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An Experimental Study of Three Component Gas Diffusion

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Equimolal countercurrent diffusions runs were made in a two bulb diffusion cell with the system hydrogen, nitrogen, and carbon dioxide. The initial bulb compositions were chosen so that various types of ternary interactions occurred. These interactions were well-described by the Maxwell-Stefan equations. The average deviation of the experimental mole fractions for all runs from those predicted by the Maxwell-Stefan equations was 0.45 mole %.

The differential equations describing isothermal, isobaric diffusion in ideal gas mixtures, the Maxwell-Stefan equations (*11, 12*), have been known for a long time. Various integrations for steady state unidirectional diffusion without reaction in three component gas mixtures have been presented. Gilliland considered diffusion with one gas stagnant (*18*), special cases of interest in the analysis of stagewise diffusional have been considered (*1, 2*), and Hoopes (*8*), as well as Keys and Pigford (*10*), presented solutions with the rates of transfer unrestricted. Hellund, who did not start with the Maxwell-Stefan equations, considered an unsteady state diffusion problem (*5, 6*). Hougen and Watson (*9*) and Wilke (*22*) developed approximate multicomponent solutions based on effective diffusivities, and Stewart presented an alternate method of computing effective diffusivities (*14*).

A solution for equimolal countercurrent diffusion, with simple approximate solutions, has been presented (*19*). The predicted behavior was found to be quite different from the behavior of corresponding binary systems. Even though the mean velocity is zero, the flux of a component may be zero in the presence of a concentration gradient of that component, a flux may exist in the absence of a gradient, or the direction of transfer may be against the concentration gradient of that component. (From the viewpoint of irreversible thermodynamics these are cross-diffusion effects.)

This behavior may be considered to be a consequence of the addition of a third component to what was originally a binary mixture and the above phenomena classed as ternary interaction phenomena. These are conveniently described as a diffusion barrier (*19*), osmotic diffusion (*5, 6*), and reverse diffusion (*19*) respectively. (Because the addition of further components to the three component mixture introduces no new effects, these interactions may also be considered to be multicomponent interaction phenomena.)

The first effect corresponds to zero values of the above mentioned effective diffusion coefficient, the second to singularities, and the third to negative values. The effective diffusivities of Wilke[*] and Stewart show this behavior but Hougen and Watson's do not (*21*). Further analysis indicated that these interaction phenomena could drastically affect design calculations, plate efficiencies for example (*20*). Recent work has shown that the above phenomena do occur in ternary mass transfer (*17*).

Papers reporting experimental work in diffusion of ternary gas mixtures are not numerous. In a few the validity of the Maxwell-Stefan equations is investigated. Fairbanks and Wilke (*4*) studied diffusion of one gas through two stagnant gases and showed that the results were in agreement with Wilke's approximate solution of the Maxwell-Stefan equations (*22*).

Keyes and Pigford investigated the separation of a binary gas mixture by passing a third gas through the mixture (*10*), and Hoopes measured both fluxes and gradients in a system in which all three fluxes were related to each other by a chemical reaction

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[*] Wilke's method 2 modified as suggested by Toor (*19*). Wilke's method 1 does not have the proper behavior.

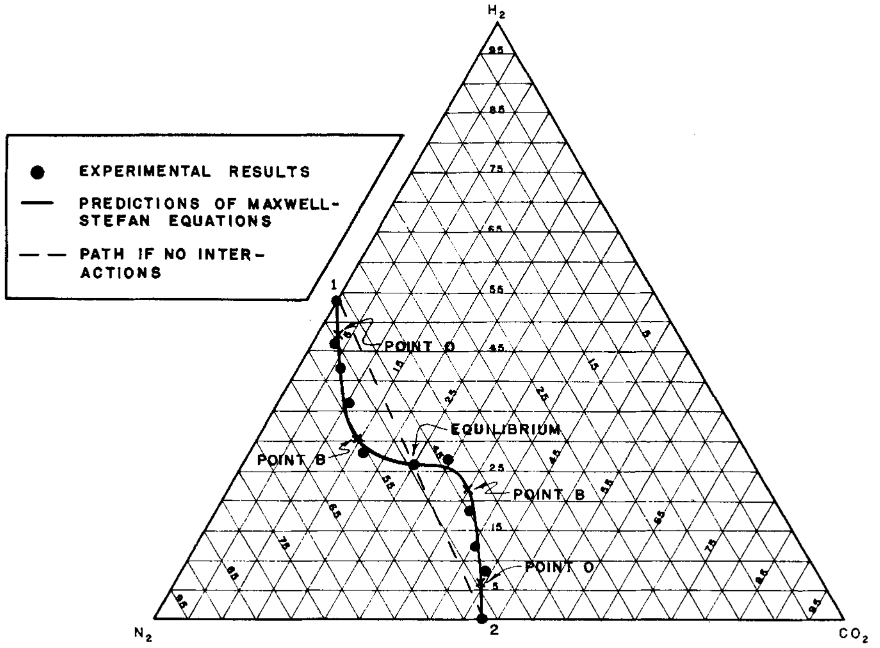

Fig. 1. Composition path.

Table 1. Effective (L/A) for Binary Pairs

Binary pair	(L/A), cm.$^{-1}$
H_2-N_2	253.1
H_2-CO_2	263.9
N_2-CO_2	258.5
average	258.1
geometric value	251.1

external to the diffusion path (8). In both cases the results agreed with the Maxwell-Stefan equations to within the experimental error.

The object of this work is to carry out a more stringent test of the Maxwell-Stefan equations by studying the regions in which the predictions of the equations differ most from equimolal countercurrent binary diffusion; that is in the regions in which reverse diffusion, osmotic diffusion, and a diffusion barrier are predicted.

EXPERIMENTAL

The apparatus and its operation have been described in detail (3). The apparatus consisted of three sections: equipment to prepare and store two gas mixtures of 500 cc. volume; a two bulb diffusion cell, bulbs with volumes of 77.99 and 78.63 cc and a capillary diffusion path 8.59 cm. long and 2.08-mm. diameter containing a stopcock; and a gas chromatograph with a silica gel column to analyze gas mixtures. The diffusion cell could be charged four times with identical gas mixtures. The cell was placed in a water bath held at 35.2 ± 0.01°C.

Two gas mixtures with different compositions were first prepared. Each bulb as well as the section of the capillary from the bulb to the closed stopcock was filled with one of the mixtures. After thermal equilibrium was reached and the pressures in each bulb had been adjusted to atmospheric, the stopcock was opened and diffusion allowed to take place. At the end of the run the stopcock was closed and the contents of the bulbs were analyzed by gas chromatography.

Three more diffusion runs were made, each with the same initial bulb concentrations, each with a different diffusion time. The data from each run consisted of six initial and six final mole fractions and a diffusion time.

Hydrogen, nitrogen, and carbon dioxide were chosen as gases. The binary diffusion coefficients are well-known, and this ternary system should give noticeable effects of reverse diffusion. The change of volume of mixing of each of the three binary pairs is small (13). Therefore it seems probable that the change of volume of mixing the ternary gas would also be small, and that the diffusion in the two bulb diffusion cell would be equimolal countercurrent diffusion. The three gases closely approximate ideal gases at this temperature and pressure.

The integrated Maxwell-Stefan equations which are available are steady state equations; the diffusion in the diffusion cell is not steady state. For this type of diffusion cell the assumption of a quasi-steady state has been used previously (15); at any time the fluxes in the diffusion cell are the steady state fluxes. For binary diffusion the difference in the mole fractions calculated with this assumption and the mole fractions calculated using the unsteady state equations is negligible (less than 1%) in a properly designed cell (3). It would be expected that the quasi-steady state assumption would be valid in a ternary system under essentially the same conditions as in a binary system, and the cell was designed on this basis. The experimental results indicate that the assumption is valid.

A second problem associated with the two bulb diffusion cell is the effective

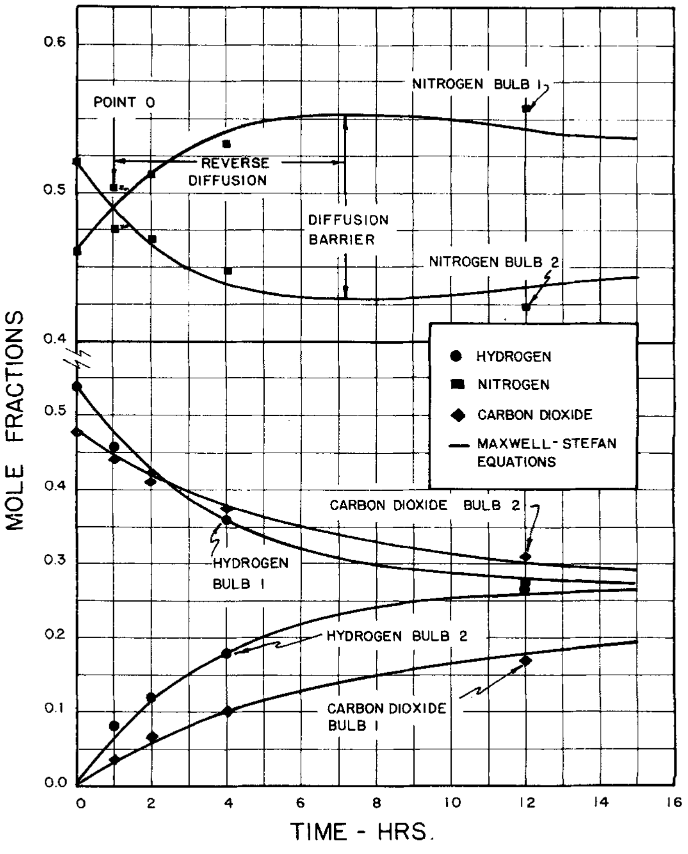

Fig. 2. Variation of composition with time.

length of the diffusion path. If some concentration gradient exists in the bulbs, then the effective length of the diffusion path is not the same as the measured geometric length. The ratio of the effective length-area ratio (L/A) appears when the Maxwell-Stefan equations are applied to the diffusion cell for binary or ternary diffusion.

An effective length-area ratio can be measured with binary diffusion runs. Whether or not this effective (L/A) is valid for ternary diffusion can be determined by comparison of accurate experimental results with predictions with this binary (L/A) ratio. However it will be seen that the ternary measurements can be also compared with the Maxwell-Stefan equations without the (L/A) ratio.

Samples of the pure gases were analyzed with the gas chromatograph at the highest attenuation, and no impurities of any significance were found. The pure gases were used for calibration, and three samples of each unknown mixture were used to determine composition.

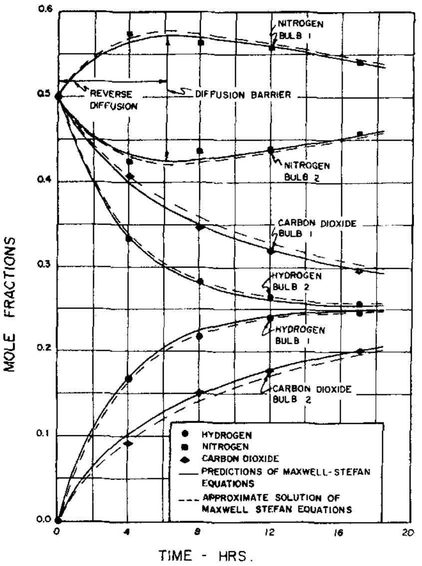

Fig. 3. Variation of composition with time.

METHODS OF CALCULATION

For binary diffusion in a two bulb diffusion cell, with the assumption of a quasi-steady state, it can be shown (*15*) that

$$\frac{L}{A} = \frac{-D_{ik}(V_1^{-1} - V_2^{-1})t}{\ln\left[\dfrac{x_i(j) - x_i^{\infty}(j)}{x_i^{\circ}(j) - x_i^{\infty}(j)}\right]} \qquad (1)$$

This equation is the basis of analysis of binary diffusion runs. All of the variables on the right-hand side of the equation are known, so the (L/A) can be calculated.

The binary diffusion coefficients used were the best experimental values available (*16*) corrected to the thermostat temperature by the method suggested by Hirschfelder, Curtiss, and Bird (*7*). The values of the diffusion coefficients at 35.2°C. and 1 atm. were nitrogen-hydrogen, 0.833 sq. cm./sec.; hydrogen-carbon dioxide, 0.680 sq. cm./sec.; carbon dioxide-nitrogen 0.168 sq. cm./sec.

For diffusion of ternary gas mixtures in the two bulb diffusion cell the following equations are used for calculation. At any time the steady state fluxes of the three components may be determined in terms of the bulb compositions from the solution to the Maxwell-Stefan equations for equimolal countercurrent transfer (*19*). The equations are (3)

$$D_{13}^{-1}(D_{12}^{-1} - D_{23}^{-1})N_1' + D_{23}^{-1}(D_{12}^{-1} - D_{13}^{-1})N_2' = (D_{12}^{-1} - D_{23}^{-1})[x_1(1) - x_1(2)] + (D_{12}^{-1} - D_{13}^{-1})[x_2(1) - x_2(2)]. \quad (2)$$

$$(D_{12}^{-1} - D_{23}^{-1})N_1' + (D_{12}^{-1} - D_{13}^{-1})N_2' =$$

$$\ln\left[\frac{\dfrac{x_1(2)}{N_1'} - \dfrac{x_2(2)}{N_2'} - \dfrac{(D_{13}^{-1} - D_{23}^{-1})}{(D_{12}^{-1} - D_{23}^{-1})N_1' + (D_{12}^{-1} - D_{13}^{-1})N_2'}}{\dfrac{x_1(1)}{N_1'} - \dfrac{x_2(1)}{N_2'} - \dfrac{(D_{13}^{-1} - D_{23}^{-1})}{(D_{12}^{-1} - D_{23}^{-1})N_1' + (D_{12}^{-1} - D_{13}^{-1})N_2'}}\right] \qquad (3)$$

and

$$N_1' + N_2' + N_3' = 0 \qquad (4)$$

where

$$N_i' = (RTL/P)\,N_i \qquad (5)$$

By a material balance

$$\frac{dx_i(1)}{d(At/LV_1)} = -N_i' \qquad (6)$$

and similarly for bulb 2. N_i' is positive if the transfer of component i is from bulb 1 to bulb 2. Equations (2) to (6) can be solved to give $x_i(j)$, $i = 1, 2, 3$, $j = 1, 2$, as a function of time with a numerical procedure on a digital computer (3). Newton's iteration method was used to solve Equations (2) to (4) with the first trials for the N_i' obtained from Toor's approximate solution, Equation (57) in (*19*). The bulb composition paths which are predicted are independent of time and (L/A) (Figure 1), so it is possible to check the Maxwell-Stefan equations independently of the quantities (L/A) and time.

BINARY RESULTS

Seven binary diffusion runs were made to evaluate the (L/A) ratio for binary experiments. The results are given in Table 1. The experimental error indicates that the (L/A) for the three binary pairs do not differ significantly. The deviation of the effective from the geometric (L/A) ratio is 2.80%.

TERNARY RESULTS AND DISCUSSION

Five sets of ternary experiments were made to cover the various types of possible interactions. On Figure 1, a triangular plot, are shown the results of four diffusion runs, with nitrogen reverse diffusing, each with the same initial bulb concentrations. The final concentrations of each run are shown as circles. Figure 2 shows the final concentrations of all three components as a function of time for the same runs with carbon dioxide and hydrogen on a reduced scale. The solid lines on the figures show the theoretical predictions of Equations (2) to (6), the Maxwell-Stefan equations as applied to this system. In Figure 2 the effective (L/A) from the binary results is used.

On Figure 1 the points labeled 1 and 2 on the edges of the triangle are the starting concentrations for all four diffusion runs. The point labeled equilibrium is calculated from the initial compositions. The dotted line represents the path of the bulb concentra-

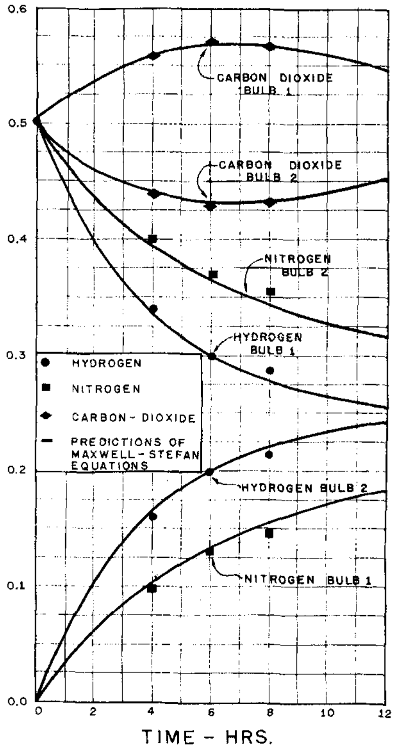

Fig. 4. Variation of composition with time.

tions if there were no reverse diffusion of nitrogen. The dotted line and the solid line do not coincide. Reverse diffusion is predicted. Point 0 represents a point of osmotic diffusion, point B a diffusion barrier. Reverse diffusion is predicted between points O and B. Similar notation is used on Figure 2.

This set of runs shows that nitrogen starts out diffusing from the bulb with high concentration to the bulb with low concentration, Figures 1 and 2. At the points O the mole fractions of nitrogen are equal in both bulbs. However the nitrogen mole fractions do not remain equal. Therefore for an instant there must be diffusion of the nitrogen when the concentration gradient of nitrogen is zero; that is there is a point of osmotic diffusion. The nitrogen mole fraction in bulb 1 increases as the mole fraction of nitrogen in bulb 2 decreases until point B is reached. Since the mole fraction of nitrogen in bulb 1 is greater than the mole fraction of nitrogen in bulb 2, this is a region of reverse diffusion of nitrogen. At point B the mole fraction of nitrogen in bulb 1 stops increasing and starts decreasing. In bulb 2 the mole fraction stops decreasing and starts increasing. For an instant there is no diffusion of nitrogen even though a concentration gradient exists; that is point B is a diffusion barrier.

Figure 2 also shows the mole fractions of carbon dioxide and hydrogen as a function of time for this set of diffusion runs. The interaction phenomena do not occur for these two components because of the choice of the initial compositions. The transfer of these two components is always from a region of high to low concentration.

This set of runs shows that reverse diffusion, osmotic diffusion, and a diffusion barrier exist. Figure 2 shows that the Maxwell-Stefan equations also predict the results quantitatively for the set of runs. The average deviation of the predictions of the Maxwell-Stefan equations from the experimental molar compositions is 0.7 mole %.

Figure 3 contains the results of a set of runs in which the initial nitrogen concentrations in both bulbs are equal. In this case the osmotic diffusion point for nitrogen occurs at time zero.

This figure also contains the concentration profiles predicted by Toor's approximate solution to the Maxwell-Stefan equations. The approximation is seen to be reasonably close to the exact solution.

Figure 4 shows the results of a set of runs with the initial compositions chosen to make carbon dioxide reverse diffuse. From these results exactly the same conclusions may be drawn as before.

Diffusion runs were also made with hydrogen reverse diffusing. It was predicted theoretically that the maximum increase in the hydrogen mole fraction in one bulb due to reverse diffusion would be only 0.5 mole %. This was verified experimentally.

For all ternary diffusion runs the average deviation of the predicted mole fractions by the Maxwell-Stefan equations from the measured mole fractions is 0.45 mole %. This is well within the expected experimental error of 2.6 mole %.

The triangular diagrams show that the composition paths followed in the bulbs are in agreement with the predictions of the Maxwell-Stefan equations. When the data are compared with theory on an explicit time scale with the binary (L/A) ratio, satisfactory agreement is also obtained, indicating that the ternary (L/A) ratio is essentially the same as the binary. The quasi-steady state assumption is apparently valid also.

It may be shown that the fractional deviation between the measured and predicted composition changes over a time interval is equal to the fractional deviation between the measured and predicted time average fluxes over the interval. Using the time interval as the entire period of a run one gets the average error between measured and computed time average fluxes for all runs as 1.5%.

CONCLUSIONS

The equimolal countercurrent diffusion experiments with hydrogen, nitrogen, and carbon dioxide are well described by the Maxwell-Stefan equations. In particular, the phenomena of reverse diffusion, osmotic diffusion, and a diffusion barrier do exist, and these phenomena are predicted within the experimental error by the Maxwell-Stefan equations.

ACKNOWLEDGMENT

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NOTATION

A = area of the diffusion path
D_{ik} = binary diffusion coefficient
L = length of the diffusion path
N_i = molar flux of ith component with respect to fixed axis
N_i' = $(RTL/P)\ N_i$
P = pressure
R = gas constant
T = temperature
t = time
V_i = volume of ith bulb of the diffusion cell
$x_i(j)$ = mole fraction of ith component in the jth bulb
$x_i^{\circ}(j)$ = mole fraction of ith component in the jth bulb at the beginning of a diffusion run
$x_i^{\infty}(j)$ = mole fraction of ith component in the jth bulb at equilibrium

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