Reprinted from AMERICAN JOURNAL OF PHYSICS, Vol. 27, No. 2, 87–89, February, 1959
Printed in U. S. A.

Theoretical Calculations and Experimental Verification for a Demonstration Thermal Diffusion Column

CARLOS E. ESPAÑOL AND CARLOS R. CARJUZAA
Comisión Nacional de Energía Atómica, Buenos Aires, República Argentina

(Received October 24, 1957)

The present paper exemplifies the theoretical calculations for a thermal diffusion column of the hot filament type, easy to build in college laboratories. The separation of a binary mixture of carbon dioxide and argon has been studied and the separation factor, theoretically calculated, has been checked against the experimental separation factor. The results show an acceptable agreement.

THE separation of a binary mixture of roughly 50% CO_2 and 50% A has been studied using a demonstration thermal diffusion column of the hot filament type available in our laboratory,[1] in order to check the separation factor theoretically calculated on the basis of the values of the components' physical constants. It was assumed that the molecular model of the (12–6) Lennard-Jones potential is valid for both components in the prevailing conditions of the experiment. In this model the intermolecular force is the result of the superposition of two force fields—one attractive and the other repulsive—which derive from a potential expressed analytically in this paper.

Although this procedure is less accurate than the method of the two bulbs, since the values of α depend on all the theoretical approximations and experimental errors, it is advantageous because it produces greater variations in the concentration, which can be easily measured. So the method is simple enough to be used in college laboratories, and illustrates typical calculations for a thermal diffusion column.

The column, whose effective length is 190 cm, is made up of a 10-mm inner diameter pyrex glass tube, cooled on the outside, having a 0.3-mm diameter nichrome axial filament. To keep the filament centered, spiral 0.3-mm nichrome spacers are placed at the top and bottom of the column.

To follow the process of separation and to find the degree of concentration of the components at both ends of the column, thermal conductivity gauges like those described previously[1] were used. It is essential to calibrate them beforehand, using CO_2-A mixtures of known proportions; this procedure assumes that the column functions symmetrically.

As it is necessary to maintain a direct current of uniform intensity ($i_k=0.5$ amp) circulating through the thermal conductivity gauges, two 400-w lamps were placed in series with them. These lamps, which were arranged to remain in a semi-incandescent state, stabilized the intensity of the current because of the variation of their resistance following any alteration of their temperature.

1. CHOICE OF A MOLECULAR MODEL

The choice of a molecular model is made by comparing the experimental values of the physical constants of the gases under survey with the theoretical values resulting from calculations based on the particular expressions for each model. Considering the available viscosity and self-diffusion values for carbon dioxide and argon gases[2] and the value of the diffusion coefficient for the carbon dioxide-argon mixture,[3] the (12–6) Lennard-Jones molecular model of potential is appropriate. In this model the intermolecular force is derived from a potential given by

$$\varphi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}],$$

where r is the distance between molecules, σ, the collision parameter, is the distance at which the potential energies of repulsion and attraction

---

[1] J. A. McMillan and C. E. Español, Am. J. Phys. 24, 287 (1956).

[2] Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), Table 8.4–2, p. 562; Table 8.4–13, p. 581. Every future reference to this book will be abbreviated as HCB.

[3] See reference 2, Table 8.4–12, p. 581.

of the field are equal, and 4ϵ is the value of each of the energies at distance σ.

2. CALCULATION OF THE CONSTANTS FOR A CARBON DIOXIDE-ARGON MIXTURE

Here, we follow the analysis in reference 2. The temperature (T_1) of the cold wall of the column is 300°K, so the constants of the mixture are calculated at this temperature.

The values of the collision integrals, necessary for the calculations, will be estimated at the reduced temperature $T^*=kT/\epsilon$; and the values of the constants ϵ and σ resulting from the application of the empirical law of combinations will be used.[4]

The subscripts 1 and 2 correspond to argon and carbon dioxide, respectively. In this way, the values indicated in Table I are obtained.

Density

$$\rho_{12}=\tfrac{1}{2}(\rho_1+\rho_2)=1.711\times10^{-3}\text{ g cm}^{-3}\text{ at }300°\text{K}.$$

Viscosity

Viscosity in a gas mixture varies with the composition, and can be greater than that of its components in certain cases.

Following HCB the viscosity coefficient of a binary mixture is given to a first approximation by

$$1/\eta_m=(X_\eta+Y_\eta)/(1+Z_\eta),$$

where

$$X_\eta=(N_1^2/\eta_1)+(2N_1N_2/\eta_{12})+(N_2^2/\eta_2),$$

$$Y_\eta=\tfrac{3}{5}A_{12}^*\left\{\frac{N_1^2}{\eta_1}\frac{M_1}{M_2}+\frac{2N_1N_2}{\eta_{12}}\frac{(M_1+M_2)^2}{4M_1M_2}\times\frac{\eta_{12}^2}{\eta_1\eta_2}+\frac{N_2^2}{\eta_2}\frac{M_2}{M_1}\right\},$$

and

$$Z_\eta=\tfrac{3}{5}A_{12}^*\left\{N_1^2\frac{M_1}{M_2}+2N_1N_2\left[\frac{(M_1+M_2)^2}{4M_1M_2}\times\left(\frac{\eta_{12}}{\eta_1}+\frac{\eta_{12}}{\eta_2}\right)-1\right]+N_2^2\frac{M_2}{M_1}\right\},$$

TABLE I. Constants for a carbon dioxide-argon mixture.

	A	Reference	CO_2	Reference	$A-CO_2$	Reference
$\sigma(A)$	3.418	a	3.996	a	3.707	b,c
$\epsilon/k(°K)$	124	a	190	a	153	b
T^*	2.419		2.1579		1.961	
$\Omega_{(T^*)}^{(11)*}$					1.082	d,e
$\Omega_{(T^*)}^{(22)*}$	1.104	d	1.286	d	1.184	d,e
$A_{(T^*)}^*$					1.094	f,e
$B_{(T^*)}^*$					1.121	f,e
$C_{(T^*)}^*$					0.833	f,e

[a] HCB, Table 8.4–1, p. 561.
[b] HCB, Table 8.4–12, p. 579.
[c] See reference 2, p. 567.
[d] HCB, Table I–M, Appendix, p. 1126.
[e] The quantities *A*, *B*, and *C* of HCB, p. 528, correspond to *A*, *B*, and *C* of S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (The Cambridge University Press, New York, 1952), p. 164, and of K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases* (The Cambridge University Press, New York, 1952), p. 26, divided by the corresponding values for the model of rigid spheres.
[f] HCB, Table I–N, Appendix, p. 1128.

in which N_1, N_2 = molar fractions of gases 1 and 2, M_1, M_2 = molecular weights of gases 1 and 2, η_1, η_2 = coefficients of viscosity of gases 1 and 2 given by

$$\eta=266.93\frac{(MT)^{\frac{1}{2}}}{\sigma^2\Omega_{(T^*)}^{(22)*}}10^{-7}\text{ g cm}^{-1}\text{ sec}^{-1},$$

η_{12} = coefficient of viscosity of an assumed pure substance of molecular weight $2M_1M_2/(M_1+M_2)$ whose potential parameters are σ_{12} and ϵ_{12}, given by

$$\eta_{12}=266.93\frac{[2M_1M_2T/(M_1+M_2)]^{\frac{1}{2}}}{\sigma_{12}^2\Omega_{12(T_{12}^*)}^{(22)*}}\times10^{-7}\text{ g cm}^{-1}\text{ sec}^{-1}.$$

For our values we get

$$\eta_m=1830\times10^{-7}\text{ g cm}^{-1}\text{ sec}^{-1}.$$

Diffusion Coefficient

The diffusion, instead of the self-diffusion coefficient, is used, as we are dealing with a common binary mixture of isotopic type.

Although the formulas given as a first approximation indicate that the diffusion coefficient is independent of the concentration of the components, to a second approximation they have a certain influence even though the calculation shows that whatever the adopted molecular model may be, its influence is not greater than 13%.

The first approximation given by HCB is

$$D_{12}=0.0026280\frac{[T^3(M_1+M_2)/2M_1M_2]^{\frac{1}{2}}}{P\sigma_{12}^2\Omega_{12(T_{12}^*)}^{(11)*}},$$

---

[4] See reference 2, p. 567.

Table II. Calculated values for thermal diffusion column.

T_2/T_1	r_1/r_2	h	k_c	k_d	$H10^6$	K_c10^5	K_d10^5	K_p10^5	$2AL$	q_e
					g sec^{-1}	g cm sec^{-1}	g cm sec^{-1}	g cm sec^{-1}		
2.4	23.3	0.074	0.0156	0.654	1.795	6.166	12.230	1.850	1.67	5.3

where P is expressed in atmospheres. Hence

$$D_{12}=0.142 \text{ cm sec}^{-1}.$$

Coefficient of Thermal Diffusion

Because the same type of molecular interactions can be assigned to both gases[5] and because the relative difference of mass $(M_1-M_2)/(M_1+M_2)$ is small with regard to the absolute values, it is possible to calculate the thermal diffusion coefficient of the mixture to a first approximation as if it were isotopic, by applying the expression of HCB,

$$\alpha=\frac{15(2A^*+5)(6C^*-5)}{2A^*(16A^*-12B^*+55)}\frac{M_1-M_2}{M_1+M_2}.$$

Hence,

$$\alpha=-0.0118.$$

The negative value of the coefficient of thermal diffusion means that the light component 1 (argon) tends to accumulate at the upper end, and the heavy one 2 (carbon dioxide) at the lower.

3. CALCULATION OF THE SEPARATION FACTOR OF THE COLUMN

The necessary data for the calculation, according to our experimental conditions, are

Inner radius of the outer tube	$r_1=0.350$ cm
Radius of filament	$r_2=0.015$ cm
Temperature of the cold wall	$T_1=300°$K
Temperature of the filament	$T_2=720°$K
Acceleration of gravity	$g=981$ cm sec^{-2}
Effective length of column	$L=190$ cm.

The physical constants of the gas have been calculated at the temperature of the cold wall since the formulas given by Jones and Furry[6] for the extreme cylindrical case have been used. These formulas assume that the largest portion of the gas is at temperature T_1.

In the extreme cylindrical case, $r_1/r_2>2.718$, and the separation factor of the column is

$$q_e=e^{2AL},$$

where $2A=H/(K_c+K_d+K_p)$, H and K_c, K_d, K_p being the coefficients of the transport equation given by

$$H=\frac{2\pi}{6!}\left[\frac{\alpha\rho^2 g}{\eta}\right]_{T_1} r_1{}^4 h, \quad K_c=\frac{2\pi}{9!}\left[\frac{\rho^3 g^2}{\eta^2 D}\right]_{T_1} r_1{}^8 k_c,$$

$$K_d=2\pi[\rho D]_{T_1} r_1{}^2 k_d, \quad K_p=0.3K_c,$$

where h, k_c, k_d, are values depending on the relations T_2/T_1 and r_1/r_2, which have been found by interpolation in Tables VI, VII, and VIII of the article already mentioned.[6] Thus the values of Table II are obtained.

4. EXPERIMENTAL CHECK

The readings for the relative concentrations of the components at both ends of the column are

Initial concentration	$N_1{}^0=57$	$1-N_1{}^0=43$
End rich in component 1	$N_1{}'=72$	$1-N_1{}'=28$
End poor in component 1	$N_1{}''=39$	$1-N_1{}''=61.$

Hence, if

$$q_{\text{exp}}=\frac{N_1{}'/(1-N_1{}')}{N_1{}''/(1-N_1{}'')},$$

then

$$q_{\text{exp}}=4.1.$$

The results show an acceptable agreement. The deviation of the experimental value from the theoretical one can be attributed to the fact that the mixture is not exactly isotopic and that the separation factor of the column has been calculated using the formulas deduced for the Maxwellian case, the only one which has been solved to date.

---

[5] K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases* (The Cambridge University Press, New York, 1952), pp. 25 and 28; reference 2, p. 542.

[6] R. Clark Jones and W. H. Furry, Revs. Modern Phys. **18**, 171 (1946); Phys. Rev. **69**, 459 (1946).