation factor as a function of pressure for two sets of cold- and hot-wall temperatures, and their data are most suitable for comparison with theory. The experimental data of Moran and Watson[27] are shown in Figs. 2 and 3. In either case, we find that the experimental data accord only moderately well even to the theoretical, qualitative form for the pressure dependence. The calculated q values according to the L-J potential are almost double the experimental values, and the pressure at which the maximum separation occurs also disagrees. Such a poor reproduction is unexpected as the L-J (12–6) potential does satisfactorily represent the behavior of neon gas in this temperature range.[9] This discrepancy between theory and experiment also cannot be attributed to the presence of parasitic convection in the column as seen from Table II. An attempt in this direction leads only to unrealistic values for K_p/K_c and b' values which are only two-thirds the theoretical values in certain cases, whereas the agreement is good for the inverse-power model $n=\frac{1}{2}$ and L-J (12–6) potential at $T_1=298$°K. From Figs. 2 and 3, we find that the agreement between theory and experiment is improved for the inverse-power model if the temperature dependence of α_T is incorporated. Viscosity and thermal-conductivity data[29] yield $n=0.630$ in the temperature range 300–1100°K. Even if the theoretical curves are interpolated for this n value, the agreement is far from satisfactory for pressures greater than one atmosphere. In particular, the maximum-separation factors are very different, the observed values being too low. Unfortunately, no reliable data for α_T as a function of temperature are available[30] to warrant an investigation for exploring this big difference between theory and experiment in the use of an incorrect temperature dependence of α_T. It will, therefore, be interesting to measure α_T as a function of temperature and q as a function of pressure to resolve this discrepancy.

Several very careful studies[17,27] of column operation have been pursued using argon gas. The pressure

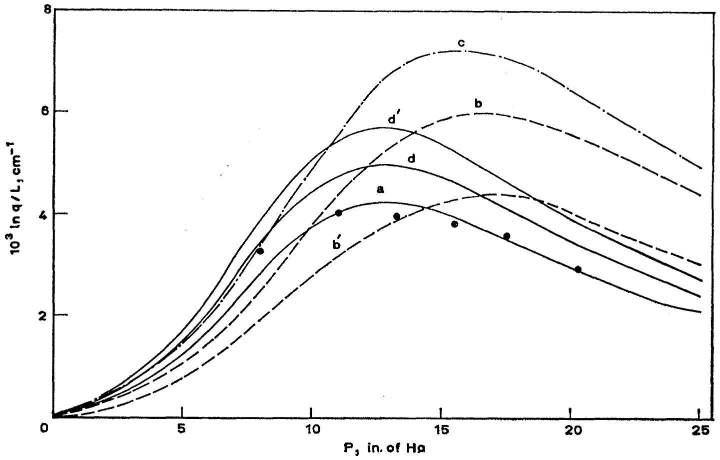

FIG. 7. Comparison of theoretical- and experimental-(ln$q$)/L values as a function of pressure for Ar. (9.7% Ar^{36}). ●—Experimental points, Moran and Watson, $T_1=288$°K.

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[29] R. S. Edwards, Proc. Roy. Soc. (London) **A119**, 578 (1928); M. Trautz and R. Zink, Ann. Physik **7**, 427 (1930); W. G. Kannuluik and E. H. Carman, Proc. Phys. Soc. (London) **B65**, 701 (1952).

[30] S. C. Saxena, J. G. Kelley, and W. W. Watson, Phys. Fluids 4, 1216 (1961).

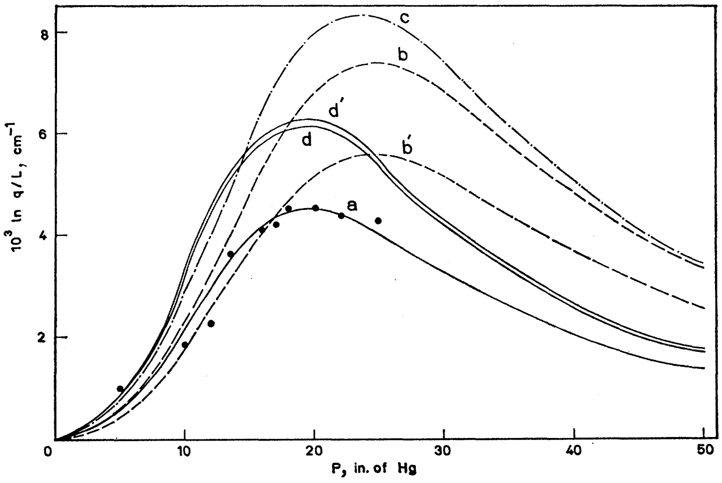

FIG. 8. Comparison of theoretical- and experimental-(ln$q$)/L values as a function of pressure for Ar. (9.7% Ar^{36}). ●—Experimental points, Moran and Watson, $T_1=358$°K.

dependence of the separation factor was extensively investigated by Simon,[17] and by Moran and Watson.[27] Both of these sets of data are considered here for comparison with theory. Simon[17] measured q for the hot-wire temperatures at 1100° and 1500°K and his data are plotted in Figs. 4 and 5, and those of Moran and Watson are plotted in Figs. 6–8. All the five sets of data can be reasonably represented by the theoretical qualitative form for the pressure dependence. The Lennard-Jones (12–6) potential gives poor agreement with the experimental data in almost all cases, the observed separation always being smaller. One would normally expect a very good agreement for this gas as L-J [12–6) potential adequately reproduces almost all the properties.[9] The inclusion of a parasitic-remixing term, unlike neon, improves the agreement in certain cases. The value of n obtained on the basis of experimental viscosity and thermal conductivity[31] is 0.72 ±0.06. Keeping in view even this value of n, we find only a poor over-all agreement between theory and experiment, the inverse-power model giving a somewhat superior agreement with the experiment than the L-J (12-6) potential.

Krypton and Xenon

Amongst all the data available for krypton[27,32] and xenon,[27,33] we have analyzed here only those of Moran and Watson[27] for krypton (Figs. 9 and 10), while for xenon, it has been done by Raman and Saxena.[16]

In Figs. 9 and 10, we have plotted $(\bar{m}/L)\ln q'^{27}$ instead of ln$q$ as a function of pressure, where $\bar{m}$ is the average mass of the two isotopes and q' is the value of q for unit-mass difference of isotopes.[27,34] Both these gases approximate better the Maxwellian behavior as far as the temperature dependence of η, λ, and D are concerned. We find from available viscosity and thermal-conductivity data that $n=0.83$ for krypton[35]

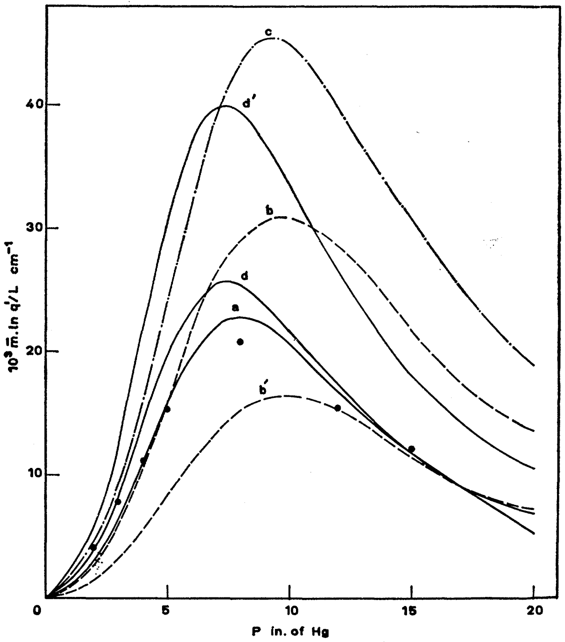

FIG. 9. Theoretical- and experimental plots of $(\bar{m}/L)\ln q'$ values vs pressure for Krypton. q' is q for unit mass difference of the two isotopes. ●—Experimental points, Moran and Watson, $T_1=298$°K.

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[31] M. Trautz and R. Zink, Ann. Physik **7**, 427, (1930); H. L. Johnston and E. R. Grilly, J. Phys. Chem. **46**, 948 (1942); V. Vasilesco, Ann. phys. **20**, 292 (1945); C. F. Bonilla, S. J. Wang, H. Weiner, Trans. Am. Soc. Mech. Engrs. **78**, 1285 (1956); W. G. Kannuluik and E. H. Carman, Proc. Phys. Soc. (London) **B65**, 701 (1952).

[32] W. Groth, Naturwiss. **27**, 260 (1939); W. Groth and P. Harteck, *ibid.* **28**, 47, (1940); K. Clusius and G. Dickel, Z. physik. Chem. **B52**, 348 (1942); **B53**, 178 (1943); J. W. Corbett and W. W. Watson, J. Chem. Phys. **25**, 385 (1956).

[33] W. Groth, Naturwiss. **27**, 260 (1939); K. Clusius, Helv. Phys. Acta. **22**, 473 (1949); K. Clusius, H. H. Bühler, H. Hürzeler, and E. Schumacher, Z. Naturforsch. **10a**, 809 (1955); **11a**, 702 (1956).

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[35] A. O. Rankine, Proc. Roy. Soc. (London) **A83**, 516 (1910). **A84**, 181 (1910); W. G. Kannuluik and E. H. Carman, Proc; Phys. Soc. (London), **B65**, 701 (1952); B. N. Srivastava and S. C. Saxena, *ibid.* **B70**, 369 (1957).

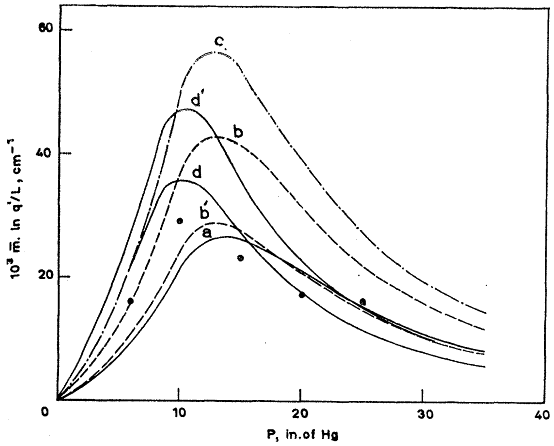

FIG. 10. Theoretical and experimental plots of $(\bar{m}/L)\ln q'$ as a function of pressure for Krypton. ●—Experimental points, Moran and Watson, $T_1=358°$K.

and $n=90$ for xenon[36] in the temperature range 300° to 600°K. On the other hand, the temperature dependence of α_T for these gases is very pronounced.[37] From the figures, we find that the theoretical qualitative form for the pressure dependence of q is preserved reasonably well. Theoretical calculated values according to L-J (12–6) potential are in extremely poor agreement with the observed values. The inverse-power model, on the other hand, gives a much better reproduction of the experimental data. An accurate knowledge of temperature variation of α_T may still improve the agreement. In this direction, further experimental work with this gas will be useful to check the theory. Analogous conclusions were arrived at by Raman and Saxena[16] while interpreting the experimental data for xenon.

B. Polyatomic gases

Rigorously speaking, the theory given in the foregoing section does not hold for polyatomic molecules because of assumption (5). (η/λ) and $(\rho D/\lambda)$ are no longer temperature-independent quantities, owing to the dependence of λ on the internal degrees of freedom.[38] If we assume that (λ/T^m) and not (λ/T^n) is independent of temperature, we obtain the following equations corresponding to Eqs. (34) and (35):

$$G(T)=-\left(\frac{QT^m}{\lambda}\right)^{3/(m+1)}\left[\frac{g\lambda_1{}^3\rho_1{}^2}{\eta_1 Q^3}\right]\frac{r_0{}^4}{t_1{}^{3m-n-2}}\gamma(t), \quad (76)$$

and

$$\frac{d}{dt}t^{-m}\exp\left(\frac{2t^{m+1}}{m+1}\right)\frac{d^2}{dt^2}t^{1-m}\exp\left(\frac{2t^{m+1}}{m+1}\right)\frac{d\gamma(t)}{dt}=t^{-2}, \quad (77)$$

where $G(T)$ and $\gamma(t)$ are new functions and satisfy the same type of boundary conditions as given by Eqs. (27) and (36), respectively. Additional complications arise in carrying the algebra further starting from Eq. (77) and calculating the expressions for K_c, K_d, and K_d' because of the temperature dependence of $(\rho D/\lambda)$ also. Probably the best solution for polyatomic gases is to perform numerical integrations for the specific cases, preceded by a numerical solution of Eq. (77).

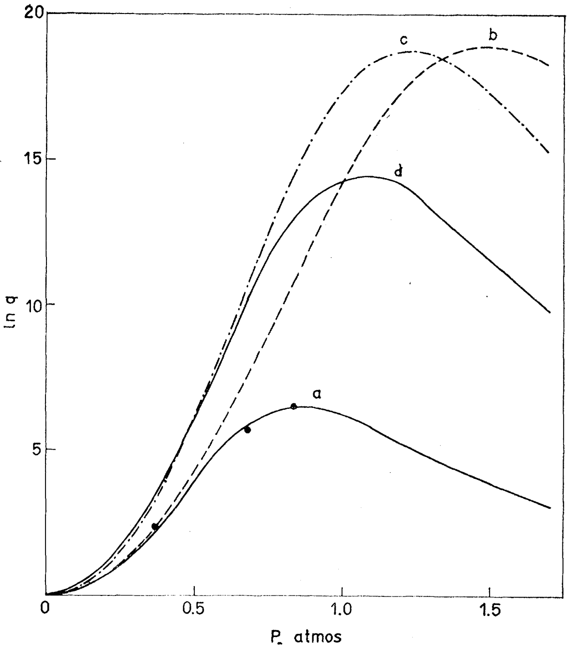

FIG. 11. Comparison of theoretical- and experimental-separation factors as a function of pressure for H_2. ●—Experimental points, Almqvist, Allen, and Sanders, $T_1=293°$K.

Hydrogen and Oxygen

A number of workers have used thermal-diffusion columns to study the isotope separation of hydrogen[39] and oxygen.[39,40] In the case of hydrogen isotopes, as the mass differences are rather big, assumption (3) does not hold in addition to the limitations mentioned in the foregoing and, unless one isotope is in trace, the composition dependence of the transport coefficients and density in the column cannot be neglected. Almqvist, Allen, and Sanders[39] measured the separation factor as a function of pressure for a mixture of hydrogen (96.5%) and tritium (3.5%). As the heavier component

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[36] A. O. Rankine, Proc. Roy. Soc. (London) **A83**, 516 (1910); M. Trautz and R. Heberling, Ann. Physik **20**, 118 (1934); W. G. Kannuluik and E. H. Carman, Proc. Phys. Soc. (London) **B65**, 701 (1952); S. C. Saxena, Indian J. Phys. **31**, 597 (1957).

[37] T. I. Moran and W. W. Watson, Phys. Rev. **109**, 1184 (1958).

[38] J. O. Hirschfelder, J. Chem. Phys. **26**, 282 (1957).

[39] G. T. Seaborg, A. C. Wahl, and J. W. Kennedy, J. Chem. Phys. **8**, 639 (1940); E. Almqvist, K. W. Allen, and J. H. Sanders, Rev. Sci. Instr. **26**, 649 (1955); G. R. Grove, K. W. Foster, and R. E. Vallee, *Proceedings International Symposium on Isotope separation* (North-Holland Publishing Company, Amsterdam, 1958), Chapter 35; C. Boorman and H. Kronberger, *ibid.* Chapter 36.

[40] I. Lauder, Trans. Faraday Soc. **43**, 620 (1947); E. Whalley, E. R. S. Winter, and H. V. A. Briscoe, *ibid.* **45**, 1085 (1949); S. B. Welles, Phys. Rev. **69**, 586 (1946); K. Clusius and G. Dickel, Z. physik. Chem. **193**, 274 (1944); K. Clusius, G. Dickel, and E. Becker, Naturwiss. **31**, 210 (1943).

is only in small proportion, we will still assume that the variation of η, λ, ρ, and D is negligible because of the change in composition. Their[39] measured separation points are shown in Fig. 11. Data of Whalley, Winter, and Briscoe[40] for oxygen isotopes are plotted in Fig. 12. The excellent agreement of the experimental points with curve a in both the cases shows that the simple theory of monatomic gases gives a qualitative form for the pressure dependence which holds well for hydrogen and oxygen. It will, therefore, be interesting to see what happens to this simple theory on the quantitative basis. For both gases, we find that the measured-separation factors are much smaller than the predicted values. From the experimental values of thermal conductivity, we find m equal to 0.818 (300° to 800°K) for hydrogen[41] and 0.911 (200° to 600°K) for oxygen[42] whereas from the viscosity data we get n equal to 0.676 (200° to 1100°K) and 0.686 (300° to 1100°K) for hydrogen[43] and oxygen,[44] respectively.

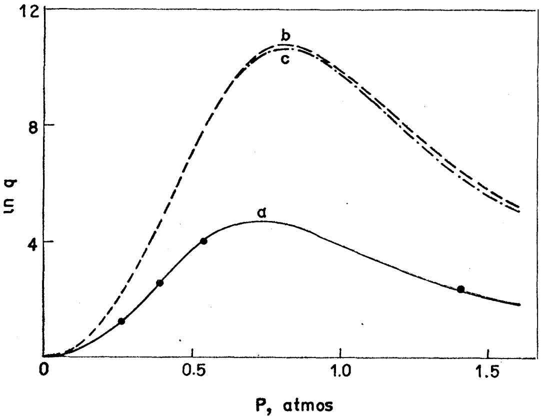

FIG. 12. Comparison of theoretical- and experimental-separation factors as a function of pressure for oxygen isotopes. ●—Experimental points, Whalley, Winter, and Briscoe.

Thus, we find that the assumption (λ/η) is temperature independent, very weak, and may indeed be the chief cause of the failure of theory. Table II also confirms that this bad agreement cannot be attributed to the presence of a parasitic-remixing effect in the columns. A slightly improved agreement will be obtained for both the gases if the experimentally available α_T values[45] are used. As the difference between theoretical and experimental α_T values is of the order of experimental uncertainty, we have used the theoretical values. However, now it has become possible to accurately determine these values by Trennschaukel.

Methane

Methane is a very interesting polyatomic molecule because it can be considered as approximately spherical in shape and because the transport theory developed for spherically symmetrical molecules also holds well[9] for this gas, except in the case of thermal conductivity. The assumption that (η/λ) and $(\rho D/\lambda)$ are not independent of temperature is also important here. From the viscosity data,[46] we find $n=0.787$, while the thermal conductivity data[47] yield $m=1.36$. Both of these values approximately correspond to the temperature range 300° to 600°K. Nier and others[48] have reported column measurements for this gas. Nier's data[48] are plotted in Fig. 13. Here again we find that the experimental data can be well represented by Eq. (73) assuming parasitic convection to be absent where a and b are according to the L-J (12-6) model, and refer to the ratio of the hot-wall to the cold-wall temperature values as 2.00 and 2.09, respectively, the experimental value[48]

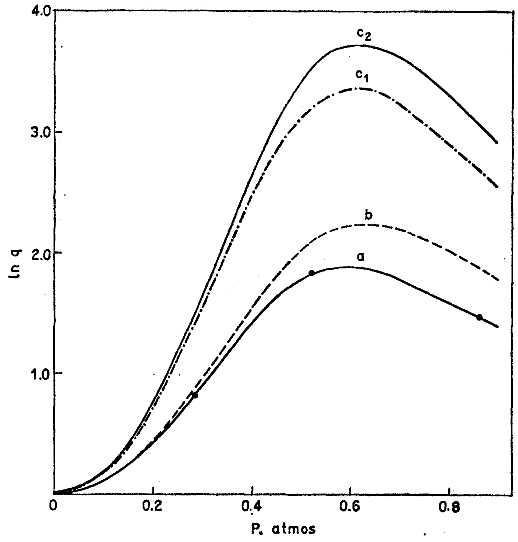

FIG. 13. Comparison of theoretical- and experimental-separation factors as a function of pressure for Methane gas, Nier. Curves c_1 and c_2 are both according to the L-J (12-6) potential for (T_2/T_1) equal to 2.0 and 2.09, respectively. ●-Experimental points.

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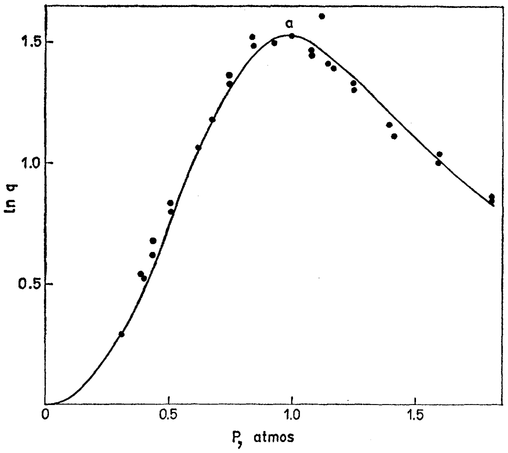

FIG. 14. Separation factors as a function of pressure for carbon dioxide and propane mixture. ●—Experimental points, Drickamer *et al.*

being 1.91 for which the tabulations are not available.[19] We find that the agreement is good with $n=1$ values and becomes still better if a parasitic-remixing term is included (Table II). We feel, in conformity with Jones and Furry,[13] that this excellent agreement is just fortuitous. Indeed, the L-J model predicts higher values in accordance with what we found for hydrogen and oxygen. In view of the widely different m and n values, the simple theory is inapplicable for methane.

C. Gaseous Mixtures

The theory described in this paper does not apply even to the mixtures of nonatomic gases because of assumption (3), while for mixtures involving polyatomic gases further complications arise because of the temperature dependence of (η/λ) and $(\rho D/\lambda)$. Drickamer, Mellow, and Tung[49] have suggested a semi-empirical modification for the theory of Furry, Jones, and Onsager[4] to suit for mixtures by analyzing the data[49,50] on the binary mixtures of Ne—Ar and CO_2—C_3H_8. Some additional support to this modified theory has been added by the later measurements of Tung and Drickamer[51] on CH_4—Xe system, of Hirota and Kobayashi[52] on H_2—N_2 mixtures, and of others.[53] Besides the inherent defect in the Drickamer *et al.* modification of the column theory of being empirical, several other doubts have been raised against it by Becker,[54] and by Davenport and Winter.[55] In view of the fact that the column theory fails badly even for pure polyatomic gases in the low-pressure region, we feel that much caution is required in putting reliance on analyzing data from the modified theory of Drickamer, Mellow, and Tung,[49] who used data for mixtures involving polyatomic gases at high pressures. The Drickamer *et al.*[50] data on CO_2—C_3H_8 system at low pressures is shown in Fig. 14. The qualitative from of the pressure dependence for q suggested by theory is quite adequate in representing this data. Unfortunately, no rigorous theory has yet been developed to compare the experimental results on a quantitative basis.

IV. CONCLUSIONS

The following conclusions seem to be reasonable in view of this detailed comparison of theory and experiment:

(1). The present form of column theory cannot be extended with any confidence for predicting the column behavior either for pure polyatomic gases or for their mixtures.

(2). The quantitative agreement between theory and experiment even for monatomic gases is, in general, quite poor. The agreement is somewhat better at low pressures, i.e., for pressures smaller than the pressure at which q is a maximum. In most of the cases, the inverse power potential gives a better reproduction of column data than the L-J (12–6) potential.

(3). The disagreement cannot be attributed, at least wholly, to the presence of a parasitic remixing in the column.

(4). The qualitative form of the theory for the pressure dependence of the separation factor holds not only for monatomic gases but may also hold for polyatomic gases and probably mixtures.

ACKNOWLEDGMENT

The authors are thankful to H. N. Sethna for his interest in this work.

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[50] H. G. Drickamer, V. J. O'Brien, J. C. Bresee, and C. E. Ockert, J. Chem. Phys. **16**, 122 (1948).

[51] L. H. Tung and H. G. Drickamer, J. Chem. Phys. **18**, 1031 (1950).

[52] K. Hirota and Y. Kobayashi, J. Chem. Phys. **21**, 246 (1953).

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