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R. B. Bernstein and T. I. Taylor

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Countercurrent Gaseous Exchange Method for the Separation of Isotopes*

R. B. BERNSTEIN** AND T. I. TAYLOR

Department of Chemistry, Columbia University, New York, New York

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A method is described for isotope enrichment by countercurrent gaseous exchange in a thermal diffusion column. The theory is derived for two cases of interest: diffusion limited and reaction-rate limited. Solutions of the equations are presented for the over-all separation S at the steady state as a function of the following: single stage enrichment factor α; diffusion constant D or exchange rate constant k; length of column Z; and the convective flow L, which in turn depends on pressure, temperature, column dimensions, etc. The results may be expressed in the usual form $S = \alpha^N$. For the diffusion-limited case $N = 4\pi D \bar{c} Z / L$, where $\bar{c} =$ moles of gas per cc. For the reaction-rate limited case the number of theoretical plates per unit length is given by the expression $N/Z = k/v$, where v is the convective velocity.

Experiments are described in which C^{13} was concentrated by the exchange reaction $C^{12}O_2 + C^{13}O \rightleftharpoons C^{13}O_2 + C^{12}O$. The observed dependence of the over-all separation upon the operational variables is consistent with the theory.

INTRODUCTION

A CONCENTRATION of the isotopes of several elements has been effected by Urey and his co-workers[1] using two-phase countercurrent systems in which favorable isotopic exchanges existed between the gaseous component and an ion in solution. Favorable isotopic exchanges also exist between two gaseous molecules, as shown by the calculations of Urey and Greiff.[2] Equilibrium constants for many such gaseous exchanges have been tabulated in a convenient form by Urey.[3] The kinetics of a number of these gaseous exchange reactions have been studied by Urey and his co-workers.[4]

A method has been devised by Taylor and Bernstein[5] in which an enrichment of isotopes may be effected in a single fluid phase by establishing countercurrent flow between the exchanging substances in a thermal diffusion column. There appear to be a number of favorable reactions in both the gaseous and the liquid phase for which the method is applicable.

Figure 1 is a diagrammatic representation of the gaseous exchange column and the flow pattern existing in it. Essentially, it consists of a cooled cylindrical column with an axial heated element which produces the desired convective flow. Thermal diffusion causes the downward moving gas stream near the cold wall to be enriched in the heavier component (CO_2, for example, in the case of a mixture of CO and CO_2). If the isotopic exchange at the hot surface favors the transfer of the heavy isotope to the heavier molecule, as is frequently the case, the heavy isotope will concentrate in the cold stream and will be carried by convection toward the bottom of the column. The analogy with a two-phase fractionating column is completed with the introduction of a chemical converter at the bottom of the column. This converts the heavy component to the light one (for example, CO_2 to CO) which then rises in the upward moving stream and undergoes further exchange. A slow stream of an equal molar mixture of the light and the heavy components (both of normal isotopic abundance) is passed across the top end of the column. This acts as an infinite reservoir supplying the heavy isotope to the column.

In order to bring about an enrichment of an isotope that concentrates in the light component, it would, of course, be necessary to place a

[1] H. C. Urey, J. R. Huffman, H. G. Thode, and M. Fox, J. Chem. Phys. **5**, 856 (1937); C. A. Hutchison, D. W. Stewart, and H. C. Urey, *ibid.* **8**, 532 (1940); D. W. Stewart and K. Cohen, *ibid.* **8**, 904 (1940).

[2] H. C. Urey and L. Greiff, J. Am. Chem. Soc. **57**, 321 (1935).

[3] H. C. Urey, J. Chem. Soc. 562 (1947).

[4] J. Brandner and H. C. Urey, J. Chem. Phys. **13**, 351 (1945); E. Leifer, *ibid.* **8**, 301 (1940).

[5] T. I. Taylor and R. B. Bernstein, J. Am. Chem. Soc. **69**, 2076 (1947); T. I. Taylor and W. Spindel, J. Chem. Phys. **16**, 635 (1948).
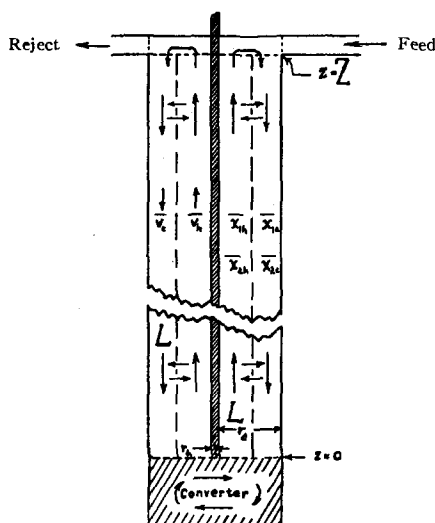
FIG. 1. Schematic representation of the gaseous exchange column. Here L is the convective flow, $\bar{v}$ is the average convective velocity, $\bar{x}_1$ and $\bar{x}_2$ represent average mole fractions of the light and heavy components. Subscripts "h" and "c" refer to the "hot" and "cold" streams.

suitable converter at the top of the column and pass the feed mixture across the bottom.

With an infinite reservoir and the condition of total reflux, the number of moles of light component leaving the top of the column per unit time is equal to the number of moles of heavy component entering the column. This method of operation prevents the formation of a vertical concentration gradient of either component. However, a vertical concentration gradient with respect to the isotopic ratio is established. At equilibrium when a steady state is reached, this isotopic gradient does not change with time. The theoretical analysis which follows applies to the above steady-state operation.

The equations already developed for the separation of isotopes in thermal diffusion columns relate the net transport of the isotopes to the operation variables. For the gaseous exchange column it is the total convective flow of the hot and the cold gas streams that is important. This flow corresponds to the throughput in a two-phase exchange column. The equations showing the dependence of the convective flow on the operating variables are given in a later section.

The mechanism of the isotopic separation process is now considered and equations are

derived for the over-all separation in two limiting cases: diffusion limited and exchange rate limited.

ISOTOPIC ENRICHMENT IN THE GASEOUS EXCHANGE COLUMN

The first case considered will be the ideal limiting situation where the isotopic exchange rate is very rapid compared to the rate of radial interdiffusion between the two opposing streams. That is, the rate-limiting process is the rate at which reactants are transported into the reaction zone and the rate at which exchange products are removed from this zone. This is analogous to the situation existing in two-phase exchange columns involving rapid exchange reactions and slow interphase transport rates. The second case considered will be one in which the isotopic exchange rate is relatively slow compared to rapid radial mixing by diffusion. In this case there is no radial isotopic gradient. The transition case in which the radial mixing rate is comparable to the isotopic exchange rate will not be treated.

In each case the simplified flow pattern described in the previous section will be assumed. It consists of two rather sharply defined opposing streams: an inner cylindrical hot stream which rises with an average convective flow of L moles/sec. and an outer cold stream descending with an equal and opposite convective flow. The reaction is assumed to take place largely in the hot zone, although not necessarily on the heated surface. Radial gradients in the isotope fractions are simplified in terms of average isotopic fractions in the hot and cold streams. Similar assumptions have often been used in treatments of thermal diffusion columns, packed fractionating towers, and two-phase exchange columns to yield expressions for the dependence of over-all separation on the operating variables. Errors which arise from the use of these simplifying assumptions are primarily errors in *magnitude* rather than in the *form* of the final equations for the over-all separation.

DIFFUSION-LIMITED CASE

At the steady state a material balance for the rare isotope of the light component in the hot zone ($C^{13}O$ in the case of a mixture of CO and

CO_2) may be written as follows:

$$L\bar{x}_{1h}(\partial\bar{\nu}_{1h}/\partial z)dz + Fdz = 0, \qquad (1)$$

where $\bar{x}_{1h}$ is the average mole fraction of light component in the hot stream, z is the vertical coordinate, and $\bar{\nu}_{1h}$ is the average value of the fraction of rare isotope of light component in the hot stream. The first term of the equation represents the difference in the number of moles of rare isotope of the light component entering and leaving an element of volume as a result of convective flow. In the second term, F represents the outward rate of diffusion of the rare isotope of the heavy component in moles per second per unit length of column ($C^{13}O_2$ in the case of a mixture of CO and CO_2). The rate of loss of rare isotope of the light component in the hot zone because of the exchange reaction is also equal to F since the rate of exchange is limited by the rate of radial outflow of the rare isotope of the heavy component produced by the exchange. This follows from the assumption that the reaction is very rapid so that the single stage equilibrium enrichment factor is always maintained in the hot zone. A term of longitudinal back diffusion caused by the vertical isotopic gradient has been neglected.

F may be evaluated in terms of the radial isotopic gradient, assuming negligible contribution from the thermal diffusion effect for the isotopic molecules. Thus if $\bar{c}$ is the average gas concentration in moles/cc, then for unit length of column:

$$F = -2\pi r D\bar{x}_2\bar{c}(\partial\nu_2/\partial r),$$

where D is the diffusion coefficient of the rare isotope of the heavy component in the presence of the remaining components, $\bar{x}_2\bar{c}$ is the average concentration of the heavy component in the tube, and ν_2 is the mole fraction of rare isotope in the heavy component. It is convenient here to simplify this equation to give a rough estimate of F in terms of mean isotope mole fractions. At the cold wall the approximate value of $r(\partial\nu_2/\partial r)$ is $r_c[(\nu_{2c}-\nu_{2h})/(r_c-r_h)] = r_c[\Delta\nu_2/(r_c-r_h)] \cong \Delta\nu_2$, since r_h is small compared to r_c. Here $\Delta\nu_2$ is the extreme difference in mole fraction of the rare isotope of the heavy component at the wall and at the filament. In terms of the difference in the mean mole fraction of the rare isotope in the

two streams, a rough first approximation gives

$$\Delta\nu_2 = 2(\bar{\nu}_{2c}-\bar{\nu}_{2h}).$$

The expression for the radial term F then becomes:

$$F = -4\pi D\bar{x}_2\bar{c}(\bar{\nu}_{2c}-\bar{\nu}_{2h}).$$

This gives the radial outflow of rare isotope of the heavy component in moles per second per centimeter length of column. The result states that the radial transport rate is proportional to the difference in mean mole fraction of the rare isotope of the heavy component in the two opposing streams. Since $\bar{\nu}_{2h} > \bar{\nu}_{2c}$ due to the isotopic exchange in the hot zone, $F > 0$.

Substituting the above value for F in Eq. (1) and solving for the vertical gradient in mole fraction of rare isotope of the light component in the hot stream, the following result is obtained:

$$\partial\bar{\nu}_{1h}/\partial z = (-4\pi D\bar{x}_2\bar{c}/L\bar{x}_{1h})(\bar{\nu}_{2h}-\bar{\nu}_{2c}). \qquad (2)$$

In a similar way a consideration of a material balance of the rare isotope of the heavy component in the cold stream leads to

$$\partial\bar{\nu}_{2c}/\partial z = (-4\pi D\bar{x}_2\bar{c}/L\bar{x}_{2c})(\bar{\nu}_{2h}-\bar{\nu}_{2c}). \qquad (3)$$

Since the column is operated at total reflux so that $\bar{x}_{1h} = \bar{x}_{2c}$, it follows that the two expressions (2) and (3) are equal.

The single stage equilibrium separation factor α for the exchange reaction at the temperature of the hot filament is defined as $\alpha = \nu_{2h}/\nu_{1h}$. For a predominantly heterogeneous exchange (which is the case for the $CO-CO_2$ exchange) the reaction at the surface may be considered to be responsible for the average enrichment $\bar{\nu}_{2h}/\bar{\nu}_{1h}$ in the hot zone. Thus, roughly, $\alpha = \bar{\nu}_{2h}/\bar{\nu}_{1h}$. Substitution of $\alpha\bar{\nu}_{1h}$ for $\bar{\nu}_{2h}$ in Eqs. (2) and (3) gives two equations with the variables $\bar{\nu}_{1h}$ and $\bar{\nu}_{2c}$ which may be written:

$$\partial\bar{\nu}_{1h}/\partial z = \partial\bar{\nu}_{2c}/\partial z$$
$$= (-4\pi D\bar{x}_2\bar{c}/L\bar{x}_{1h})(\alpha\bar{\nu}_{1h}-\bar{\nu}_{2c}). \qquad (4)$$

This shows that the vertical gradient in $\bar{\nu}_{1h}$ must be identical with that of $\bar{\nu}_{2c}$. At the bottom of the column, the converter chemically changes the heavy component into the light one so that $\bar{\nu}_{2c} = \bar{\nu}_{1h}$ at $z = 0$. Consequently, at the steady state, $\bar{\nu}_{1h}$ must equal $\bar{\nu}_{2c}$ at every height z in the column. This is analogous to the circumstances existing in a two-phase exchange column where

interphase diffusion is the limiting factor. Here the concentration of the desired isotope in the rising gas phase is equal to that in the downward flowing liquid phase at any height in the column.

Integration of Eq. (4) with the omission of subscripts on ν gives

$$\log\nu = (-4\pi D\bar{x}_2\bar{c}z/L\bar{x}_{1h})(\alpha-1)+\text{const.} \quad (5)$$

The over-all separation S is now defined for separations not too large as the ratio of the concentration of rare isotope at the bottom of the column ($\nu(0)$ at $z=0$) to its concentration at the top of the column ($\nu(Z)$ at $z=Z$) or $S=\nu(0)/\nu(Z)$. It follows that

$$\log S = (4\pi D\bar{x}_2\bar{c}Z/L\bar{x}_{1h})(\alpha-1). \quad (6)$$

This equation gives the maximum over-all separation to be expected for a column of length Z.

NUMBER OF THEORETICAL PLATES

For most isotopic exchanges, α is small and $(\alpha-1)$ can be replaced by $\log\alpha$. Furthermore, $\bar{x}_2\cong\bar{x}_{1h}$ to a fair approximation so that

$$S = \alpha^{4\pi D\bar{c}Z/L}. \quad (7)$$

This is the familiar form of the equation for the over-all separation of fractionating columns and exchange columns:[6]

$$S = \alpha^N,$$

where N is the number of theoretical plates. Consequently, in the diffusion-limited case

$$N = 4\pi D\bar{c}Z/L. \quad (8)$$

It will be shown in a later section that L is proportional to P^2r^4. Thus the number of plates should be proportional to the length Z of the column; to $1/P^2$ and to $1/r^4$. Only a slight positive temperature dependence should be expected for L; the over-all separation α^N would therefore be expected to follow the temperature dependence of α.

REACTION-RATE LIMITED CASE

In most actual cases involving gases, the over-all separation will be limited by the rate of the isotope exchange rather than by radial diffusion. This will result in a smaller number of

theoretical plates than would be calculated from Eq. (8).

In the reaction-rate limited case a material balance equation is again written for the rare isotope of the light component in the hot stream:

$$L\bar{x}_{1h}(\partial\nu_1/\partial z)dz+Gdz=0. \quad (9)$$

The quantity G is defined as the net rate in moles per second per unit length of column at which the rare isotope of the light component disappears as a result of isotopic exchange. It is assumed here that the radial mixing rate is sufficient to insure the presence of no gradient in the mole fraction of the rare isotope of either component. Subscripts h and c may, therefore, be omitted from the isotopic fractions, ν.

The loss of rare isotope G in Eq. (9) may be written as:

$$G = -A_h(\partial/\partial t)(\bar{x}_{1h}\bar{c}_h\nu_1),$$

where A_h is the cross-sectional area of the hot zone, $\bar{x}_{1h}\bar{c}_h$ is the mean concentration of light component in the hot zone, and ν_1 is the fraction of rare isotope in the light component. Substitution for G in Eq. (9) leads to the following expression for the vertical isotopic gradient:

$$\partial\nu_1/\partial z = (A_h/L)\bar{c}_h(\partial\nu_1/\partial t).$$

It has been shown by McKay[7] that isotopic exchange reactions in general are apparent first order with respect to the rare isotope. This is, of course, true only because the chemical composition of an exchanging mixture is invariant during the exchange process. That is, there is no change in the mole fraction of the heavy and light component as a result of isotopic exchange regardless of the exchange mechanism. This is expressed here in terms of the isotopic exchange rates in the forward and reverse direction:

$$\partial\nu_1/\partial t = -k_1\nu_1+k_2\nu_2, \quad (10)$$

where k_1 and k_2 are the rate constants for the forward and the reverse reactions, respectively. The ratio k_1/k_2 is the equilibrium constant α for the exchange at the temperature of the hot wire.

Hence, substituting $k_2\alpha$ for k_1,

$$\partial\nu_1/\partial t = -k_2(\alpha\nu_1-\nu_2).$$

Combining this with the previous expression for the vertical gradient, one obtains the fol-

[6] K. Cohen, J. Chem. Phys. 8, 588 (1940).

[7] H. A. McKay, Nature 142, 997 (1938).

lowing equation:

$$\partial \nu_1/\partial z = (-A_h \bar{c}_h k_2/L)(\alpha \nu_1 - \nu_2). \qquad (11)$$

In the steady state the rate of accumulation of the rare isotope of the heavy component in the cold stream is equal to the rate of disappearance of the rare isotope of the light component in the hot stream. A material balance equation may be set up for the cold stream as was done in Eq. (9) for the hot stream. The two material balance equations simplify to

$$G = -L\bar{x}_{1h}(\partial \nu_1/\partial z) = -L\bar{x}_{2c}(\partial \nu_2/\partial z). \qquad (12)$$

Since $\bar{x}_{1h} = \bar{x}_{2c}$, the two gradients are equal, and

$$\partial \nu_1/\partial z = \partial \nu_2/\partial z = (-A_h \bar{c}_h k_2/L)(\alpha \nu_1 - \nu_2). \qquad (13)$$

With the two gradients equal and with $\nu_1 = \nu_2$ at the bottom of the column, it follows that at the steady state $\nu_1 = \nu_2$ at all heights z. Consequently, the subscripts on the isotope fractions may be omitted and Eq. (13) may be integrated with the boundary condition that $S = \nu(0)/\nu(Z)$. The result is

$$\log S = (A_h \bar{c}_h k_2 Z/L)(\alpha - 1). \qquad (14)$$

RELATION OF NUMBER OF THEORETICAL PLATES TO REACTION RATE

Using the logarithmic approximation for $(\alpha - 1)$, the over-all separation becomes

$$S = \alpha^N,$$

where N is the number of theoretical plates given by

$$N = k_2 A_h \bar{c}_h Z/L. \qquad (15)$$

This equation may be simplified further by expressing L in terms of the mean convective velocity of the hot stream, $L = A_h \bar{c}_h \bar{v}_h$. This gives the interesting result that the number of plates per unit length of column is the ratio of the exchange rate constant (sec.$^{-1}$) to the average convective velocity in cm/sec., or

$$N/Z = k/v. \qquad (16)$$

In other words the H.E.T.P. for this case is simply v/k.

DEPENDENCE OF OVER-ALL SEPARATION ON EXPERIMENTAL VARIABLES

The number of theoretical plates for a reaction rate limited process is then proportional to the length of the column Z; to $1/p$ (modified by any pressure dependence of k); and to $1/r^2$. Since the predominant temperature dependent term is the rate constant k, the number of plates should be expected to increase rapidly with temperature. However, since α usually decreases with increasing temperature, the over-all separation as given by Eq. (14) should not be expected to increase markedly. Ultimately, at temperatures where α approaches unity no enrichment should be obtained.

CONVECTIVE FLOW FROM THE NET TRANSPORT

It is now necessary to evaluate the dependence of the convective flow upon the operating variables. It is also of interest to obtain an estimate of its magnitude. This is an important quantity in determining the over-all isotope separation.

One method of determining the convective flow is by obtaining a relation between the net transport (a measurable quantity) and the convective flow. The net transport of one component in the gaseous exchange column can be calculated directly from the measured concentration of the light component in the reject stream from the top of the column. Equations for the convective flow are derived for the two major components (CO and CO_2, for example) with no consideration given to the relative isotopic abundance in the two components or to the isotopic exchange process.

Jones and Furry[8] in their review of the theory of thermal diffusion for the separation of isotopes have derived equations for the net transport in the vertical direction for one component of an *isotopic mixture*. For the gaseous exchange column described here it is necessary to estimate the net transport and convective flow for a mixture of the two main components which may differ considerably in molecular weights.

The equation given by Jones and Furry for the net transport τ of light component in grams per second up the column is

$$\tau_1 = H\bar{x}_1\bar{x}_2 - K(dx_1/dz), \qquad (17)$$

where $\bar{x}_1$ and $\bar{x}_2$ are the mean values of the mole fractions of the light and the heavy component,

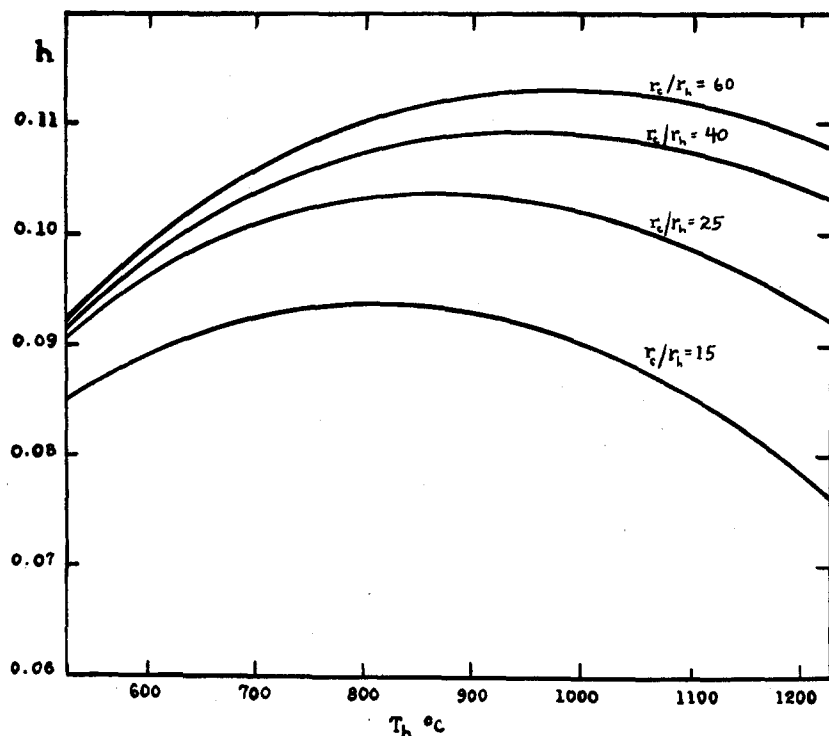[8] R. C. Jones and W. H. Furry, Rev. Mod. Phys. 18, 151 (1947).

FIG. 2. Dependence of parameter h upon temperature ($T_h°C$) at different ratios of cylindricity (r_c/r_h), assuming $T_c = 300°A$—from Jones and Furry (reference 8, Table VI) for a "Maxwellian" gas.

respectively, and z is the distance from the bottom of the column. The transport coefficients H and K are constants which have been shown to depend upon the nature of the gas mixture, the dimensions and shape of the apparatus and the temperature difference maintained in the column. K is the sum of coefficients which take into account the various re-mixing effects. However, for the steady-state operation of the gaseous exchange column at total reflux with an infinite reservoir, no concentration gradient of either light or heavy component exists ($dx_1/dz = dx_2/dz = 0$) and the second term of Eq. (17) becomes zero. They evaluate H in terms of the geometry and operating variables of the column as follows:

$$H = (2\pi/6!)\alpha_i(\rho_c^2 g/\eta_c)r_c^4 h(T_h/T_c; r_c/r_h). \quad (18)$$

Here α_i is the thermal diffusion constant, ρ_c and η_c the density and viscosity of the gas mixture at the temperature T_c of the cold wall, g the acceleration of gravity, r_c the radius of the tube, r_h the radius of the hot wire, T_h and T_c the absolute temperature of the hot wire and cold wall, respectively. The function h has been tabulated by Jones and Furry[8] for a Maxwellian gas ($\lambda \propto T$) in the "extreme cylindrical" case where $r_c/r_h \gg 1$ (see Fig. 2).

In order to apply Eqs. (17) and (18) to the gaseous exchange column where a large mass difference may exist between the two main components, a modification appears necessary to satisfy the condition that the net transport of the light component in moles per second equals that of the heavy component in moles per second in the opposite direction. The experimental requirement of constant pressure (no accumulation of material) in the apparatus would not be met by these equations in their present form with τ_1 given in grams per second. For the case under consideration, the revised transport equation after substitution for H becomes:

$$\tau_1 = (2\pi/6!)\alpha_i(\rho_c^2 g/\eta_c)r_c^4(M_1/\bar{M})\bar{x}_1\bar{x}_2 h, \quad (19)$$

where M_1 is the molecular weight of the light component and $\bar{M}$ is the mean molecular weight of the mixture given by $\bar{x}_1 M_1 + \bar{x}_2 M_2$. ρ_c is the mean density of the mixture at the temperature of the cold wall. If the transport τ_2 of the heavy component down the tube is desired, M_1 is replaced by M_2. This equation satisfies the condition of equal molar transport rates of light and heavy components, since now

$$\tau_1/M_1 = \tau_2/M_2 = \tau',$$

where τ' is the net transport rate of either component in moles per second. In the case of two isotopic molecules, Eq. (19) reduces to the usual form since $M_1/\bar{M} \doteq 1$.

The density ρ_c may be expressed in terms of the mean molecular weight by $\rho_c = P\bar{M}/RT_c$ where P is the pressure in atmospheres and R is the gas constant in cc atm./°A mole. Substitution in Eq. (19) gives the following expression for the net transport of either component in moles per second:

$$\tau' = \tau_1/M_1 = \tau_2/M_2$$
$$= (2\pi/6!)\alpha_t(P^2\bar{M}/\eta_c R^2 T_c^2)gr_c^4\bar{x}_1\bar{x}_2 h. \quad (20)$$

A relation between this quantity and the convective flow may now be obtained by noting

that the net upward transport of the light component, for example, is equal to the difference between the total upward and downward flow rates of the light component in the hot and cold streams. Thus,

$$\tau' = \bar{x}_{1h}L_h - \bar{x}_{1c}(-L_c),$$

where $\bar{x}_{1h}$ and $\bar{x}_{1c}$ are the mean mole fractions of light component in the rising hot stream and descending cold stream, respectively. L_h is the convective flow rate in the hot stream in total number of moles of gas per second. It is considered positive since it flows in the positive z direction. L_c is thus negative and for total reflux $L_h = -L_c$. In general, only the positive quantity will be referred to and the subscript will be

FIG. 3a. Radial temperature distribution calculated for a Maxwellian gas for two values of $T_h = 1000°A$, $1300°A$, and for two values of the cylindricity: $r_c/r_h = 10, 20$.
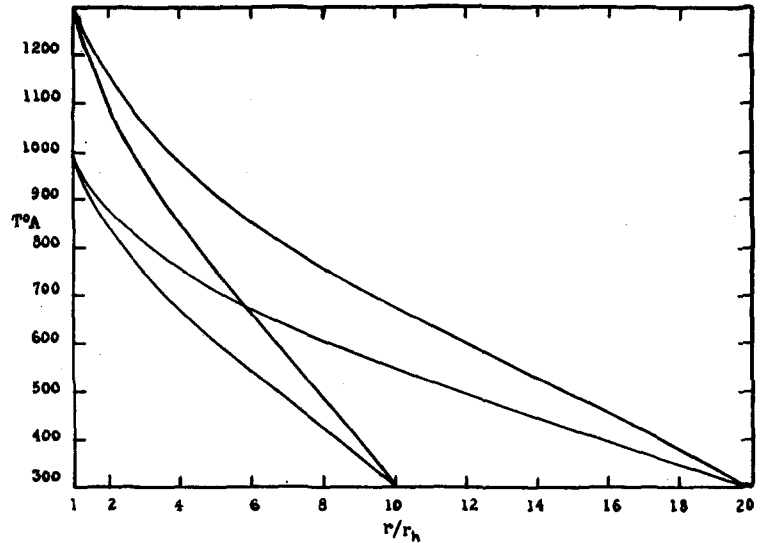

FIG. 3b. Radial concentration distribution due to effect of thermal diffusion. Calculated for the various temperature distributions shown in Fig. 3a.
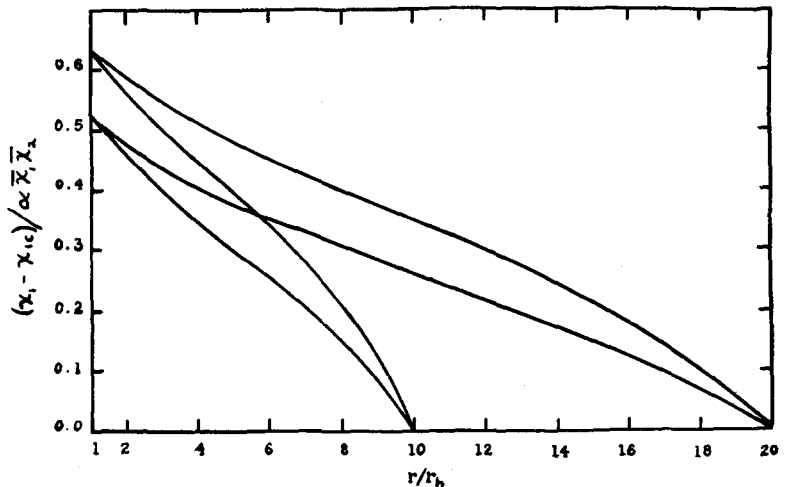
TABLE I. Equilibrium constant, α, as function of temperature.

Temperature		Equilibrium constant, α
°A	°C	
273	0	1.098
298	25	1.086
600	327	1.029
1000	727	1.012
1400	1127	1.0064

omitted, so that

$$L = \tau'/(\bar{x}_{1h} - \bar{x}_{1c}). \qquad (21)$$

The difference in mean concentration $\bar{x}_{1h} - \bar{x}_{1c}$ established between the hot and cold streams as a result of thermal diffusion may be derived from the following equation of diffusion as given by Jones and Furry:[8]

$$x_1(v_1 - v) = D_{12}(\alpha_t x_1 x_2 \text{ grad } \log T - \text{grad} x_1). \qquad (22)$$

Here $(v_1 - v)$ is the net advance velocity of the light component and D_{12} is the ordinary mutual diffusion coefficient of the mixture. For the particular conditions of operation of the gaseous exchange column at the steady state where $dx_1/dz = 0$ it can be seen that $(v_1 - v) = 0$ and Eq. (22) reduces to

$$\text{grad} x_1 = \alpha_t x_1 x_2 \text{ grad } \log T.$$

With cylindrical symmetry and no vertical gradient this becomes

$$dx_1/dr = \alpha_t x_1 x_2 (d/dr)(\log T). \qquad (23)$$

Replacing $x_1 x_2$ in the usual manner by the average value $\bar{x}_1 \bar{x}_2$ across the tube and integrating, the extreme radial concentration difference becomes

$$x_{1h} - x_{1c} = \alpha_t \bar{x}_1 \bar{x}_2 \log(T_h/T_c), \qquad (24)$$

in which x_{1h} is the concentration of the light component at the hot wire whose temperature is T_h and x_{1c} is the concentration of the light component near the cold wall where the temperature is T_c.

Before approximating the difference in mean concentration of the light component $(\bar{x}_{1h} - \bar{x}_{1c})$ in the hot and cold streams from Eq. (24), it is instructive to examine the temperature distribution and the concentration gradient across the column. The heat loss by conduction through a Maxwellian gas (coefficient of heat conductivity

proportional to T) in a concentric cylinder system is given by

$$Q = 2\pi r \lambda_0 T(dT/dr),$$

where Q is the heat loss per unit length of heated cylinder and $\lambda_0 T$ is the coefficient of heat conductivity. With the boundary conditions that $T = T_h$ at $r = r_h$ and $T = T_c$ at $r = r_c$, the radial temperature distribution becomes

$$(T_h^2 - T^2)/(T_h^2 - T_c^2) = (\log r/r_h)/(\log r_c/r_h).$$

Figure 3a shows a set of curves of T as a function of the ratio r/r_h for $T_c = 300°A$ with T_h at 1000°A and 1300°A at cylindricity ratios r_c/r_h of 10 and 20 for each case. It can be seen that the temperature gradient is greatest in the neighborhood of the wire. In Fig. 3b a quantity proportional to the concentration difference $(x_1 - x_{1c})$ is plotted against the ratio r/r_h for each of the above conditions. This shows the concentration gradient to be approximately linear, as has been assumed in most simplified treatments of the thermal diffusion column.

From the above result, the desired difference in mean concentrations of light component in the hot and cold streams is approximated as

$$\bar{x}_{1h} - \bar{x}_{1c} \cong \tfrac{1}{2}(x_{1h} - x_{1c}) = \tfrac{1}{2}\alpha_t \bar{x}_1 \bar{x}_2 \log(T_h/T_c). \qquad (25)$$

The convective flow L may now be obtained by combining Eqs. (20), (21), and (25) with the result that

$$L = (4\pi/6!)[P^2 \bar{M} g r_c^4 h / \eta_c R^2 T_c^2 \log(T_h/T_c)]. \qquad (26)$$

Substituting for the constants, the convective flow in moles/sec. becomes

$$L = 2.5 \times 10^{-3}[P^2 \bar{M} r_c^4 h / \eta_c T_c^2 \log(T_h/T_c)]. \qquad (27)$$

Values of the function h for different ratios of T_h/T_c and r_c/r_h are plotted in Fig. 2 from the table given by Jones and Furry.[8] It can be seen that h is rather insensitive to the temperature and cylindricity. Consequently, the convective flow is proportional to the square of the pressure and to the fourth power of the tube radius. It is inversely proportional to $\log(T_h/T_c)$ but is not a function of the thermal diffusion constant α_t.

The convective flow L may also be evaluated from the experimentally determined values of τ' and α_t by means of Eqs. (21) and (25). Thus

$$L = \tau'/\tfrac{1}{2}\alpha_t \bar{x}_1 \bar{x}_2 \log(T_h/T_c). \qquad (28)$$

Approximate agreement of these experimental values with the values calculated from Eq. (27) will be shown in a later section.

EXPERIMENTAL TESTS OF THE THEORY

The isotopic exchange reaction $C^{13}O + C^{12}O_2 \rightleftharpoons C^{12}O + C^{13}O_2$ was selected for an investigation of the countercurrent gaseous exchange method of isotope separation. The equilibrium constant for this exchange at several temperatures has been calculated by Urey and Greiff.[2] Their values along with those calculated for the higher temperatures using the method of Bigeleisen and Mayer[9] are summarized in Table I.

The kinetics of the exchange in the region of 900°C have been studied by Brandner and Urey.[4] They found the reaction to be primarily heterogeneous and surface-catalyzed. The rate of the exchange was markedly increased by the presence of H_2 or H_2O. The rate constants were shown to be independent of the pressure and of the composition of the mixture in the ranges studied. Values varied, for example, from 2×10^{-5} sec.$^{-1}$ in a quartz vessel at 898°C to 1×10^{-3} sec.$^{-1}$ in the presence of gold at 898°C where the total pressure was about 11 mm Hg.

Apparatus

A small gaseous exchange column was constructed, as illustrated in Fig. 4. It consisted of a water-jacketed glass tube 1.0 cm in diameter and 110 cm long. A number of filaments were tested; a platinum wire (B. and S. No. 22) 0.64 mm in diameter seemed to be most satisfactory. Small cross pieces of platinum wire were spot-welded onto the filament to center it in the column. A 100-g weight attached to the lower end of the filament was used to keep the filament taut. Electrical contact was made to a pool of mercury in a glass well at the bottom of the column. The temperature of the filament was estimated to within ±50°C from measurements of the resistance of the wire. In one set of experiments CO_2 was supplied to the top of the column from a 20-liter reservoir. Convection, produced by heating one of the tubes leading from the tank to the column, served to circulate gas across the top of the column. Provision was

[9] J. Bigeleisen and M. G. Mayer, J. Chem. Phys. **15**, 261 (1947).

made for withdrawing samples periodically from the reservoir. Microanalyses of these samples were performed to measure the rate at which the concentration of CO increased in the tank.

In other sets of experiments CO_2 was metered across the top of the column. For analysis, the reject gas was passed into an Orsat analysis unit. From the CO_2 flow (measured by a capillary flowmeter) and the concentration of CO in the exit gases, the net CO transport was calculated.
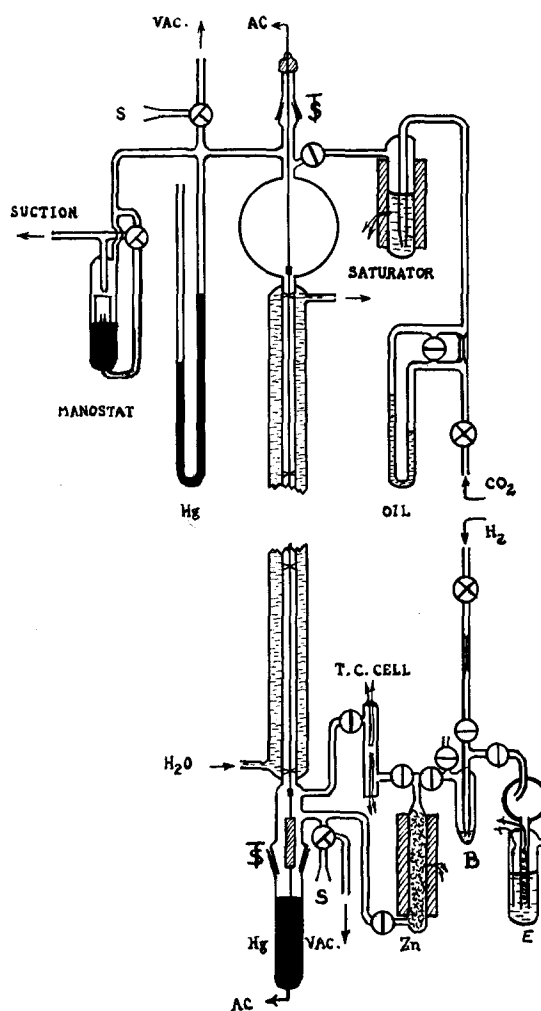

FIG. 4. Experimental apparatus (glass column). The column is shown with filament, spacers, weight, and Hg pool. Ground joints allow for removal of the filament. The standard taper joints "S" for sample withdrawal are indicated at top and bottom. The Zn converter and thermal conductivity cell are shown. The bubbler flowmeter "B" and the auxiliary electrolysis unit "E" for calibration are indicated. The CO_2 may be saturated with H_2O before passing across the top of the column. The manostat leading to the rough vacuum line is shown.

A cartesian manostat in the reject line maintained constant pressure.

At the bottom of the column, zinc at 400°C was used to convert CO_2 to CO.[10] With the converter in a vertical position the convective circulation rate was several times greater than the net transport of CO_2 to the bottom of the column. This insured a condition of total reflux. A small thermal conductivity cell in series with the converter gave a continuous indication of the conversion efficiency, usually greater than 95 percent.

In some of the experiments hydrogen was introduced into the bottom of the column as a catalyst. This was done by means of a small electrolysis unit. By adjusting the current through the cell a small constant flow of hydrogen could be admitted to the exchange column. For the experiments at other than atmospheric pressure it was found more convenient to supply hydrogen from a tank through a small metal capillary leak. Flow rates were measured by means of a special bubbler flowmeter previously calibrated with the electrolysis unit.

Water instead of hydrogen was introduced as a catalyst in a number of experiments. This was done by means of a water saturator in the carbon dioxide inlet line at the top of the column. The temperature of the saturator was high enough to insure condensation of a small amount of water on the cold tube. This water then covered the walls of the column, thereby maintaining in the column a partial pressure of water vapor. The existence of the water gas reaction, $CO + H_2O \rightleftharpoons$
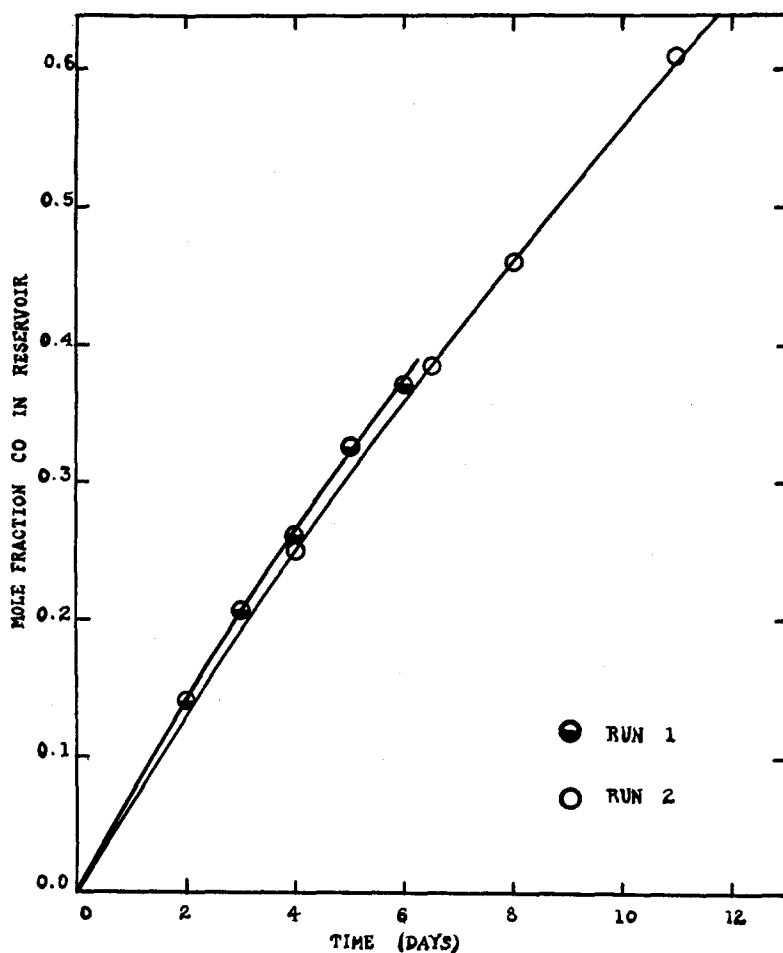

FIG. 5. Time dependence of CO concentration in the 20-liter reservoir at top of gaseous exchange column for two runs. Run 1, $T_h = 700°C$; run 2, $T_h = 800°C$.

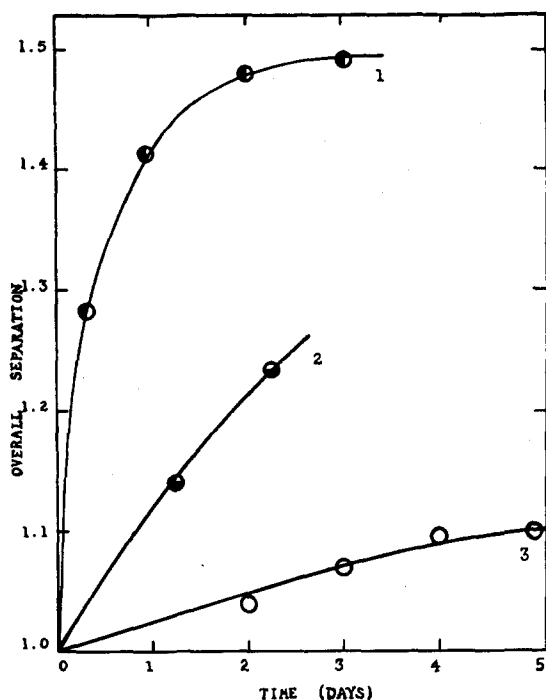[10] R. B. Bernstein and T. I. Taylor, Science 106, 498(1947).

FIG. 6. Dependence of over-all separation at 1.0 atmos. upon time. Three runs under different conditions of temperature, catalyst, and filament. Curve 1: platinum filament, $T_h = 1150°C$; presence of H_2O vapor (run 11). Curve 2: platinum filament, $T_h = 800°C$; presence of H_2O vapor (run 7). Curve 3: nichrome filament, $T_h = 700°C$; no H_2O (run 1).

FIG. 7. Dependence of over-all separation on time and filament temperature at 1 atmos. total pressure with constant H_2O vapor pressure. Pt filament 0.64 mm in diameter. Column length, 1.1 meter. Data from runs 9, 10, and 11.

$CO_2 + H_2$ with an equilibrium constant of unity at about $800°$[11] insures the presence of hydrogen which may also aid in catalyzing the exchange.

Convective Flow

The rate of increase in concentration of CO in the 20-liter reservoir attached to the top of the column was determined by analysis with a Blacet microgas analysis unit (A. H. Thomas Company). Figure 5 shows the results of two such experiments. Net transport rates of CO were calculated from the initial slopes of each curve. Thus:

$$\text{net transport (cc/min.)} = V(dx/dt)_0,$$

where V is the volume of the reservoir (2×10^4 cc) and $(dx/dt)_0$ is the initial rate of increase in mole fraction of CO in the reservoir. In those experiments in which CO_2 was passed across the top of

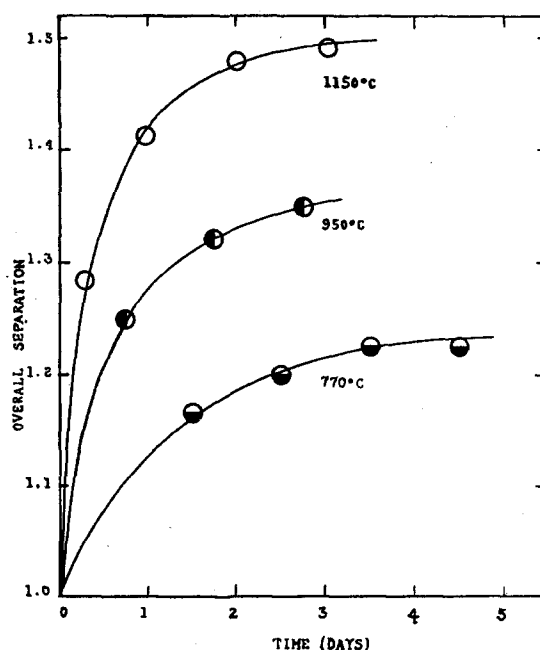the column the net transport of CO was obtained from the product of the mole fraction of CO in the reject gas stream and the total flow rate in cc/min. The results of these experiments are given in Table II to show the dependence of net transport on the temperature of the filament and on the pressure. The small decrease in net transport of CO with increase in temperature is in qualitative agreement with the temperature variation of the parameter h (Fig. 2). The increase of the net transport with the pressure agrees quite well with that expected from Eq. (20) in which τ' is seen to be proportional to P^2. The experiments of Clusius and Dickel[12] with the

TABLE II. Determinations of the net transport of CO.

Filament	Diameter (mm)	Temperature °C($\pm 50°$)	Pressure (atmos.)	Net transport (std. cc/min.)
Nichrome	0.30	700	1.00	0.97
Nichrome	0.30	800	1.00	0.93
Platinum	0.64	770	1.00	0.88
Platinum	0.64	950	1.00	0.62(?)
Platinum	0.64	1150	1.00	0.79
Platinum	0.64	1150	1.48	1.47

[11] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, J. Research Nat. Bur. Stand. 34, 143 (1945).

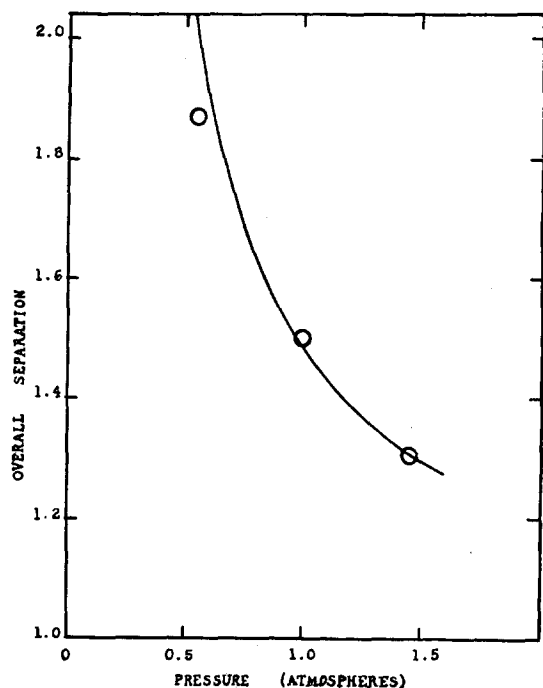[12] K. Clusius and G. Dickel, Zeits. f. physik. Chemie B44, 397, 451 (1939).

FIG. 8. Dependence of over-all separation on pressure (atmospheres) at about 1100°C. Solid curve calculated from expected pressure dependence (theoretical). Data from runs 11, 12b, and 13b.

mixture O_2 and N_2 have amply verified the pressure dependence given by the theoretical equations of Jones and Furry.[8]

The convective flow L, which is an important quantity in determining over-all isotope separation, may be calculated from Eq. (28) using the experimental net transport along with the thermal diffusion constant α_t. A value of $\alpha_t = 0.10$ was obtained by extrapolating the data of Kitagawa and Wakao[13] for a mixture of CO_2 and CO to 1000°C. Substitution of $\tau' = 0.8$ cc/min. at $T_h = 1000°C$ and $P = 1.0$ atmos. into Eq. (28) leads to the following value for the convective flow L:

$$L = \frac{0.8}{(0.5)(0.10)(0.5)(0.5) \log_e(1273/298)}$$

$$= 43.5 \text{ cc/min.} = 3.0 \times 10^{-5} \text{ mole/sec.}$$

This result may be compared with the theoretical value obtained by substituting into Eq.

[13] H. Kitagawa and M. Wakao, J. Chem. Soc. Japan, **62**, 100 (1941).

(27) the following:

$$P = 1.00 \text{ atmos.}; \quad T_h = 1273°A;$$
$$T_c = 298°A; \quad r_h = 0.032 \text{ cm};$$
$$r_c = 0.50 \text{ cm}; \quad \eta_c = 1.7 \times 10^{-4} \text{ poise};$$
$$\bar{M} = 36; \quad h = 0.09$$

Thus,

$$L = \frac{(2.5 \times 10^{-3})(1.00)^2(36)(0.5)^4(0.09)}{(1.7 \times 10^{-4})(298)^2 \log_e(1273/298)}$$

$$= 2.3 \times 10^{-5} \text{ mole/sec.}$$

The numerical agreement with the previous value from the experimental data may be somewhat fortuitous in view of the approximations in the theory, but it seems reasonable to expect that the correct dependence of the convective flow upon the variables is given by Eqs. (27) and (28).

Over-All Isotope Separation

Carbon isotope abundance ratios of the samples withdrawn periodically from the column were determined to a precision of about 1 percent by measurement of the 44 and 45 peaks of the CO_2 with a Nier-type mass spectrometer.

The effect of the presence of water or hydrogen and the effect of change in filament temperature are shown in Fig. 6 where the over-all isotope separation is plotted against time. The upper curves, 1 and 2, show qualitatively that the over-all separation is increased by the presence of the catalyst and by the temperature increase. In curve 1, H_2 was admitted at a rate of about 0.2 cc/min., which appeared to be equivalent to the addition of water vapor. This is, of course, expected from the equilibria involved in the water gas reaction. Brandner and Urey[4] had previously shown this catalytic effect in their kinetic measurements.

The effect of filament temperature is more clearly illustrated by the experiments shown in Fig. 7. Here the total pressure was maintained at 1.00 atmosphere with a constant flow of H_2 into the column. The over-all separation increases with T_h even though α decreases with increasing temperature (Table I). This is attributed to the increase in exchange rate with temperature. In principle, however, temperatures would be

reached where α approaches 1, resulting in no separation.

The effect of the variation in pressure on the over-all separation is illustrated by the data plotted in Fig. 8. Here, the values for the over-all separation are those taken from the end points of curves of separation against time at three pressures. The temperature was maintained at approximately 1100°C and the water vapor pressure was about 20 mm Hg. This dependence on pressure is expected from an analysis of Eq. (14), where it was previously shown that the over-all separation should increase with decreasing pressure. This agreement with the theory is demonstrated by the solid curve calculated from the pressure dependence of the terms in the relation $N/Z = k/v$. Here the convective velocity is proportional to the first power of the pressure and k is assumed to be independent of pressure as was demonstrated by Brandner and Urey.[4]

An interesting application of Eq. (16), $N/Z = k/v$, is its use in determining experimentally rather fast exchange rates from a knowledge of the convective flow and the equilibrium constant for the exchange. In the experiment at 1150°C at 1 atmos. of pressure, for example, the measured net transport of CO (0.79 cc/min.) corresponds to a convective flow rate of 43.5 cc/min. or to a convective velocity of about 1.9 cm/sec. (This might be measured more precisely by the use of an added trace of radioactive isotopes.) At 1150°C the value of α is 1.006 and with an over-all separation S of 1.5, the number of plates in the 1.1 meter column is 68. The height equivalent to each theoretical plate (H.E.T.P.) is thus 1.6 cm. This corresponds to a reaction velocity constant of $k = vN/Z = 1.9 \times (68/110) = 1.2$ sec.$^{-1}$. Because of the large temperautre uncertainty, it was not possible to obtain a reliable value for the apparent activation energy of the exchange. However, the results indicate a considerably lower value than that reported by Brandner and Urey.[4]

As the reaction rate increases, the H.E.T.P. will approach that for the diffusion-limited case. Substituting in Eq. (8) $L = 3 \times 10^{-5}$ mole/sec. and evaluating the quantity cD at the mean temperature of about 800°K as $(4.1 \times 10^{-5}) \times (0.2) \times (800/300)^{0.8} = 1.8 \times 10^{-5}$ mole cm sec.$^{-1}$, the

estimated limiting value of the H.E.T.P. is 1.3 mm. This implies that if the rate constant could be increased by catalysis or by an increase in surface, a greater isotope concentration could be achieved in a given column. Such conditions might also allow operation at lower temperatures where the isotopic exchange equilibrium constant is larger.

Comparison with Other Methods

It is of interest to compare the results of these experiments with isotope separations obtained by other methods. For the separation of $C^{13}H_4$ by ordinary thermal diffusion of methane, Nier[14] used a concentric tube column 730 cm long with a spacing of 0.71 cm and a temperature difference of about 300°C. At a pressure of 46 cm approximately 4.5×10^{-8} g/sec. of C^{13} was transported and collected as 4.5 percent $C^{13}H_4$ gas. The transport of isotope in the gaseous exchange column as measured by the initial increase in concentration of C^{13} in the bottom assembly of the column (180 cc) is about 1×10^{-8} g/sec. A value of 3×10^{-8} g/sec. may be calculated from the simple transport equation $Lv_0(\alpha - 1)$. This transport rate is less than that obtained in the ordinary thermal diffusion column, but it might be pointed out that the area of the annular space was 9.4 cm^2 for Nier's column compared to 0.8 cm^2 for the gaseous exchange column. A comparison of separations can be made by calculating the over-all separation obtainable in a 1.1-meter length of Nier's thermal diffusion column. The constant A (reference 8, p. 177, Eq. (149)) for the column was 0.81×10^{-3} cm^{-1} (reference 8, p. 207, Eq. (363)) so that the over-all separation at equilibrium (reference 8, p. 178, Eq. (150)) would be 1.2 at one atmosphere. An over-all separation of 1.5 was obtained with the exchange column (Fig. 7). Consequently, for a given length of column a higher separation may be achieved in the exchange column.

The power required for the gaseous exchange column was approximately 0.2 kw/meter as compared with 0.38 kw/meter for Nier's column. Considering the differences in the transport rates and lengths of columns required, it can be seen that the power required to produce C^{13} at a

[14] A. O. Nier, Phys. Rev. **57**, 30 (1940).

given concentration is approximately the same as for the thermal diffusion column.

The two-phase counter-current exchange methods developed by Urey and his co-workers[1] have been used to produce concentrations as high as 25 percent C^{13} at high transport rates of 2×10^{-6} g/sec. of C^{13}. The power requirements with these methods are low; they are therefore much more economical.

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# The Mercury Photosensitized Hydrogenation of Propylene*

WALTER J. MOORE
*Department of Chemistry, Catholic University of America, Washington, D. C.*
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The mercury photosensitized hydrogenation of propylene has been investigated at 30°, 110°, and 200°, using an 8/1 ratio of hydrogen to propylene. The hydrocarbon products were analyzed with a mass spectrometer. The occurrence of 2,3-dimethylbutane as the principal C_6 product indicates that a hydrogen atom adds preferentially to the terminal carbon atom of propylene to form the isopropyl radical. Analyses of the C_6 and C_9 products suggests that the isopropyl radical adds preferentially to the middle carbon atom of propylene.

A CONVENIENT source of hydrogen atoms in low concentrations is provided by the reaction of excited mercury atoms with molecular hydrogen:

$$Hg(^1S_0) + h\nu(2537 \text{ A.U.}) = Hg(^3P_1)$$
$$Hg(^3P_1) + H_2 = Hg(^1S_0) + 2H.$$
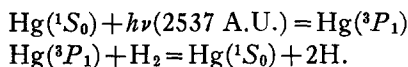
If hydrogen atoms are produced in this way in a mixture of hydrogen and an olefin, the subsequent addition of a hydrogen atom to the olefinic double bond will yield an aliphatic free radical. For example:

$$H + C_2H_4 = C_2H_5.$$
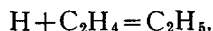
The reaction products from the mercury photosensitized hydrogenation at 25°C of ethylene, propylene, and butene-2 were analyzed by Moore and Taylor,[1] who found a considerable formation of the radical recombination products, butane, hexane, and octane, respectively. Thus,

$$2C_2H_5 = C_4H_{10}; \quad 2C_3H_7 = C_6H_{14}; \quad 2C_4H_9 = C_8H_{18}.$$

These reactions were carried out with a high (about 8 to 1) ratio of hydrogen to olefin. This

has the effect of minimizing photosensitized reactions of the olefins themselves, which might otherwise obscure the simple atomic hydrogen reactions. The quenching cross section of propylene is probably around ten times[2] that of hydrogen for $Hg(^3P_1)$. In the absence of hydrogen excited ethylene or propylene molecules are readily deactivated without undergoing chemical reaction.[3] It is probable, however, that some formation of hydrogen atoms and propyl radicals occurs through the reaction of excited propylene with molecular hydrogen:

$$C_3H_6^* + H_2 = C_3H_7 + H.$$
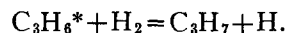
The quenching cross sections of the saturated hydrocarbons are much lower than those of the olefins. With the excess of hydrogen used it is therefore possible to study the hydrogenation reactions of the olefins without undue complications from the mercury photosensitized reactions of the hydrocarbon reactants and products.

The present work is a more extended investigation of the mercury photosensitized hydrogenation of propylene over a range of tempera-

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[1] W. J. Moore and H. S. Taylor, J. Chem. Phys. 8, 504 (1940).

[2] K. J. Laidler, J. Chem. Phys. 15, 718 (1947).
[3] H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. 14, 57 (1946).