Diffusion in Three-component Gas Mixtures

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A solution to the Stefan-Maxwell diffusion equations for equimolal countercurrent diffusion in a three-component gas mixture is obtained which is similar in form to Gilliland's equation for diffusion of two gases through a third inert gas. The important features of both types of diffusion are investigated and the conditions under which the following phenomena occur are determined: (1) diffusion barrier (the rate of diffusion of a component is zero even though its concentration gradient is not zero); (2) osmotic diffusion (the rate of diffusion of a component is not zero even though its concentration gradient is zero); (3) reverse diffusion (a component diffuses against the gradient of its concentration).

A generalized driving force which describes these phenomena is introduced, and approximate equations are developed which give the individual rates of diffusion directly.

PART I

Almost all the theories of mass transfer are based to some extent on molecular diffusion (*5, 6, 18*). Although binary-diffusion theory is well understood, the theory for multicomponent diffusion is less satisfactory, even though the basic diffusion equations have long been available. This paper will be restricted to the study of steady state diffusion in the simplest multicomponent gas, the ternary.

The equations for diffusion in ideal multicomponent gases were developed by Stefan (*16, 17*) and Maxwell (*11, 12*). For ideal binary gas mixtures the more rigorous Chapman-Enskog (*2*) equations can be shown to reduce to the Maxwell equations when the temperature and total pressure are constant. Similarly, under the same conditions the Curtiss-Hirschfelder (*4*) extension of the Chapman-Enskog equations can be shown to reduce to the Maxwell-Stefan equations for ideal multicomponent gas mixtures. The predictions of the Maxwell equations for three-component mixtures have been shown to be in good accord with experiment for various types of diffusion (*7, 10*).

For the general n-component system there are n Maxwell equations of the form

$$-\frac{P}{RT}\frac{dy_A}{dx} = \frac{N_A y_B - N_B y_A}{D_{AB}} + \frac{N_A y_C - N_C y_A}{D_{AC}} + \cdots \qquad (1)$$

When the total pressure is constant, as assumed in the equation, the number of equations is reduced to $n - 1$. For steady state diffusion in the x direction only, these $n - 1$ differential equations can be solved to give $n - 1$ algebraic equations relating the rates of diffusion of the n different molecular species. Therefore the resulting equations will be indeterminate, and one more restriction is necessary to make the system determinate. This restriction is obtained by fixing the rate of diffusion of any one of the components or by relating any two or more of the diffusion rates.

For a binary system the two simplest and most useful special cases of these general restrictions are the stagnant-gas case and the equimolal countercurrent diffusion case. The former sets the rate of diffusion of one component equal to zero by placing a barrier to the transfer of this component (which will be called an absorption barrier), and the latter usually sets the total net rate equal to zero by an energy balance.

These two restricted types of diffusion appear to be of most utility in multicomponent systems as well as in binary systems. The case of one stagnant gas corresponds to absorption in which one component of the mixture is insoluble in the liquid phase, and equimolal countercurrent diffusion (hereafter referred to as *equimolal diffusion*) corresponds to distillation of a multicomponent mixture. Equimolal diffusion is closely approximated (*14*) when the distillation column is adiabatic, molal heats of vaporization are approximately the same for all components, etc.

Gilliland (*15*) solved the diffusion equations for a ternary system by setting the rate of diffusion of one of the components equal to zero, and Hoopes (*10*) solved the same equation with the rates of transfer unrestricted. Hoopes also presented a solution for the case of equimolal diffusion. Solutions for other special cases of ternary diffusion have been obtained by Benedict and Boas (*1*) and Cichelli, Weatherford, and Bowman (*3*).

The integrated equations, even for a three-component system, are highly complex and numerical results usually can be calculated from the equations only by trial-and-error. In addition, the physical significance of the equations is not at all apparent. Wilke (*19*) has developed approximate methods of solving Maxwell's equations, but his method necessitates a trial-and-error solution and consequently does not bring out the important features of the diffusion process.

This paper will be concerned with the two types of diffusion in three-component gas mixtures: diffusion of two gases through a third stagnant gas and equimolal diffusion. The object is to determine the important characteristics of the diffusion process and to develop approximate equations which will show these characteristics and still retain, as far as possible, the familiar forms of the binary-diffusion equations.

SOLUTIONS OF THE MAXWELL DIFFUSION EQUATIONS

It is simplest and most informative to obtain directly the desired solution for equimolal diffusion.

For a three-component system Equation (1) can be written for each component, and since the summation of the mole fractions is 1, the equation for component C can be eliminated. At a constant total pressure $D_{ij} = D_{ji}$ and the equations become

$$-\frac{P}{RT}\frac{dy_A}{dx} = -\left(\frac{N_B}{D_{AB}} + \frac{N_A + N_C}{D_{AC}}\right)y_A + \left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right)N_A y_B + \frac{N_A}{D_{AC}} \qquad (2)$$

$$-\frac{P}{RT}\frac{dy_B}{dx} = -\left(\frac{N_A}{D_{AB}} + \frac{N_B + N_C}{D_{BC}}\right)y_B + \left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}}\right)N_B y_A + \frac{N_B}{D_{BC}} \qquad (3)$$

Since $D_{ij}P$ is independent of P it can be seen that the diffusion rates are independent of the total pressure and proportional to $1/RTx$, where x is the length of the diffusion path. This is also true for an n-component mixture.

For equimolal diffusion

$$N = N_A + N_B + N_C = 0 \qquad (4)$$

and with this restriction Equations (2) and (3) reduce to

$$-\frac{P}{RT}\frac{dy_A}{dx} = -\left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right)N_B y_A + \left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right)N_A y_B + \frac{N_A}{D_{AC}} \qquad (5)$$

$$-\frac{P}{RT}\frac{dy_B}{dx} = -\left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}}\right)N_A y_B + \left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}}\right)N_B y_A + \frac{N_B}{D_{BC}} \qquad (6)$$

Part of the solution to these equations may be obtained directly by first multiplying both sides of Equation (5) by $(1/D_{AB}) - (1/D_{BC})$, both sides of Equations (6) by $(1/D_{AB}) - (1/D_{AC})$, and then adding the resulting equations:

$$-\frac{P}{RT}\left[\left(\frac{1}{D_{AB}}-\frac{1}{D_{BC}}\right)\frac{dy_A}{dx}+\left(\frac{1}{D_{AB}}-\frac{1}{D_{AC}}\right)\frac{dy_B}{dx}\right]=\left(\frac{1}{D_{AB}}-\frac{1}{D_{BC}}\right)\frac{N_A}{D_{AC}}+\left(\frac{1}{D_{AB}}-\frac{1}{D_{AC}}\right)\frac{N_B}{D_{BC}} \tag{7}$$

This may be integrated in terms of the variable

$$\left(\frac{1}{D_{AB}}-\frac{1}{D_{BC}}\right)y_A+\left(\frac{1}{D_{AB}}-\frac{1}{D_{AC}}\right)y_B$$

from $x = 0$ where $y_A = y_{A_1}$ and $y_B = y_{B_1}$
to $x = x$ where $y_A = y_{A_2}$ and $y_B = y_{B_2}$ (8)

to give

$$\frac{1}{D_{AC}}\left(\frac{1}{D_{AB}}-\frac{1}{D_{BC}}\right)N_A+\frac{1}{D_{BC}}\left(\frac{1}{D_{AB}}-\frac{1}{D_{AC}}\right)N_B=\frac{P}{RTx}\left[\left(\frac{1}{D_{AB}}-\frac{1}{D_{BC}}\right)(y_{A_1}-y_{A_2})+\left(\frac{1}{D_{AB}}-\frac{1}{D_{AC}}\right)(y_{B_1}-y_{B_2})\right] \tag{9}$$

The second part of the solution may be obtained by use of the Laplace Transform. (*13*), and the result is

$$\left(\frac{1}{D_{AB}}-\frac{1}{D_{BC}}\right)N_A+\left(\frac{1}{D_{AB}}-\frac{1}{D_{AC}}\right)N_B=\frac{P}{RTx}\ln\left[\frac{\dfrac{y_{A_2}}{N_A}-\dfrac{y_{B_2}}{N_B}-\dfrac{\dfrac{1}{D_{AC}}-\dfrac{1}{D_{BC}}}{\left(\dfrac{1}{D_{AB}}-\dfrac{1}{D_{BC}}\right)N_A+\left(\dfrac{1}{D_{AB}}-\dfrac{1}{D_{AC}}\right)N_B}}{\dfrac{y_{A_1}}{N_A}-\dfrac{y_{B_1}}{N_B}-\dfrac{\dfrac{1}{D_{AC}}-\dfrac{1}{D_{BC}}}{\left(\dfrac{1}{D_{AB}}-\dfrac{1}{D_{BC}}\right)N_A+\left(\dfrac{1}{D_{AB}}-\dfrac{1}{D_{AC}}\right)N_B}}\right] \tag{10}$$

Equations (9) and (10) together satisfy Equations (5) and (6) as well as the boundary conditions (8), and N_A and N_B may be obtained from them by trial and error; N_C is then fixed by Equation (4).

The parametric solution to the ternary-diffusion problem obtained by Gilliland (*15*) when one gas is stagnant ($N_C = 0$) is given below:

$$\frac{N_A}{D_{AC}}+\frac{N_B}{D_{BC}}=\frac{P}{RTx}\ln\frac{y_{C_2}}{y_{C_1}} \tag{11}$$

$$N_A+N_B=\frac{D_{AB}P}{RTx}\ln\left[\frac{\dfrac{N_A+N_B}{N_A}y_{A_2}-\left(\dfrac{\dfrac{1}{D_{AB}}-\dfrac{1}{D_{AC}}}{\dfrac{1}{D_{AB}}-\dfrac{1}{D_{BC}}}\right)\dfrac{N_A+N_B}{N_B}y_{B_2}-\dfrac{\dfrac{1}{D_{AC}}-\dfrac{1}{D_{BC}}}{\dfrac{1}{D_{AB}}-\dfrac{1}{D_{BC}}}}{\dfrac{N_A+N_B}{N_A}y_{A_1}-\left(\dfrac{\dfrac{1}{D_{AB}}-\dfrac{1}{D_{AC}}}{\dfrac{1}{D_{AB}}-\dfrac{1}{D_{BC}}}\right)\dfrac{N_A+N_B}{N_B}y_{B_1}-\dfrac{\dfrac{1}{D_{AC}}-\dfrac{1}{D_{BC}}}{\dfrac{1}{D_{AB}}-\dfrac{1}{D_{BC}}}}\right] \tag{12}$$

If y_A and y_B are assumed small, Equations (2) and (3) may be integrated separately:

$$N_A=\frac{D_{AC}P}{RTx}(y_{A_1}-y_{A_2}) \tag{13}$$

$$N_B=\frac{D_{BC}P}{RTx}(y_{B_1}-y_{B_2}) \tag{14}$$

Although these are the equations for binary equimolal diffusion, as well as the limiting forms for diffusion of one dilute gas through a second stagnant gas, Equation (13) applies to a system consisting of A and C, and Equation (14) applies to a system consisting of B and C. Thus, when gases A and B are dilute they diffuse through the third gas with no interaction among themselves.

The differences in mole fraction in these equations can be conveniently considered to be the driving forces for diffusion in binary systems, and with this picture the first terms on the right of the equations may be considered to be reciprocal resistances. Since mole fraction is proportional to concentration in ideal gases, this is the same as considering a concentration difference to be the driving force.

DIFFUSION BARRIER

Equimolal Diffusion

If N_C is set equal to zero, $N_A + N_B = 0$ from Equation (4), and the equimolal diffusion equations, (9) and (10), give the rates of transfer of A and B directly,

$$N_A=-N_B=\frac{1}{\left(\dfrac{1}{D_{AC}}-\dfrac{1}{D_{BC}}\right)}\cdot\frac{P}{RTx}\ln\frac{y_{C_2}}{y_{C_1}} \tag{15}$$

However, they also yield the additional equation

$$\left(1-\frac{D_{AB}}{D_{BC}}\right)(y_{A_1}-y_{A_2})+\left(1-\frac{D_{AB}}{D_{AC}}\right)(y_{B_1}-y_{B_2})=\ln\frac{y_{C_2}}{y_{C_1}} \tag{16}$$

This indicates, as expected, that N_C could not be arbitrarily set equal to zero, as all the degrees of freedom were removed by fixing $N = 0$. Thus Equation (15) gives the rate of transfer of components A and B when $N_C = 0$ but $N_C = 0$ only when the mole fractions are related in such a way that they satisfy Equation (16). This result throws light on Gilliland's solution to the ternary diffusion problem where N_C is fixed equal to zero. As pointed out by Wilke (*19*), Equations (11) and (12) are always satisfied by $N_A + N_B = 0$ and there are usually at least two solutions to the equations. Consequently, as N_A approaches N_B, it becomes more and more difficult to determine the correct solution. This difficulty occurs because when $N_A + N_B = 0$, Gilliland's equation is a special case of equimolal diffusion.

Although the same physical situation is described regardless of the order in which the limit $N_A + N_B = N_C = 0$ is approached, Gilliland's solution in the limit gives Equation (15), but it fails to give Equation (16). It can be shown by substituting $N_A + N_B = N_C = 0$ into the original differential equations, (2) and (3), that Equations (15) and (16) are the correct solutions for this situation. Therefore, when N_C is fixed equal to zero, by a solubility barrier, for example, equimolal diffusion of the remaining two components occurs when Equation (16) is satisfied and the rate is given by Equation (15). Equation (16) thus complements Gilliland's solution. When it is not satisfied, the solution $N_A + N_B = 0$ is a ficticious one.

When N is set equal to zero, by an energy balance, for example, then when Equation (16) is satisfied N_C goes to zero and Equation (15) gives the rate of diffusion of the other two components. The interesting result is that if component C is not in equilibrium its rate of diffusion, even if there is no apparent barrier to its transfer, will be zero if the components are distributed so that Equation (16) is satisfied.

(The concept of equilibrium is being used in a restricted sense to indicate the condition when $y_{i_1} = y_{i_2}$; i.e., the ordinary binary driving force is zero. *This is really* a pseudoequilibrium for each component.) Using the ordinary concept of diffusion in a binary gas, one might say the resistance of the gas to the transfer of component C is infinite, and this condition will be defined as a *diffusion barrier* to differentiate it from the *solubility barrier*, which exists in gas absorption.

The physical situation is clarified if one considers the theoretical situation in which the two independent restrictions, $N_C = 0$ and $N_A + N_B = 0$, are simultaneously placed in the system. Maxwell's equations then yield Equations (15) and (16); the first equation gives the rates of diffusion and the second describes the manner in which the gases arrange themselves. If either of the original restrictions is placed separately on the system, the preceding situation is reproduced identically if a second restriction is that the compositions must satisfy Equation 16).

When $D_{AC} = D_{BC}$ it can be shown that the only physically possible solution to Equation (16) is $y_{C_1} = y_{C_2}$, and so Equation (15) does not go to infinity, but becomes indeterminate under this restriction. The rates of diffusion of A and B under these conditions are shown below to be given by Equations (43) and (44).

Figure (1) shows some concentration relationships which cause diffusion barriers in the system H_2, H_2O, and CO_2. These curves were determined from Equation (16) by use of binary diffusion coefficients from Table 1. The curves are independent of the total pressure. All the subsequent calculations are based on these same diffusion coefficients. Equation (16), which gives the conditions for $N_C = 0$, was applied to each of the components in turn. Two of the four independent variables were removed by setting the mole fraction of one of the diffusing gases equal to zero at point 1 and setting the mole fraction of the other diffusing gas equal to zero at point 2. This allows the compositions at points 1 and 2 to be given by one point on a curve and also shows the greatest effect of the diffusion barrier.

TABLE 1.

BINARY-DIFFUSION COEFFICIENTS

(sq. cm./sec.)

$i = CO_2$	$D_{ij} = 0.9220$
$j = H_2O$	$D_{ik} = 2.7064$
$k = H_2$	$D_{jk} = 3.4576$

Approximate values at 40°C. and 155 mm. Hg, from Wilke (*19*).

A point on any of the curves gives the compositions of that component at the terminal points when that component is stopped from diffusing by a diffusion barrier. The 45-deg. line indicates the absence of a diffusion barrier, for this line corresponds to no diffusion when $y_{C_1} = y_{C_2}$. The difference between any of the curves and the 45-deg. line therefore gives the driving force, $y_{C_1} - y_{C_2}$, for the component which is not diffusing. This difference can be considered in a sense as the strength of the diffusion barrier. The curves show that the maximum strength of the diffusion barrier for hydrogen, the light component, is considerably less than the maximum strength of the barriers for the two heavier components.

Just as in Gilliland's equation, the equations for equimolal diffusion also contain a solution which is usually fictitious for it can be seen that Equation (10) is always satisfied by

$$N_A\left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}}\right) + N_B\left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right) = 0 \qquad (17)$$

Under these conditions Equation (9) gives

$$N_A = \frac{P/RTx}{\left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}}\right)\left(\frac{1}{D_{AC}} - \frac{1}{D_{BC}}\right)} \cdot \left[\left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}}\right)(y_{A_1} - y_{A_2}) + \left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right)(y_{B_1} - y_{B_2})\right] \qquad (18)$$

As before, this solution is true for only one particular relationship among the mole fractions and here the extra equation must be obtained by solving the original differential equations with restrictions given by Equations (17) and (4). The solution gives Equation (18) and the additional relationship

$$\frac{\left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right)(y_{B_1} - y_{B_2})}{\left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}}\right)(y_{A_1} - y_{A_2})} = -\frac{\left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}}\right)(y_{A_1} + y_{A_2}) + \left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right)(y_{B_1} + y_{B_2}) + \frac{2}{D_{BC}}}{\left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}}\right)(y_{A_1} + y_{A_2}) + \left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right)(y_{B_1} + y_{B_2}) + \frac{2}{D_{AC}}} \qquad (19)$$

The solution to the equimolal diffusion equations given by Equation (18) is correct only when Equation (19) is satisfied.

One Gas Stagnant

The previous results suggest the possibility of a diffusion barrier when two gases are diffusing through a third gas which cannot diffuse because of a solubility barrier. If N_B is set equal to zero in Equation (11),

$$N_A = \frac{D_{AC}P}{RTx} \ln \frac{y_{C_2}}{y_{C_1}} \qquad (20)$$

Equations (11) and (12) together also yield

$$\frac{y_{B_2}}{y_{B_1}} = \left(\frac{y_{C_2}}{y_{C_1}}\right)^{D_{AC}/D_{AB}} \qquad (21)$$

and so a diffusion barrier exists here also. Gas C therefore cannot diffuse because of a solubility barrier and when Equation (21) holds, gas B cannot diffuse because of a diffusion barrier.

It can be shown (*10*) that Equations (20) and (21) are the solutions to the diffusion equations, (2) and (3), when N_B and N_C are both set equal to zero. Therefore, when two of the three gases are stagnant, the stagnant gas concentrations adjust themselves to satisfy Equation (21), and the diffusion rate is given by Equation (20). If only one gas is initially stagnant owing to a solubility barrier, the system containing two stagnant gases can be exactly reproduced by fixing the compositions of the components at both ends of the diffusion path so that Equation (21) is satisfied.

The fact that two stagnant gases will partially separate when a third gas is passed through them, as shown by Equation (21), is the basis of the sweep-diffusion separation process (*3*). Hellund (*9*) has considered the unsteady state analogue of the sweep-diffusion process using his extension of the Chapman-Enskog theory.

Figure 2 shows some concentration relationships when H_2O is restrained by a diffusion barrier. The terminal concentrations of the diffusing component have been fixed at 0 at point 1 and 0.5 at point 2. The conditions when CO_2 is diffusing and H_2 is stagnant are shown by curve *a*, and curve *b* shows the conditions when H_2 is diffusing and CO_2 is stagnant. It can be seen that CO_2 is more effective than H_2 in stopping the diffusion of the H_2O.

When y_{B_1} approaches 1, y_{C_1} approaches 0 and y_{B_2} must approach 0.5 in order for a solution to exist. At this limit the system is reduced to a binary gas and this binary system is indeterminate as the removal of the stagnant gas removes the determinancy condition. Since Equation (21) gives the conditions under which $N_B = 0$, it yields $y_{B_2} = 0.5$ when $y_{B_1} = 1.0$, the

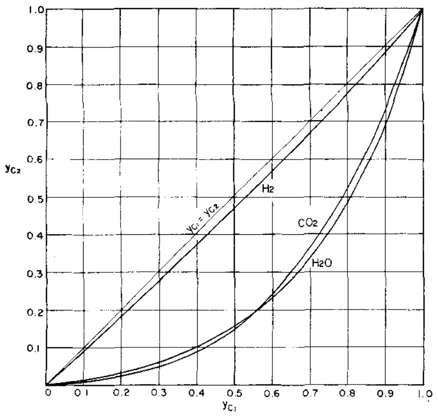

Fig. 1. Diffusion-barrier conditions for component *C*, equimolal diffusion.

H_2 = C		CO_2 = C		H_2O = C	
1	2	1	2	1	2
H_2O	CO_2	H_2	H_2O	H_2	CO_2
H_2	H_2	CO_2	CO_2	H_2O	H_2O

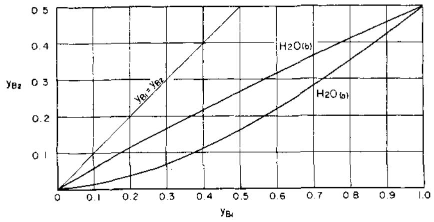

Fig. 2. Diffusion-barrier conditions for component *B*; component *C* is stagnant.

$y_{A_1} = 0$ $\qquad y_{A_2} = 0.5$
$y_{C_1} = 1 - y_{B_1}$ $\qquad y_{C_2} = 0.5 - y_{B_2}$

Curve	Component		
	A	*B*	*C*
a	CO_2	H_2O	H_2
b	H_2	H_2O	CO_2

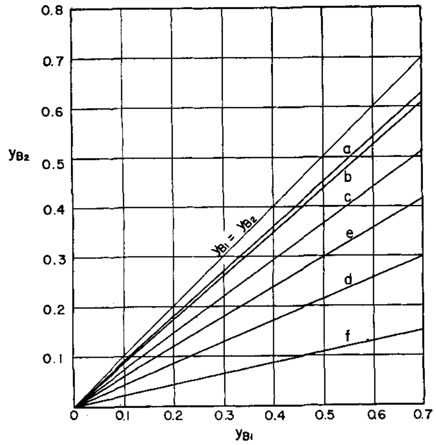

Fig. 3. Diffusion-barrier conditions for component *B*; component *C* is stagnant.

$y_{A_1} = 0.7 - y_{B_1}$ $\qquad y_{A_2} - 0.8 - y_{B_2}$
$y_{C_1} = 0.3$ $\qquad y_{C_2} - 0.2$

Curve	Components		
	A	*B*	*C*
a	H_2O	H_2	CO_2
b	CO_2	H_2	H_2O
c	H_2	H_2O	CO_2
d	CO_2	H_2O	H_2
e	H_2	CO_2	H_2O
f	H_2O	CO_2	H_2

only composition at point 2 which can exist in this binary system.

Figure 3 shows the diffusion-barrier conditions when the terminal concentrations of the stagnant gas are held constant. There are six different combinations of CO_2, H_2O and H_2, all of which are shown. The strength of the diffusion barrier clearly increases as the mass of the restrained and diffusing components increases.

GENERALIZED DRIVING FORCE

When a diffusion barrier exists for a particular component, it cannot diffuse even though it is distributed nonuniformly in the gas. This can be pictured as a dynamic equilibrium between the tendency of the restrained component to diffuse in the direction of decreasing concentration because of the usual concentration driving force and the tendency of the component to be forced in the reverse direction by interactions with the other two diffusing components.

A small increase in the driving force at this point, therefore, should allow it to overcome the interactions and cause the transfer to take place in the direction of the driving force (high to low concentrations) and a small decrease in the driving force should make the transfer take place in the direction opposite to the driving force.

Equimolal Diffusion

This conclusion has been tested numerically for equimolal diffusion by use of Equations (9), (10), (4), and (16). Figure 4 shows the rate of diffusion of CO_2 as a function of its mole fraction at point 2, when its mole fraction at point 1 is constant at 0.5. It is assumed for simplicity that the mole fraction of H_2O is zero at point 1 and the mole fraction of H_2 is zero at point 2. The rates of diffusion of H_2O and H_2 are also shown on the figure. The dotted lines are approximate equations developed in a later section.

It can be seen that the rate of diffusion of CO_2 is close to a linear function of y_{A_2}. At $y_{A_2} = 0.159$, N_A is zero, as this is the diffusion-barrier concentration. As y_{A_2} decreases from this value, the driving force $y_{A_1} - y_{A_2}$ increases and overcomes the interactions and N_A increases in the positive direction. As y_{A_2} increases from the diffusion-barrier value, the driving force decreases, the interactions overcome the driving force, and the diffusion increases in the negative direction. The direction of diffusion is now opposite to the direction of the driving force.

As y_{A_2} continues increasing the driving force decreases and the magnitude of N_A increases. At $y_{A_2} = 0.5 = y_{A_1}$ the driving force is now zero but N_A is not zero. This point is labeled *osmotic diffusion* and is considered later. When y_{A_2} becomes greater than y_{A_1} the direction of diffusion is unchanged, but the direction of the driving force is reversed so that the diffusion is again in the direction of the driving force. When y_{A_2} equals 1 the system is reduced to a binary gas consisting of CO_2 and H_2. $N_A = -N_B$ and the rates are the same as those given by the usual equation for binary equimolal diffusion.

The same conclusions can be reached analytically for the special case of diffusion in which two of the binary-diffusion coefficients are equal. [*See* Equation (36).]

No diffusion barrier occurs for H_2O and H_2 because of the way the compositions were fixed.

There are two separation processes which take advantage of the phenomenon of diffusion from regions of low to high concentrations. They differ from themselves, and from the conditions considered here, by the restrictions placed on N. One has been defined as *mass diffusion* (*1*) or *atmolysis*, and the other as *sweep diffusion* (*3*).

It seems useful to define as *reverse diffusion* the diffusion of a constituent of a multicomponent gas from a region where its concentration is low to a region where it is high when it is caused by the action of the other constituents of the gas. The region in which reverse diffusion takes place is indicated in Figure 4.

In one sense the diffusion-barrier concentrations of the restrained component correspond to a zero concentration gradient in a binary gas. When the restrained component is at the concentrations corresponding to a diffusion barrier, its rate of transfer is zero, just as it is zero in a binary gas when $y_1 = y_2$. In the ternary gas mixture the diffusion of a component is from point 1 to point 2 when the concentration of the component at 1 is greater than the concentration at 1 corresponding to the diffusion barrier, just as the diffusion in a binary system is from 1 to 2 when y_1 is greater than the value corresponding to zero concentration gradient y_2. As the displacement from the barrier condition increases, the rate of diffusion increases; therefore, the driving force in a ternary gas which should correspond to $y_1 - y_2$ in a binary gas is, for component i,

$$(y_{i_1} - y_{i_1}{}^*) \qquad (22)$$

or

$$(y_{i_2}{}^* - y_{i_2}) \qquad (23)$$

where $y_{i_1}{}^*$ is the mole fraction which would have to exist at point 1 for a diffusion barrier to exist for component i when the mole fractions at point 2 are held constant and $y_{i_2}{}^*$ is the mole fraction necessary at point 2 for a diffusion barrier to exist when the mole fractions at point 1 are held constant.

Equation (16), when A and C are

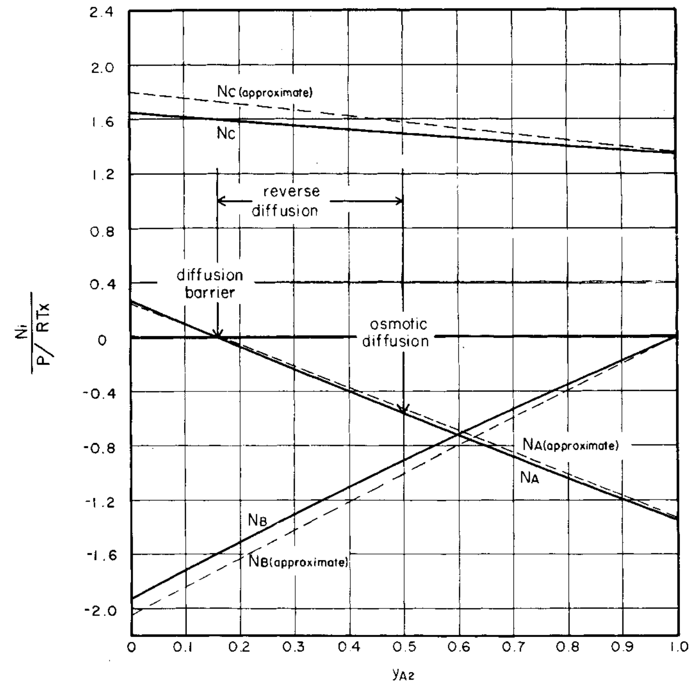

Fig. 4. Diffusion rates as a function of y_{A_2}, equimolal diffusion.

$y_{A_1} - 0.5$
$y_{B_1} = 0$
$y_{C_1} = 0.5$

y_{A_2}
$y_{B_2} = 1 - y_{A_2}$
$y_{C_2} = 0$

A	B	C
CO_2	H_2O	H_2

interchanged, gives for component A

$$\frac{y_{A_2}}{y_{A_1}} = \exp\left[\left(1 - \frac{D_{BC}}{D_{AB}}\right)(y_{C_1} - y_{C_2}) + \left(1 - \frac{D_{BC}}{D_{AC}}\right)(y_{B_1} - y_{B_2})\right] = \delta_A \quad (24)$$

and either y_{A_1} or y_{A_2} can be considered to be the starred value. When y_{A_1} is taken as $y_{A_1}{}^*$, Equation (22) becomes for component A

$$\frac{1}{\delta_A}(\delta_A y_{A_1} - y_{A_2}) \qquad (25)$$

and when y_{A_2} is taken as $y_{A_2}{}^*$ Equation (23) yields for component A

$$\delta_A(y_{A_1} - y_{A_2}) \qquad (26)$$

There are similar equations for the other two components obtained by interchanging subscripts in the above equations. It can be shown that

$$\delta_i = \delta_j^{D_{jk}/D_{ik}} \qquad (27)$$

It is immaterial whether Equation (25) or (26) is considered to represent the generalized driving force; so, for simplicity, the second one will be used. The function defined by Equation (26) satisfies the necessary conditions for a driving force. First, it gives the correct direction of diffusion; when it is positive the direction of diffusion is positive and when it is negative the direction of diffusion is negative. Second, the rate of diffusion is zero when the function is zero. Since the relationship between the rate of diffusion and the generalized driving force must be single valued, the first two conditions require that the rate of diffusion be a monatonic increasing function of the generalized driving force.

A final condition which is desirable but not necessary is that the rate of diffusion should be proportional, or approximately proportional, to the driving force. The rate of diffusion of each of the three components is plotted against its generalized driving force in Figure 5. The curves were obtained by the use of Figure 4 and Equations (24) and (26) and the curves are close to straight lines. In this example no diffusion barrier occurs for H_2 and H_2O since the composition of both components is fixed at zero at one or the other end of the diffusion path. The rates of diffusion of these two components are roughly proportional to their binary driving forces, and their generalized driving forces are essentially the same as their binary ones. However, CO_2, for which a diffusion barrier exists, diffuses quite independently of its binary driving force, and its diffusion rate is closely proportional to its generalized driving force. It can be seen that reverse diffusion takes place when the generalized driving force is of opposite sign to the binary driving force, and this would be expected to be the case in general.

The reciprocal slopes of the curves in Figure 5 are a measure of the generalized resistances to the diffusion of each component (the generalized driving force divided by the diffusion rate). The mean slopes of the lines decrease with increasing molecular weight, an indication, at least for this example, that the generalized resistances increase with the mass of the component. Since the curves for CO_2 and H_2O have opposite curvatures, their generalized resistances approach each other when the generalized driving forces are small.

In general, the relationship between the rates of diffusion and the generalized driving forces would not be expected to be as linear as in this particular case, and so the generalized resistances for each component would vary more with the composition of the system. In this instance the generalized driving force has the same utility as the one used in the diffusion of one gas through a second inert gas, quantitatively it can be somewhat misleading, but it always gives the correct direction of diffusion and the correct zero condition.

One Gas Stagnant

The generalized-driving-force viewpoint can also be applied to transfer when one gas is stagnant by using the displacement from a diffusion barrier as a measure of the driving force.

Figure 6 shows the rates of diffusion of CO_2 and H_2O through stagnant H_2 as a function of the mole fraction of CO_2 at point 2. The solid curves were calculated from Equations (11) and (12) and the dotted ones are approximations developed in a later section. The terminal concentrations are fixed as shown in the figure. The inert-gas concentrations are fixed at both ends of the diffusion path, and the concentrations of CO_2 and H_2O are fixed only at point 1.

These curves bear a resemblance to those shown in Figure 4 for equimolal diffusion, although the conditions are quite different. There is no diffusion barrier for H_2O, as its concentration at point 1 is zero, but the CO_2 diffusion barrier occurs at $y_{B_2} = 0.152$. At this point the tendency for CO_2 to diffuse in the direction of decreasing CO_2 concentration is just balanced by collisions with H_2O, which is diffusing in the opposite direction.

In this system, contrary to the equimolal one previously discussed, there is a net molal transfer for all values of y_{B_2}. N_A never equals $-N_B$ since Equation (16), the criterion for this condition, cannot be satisfied by any physically possible value of y_{B_2} in this example.

When y_{B_2} is less than the diffusion-barrier concentration, N_B is positive and in the direction of decreasing CO_2 concentration. When y_{B_2} is between the diffusion-barrier concentration and y_{B_1}, 0.7, N_B is negative and reverse diffusion takes place. When y_{B_2} is greater than y_{B_1} the diffusion is again in the direction of of decreasing CO_2 concentration. When $y_{B_2} = 0.8$, the system reduces to a binary one in which CO_2 is diffusing through stagnant H_2 and the rate of diffusion of CO_2 is given by the binary equation.

Since the diffusion phenomena when one gas is stagnant are similar to the phenomena when the transfer is equimolal, the generalized driving force given by Equation (23) applies here also. The only difference is that $y_{i_2}{}^*$ is now given by Equation (21). Thus for component B,

$$\frac{y_{B_2}{}^*}{y_{B_1}} = \left(\frac{y_{C_2}}{y_{C_1}}\right)^{D_{AC}/D_{AB}} = \delta_B' \qquad (28)$$

and the generalized driving force for component B is obtained by combining Equations (23) and (28),

$$(\delta_B' y_{B_1} - y_{B_2}) \qquad (29)$$

The equation for component A is obtained by interchanging the A and B subscripts in the preceding equations. δ_A' and δ_B' are related to each other in the same way as δ_i and δ_j [Equation (27)]. As before, the generalized driving force gives the correct direction of diffusion as well as the correct zero condition.

The rate of diffusion of both components is shown plotted against their generalized driving forces in Figure 7. The data are from Figure 6 and Equations (28) and (29). The generalized driving force for component A, H_2O, reduces to the binary one because of the terminal concentrations which were used and the rate of diffusion of H_2O is approximately proportional to this quantity. The generalized driving force for CO_2, however, is markedly different from the binary one, and only the generalized driving force has the characteristics of a driving force.

The generalized resistances to the diffusion of the two components are not the same although they approach one another as the generalized driving forces approach zero, and the generalized resistance for CO_2 is greater than that for H_2O.

Simplified approximate equations for the rates of diffusion, developed in a later section both when the diffusion is equimolal and when one gas is stagnant, allow analytic confirmation of the conclusions reached in this section.

NOTATION

D_{ij} = diffusion coefficient for binary mixture of components i and j, sq. cm./sec.

D_m = mean diffusion coefficient defined by Equation (56), sq. cm./sec.

N = total net diffusion rate, g.-mole/(sq. cm.)(sec.)

N_i = diffusion rate for component i, g.-mole/(sq. cm.)(sec.)

P = total pressure, atm.

R = gas constant, (cc.)(atm.)/(g.-mole)(°K.)

T = temperature, °K.

x = distance in direction of diffusion or length of diffusion path, cm.

y_i = mole fraction of component i

$y_i{}^*$ = value of y_i when component i is restrained by a diffusion barrier

y_{im} = log mean of y_i

Greek Letters

$\delta, \delta_i, \delta_m, \varphi_C$ = functions used in equimolal diffusion equations, defined by Equations (35), (24), (59), and (60), respectively

$\delta', \delta_i', \delta_m', \varphi_C'$ = functions used in stagnant-gas diffusion equations, defined by Equations (49), (28), (65), and (66), respectively

Subscripts

A, B, C = components of a mixture

i, j, k = indexes which refer to components A, B, or C

1, 2 = terminal conditions of the diffusion path

PART II

OSMOTIC DIFFUSION

It has been shown that a component not in equilibrium under certain conditions may not diffuse even if there is no barrier to its diffusion, and it has also been shown for a particular example that the converse is true, i.e., that a component which is in equilibrium may diffuse.

Equimolal Diffusion

It has already been demonstrated that Equation (16) must be satisfied for N_C to equal zero when $N = 0$. If component C is in equilibrium, $y_{C_1} = y_{C_2}$, and since the sum of the mole fractions at any point is equal to 1, Equation (16) is satisfied with these restrictions only if one of the following conditions is satisfied:

$$y_{A_1} = y_{A_2} \qquad (30)$$

and consequently

$$y_{B_1} = y_{B_2}$$

or

$$D_{AC} = D_{BC} \qquad (31)$$

The first condition is trivial, as it gives the obvious result that there is no transfer if there is complete equilibrium in the system. The second condition shows that $N_C = 0$ only when the diffusivity of A through C equals the diffusivity of B through C (when $y_{C_1} = y_{C_2}$). When this condition holds, Equation (15) is indeterminate and the diffusion equations reduce to Equations (43) and (44). When D_{AC} does not equal D_{BC}, the rates of diffusion are given by the general equations.

From the generalized-driving-force viewpoint, $N_C = 0$ for $y_{C_1} - y_{C_2} = 0$ only when the generalized driving force, $\delta_C y_{C_1} - y_{C_2}$, is equal to the usual binary driving force, that is, when $y_{C_1} = y_{C_2}$ and Equation (30) or (31) is satisfied. The point at which osmotic diffusion occurs is shown in Figures 4 and 5.

The phenomenon of diffusion of a component which is in equilibrium was predicted by Hellund (*8*), who extended the Chapman-Enskog equations to a ternary system and obtained a solution for diffusion in the unsteady state. He named the phenomenon *osmotic diffusion* by analogy to liquids.

One Gas Stagnant

When N_C is fixed equal to zero by a solubility barrier, N_B is zero when Equation (21) holds. If component B is in equilibrium, $y_{B_1} = y_{B_2}$ and the condition for $N_B = 0$ becomes $y_{C_1} = y_{C_2}$. This is the condition which reduces the generalized driving force to the binary driving force as well as the condition for complete equilibrium, and so in this system a component which is in equilibrium will always diffuse unless the entire system is in equilibrium. The point at which osmotic diffusion occurs is shown in Figures 6 and 7.

In general, reverse diffusion, both in equimolal diffusion and diffusion with one gas stagnant, would be expected to occur when the generalized driving force lies between zero and the value corresponding to osmotic diffusion.

TWO DIFFUSION COEFFICIENTS EQUAL

By setting two of the three binary diffusion coefficients equal to each other, one may obtain simplified forms of the diffusion equations.

Equimolal Diffusion

If $D_{AC} = D_{BC}$ Equations (9) and (10) reduce to

$$N_A + N_B = \frac{D_{AC}P}{RTx} \cdot [(y_{A_1} + y_{B_1}) - (y_{A_2} + y_{B_2})] = \frac{D_{AC}P}{RTx}(y_{C_2} - y_{C_1}) \qquad (32)$$

and

$$\left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right)(N_A + N_B) = \frac{P}{RTx} \ln \frac{\dfrac{y_{A_2}}{N_A} - \dfrac{y_{B_2}}{N_B}}{\dfrac{y_{A_1}}{N_A} - \dfrac{y_{B_1}}{N_B}} \qquad (33)$$

equating the last two equations yields

$$\frac{N_A}{N_B} = \frac{\delta y_{A_1} - y_{A_2}}{\delta y_{B_1} - y_{B_2}} \qquad (34)$$

where

$$\delta = \exp\left[\left(1-\frac{D_{AC}}{D_{AB}}\right)(y_{C_1}-y_{C_2})\right] \qquad (35)$$

Substituting Equation (34) into Equation (32) leads to

$$N_A = \frac{y_{C_1} - y_{C_2}}{(1 - y_{C_2}) - \delta(1 - y_{C_1})} \cdot \frac{D_{AC}P}{RTx}(\delta y_{A_1} - y_{A_2}) \qquad (36)$$

and

$$N_B = \frac{y_{C_1} - y_{C_2}}{(1 - y_{C_2}) - \delta(1 - y_{C_1})} \cdot \frac{D_{BC}P}{RTx}(\delta y_{B_1} - y_{B_2}) \qquad (37)$$

Equation (32) with the equimolal condition gives

$$N_C = \frac{D_{AC}P}{RTx}(y_{C_1} - y_{C_2}) \qquad (38)$$

This is the equation for equimolal diffusion in a binary system consisting of A and C. Hence the rate of diffusion of component C is the same as it would be if A and B were one gas; indeed, as far as C is concerned A and B are the same gas, for their interactions with C were assumed identical. Equation (32) shows that the hypothetical gas consisting of A and B also diffuses through C as if it were the second gas in a binary mixture.

In a sense the ternary mixture has been reduced to a binary one in which part of the molecules of one component are tagged to distinguish them from the other part of the same component. The diffusion coefficient D_{AB} then represents the coefficient of self-diffusion of components A and B. Although the net rate of diffusion of the tagged and untagged molecules, A and B, follows the binary equation, the individual components deviate from the binary equation as shown by Equations (36) and (37).

If the composition of the gas A and B is the same at both ends of the diffusion path,

$$\frac{y_{A_1}}{y_{B_1}} = \frac{y_{A_2}}{y_{B_2}} \qquad (39)$$

and Equations (36) and (37) show that

$$\frac{N_A}{N_B} = \frac{y_{A_1}}{y_{B_1}} = \frac{y_{A_1}/(y_{A_1} + y_{B_1})}{y_{B_1}/(y_{A_1} + y_{B_1})} \qquad (40)$$

Equation (32) then yields

$$N_A = \left(\frac{y_{A_1}}{y_{A_1} + y_{B_1}}\right) \cdot \frac{D_{AC}P}{RTx}(y_{C_2} - y_{C_1}) \qquad (41)$$

$$N_B = \left(\frac{y_{B_1}}{y_{A_1} + y_{B_1}}\right) \cdot \frac{D_{BC}P}{RTx}(y_{C_2} - y_{C_1}) \qquad (42)$$

so that components A and B deviate from the binary rate of diffusion of gas A and B by their mole fractions in the mixture A and B, and the composition of the gas A and B is unchanged by the diffusion through component C.

As D_{AB} approaches D_{AC}, δ approaches 1 and Equations (36) and (37) approach the binary equimolal equations (13) and (14), as expected. When y_{C_1} approaches y_{C_2}, Equations (36) and (37) reduce to

$$N_A = \frac{D_{AC}P/RTx}{y_C\left(1 - \frac{D_{AC}}{D_{AB}}\right) + \frac{D_{AC}}{D_{AB}}} \cdot (y_{A_1} - y_{A_2}) \qquad (43)$$

$$N_B = \frac{D_{BC}P/RTx}{y_C\left(1 - \frac{D_{BC}}{D_{AB}}\right) + \frac{D_{BC}}{D_{AB}}} \cdot (y_{B_1} - y_{B_2}) \qquad (44)$$

and this is the special case discussed previously where N_C is zero and $N_A = -N_B$. The presence of component C under these conditions merely causes the rates of diffusion of the other two components to deviate from the binary rates by a constant amount.

When gas C is dilute, the equations further simplify to the equimolal diffusion equations for the binary system consisting of A and B. When A and B are dilute, y_C approaches 1 and the binary equimolal diffusion equations are again obtained, although in this case the diffusion coefficient D_{AC} or D_{BC} replaces the coefficient D_{AB}, giving Equations (13) and (14). If either A or B alone is dilute, the rate of diffusion of the other component is given by Equation (13) or (14).

Equations (36) and (37) are very closely related to the idea of a generalized driving force. The last terms on the right of the equations are special cases of the generalized driving force defined by Equations (24) and (26) since δ_A and δ_B are both equal to δ. The remaining terms on the right of the equations are therefore reciprocals of the generalized resistances for this special case. The generalized resistance is the same for components A and B and, for any particular system, is a function of the concentration of component C only. When the terminal concentrations of component C are held constant, the generalized resistance is constant and the diffusion rates are directly proportional to the generalized driving forces, but when the concentrations of component C are allowed to vary this proportionality does not exist. It can be shown that the generalized resistance in Equations (36) and (37) is always positive, finite, and nonzero, as indeed is nesessary if the driving-force viewpoint is to be meaningful.

The rate of diffusion of component C, which is given by the binary-diffusion equation, (38), apparently is not a function of its generalized driving force. To determine the cause of this inconsistency it is necessary to consider the original derivation of the generalized driving force. Applying Equation (24) to component C with $D_{AC} = D_{BC}$ yields

$$\delta_C = \frac{y_{C_2}}{y_{C_1}} = \exp\left[\left(\frac{D_{AB}}{D_{AC}} - 1\right)(y_{C_1} - y_{C_2})\right] \qquad (45)$$

and y_{C_2}, which can be taken as $y_{C_2}^*$, is the mole fraction of C at point 2, which causes a diffusion barrier. If this equation is combined with Equation (23) as usual, it does not yield the binary driving force which appears in Equation (38), because there is only one solution to Equation (45) which has any physical significance and that solution is $y_{C_2} = y_{C_1}$, or $y_{C_2}^* = y_{C_1}$. Therefore, δ_C must always be 1 and Equation (23) does yield $y_{C_1} - y_{C_2}$ as the generalized driving force for this limit. There can be no diffusion barrier for component C and the only condition for zero diffusion is $y_{C_1} = y_{C_2}$.

One Gas Stagnant

When $D_{AC} = D_{BC}$ Equations (11) and (12) yield

$$N_A + N_B = \frac{D_{AC}P}{RTx}\ln\frac{y_{C_2}}{y_{C_1}} \qquad (46)$$

and

$$N_A + N_B = \frac{D_{AB}P}{RTx}\ln\frac{\frac{y_{A_2}}{N_A} - \frac{y_{B_2}}{N_B}}{\frac{y_{A_1}}{N_A} - \frac{y_{B_1}}{N_B}} \qquad (47)$$

and by equating these the counterpart of Equation (34) is obtained,

$$\frac{N_A}{N_B} = \frac{\delta' y_{A_1} - y_{A_2}}{\delta' y_{B_1} - y_{B_2}} \qquad (48)$$

where

$$\delta' = \left(\frac{y_{C_2}}{y_{C_1}}\right)^{D_{AC}/D_{AB}} \qquad (49)$$

and so

$$N_A = \frac{\ln\frac{y_{C_1}}{y_{C_2}}}{(1 - y_{C_2}) - \delta'(1 - y_{C_1})} \cdot \frac{D_{AC}P}{RTx}(\delta' y_{A_1} - y_{A_2}) \qquad (50)$$

$$N_B = \frac{\ln \frac{y_{C_1}}{y_{C_2}}}{(1 - y_{C_2}) - \delta'(1 - y_{C_1})} \cdot \frac{D_{BC}P}{RTx}(\delta' y_{B_1} - y_{B_2}) \qquad (51)$$

Equation (46) shows that the hypothetical gas $A + B$ diffuses through the stagnant gas C at the same rate that one gas diffuses through a second inert gas, but Equations (50) and (51) indicate that components A and B individually do not follow the binary equations.

When the ratio of A to B is the same at both ends of the diffusion path,

$$N_A = \left(\frac{y_{A_1}}{y_{A_1} + y_{B_1}}\right) \frac{D_{AC}P}{RTxy_{C_m}} \cdot (y_{C_2} - y_{C_1}) \qquad (52)$$

$$N_B = \left(\frac{y_{B_1}}{y_{A_1} + y_{B_1}}\right) \frac{D_{BC}P}{RTxy_{C_m}} \cdot (y_{C_2} - y_{C_1}) \qquad (53)$$

where

$$y_{C_m} = \frac{y_{C_1} - y_{C_2}}{\ln \frac{y_{C_1}}{y_{C_2}}} \qquad (54)$$

At this limit the diffusion rates when one gas is stagnant differ from the rates for equimolal transfer by the term y_{C_m}, just as in binary diffusion. Under these conditions the composition of the gas $A + B$ is unchanged by its diffusion through gas C.

Equations (50) and (51) differ from the analogous equimolol equations in that they do not reduce to the binary equations when all the diffusion coefficients are equal.

When y_{C_1} approaches y_{C_2}, Equations (50) and (51) reduce to Equations (43) and (44), as do the equimolal equations, since $N_A = -N_B$. When the diffusing gases are dilute, Equations (13) and (14) are again obtained, and when only one of the diffusing gases is dilute, the binary stagnant gas equation applies to the other gas.

When the stagnant gas is dilute, the limiting forms of the equations depend, in this case, on how the limit is approached. This would be expected since when component C is removed, the restriction which makes the system determinate is removed and the resulting binary system is indeterminate. Thus, when $y_{C_1} = y_{C_2} = 0$, Equation (47) reduces to the general equation for binary diffusion,

$$N_A + N_B = \frac{D_{AB}P}{RTx} \cdot \ln \left[\frac{1 - \frac{N_A + N_B}{N_A} y_{A_2}}{1 - \frac{N_A + N_B}{N_A} y_{A_1}} \right] \qquad (55)$$

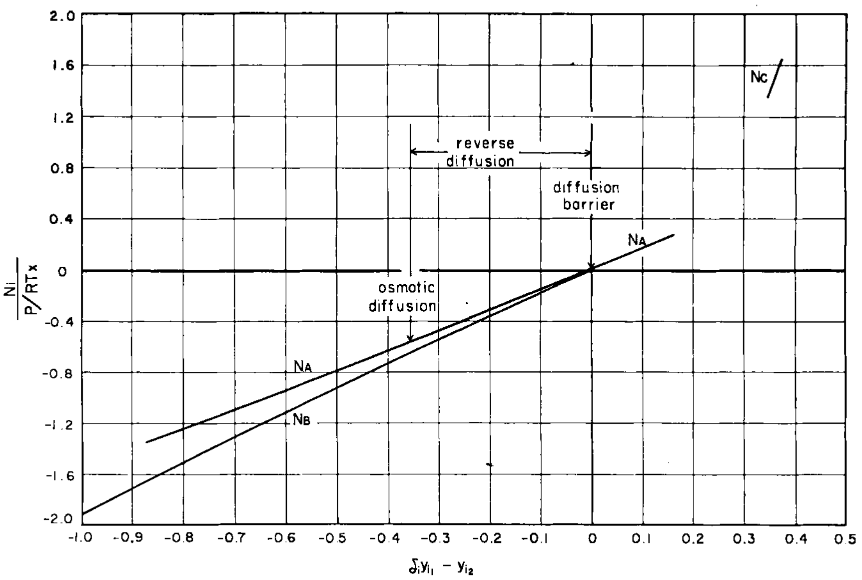

Fig. 5. Diffusion rates as a function of the generalized driving forces, equimolal diffusion.

$y_{A_1} = 0.5$ $\quad$ y_{A_2}

$y_{B_1} = 0$ $\quad$ $y_{B_2} = 1 - y_{A_2}$

$y_{C_1} = 0.5$ $\quad$ $y_{C_2} = 0$

A	B	C
CO_2	H_2O	H_2

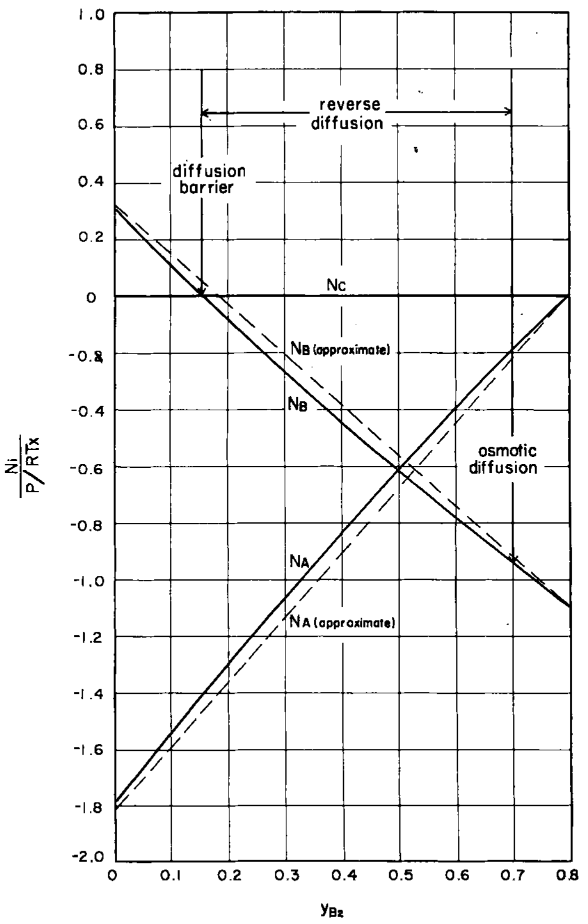

Fig. 6. Diffusion rates as a function of y_{B_2}; H_2 is stagnant.

$y_{A_1} = 0$ $\quad$ $y_{A_2} = 0.8 - y_{B_2}$

$y_{B_1} = 0.7$ $\quad$ y_{B_2}

$y_{C_1} = 0.3$ $\quad$ $y_{C_2} = 0.2$

A	B	C
H_2O	CO_2	H_2

and another restriction is now needed to define N_A and N_B.

The last terms on the right of Equations (50) and (51) are special cases of the generalized driving force defined by Equations (28) and (29) and the remaining terms on the right are the generalized resistances, which are the same for both components. This generalized resistance is positive, finite, and nonzero for all conditions of physical significance.

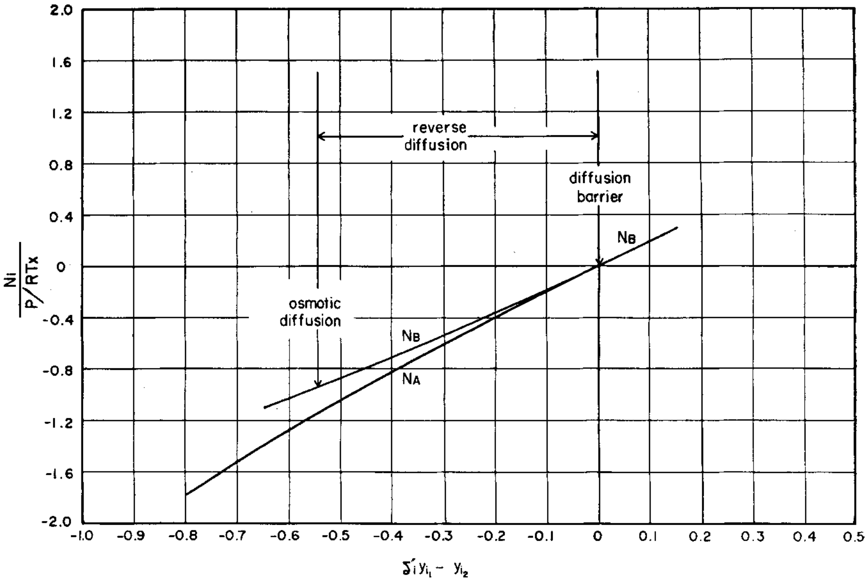

Fig. 7. Diffusion rates as a function of the generalized driving forces; H_2 is stagnant.

$y_{A_1} = 0$ $\quad$ $y_{A_2} = 0.8 - y_{B_2}$
$y_{B_1} = 0.7$ $\quad$ y_{B_2}
$y_{C_1} = 0.3$ $\quad$ $y_{C_2} = 0.2$

A	B	C
H_2O	CO_2	H_2

APPROXIMATE DIFFUSION EQUATIONS

Since the equations developed in the last two sections apply to a ternary gas in which two of the three binary-diffusion coefficients are equal, it seems possible that they could be modified to approximate the general equations when all the diffusion coefficients are unequal.

Equimolal Transfer

The simplest useful modifications of Equations (35) to (37) are obtained by replacing D_{AC} in Equation (35) by

$$D_m = \frac{D_{AC} + D_{BC}}{2} \tag{56}$$

so that

$$N_A = \frac{D_{AC}P}{RTx}\varphi_C(\delta_m y_{A_1} - y_{A_2}) \tag{57}$$

$$N_B = \frac{D_{BC}P}{RTx}\varphi_C(\delta_m y_{B_1} - y_{B_2}) \tag{58}$$

where

$$\delta_m = \exp\left[\left(1 - \frac{D_m}{D_{AB}}\right)(y_{C_1} - y_{C_2})\right] \tag{59}$$

and

$$\varphi_C = \frac{y_{C_1} - y_{C_2}}{(1 - y_{C_2}) - \delta_m(1 - y_{C_1})} \tag{60}$$

Once N_A and N_B are obtained, N_C can be determined from Equation (4). Although the equations are symmetrical with respect to A and B, they are not symmetrical with respect to C. Therefore, the results obtained from them depend on which of the three components is chosen to be component C. The most accurate results should be obtained when component C is chosen so that D_{AC} and D_{BC} are the two diffusion coefficients which are closest to each other, since this choice makes the system approximate as closely as possible the conditions under which Equations (57) and (58) are exact.

The preceding approximate equations are compared with the exact ones in Figure 4, where the approximate equations are shown by dotted lines. The error for CO_2 is very small and the diffusion-barrier conditions predicted by Equation (57) are close to the true diffusion-barrier conditions. This may not be the case in general, and when y_{A_2} is between the approximate and exact diffusion barrier values the direction of diffusion given by Equation (57) is incorrect. In this example this region is extremely narrow.

If more accurate values are desired near the diffusion barrier, the approximate generalized driving force in Equation (57) may be replaced by the true generalized driving force given by Equations (24) and (26). Thus, for component A

$$N_A = \frac{D_{AC}P}{RTx}\varphi_C(\delta_A y_{A_1} - y_{A_2}) \tag{61}$$

This equation is not symmetrical with respect to positions 1 and 2. The equation can be made symmetrical by replacing δ_m by δ_A in Equation (60), although better results are obtained by taking the average of the two values given by interchanging points 1 and 2 in Equation (61),

$$N_A = \frac{D_{AC}P}{RTx}\varphi_C\left(\frac{\delta_A + \delta_m}{2\delta_m}\right) \cdot(\delta_A y_{A_1} - y_{A_2}) \tag{62}$$

The equation can be written for the other components by interchanging subscripts. It is a good approximation when the generalized driving force is not too large, as it gives the correct zero condition, but it is usually less accurate than (57) when the generalized driving force is large. For the conditions of Figure 4 it is actually a better approximation to N_A than Equation (57) over a large part of the range of y_{A_2}.

The difference between the approximate and true diffusion rates for H_2O is larger than that for CO_2 and the rate of diffusion of H_2 is fixed by the equimolal condition, Equation (4). Consequently if H_2 were diffusing at a relatively low rate compared with that of the other two components, calculating H_2 by difference could lead to large relative errors in N_C.

In order to test the methods under other conditions, the test examples set up by Wilke (*19*) were used. The system is H_2, CO_2, and H_2O, as before, and the results obtained by use of Equations (56) to (60) and (4), defined as method 1, in most cases check those calculated from the exact equations within 10%. They are tabulated in Tables 2 and 3.[*] However, when the generalized driving force for H_2, which is the recommended choice for component C, is much smaller than the other generalized driving forces, this method causes large errors. (The direction as well as the magnitude is incorrect.) This is due to the fact that H_2 is obtained by difference. Calculating H_2 directly by this method also gives poor results because the generalized driving forces are small. In this case Equation (62) is a much better approximation since it uses the correct generalized driving force (method 2). With both methods, the maximum error is 20% although the absolute errors are generally very small.

At present the recommended procedure for equimolal diffusion is to use method 1 in all cases where the generalized driving force is not small and method 2 if the generalized driving force for a component is small. The results may be checked for consistency by use of Equations (4) and (9) without solving the general equations.

The errors in the approximate methods should increase as the difference between the diffusion coefficients increases.

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[*] Tables 2, 3, and 4 have been deposited as document 5210 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$2.50 for photoprints or \$1.75 for 35-mm. microfilm.

One Gas Stagnant

In this case the approximate diffusion equations are obtained by replacing D_{AC} in Equation (49) by D_m; so from Equations (49) to (51):

$$N_A = \frac{D_{AC}P}{RTx}\varphi_C'(\delta_m' y_{A_1} - y_{A_2}) \qquad (63)$$

$$N_B = \frac{D_{BC}P}{RTx}\varphi_C'(\delta_m' y_{B_1} - y_{B_2}) \qquad (64)$$

where

$$\delta_m' = \left(\frac{y_{C_2}}{y_{C_1}}\right)^{D_m/D_{AB}} \qquad (65)$$

and

$$\varphi_C' = \frac{\ln \dfrac{y_{C_1}}{y_{C_2}}}{(1 - y_{C_2}) - \delta_m'(1 - y_{C_1})} \qquad (66)$$

Since there are only two diffusion rates which are unknown, there is no problem with the third component as there was in equimolal diffusion. The equations are now completely symmetrical, but here there is no freedom in choosing the constituent which is to be considered as component C: it must be the stagnant gas. Therefore, the accuracy of the approximate equations would be expected to decrease as the dissimilarity between the two diffusing gases increases.

The approximate equations are compared with Gilliland's equation in Figure 6, where H_2 is the stagnant gas. When $y_{B_2} = 0.8$, the system reduces to a binary gas and the approximate equations are exact at this point. At $y_{B_2} = 0$, the approximate equations differ very slightly from the exact ones, but between these two extremes the error is larger because of the curvature in the correct curves.

The diffusion rates are reproduced quite well by the approximate equations, except for CO_2 near its diffusion barrier. The diffusion barrier predicted by the approximate equations occurs at a value of y_{B_2} slightly different from the correct diffusion barrier, so that in this region the percentage error in N_B can be very large, although the absolute error is small. In addition, when y_{B_2} is between the values corresponding to the two diffusion barriers, the approximate equation gives the wrong direction of diffusion for CO_2.

If the correct generalized driving force is used to replace the approximate one in Equation (63), the equation can be made to yield the correct diffusion-barrier conditions, and when the equation is made symmetrical as in the equimolal case,

$$N_A = \frac{D_{AC}P}{RTx}\varphi_C'\left(\frac{\delta_A' + \delta_m'}{2\delta_A'}\right) \cdot (\delta_A' y_{A_1} - y_{A_2}) \qquad (67)$$

The equation for N_B is similar.

It is interesting to note here that

$$\delta_m' = \sqrt{\delta_A' \delta_B'} \qquad (68)$$

As Equation (67) is exact when $N_A = 0$, it should be a good approximation when the generalized driving force is small. If it is applied to CO_2 in Figure (6) by interchanging A and B, it reproduces the correct diffusion rate very accurately in the vicinity of the diffusion barrier and it is a better approximation than Equation (64) over the range of y_{B_2} from 0 to 0.5.

The previous test examples were used here also. N_C instead of N is set equal to zero and method 1, with Equations (63) to (66), is generally very accurate—appreciably more so than the analogous method for equimolal diffusion. The average error is a few per cent and the maximum error is 18%. This error is very small compared with the total diffusion rate. Method 2, which uses the correct generalized driving force, Equation (67), is in general less accurate than method 1 in these examples. The results are in Table 4.*

The recommended procedure for calculating the rates of diffusion of two gases through a third stagnant gas is to use method 1 except when the generalized driving force is very small, a point at which method 2 should be more reliable.

Wilke's (*19*) approximate methods for solving Maxwell's equations have not been checked extensively, but it appears that the equations are not inconsistent with the phenomena discussed above if the negative partial film pressure factors which occur in the procedure are not rejected as he suggested, but are retained. This makes the average effective diffusion coefficient used by Wilke negative in the reverse diffusion region.

CONCLUSIONS

It is clear that in general there are marked qualitative as well as quantitative differences between binary and ternary diffusion. The approximate Equations (57) and (63) show explicity that in both equimolal diffusion and diffusion of two gases through a third stagnant gas, the usual concept of a driving force, $(y_{A_1} - y_{A_2})$, is inapplicable and the rate of transfer of one component is not only a function of its own concentration gradient but is also a function of the concentrations of the other components. This interaction is the cause of the diffusion barriers, reverse diffusion, and osmotic diffusion which are predicted by the more rigorous diffusion equations as well as by the new approximate equations.

How great an effect these results have on mass transfer in operations such as ternary distillation or in the absorption of two gases from a third stagnant gas depends both on whether an actual region exists in which steady state molecular diffusion controls the transfer rate (i.e., the usual laminar film) and on what percentage of the total resistance to transfer resides in this region if it does exist.

Without going too far astray from the purposes of this paper, one might point out that if a laminar gas film exists at all, even if it is so thin that it would have no over-all effect in binary transfer, it would still stop the transfer of any component which is prevented from diffusing by a diffusion barrier. In other words, if a diffusion barrier exists, then the resistance of the film, no matter how thin it is, is infinite as far as one component is concerned, and the film then completely stops the transfer of this component. Thus a laminar film may be controlling in the usual sense for one component only while the transfer of the other components is controlled by some other resistance in the system.

NOTATION

The notation for this article appears on Page 203.

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*See footnote on page 206.