Effects of column asymmetry on thermal diffusion separations

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The theory of the Clusius–Dickel column in static operation is extended to include eccentric misalignment of the inner cylinder. Variable-property effects are included. An orthogonal expansion method is used, and a computer program is provided for general application of the method. The new theory is useful for determining alignment tolerances in commercial separation columns or in absolute measurements of α_T . The theory is supported by experiments on separation of gaseous ^{20}Ne from ^{22}Ne .

INTRODUCTION

The detrimental effects of column asymmetries on thermal diffusion separations were recognized in early studies of the Clusius–Dickel column.^{1,2} Estimates of these ‘parasitic effects’ were given by the foregoing authors and by Dickel,³ but the agreement with experiments was poor.³ In view of the need for an accurate theory to establish tolerances for column design, we treat the performance of ec-

centric columns here in greater detail.

For asymmetric columns it is preferable to solve the equations of change directly for the temperature, velocity and composition profiles, rather than use the conventional method^{1–4} of partial integration. The direct approach gives a clearer physical picture of the interaction of the flow and diffusion phenomena, and also is easier for this three-dimensional problem.

NOTATION

A_{ijk}	Trial function coefficients for the composition
a	Dimensionless y coordinate of pole at $\eta = \infty$
b_1, b_2, b_3	Constants, Eq. (47)
C_{ijk}, C_{ijp}	Trial function coefficients for the velocity
c_1, c_2	Constants, Eq. (39)
$D_{AA^*}(T)$	Isotopic ordinary diffusivity
E	Dimensionless constant, Eq. (30)
$e_D, e_k, e_\alpha, e_\mu$	Exponents for temperature dependence of physical properties
$G(\eta, \xi)$	Transformation function, $(\cosh \eta - \cos \xi)^2$
g	Gravitational acceleration
$H = H'p^2,$	
$K = K_c + K_p + K_d$	
$\quad = (K'_c + K'_p)p^4 + K_d$	Column transport coefficients
$k(T)$	Thermal conductivity
L	Distance between column sampling points
N_η, N_ξ	Numbers of collocation points in η and ξ directions
p	Pressure
q	Column separation factor, Eq. (43)
R	Tube radius
$T(\eta)$	Absolute temperature

$u(\eta)$	Coordinate, Eq. (17)
$v_z(\eta, \xi)$	Upward velocity component
V_g, V_p, V	Dimensionless velocity components, Eqs. (9) and (12)
x, y, z	Rectangular coordinates
Greek letters	
$\alpha_T(T)$	Thermal diffusion factor
ϵ	Dimensionless displacement of inner cylinder from tube axis
η, ξ, ζ	Bipolar coordinates, Eqs. (1), (2), and (3)
κ	Ratio of inner cylinder radius to tube radius
λ_1	Dominant non-zero eigenvalue in Eq. (33)
$\mu(T)$	Fluid viscosity
$\rho(T)$	Fluid density
$\omega(\eta, \xi, \zeta)$	Mass fraction of ascending isotope
$\omega_s(\zeta)$	Mean surface composition, Eq. (41)
$\omega_{12}(\xi, \zeta)$	Mean surface composition, Eq. (26)
Subscripts	
0	Reference value for linearization of $\omega(1 - \omega)$
1, 2	Cold and hot wall
B, T	Bottom and top sampling points
g	Gravity contribution to the velocity profile
p	Pressure contribution to the velocity profile

SYSTEM DESCRIPTION

The ideal Clusius–Dickel column consists of a vertical tube of radius R maintained at a uniform temperature T_1 , and a coaxial rod of radius κR heated electrically to a higher temperature T_2 . We consider here the effect of a deviation, ϵR , from coaxial alignment of the rod and tube.

The system is analyzed in bipolar coordinates η, ξ, ζ , related to the rectangular coordinates as follows (see Fig. 1)

$$x/aR = \sin \xi / (\cosh \eta - \cos \xi), \quad (1)$$

$$y/aR = \sinh \eta / (\cosh \eta - \cos \xi), \quad (2)$$

$$z/R = R^3 \bar{\rho} g \zeta / \bar{D}_{AA} \bar{\mu}. \quad (3)$$

The outer and inner wall are at $\eta = \eta_1$ and $\eta = \eta_2$, respectively.

We assume quasisteady operation^{1,2,5} with a gaseous mixture of heavy isotopes A and A*. The mixture velocity is purely vertical, and the temperature and velocity are considered independent of ζ . The fluid properties μ , ρ , k , D_{AA^*} , and α_T

depend only on T in a given column. The Dufour effect is small here and is omitted, as usual,^{1–5} to allow an uncoupled solution of the problem.

SOLUTION FOR THE TEMPERATURE

The temperature satisfies the differential equation

$$\frac{\partial}{\partial \eta} \left(k \frac{\partial T}{\partial \eta} \right) + \frac{\partial}{\partial \xi} \left(k \frac{\partial T}{\partial \xi} \right) = 0. \quad (4)$$

The solution for uniform wall temperatures at η_1 and η_2 is that $\int k dT$ depends linearly on η and is independent of ξ as well as ζ . The fluid properties are correspondingly independent of both ξ and ζ . Then, if k is a power function of T ,

$$k/\bar{k} = (T/\bar{T})^{e_k} \quad (5)$$

the solution becomes

$$\left(\frac{T}{\bar{T}} \right) = \left\{ \left(\frac{T_1}{\bar{T}} \right)^{1+e_k} + \frac{\eta - \eta_1}{\eta_2 - \eta_1} \left[\left(\frac{T_2}{\bar{T}} \right)^{1+e_k} - \left(\frac{T_1}{\bar{T}} \right)^{1+e_k} \right] \right\}^{1/(1+e_k)}. \quad (6)$$

Note that the reference conductivity $\bar{k}$ does not appear in the solution.

FIG. 1. Column cross section and bipolar coordinate grid.

SOLUTION FOR THE VELOCITY

In view of Eq. (6) and the assumptions previously stated, the equation of motion reduces to

$$\left[\frac{\partial}{\partial \eta} \left(\mu \frac{\partial v_z}{\partial \eta} \right) + \mu \frac{\partial^2 v_z}{\partial \xi^2} \right] \frac{G}{a^2 R^2} = \frac{dp}{dz} + \rho g, \quad (7)$$

where $G = (\cosh \eta - \cos \xi)^2$. Equation (7) is to be solved with no-slip conditions at the inner and outer walls and with a pressure gradient corresponding to zero net mass flow (static column operation)

$$\int_S \rho v_z dS = 0. \quad (8)$$

Here S is the fluid cross section at any given value of ζ . The hydrostatic solution $dp/dz = -\bar{\rho}g$ is not appropriate here, though it does hold for small temperature differences in columns with parallel plane boundaries.

We represent v_z as the sum of a gravity term and a pressure term

$$v_z = (\bar{\rho}gR^2/a^2\bar{\mu})V_g + [(R^2/a^2\bar{\mu})(dp/dz)]V_p. \quad (9)$$

With these substitutions Eq. (7) yields the following dimensionless equations for V_g and V_p

$$\frac{\partial}{\partial \eta} \left[\frac{\mu}{\bar{\mu}} \frac{\partial V_g}{\partial \eta} \right] + \frac{\mu}{\bar{\mu}} \frac{\partial^2 V_g}{\partial \xi^2} = \frac{\rho a^4}{\bar{\rho} G}, \quad (10)$$

$$\frac{\partial}{\partial \eta} \left[\frac{\mu}{\bar{\mu}} \frac{\partial V_p}{\partial \eta} \right] + \frac{\mu}{\bar{\mu}} \frac{\partial^2 V_p}{\partial \xi^2} = \frac{a^4}{G}. \quad (11)$$

Elimination of dp/dz from Eq. (9) by use of Eq. (8) gives

$$(a^2\bar{\mu}/\bar{\rho}gR^2)v_z = V_g - V_p \int \rho V_g dS / \int \rho V_p dS. \quad (12)$$

The functions $V_g(\eta, \xi)$ and $V_p(\eta, \xi)$ will now be determined using

$$\mu/\bar{\mu} = (T/\bar{T})^{\epsilon\mu}, \quad (13)$$

$$\rho/\bar{\rho} = (\bar{T}/T) \quad (14)$$

as the property functions.

Each of the functions V_g and V_p can be represented in terms of a corresponding stream function ψ as follows

$$\rho V = \bar{\rho} G(\partial\psi/\partial\eta). \quad (15)$$

The function ψ can be approximated by a finite expansion in trial functions of η and ξ

$$\psi = \sum_{i=0}^{N_\eta-1} \sum_{j=0}^{N_\xi-1} C_{ij} f_i(u) \cos(j\xi). \quad (16)$$

Here

$$u = \frac{\ln(\eta/\eta_1)}{\ln(\eta_2/\eta_1)}, \quad (17)$$

$$f_0(u) = \frac{1}{2}u^2 - \frac{1}{3}u^3, \quad (18)$$

$$f_i(u) = u^{i+1}(1-u)^2 \quad i \geq 1. \quad (19)$$

The transformation in Eq. (17) was selected on the basis of numerical studies of the convergence of the approximation scheme. Equations (18) and (19) ensure satisfaction of the no-slip conditions. The cosine functions in Eq. (16) provide the required symmetry of the solution with respect to x .

Integration of Eq. (15) over the fluid cross section gives

$$\int_S \rho V dS = 2 \int_{\eta_1}^{\eta_2} \int_0^\pi (a^2 R^2 / G) \rho V d\eta d\xi = (\pi/3) \bar{\rho} a^2 R^2 C_{00}, \quad (20)$$

whence

$$\int \rho V_g dS / \int \rho V_p dS = C_{00g} / C_{00p}. \quad (21)$$

The coefficients C_{ijg} and C_{ijp} are determined by collocation, that is, by requiring that Eqs. (15) and (16) satisfy Eqs. (10) and (11), respectively, at a chosen set of points in the fluid cross section of Fig. 1. This yields linear equations which can be solved numerically for the coefficients.

The departures of the approximate solutions from Eqs. (10) and (11) are made small in the mean by choosing the collocation points as Gaussian quadrature points in $(0 < u < 1)$ and Mehler quadrature points in $(0 < \xi < \pi)$. The latter are given by

$$\xi_j = (j - \frac{1}{2})\pi/N_\xi \quad j = 1, 2, \dots, N_\xi \quad (22)$$

and lie in the first quadrant of Fig. 1.

The convergence of the leading coefficients C_{00g} and C_{00p} with respect to N_η and N_ξ is illustrated in Table I. Three-figure convergence is achieved in

TABLE I. Convergence of the flow coefficients.

ϵ	N_ξ	Values ^a of C_{00g} and C_{00p} . ^b		
		$N_\eta=8$	$N_\eta=10$	$N_\eta=12$
0°	1	-0.184838	-0.184588	-0.184583
		-0.199933	-0.199771	-0.199768
0.1685	4		-0.196825	
			-0.209967	
	5	-0.198523	-0.196827	-0.196797
		-0.211082	-0.209969	-0.209950
	6		-0.196827	
			-0.209969	
0.3370	4		-0.233512	
			-0.239955	
	5	-0.236172	-0.234039	-0.233999
		-0.241671	-0.240386	-0.240363
	6		-0.234108	
			-0.240441	

^aThe upper number in each pair is C_{00g} .

^bConstants: $\kappa=0.08525$, $T_1=288^\circ\text{K}$, $T_2=1098^\circ\text{K}$, $\bar{T}=450^\circ\text{K}$, $e_k=0.65$, $e_\mu=0.65$.

^cFor this case (centered rod) the solution is axially symmetric and was done in polar coordinates.

each case with $N_\eta \geq 10$ and $N_\xi \geq 5$ (or $N_\xi=1$ for $\epsilon \approx 0$). This high accuracy is necessary since V_g and V_p are opposed in Eq. (12). The convergence of the remaining coefficients C_{ijg} and C_{ijp} is indicated by the results obtained below for the diffusion problem. The validity of the procedure is further indicated by the close agreement of V_p in the constant-property limit with the known exact solution.^{6,7}

The velocity field for one of the cases in Table I

is shown in Fig. 2. The asymmetry of the flow is evident.

SOLUTION FOR THE COMPOSITION

The equation of continuity for the ascending isotope is

$$\rho v_z \frac{\partial \omega}{\partial z} = \left[\frac{\partial}{\partial \eta} (\rho D_{AA}^* \phi_\eta) + \rho D_{AA}^* \frac{\partial^2 \omega}{\partial \xi^2} \right] \frac{G}{a^2 R^2} + \rho D_{AA}^* \frac{\partial^2 \omega}{\partial z^2}, \quad (23)$$

where

$$\phi_\eta = \partial \omega / \partial \eta + \omega(1-\omega) \alpha_T (\partial \ln T / \partial \eta). \quad (24)$$

The impermeability of the wall gives the boundary condition

$$\phi_\eta = 0 \text{ at } \eta = \eta_1 \text{ and } \eta = \eta_2. \quad (25)$$

The end conditions will be discussed after the general solution of these equations is indicated.

The nonlinear term $\omega(1-\omega)$ can be closely approximated by inserting the following average of the surface compositions

$$\omega_{12}(\xi, \eta) = \frac{1}{2} [\omega(\eta_1, \xi, \xi) + \omega(\eta_2, \xi, \xi)]. \quad (26)$$

This is a refinement of the standard practice¹⁻⁵ of taking $\omega(1-\omega)$ at the cold-wall composition. Expanding this product and truncating to linear terms, we obtain

$$\omega(1-\omega) \approx \omega_{12}(1-2\omega_0) + \omega_0^2, \quad (27)$$

where ω_0 is the value of ω_{12} at a reference point on the plane $\xi = \xi_0$.

FIG. 2. Isometric view of velocity profile of Eq. (12) for an eccentric column with $\epsilon=0.1685$.

TABLE II. Convergence of the dominant eigenvalue.

ϵ	N_ξ	Values ^a of $1/\lambda_1$		
		$N_\eta=8$	$N_\eta=10$	$N_\eta=12$
0	1	0.032608	0.032716	0.032718
0.1685	4		0.081702	
	5	0.082489	0.081772	0.081744
	6		0.081775	
0.3370	4		0.16540	
	5	0.17270	0.17292	0.17290
	6		0.17453	

^aThe constants of Table I are used here. In addition, $\bar{\alpha}_T(1-2\omega_0)=0.0227$, $e_D=1.65$, $e_\alpha=0.35$, and $E=0$.

Equations (23) and (24) can now be rewritten as

$$V \frac{\partial \omega}{\partial \xi} = \frac{G}{\rho D_{AA}^*} \left[\frac{\partial}{\partial \eta} (\rho D_{AA}^* \phi_\eta) + \rho D_{AA}^* \frac{\partial^2 \omega}{\partial \xi^2} \right] + \frac{D_{AA}^*}{D_{AA}^*} a^2 E^2 \frac{\partial^2 \omega}{\partial \xi^2}, \quad (28)$$

$$\phi_\eta = (\partial \omega / \partial \eta) + [\omega_{12}(1-2\omega_0) + \omega_0^2] \alpha_T (\partial \ln T / \partial \eta), \quad (29)$$

where

$$E = \bar{D}_{AA}^* \bar{\mu} / R^3 \bar{\rho} g. \quad (30)$$

The solution for $\omega(\eta, \xi, \zeta)$ will be determined from Eqs. (25), (28) and (29) using

$$D_{AA}^* / \bar{D}_{AA}^* = (T/\bar{T})^{e_D}, \quad (31)$$

$$\alpha_T / \bar{\alpha}_T = (T/\bar{T})^{e_\alpha} \quad (32)$$

as the property functions.

The general solution for ω can be approximated as closely as desired, in the neighborhood of the composition ω_0 , by taking enough terms in the following trial function

$$\omega(1-2\omega_0) + \omega_0^2 = \sum_k e^{\lambda_k(\xi-\xi_0)} \sum_{i=0}^{N_\eta-1} \sum_{j=0}^{N_\xi-1} A_{ijk} F_i(u) \cos(j\xi). \quad (33)$$

Equation (25) is satisfied for ϕ_η of Eq. (29) by taking the functions $F_i(u)$ as follows

$$F_0(u) = 1 + B \frac{1 - (T/\bar{T})^{e_\alpha}}{e_\alpha}, \quad (34)$$

$$F_1(u) = \frac{1}{2}u^2 - \frac{1}{3}u^3 - \frac{1}{12}, \quad (35)$$

$$F_i(u) = u^i(1-u)^2 \quad i \geq 2, \quad (36)$$

where

$$B = \frac{2\bar{\alpha}_T(1-2\omega_0)}{2 + \bar{\alpha}_T(1-2\omega_0)[(T_2/\bar{T})^{e_\alpha} + (T_1/\bar{T})^{e_\alpha} - 2]} e_\alpha^{-1}. \quad (37)$$

For constant α_T , Eq. (34) is rendered determinate by the substitution

$$\lim_{e_\alpha \rightarrow 0} \left[\frac{1 - (T/\bar{T})^{e_\alpha}}{e_\alpha} \right] = \ln(\bar{T}/T). \quad (38)$$

The coefficients A_{ijk} and eigenvalues λ_k are found by requiring Eq. (33) to satisfy Eq. (28) at the same collocation points used in the solution for V . The number of eigenvalues is $N_\eta N_\xi$ if axial diffusion is neglected, and $2N_\eta N_\xi$ if axial diffusion is included. Each value of k gives an eigenfunction of the diffusion problem.

A single exponential term, $\exp(\lambda_1 \xi)$, suffices in Eq. (33) for all cases studied here. The higher eigenvalues are so large (at least 1000 times λ_1 in magnitude) that their contributions can be neglected in the usual mode of operation, which excludes the end regions of the column. As shown below, λ_1 is proportional to the separation accomplished per unit length of column.

The convergence of the dominant eigenvalue with respect to N_η and N_ξ is illustrated in Table II for several column geometries. The convergence becomes slower with increasing ϵ , but is more than adequate for practical needs.

The eigenvalue λ_1 is proportional to $(1-2\omega_0)\bar{\alpha}_T$ within terms of order $\bar{\alpha}_T$, e.g., within 1% for ^{20}Ne – ^{22}Ne . The composition enters the calculation of λ_1 only through the specification of the product $(1-2\omega_0)\bar{\alpha}_T$.

The influence of axial diffusion on λ_1 is shown in Table III. The relation

$$\bar{\alpha}_T(1-2\omega_0)/\lambda_1 = c_1 + c_2 E^2 \quad (39)$$

fits the results almost exactly, as can be seen from the final column of the table.

COLUMN COEFFICIENTS

The ratio of the column coefficients H and K for static separation is, by definition¹

$$H/K = [1/\omega_s(1-\omega_s)](d\omega_s/dz) \quad (40)$$

in which ω_s is a representative composition at the given height in the column. We use

$$\omega_s = (1/\pi) \int_0^\pi \omega_{12}(\xi, \xi) d\xi. \quad (41)$$

Evaluation of H/K from the dominant term of Eq.

TABLE III. Effect of axial diffusion on the dominant eigenvalue.

$E^2 \times 10^8$	$1/\lambda_1^a$	$1/\lambda_1 - (1/\lambda_1)_{E=0}$
0	0.081744	0
25	0.091225	0.00948
50	0.100695	0.01895
75	0.110156	0.02841
100	0.119611	0.03787
200	0.157389	0.07565

^aConstants are the same as in Table II except that here E is varied, $\epsilon=0.1685$, $N_\eta=12$, and $N_\xi=5$.

TABLE IV. Effect of column geometry and axial diffusion on the dominant eigenvalue.

κ	b_1^a	b_2^a	b_3^a
0.08525	0.04673	34800	2.38
0.2	0.03545	39000	1.59
0.5	0.02591	50500	0.914
0.8	0.02182	63200	0.624
0.9	0.02086	67500	0.515
0.95	0.02042	69600	0.386
0.99	0.02009	71300	0.31
1	0.02001 ^b	71800 ^b	

^aComputed with $N_\eta=12$, $N_\xi=5$, and the following constants: $T_1=288^\circ\text{K}$, $T_2=1098^\circ\text{K}$, $\bar{T}=450^\circ\text{K}$, $e_k=e_\mu=0.65$, $e_D=1.65$, $e_\alpha=0.35$, $\bar{\alpha}_T(1-2\omega_0)=0.0227$.

^bObtained by linear extrapolation.

(33) then gives the predicted value

$$H/K = \lambda_1 E / (1 - 2\omega_0) R. \quad (42)$$

Since λ_1 is essentially proportional to $(1 - 2\omega_0)$ as noted above, the calculated ratio H/K is essentially independent of the mass fraction at which the linearization is performed. This is consistent with known results⁴ which show H/K to be independent of ω_s for heavy isotopes in axially symmetric columns.

Integration of Eq. (40) for a column of length L gives the column separation factor

$$\ln q = \ln[\omega_T(1 - \omega_B)/\omega_B(1 - \omega_T)] = HL/K. \quad (43)$$

Equations (39), (42), and (43) give

$$\ln q = \frac{LE\bar{\alpha}_T/R}{c_1 + c_2 E^2}. \quad (44)$$

Since E varies inversely with the square of the pressure for ideal gases, Eq. (44) can be written in the form²

$$\ln q = LH'p^2 / [(K'_c + K'_p)p^4 + K_d] \quad (45)$$

which shows the dependence of the separation factor on the pressure and length of column. Thus our results for c_1 and c_2 can be used to determine the ratios $(K'_c + K'_p)/H'$ and (K_d/H') as functions of the fluid properties and column geometry.

The solution method used here is different from that of Jones and Furry, but agrees closely with their calculations for axisymmetric columns.⁴ For example, the coefficients in their Eq. (85)

$$\ln q = \frac{1.710/p^2}{1 + 0.1628/p^4} \quad (46)$$

are reproduced within 0.5%, and this small deviation is attributable to different definitions of ω_s . The agreement for K_d/H' is particularly remarkable in view of their artificial way of handling axial diffusion. The following constants were used: $\kappa = 0.710$, $\epsilon = 0$, $R = 2.458$ cm, $T_1 = 300^\circ\text{K}$, $T_2 = 573^\circ\text{K}$, $\bar{T} = 436.5^\circ\text{K}$, $\bar{\mu} = 1.51 \times 10^{-4}$ g cm⁻¹ sec⁻¹, $\bar{\rho} = 4.47 \times 10^{-4}$ g cm⁻³, $p\bar{D}_{AA}^* = 0.475$ atm cm² sec⁻¹, $\bar{\alpha}_T = 0.0077$, $L = 730$ cm, $e_k = e_\mu = 1$, $e_D = 2$, and $e_\alpha = 0$.

The influence of ϵ , E , and κ on the column performance is illustrated in Table IV. For small displacements, $\epsilon \leq 0.04(1 - \kappa)$, the dominant eigen-

TABLE V. Observed and predicted column coefficients.

ϵ	$(K'_c + K'_p)/H'$			K_d/H'		
	exptl.	predicted	exptl./predicted	exptl.	predicted	exptl./predicted
0	29.3	35.7 ^a	0.82	38.2	34.0 ^a	1.13
		32.6 ^b	0.90		31.0 ^b	1.23
		27.4 ^c	1.07		40.2 ^c	0.95
0.1685	68.4	89.1 ^a	0.77	30.5	30.9 ^a	0.99
		81.4 ^b	0.84		28.3 ^b	1.08
		68.4 ^c	1.00		36.6 ^c	0.83
0.3370	127	188. ^a	0.67	36.1	24.9 ^a	1.45
		172. ^b	0.74		22.8 ^b	1.58
		145. ^c	0.88		29.5 ^c	1.22

^aPredicted with $N_\eta=12$, $N_\xi=5$, and the following constants: $T_1=288^\circ\text{K}$, $T_2=1098^\circ\text{K}$, $\bar{T}=450^\circ\text{K}$, $\bar{\mu}=4.0 \times 10^{-4}$ g cm⁻¹ sec⁻¹, $\bar{\rho}/p=5.47 \times 10^{-4}$ g cm⁻³ atm⁻¹, $p\bar{D}_{AA}^*=0.97$ atm cm² sec⁻¹, $\bar{\alpha}_T=0.0227$, $e_k=e_\mu=0.65$, $e_D=1.65$, $e_\alpha=0.35$. $\bar{\alpha}_T$ is from Ref. 8, and other physical properties are obtained from collision integrals⁹ for the Lennard-Jones 12-6 potential.

^bPredicted as in Footnote a except that $\bar{\alpha}_T=0.0248$ as determined by a least-squares fit of these experiments. The measured values of q are fitted with a standard error of 14%.

^cPredicted as in Footnote a except that $\bar{\alpha}_T=0.0238$ and $p\bar{\mu}\bar{D}_{AA}^*=4.82 \times 10^{-4}$ atm g cm sec⁻² as determined by a least-squares fit of these experiments. The measured values of q are fitted with a standard error of 5.7%.

value λ_1 is fitted within 1% by the following expression

$$1/(1-\kappa)^4 \lambda_1 = b_1 + b_2 E^2/(1-\kappa)^6 + b_3 \epsilon^2/(1-\kappa)^2. \quad (47)$$

The corresponding behavior of q can be determined by insertion of this expression into Eqs. (42) and (43). Over this small range of displacements, the axial diffusion contribution is negligibly affected by misalignment, in accord with the assumptions of Jones and Furry.²

Equation (47) and Table IV show that very close alignment is necessary when the gap between the rod and the tube is small. The results shown here are for gaseous ^{20}Ne – ^{22}Ne , but indicate the expected magnitude of the misalignment effects for other systems.

COMPARISON WITH EXPERIMENTS

The effect of column misalignment was studied experimentally⁸ by conducting static separations of ^{20}Ne – ^{22}Ne mixtures at pressures from 500 to 1500 torr in a length $L = 152.4$ cm of a column with radii $R = 0.9430$ cm and $\kappa R = 0.08039$ cm. Experiments were done with the wire centered in the tube ($\epsilon = 0$) and also with displacements $\epsilon R = 0.15875$ and 0.3175 cm of the wire from the tube axis. The tube and wire were maintained at 288 and 1098 °K.

Column coefficients $(K'_c + K'_p)/H'$ and K_d/H' were determined by plotting the data according to Eq. (45). The results are shown in Table V. For comparison, predicted values are also given based on the constants of Eq. (44).

The agreement is reasonable in view of the uncertainties of the experimental parameters $(K'_c + K'_p)/H'$ and K_d/H' . The best measure of agreement is that of the separation factors q , which are fitted within 5.7% in Case c, using reasonable property values.

CONCLUSION

The theory developed here provides a detailed description of the effects of column eccentricity on thermal diffusion separations. The resulting loss of separation capacity is most serious for large values of κ (small radial clearances) as shown in Table IV. For small κ values the effect is less im-

portant.

For small displacements, ϵ , of the rod from the axis of the tube, the loss of separation power varies as $\epsilon^2/(1-\kappa)^2$. Thus, with a thin, well aligned center rod, it should be possible to determine accurate values of $\bar{\alpha}_T$ and $\bar{\mu}D_{AA}$ * from measurements of q at various pressures. The recent results of Rutherford¹⁰ are in accord with this.

A computer program has been provided for general use of our solution method. See NAPS Document No. 2146 for 21 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. Remit in advance for each NAPS accession number \$1.50 for microfiche or \$5.00 for photocopies. Make checks payable to Microfiche Publications.

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