

TABLE A-1. REPRESENTATIVE DATA OF ISOTHERMAL RUNS, RUN I-14

Coolant temperature	96° to 97°C.				
W_A	0.00887 g. moles/min.				
W_{NO}	0.00152 g. moles/min.				
y_{NO}^o	0.146				
n_{NO}^o	0.00500 moles nitric-oxide converted/unit mass feed				
X_1^o	0.000807 moles nitric-oxide converted/unit mass feed				
X_2^o	0.00401 moles nitric-oxide converted/unit mass feed				
X_3^o	0.00421 moles nitric-oxide converted/unit mass feed				
X_3/n_{NO}^o	0.843				
Station through bed	1	2	3	4	5
Pressure, atm. abs.	1.029	—	1.020	1.013	1.007
Temperature, °C.	96	96	96	96	96

* X_3 is a measured quantity; X_2 is calculated from it as a correction for the homogeneous reaction. X_1 is calculated for the homogeneous reaction.

pressure was not specifically studied in this investigation, it was necessary to assume a pressure dependence on the basis of available data. Although there is little agreement in the literature in this regard, proportionality of the rate to the square of absolute pressure represents a reasonable compromise between reported correlations (2, 4, 8, 10). This relationship was assumed in deriving the reaction rates reported here.

Rates of Isothermal Reaction. The calculated rates of isothermal reaction are plotted in Figures A-2, 3, 4, 5, and 6. The ordinate is R , for use in the equation

$$X_2 - X_1 = \frac{1}{F} \int_0^{V_R} R p^2 dV \quad (A-3)$$

The abscissas are fractional conversions and the parameter temperature. A separate curve is given for each value of n_{NO}^o .

Tabulated values are given by Jaffer (7). No empirical or semitheoretical equation has been found to correlate these rates, although there is evidence for strong adsorption of nitrogen dioxide in the practically zero rates at high conversions. Negative rates shown in some curves and in the tables at very high conversions reflect slight errors, of course. Such rates are, for all practical purposes, zero. The absence of a significant effect of gas-phase diffusion on this catalytic reaction has been reported by Baker *et al.* (2); accordingly any effect of velocity of flow has been neglected in interpreting these rate data.

Comparison of these results with those of others is difficult because conditions were

not at all comparable. While the temperature range is considerably different from that used by Baker, Wong, and Hougen (2), their results and these seem to be consistent. For $n_{NO}^o = 0.003$, a conversion of 0.578, and a temperature of 60°C., the equation given by Baker, Wong, and Hougen predicts a rate of 0.000065 g. moles nitric oxide converted/(min.) (cc.) at 1 atm. An extrapolation of the present results to 60°C. yields a rate of 0.000075. The temperature dependence of this reaction is the same in direction as that observed by all previous workers. The decrease of the temperature dependence at higher temperatures conforms to the observations of Kurin and Blokh (8) and the theoretical treatment of Glasstone, Laidler, and Eyring (6).

It will be noted that for high initial nitric oxide concentrations and high conversion of nitric oxide, reaction rates at 103°C. are shown to be higher than those at 96°C. Such a reversal of the effect of temperature on the reaction has not been reported previously. No successful attempt has been made in the present investigation to explain this phenomenon; the effect is not large and occurs only at high conversion of nitric oxide.

A good verification of the method and of the accuracy of these rate data is that they can be used to reproduce by calculation the integral conversion data observed with excellent agreement. In run I-14 the measured value of X_2 was 0.00401; when one integrates Equation (A-3) with these rate data, the calculated value is 0.00412. The absolute magnitude of the rate in this calculation varied thirty-fold from entrance to exit of bed.

Multicomponent Diffusion Problems

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Analysis of four three-component diffusion problems by means of the Stefan-Maxwell equations is presented. In three of these problems heterogeneous chemical reactions are occurring at a catalytic surface. Characteristic curves are presented for the better understanding of the analytical solutions. The results of one of the exact solutions are compared with those by the effective diffusion-coefficient approach.

The equations describing the diffusion in a ν -component mixture of gases are the Stefan-Maxwell equations (1):

$$\nabla x_i = \sum_{j=1}^{\nu} (c \mathcal{D}_{ij})^{-1} (x_i \vec{N}_j - x_j \vec{N}_i) \quad i = 1, 2, \dots, \nu \quad (1)$$

The derivation of Equation (1) from the kinetic theory of gases has been given by Curtiss and Hirschfelder (3). Only $\nu - 1$ of these equations are independent because $\sum x_i = 1$.

Specific solutions to the Stefan-Maxwell equations have been given by Gilliland (4), Hoopes (5), Benedict and Boas (2), Keyes and Pigford (8), and Toor (10) for multicomponent systems. It is the purpose of this publication to extend the "dictionary" of solutions for steady state multicomponent diffusion, particularly those with chemical reactions involved. The latter are of course interesting in connection with the study of diffusion-controlled heterogeneous reactions.

DIFFUSION OF A THROUGH A STAGNANT FILM OF B AND C OF KNOWN AVERAGE COMPOSITION

Gas A is diffusing in steady state through a stagnant film of thickness δ , which consists of species B and C, as shown in Figure 1a. If no A were present, the film would contain B and C in concentration x_B^0 and x_C^0 (with $x_B^0 + x_C^0 = 1$). The authors select as the two independent equations those for B and C:

$$\frac{dx_B}{d\zeta} = \nu_{AB} x_B \quad (2)$$

$$\frac{dx_C}{d\zeta} = \nu_{AB} x_C \quad (3)$$

which are to be integrated with the boundary conditions: at $\zeta = 0$, $x_A = x_{A0}$, and at $\zeta = 1$, $x_A = x_{As}$. Integration of Equations (2) and (3) gives the following concentration profiles:

$$x_B = \frac{(1 - x_{A0}) \alpha_{AC} - (1 - x_{As})}{(\alpha_{AC} - \alpha_{AB})} \alpha_{AB}^{\zeta} \quad (4)$$

$$x_C = \frac{(1 - x_{A0}) \alpha_{AB} - (1 - x_{As})}{(\alpha_{AB} - \alpha_{AC})} \alpha_{AC}^{\zeta} \quad (5)$$

in which $\alpha_{ij} = \exp [N_A \delta / c \mathcal{D}_{ij}]$ and $\zeta = z/\delta$.

An expression for \bar{N}_A in terms of x_{A0} , x_{As} , x_B^0 , and $r = \mathcal{D}_{AB}/\mathcal{D}_{AC}$ may be obtained by calculating x_B^0 from the above concentration profiles:

$$x_B^0 = \frac{\int_0^1 x_B dz}{\int_0^1 (x_B + x_C) dz} \quad (6)$$

Inserting Equations (4) and (5) and performing the integrations one gets

$$x_B^0 = \left[1 - \frac{1}{r} \left(\frac{\alpha_{AB}^r - 1}{\alpha_{AB}^r - Q} \right) \left(\frac{\alpha_{AB} - Q}{\alpha_{AB} - 1} \right) \right]^{-1} \quad (7)$$

in which $Q = (1 - x_{As})/(1 - x_{A0})$.

Equation (7) has been used to calculate the values of α_{AB} in terms of Q , x_B^0 , and r by an IBM 650 digital com-

puter. The results are presented in graphical form in Figure 2 and in tabular form in Table 1*. The tabulated values of α_{AB} are reported to five significant figures with the range of $Q = 1.2 \rightarrow 80$, $r = 0.10 \rightarrow 0.95$ with 0.10 intervals to 0.90, and $x_B^0 = 0.00 \rightarrow 1.00$ with 0.05 intervals. From this table the mass transfer rate can be calculated. This table has been used by Huebner in connection with studies on psychrometry in three-component systems (7).

It can be seen both from the table and the figure that α_{AB} increases with increasing Q , with decreasing r , and with decreasing x_B^0 .

DIFFUSION OF A THROUGH A STAGNANT FILM OF B TO FORM A_n AT A CATALYTIC SURFACE

Gas A is diffusing in steady state through a stagnant film of B to a catalytic surface, where A disappears by an irreversible chemical reaction of order h (see Figure 1b). The surface reaction whereby A disappears may be described stoichiometrically as



Note that n and h do not necessarily have to be the same. Values of $n = 2, 3, 4 \dots$ correspond to polymerization reactions, whereas values of $n = 1/2, 1/3, 1/4, \dots$ correspond to depolymerization at the catalytic surface. The relative molar fluxes are determined by the stoichiometry of the reaction (and not by the order of the chemical reaction); that is $N_A = -nN_{A_n}$. For this case the Stefan-Maxwell equations for A and B are

$$\frac{1}{\nu_{AB}} \cdot \frac{dx_A}{d\zeta} = r_{An} \left(1 - \frac{1}{n} \right) x_A + (r_{An} - r_B) x_B - r_{An} \quad (9)$$

$$\frac{1}{\nu_{AB}} \cdot \frac{dx_B}{d\zeta} = \left(r_B - \frac{1}{n} \right) x_B \quad (10)$$

in which $\nu_{AB} = [N_A \delta / c \mathcal{D}_{AB}]$, $r_B = \mathcal{D}_{AnB}/\mathcal{D}_{AB}$, and $r_{An} = \mathcal{D}_{AnB}/\mathcal{D}_{AAn}$. These equations may be integrated with the boundary conditions that $x_A = x_{A0}$ and $x_B = x_{B0}$ at $\zeta = 0$. The integration of the x_B equation is done first; the result is then substituted into Equation (9), and the resulting first-order linear differential equation is integrated:

$$x_B = x_{B0} \exp [R \nu_{AB} \zeta] \quad (11)$$

$$x_A = [x_{A0} - N^{-1} + M^{-1} x_{B0}] \exp [N r_{An} \nu_{AB} \zeta] + N^{-1} - M^{-1} x_{B0} \exp [R \nu_{AB} \zeta] \quad (12)$$

in which

$$N = 1 - \frac{1}{n}, M = 1 - \frac{1}{n} \left(\frac{1 - r_{An}}{r_B - r_{An}} \right),$$

$$\text{and } R = r_B - \frac{1}{n} \quad (13 a, b, c)$$

The condition that there be an h th order reaction at the catalytic surface is that at $\zeta = 1$

$$N_A = k_h x_A^h \text{ or } \nu_{AnB} = K x_A^h \quad (14)$$

where $K = [k_h \delta / c \mathcal{D}_{AnB}]$. Applying this condition to Equation (12) one gets the following transcendental equation for ν_{AB} :

$$\sqrt[n]{\frac{\nu_{AB}}{K}} = [x_{A0} - N^{-1} + M^{-1} x_{B0}] \exp (N r_{An} \nu_{AB}) + N^{-1} - M^{-1} x_{B0} \cdot \exp (R \nu_{AB}) \quad (15)$$

Equations (12) and (15) do not hold for several special cases. For these cases the mass transfer rate ν_{AB} is calculated from the following formulas:

Case I

$r_{An} = r_B$; the binary diffusivities \mathcal{D}_{AAn} and \mathcal{D}_{AB} are equal. In this case the $(r_{An} - r_B)x_B$ term in Equation (9) disappears, and the solution is independent of the concentration x_{B0} at the outer edge of the film:

$$\nu_{AB} = \frac{1}{N r_{An}} \ln \frac{1 - N \sqrt[n]{\nu_{AB} B / K}}{1 - N x_{A0}} \quad (16)$$

Case II

$n = 1$; a unimolecular rearrangement is taking place at the catalytic surface. In this case the $r_{An}(1 - 1/n)x_A$ term in Equation (9) disappears, and the solution gives

$$\sqrt[n]{\frac{\nu_{AB}}{K}} = x_{A0} - \left(\frac{r_B - r_{An}}{r_B - 1} \right) \cdot x_{B0} \{ \exp [\nu_{AB} (r_B - 1)] - 1 \} - r_{An} \nu_{AB} \quad (17)$$

Case III

$n r_B - 1 = r_{An}(n - 1)$; in this special case the solution is

$$\sqrt[n]{\frac{\nu_{AB}}{K}} = [x_{A0} - N^{-1} + x_{B0} \left(\frac{r_B - 1}{n - 1} \right) \nu_{AB}] \exp (R \nu_{AB}) + N^{-1} \quad (18)$$

* Tabular material has been deposited as document 6266 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$7.50 for photoprints or \$2.75 for 35-mm. microfilm.

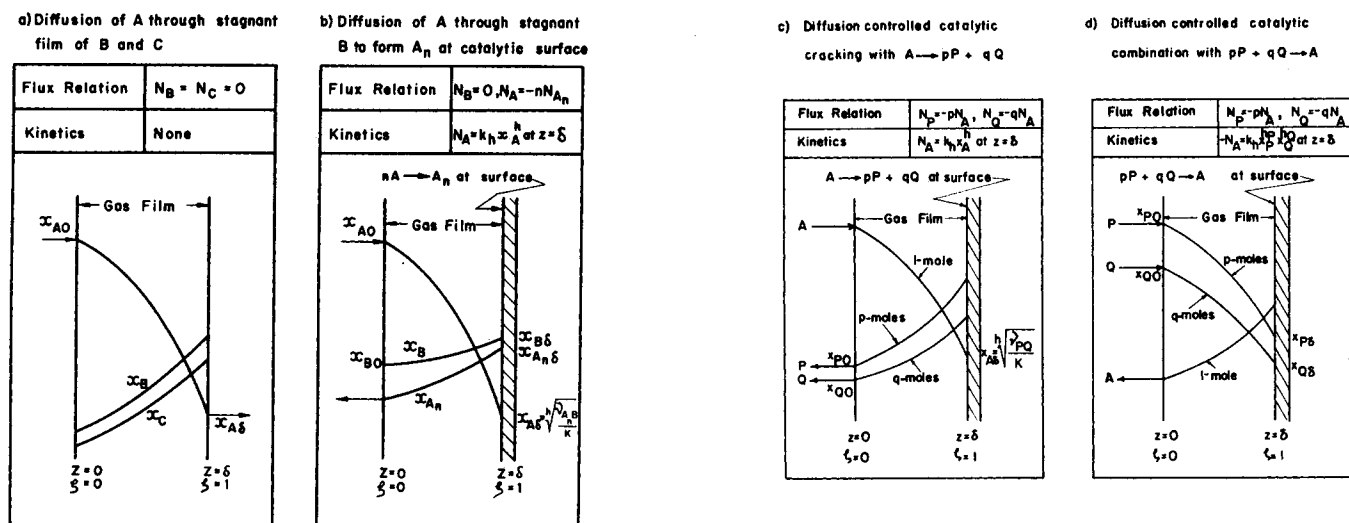


Fig. 1. Three component diffusion problems.

Equations (15), (16), and (18) have been used to tabulate $\nu_{A_n B}$ for various values of n, r_B, r_{A_n}, x_{A0} , and x_{B0} for $K = \infty$ by an IBM 650 digital computer. The results are presented in tabular form in Table 2*, and some of the characteristic results are plotted in Figure 3. The tabulated results are reported to four significant figures with the following parameters:

$$\begin{aligned} n &= 2, 3, 4, 1/2, 1/3, 1/4 \\ r_{A_n}, r_B &= 0.4, 0.8, 1.2, 2.0, 4.0, 6.0 \\ x_{A0} &= 0.3, 0.4, 0.5, 0.6, 0.7 \\ x_{B0} &= 0.1, 0.2, 0.3, 0.4 \end{aligned}$$

In Figure 3 $\nu_{A_n B}$ is plotted against r_{A_n} for the following cases:

$$\begin{aligned} n &= 2, \quad x_{A0} = 0.3, \quad x_{B0} = 0.1: \\ &\quad \text{for various values of } r_B \\ n &= 2, \quad x_{A0} = 0.3, \quad r_B = 1.2: \\ &\quad \text{for various values of } x_{B0} \\ n &= 2, \quad x_{B0} = 0.1, \quad r_B = 0.4: \\ &\quad \text{for various values of } x_{A0} \\ x_{A0} &= 0.3, \quad x_{B0} = 0.1, \quad r_B = 0.4: \\ &\quad \text{for various values of } n \end{aligned}$$

This figure shows the dependence of $\nu_{A_n B}$ on the main variables.

DIFFUSION-CONTROLLED CATALYTIC CRACKING WITH $A \rightarrow pP + qQ$

Substance A diffuses through a gas film of thickness δ containing A, and the reaction products (see Figure 1c). At the catalytic surface A disappears by an irreversible chemical reaction of order h . Stoichiometrically the reaction is represented by the cracking reaction:



The relative molar fluxes are determined by the stoichiometry (and not

by the order of the reaction); that is, $pN_A = -N_P$ and $qN_A = -N_Q$. For this problem the Stefan-Maxwell equa-

$$\bar{x}_P(s) = \frac{[x_{P0}]s^2 + [-A_0 x_{P0} + B_P x_{Q0} + C_P]s + [B_P C_Q - C_P A_Q]}{s^2 - [A_P + A_Q]s + [A_P A_Q - B_P B_Q]} \quad (23)$$

tions for components P and Q are

$$\frac{1}{\nu_{PQ}} \cdot \frac{dx_P}{d\zeta} = A_P x_P + B_P x_Q + C_P \quad (20)$$

$$\frac{1}{\nu_{PQ}} \cdot \frac{dx_Q}{d\zeta} = A_Q x_Q + B_Q x_P + C_Q \quad (21)$$

in which

$$A_P = (1-p)r_P - q, \quad B_P = (1-r_P)p,$$

$$\text{and } C_P = pr_P \quad (22 a, b, c)$$

and

$$r_P = \frac{D_{PQ}}{D_{AP}} \quad \text{and} \quad r_Q = \frac{D_{PQ}}{D_{AQ}} \quad (22 d, e)$$

two algebraic equations result, which may be solved for the transform functions $\bar{x}_P(s)$ and $\bar{x}_Q(s)$:

and an analogous expression for $\bar{x}_Q(s)$ obtained by interchanging all p and q and all P and Q .

In order for Equation (23) to be inverted, the denominator has to be factored into $(s-s_+)(s-s_-)$, in which

$$s_{\pm} = \frac{1}{2} [(A_P + A_Q) \pm \sqrt{(A_P - A_Q)^2 + 4 B_P B_Q}] \quad (24)$$

One now has to consider three cases, namely $s_+ \neq s_-$, $s_+ = s_- = s_e$, and $s_{\pm} = s_0$ when $s_- = 0$.

Case I

Unequal roots, $s_+ \neq s_-$. In this case the inversion of Equation (23) yields

$$x_P(\zeta) = \frac{1}{(s_+ - s_-)} \left\{ \begin{aligned} &[x_{P0}][s_+ \exp(s_+ \nu_{PQ} \zeta) - s_- \exp(s_- \nu_{PQ} \zeta)] + [-A_0 x_{P0} + B_P x_{Q0} + C_P][\exp(s_+ \nu_{PQ} \zeta) - \exp(s_- \nu_{PQ} \zeta)] + [B_P C_Q - C_P A_Q] \\ &\cdot \left[\frac{\exp(s_+ \nu_{PQ} \zeta) - 1}{s_+} - \frac{\exp(s_- \nu_{PQ} \zeta) - 1}{s_-} \right] \end{aligned} \right\} \quad (25)$$

The quantities A_0, B_0 , and C_0 are defined analogously by interchanging all p and q and P and Q . Equations (20) and (21) are to be solved with the boundary conditions that at $\zeta = 0$, $x_P = x_{P0}$ and $x_Q = x_{Q0}$.

When the $(s$ multiplied) Laplace transform of both equations is taken,

with a similar expression for $\bar{x}_Q(\zeta)$. The condition that there be an h th-order reaction at the catalytic surface which is similar to Equations (14) is that at $\zeta = 1$

$$N_A = k_h x_A^h \quad \text{or} \quad \nu_{PQ} = K_h x_A^h \quad (26)$$

where $K_h = [k_h \delta / c D_{PQ}]$. Thus when

* See footnote on page 517.

one sets $x_p + x_q = 1 - x_A$ at $\zeta = 1$, one obtains

$$\begin{aligned} & [Xs_+ + Y + Zs_+^{-1}] \exp(s_+ \nu_{PQ}) \\ & - [Xs_- + Y + Zs_-^{-1}] \exp(s_- \nu_{PQ}) \\ & = (s_+ - s_-) \left[1 - \frac{Z}{s_+ s_-} - \sqrt{\nu_{PQ}/K_h} \right] \end{aligned} \quad (27)$$

in which

$$X = x_{p0} + x_{q0} \quad (28)$$

$$s_{\pm} = \frac{1}{2} \left[\frac{(1-p)r_p + (1-q)r_q - (p+q)}{\pm \sqrt{\{(1-p)r_p - (1-q)r_q + (p-q)\}^2 + 4pq(1-r_p)(1-r_q)}} \right] \quad (31)$$

$$Y = x_{p0}(p+q-r_q) + x_{q0}(p+q-r_p) + (pr_p + qr_q) \quad (29)$$

$$Z = pq(r_p + r_q) - r_p r_q(p+q) + (p^2 r_p + q^2 r_q) \quad (30)$$

[Equation (31) is the simplified form of Equation (24).]

Case II

Equal roots, $s_+ = s_- = s_e$

In this case the inversion of Equation (23) leads to

$$\begin{aligned} x_p(\zeta) = & [x_{p0}] [1 + s_e \nu_{PQ} \zeta] \\ & \cdot \exp(s_e \nu_{PQ} \zeta) + [-A_q x_{p0} + B_p x_{q0} \\ & + C_p] \nu_{PQ} \zeta \exp(s_e \nu_{PQ} \zeta) + [B_p C_q \\ & - C_p A_q] (s_e \nu_{PQ})^{-2} [s_e \nu_{PQ} \zeta \exp \\ & (s_e \nu_{PQ} \zeta) - \exp(s_e \nu_{PQ} \zeta) + 1] \end{aligned} \quad (32)$$

with a similar expression for $x_q(\zeta)$. Then application of the conditions that $x_p + x_q = 1 - x_A$ at $\zeta = 1$ gives

$$\begin{aligned} & [X + Ys_e^{-1} + Zs_e^{-2}] s_e \nu_{PQ} \exp(s_e \nu_{PQ}) \\ & + [X - Zs_e^{-2}] \exp(s_e \nu_{PQ}) = \\ & 1 - Zs_e^{-2} - \sqrt{\nu_{PQ}/K_h} \end{aligned} \quad (33)$$

in which X, Y, Z are defined in Equations (28) to (30) and $s_e = (1/2)[(1-p)r_p + (1-q)r_q - (p+q)]$.

Case III

One root is zero; $s_{\pm} = s_0$ when $s_{\mp} = 0$

In this case the inversion of Equation (23) gives

$$\begin{aligned} x_p(\zeta) = & [x_{p0}] \exp(s_0 \nu_{PQ} \zeta) \\ & + [-A_q x_{p0} + B_p x_{q0} + C_p] s_0^{-1} \\ & [\exp(s_0 \nu_{PQ} \zeta) - 1] \\ & + [B_p C_q - C_p A_q] s_0^{-2} [\exp \\ & (s_0 \nu_{PQ} \zeta) - 1 - s_0 \nu_{PQ} \zeta] \end{aligned} \quad (34)$$

with a similar expression for $x_q(\zeta)$. At $\zeta = 1$ it is known that $x_p + x_q = 1 - x_A$, so that

$$\begin{aligned} & [X + Ys_0^{-1} + Zs_0^{-2}] \exp(s_0 \nu_{PQ}) \\ & - Zs_0^{-1} \nu_{PQ} = [1 + Ys_0^{-1} + Zs_0^{-2}] \\ & - \sqrt{\nu_{PQ}/K_h} \end{aligned}$$

in which X, Y, Z are defined in Equation (28) to (30) and $s_0 = (1-p)r_p + (1-q)r_q - (p+q)$.

Equations (27), (33), and (35) have been used to tabulate ν_{PQ} for various values of $p, q, x_{p0}, x_{q0}, r_p$, and r_q for $K = \infty$ by an IBM 650 digital computer. The results are presented in tabular form in Table 3*, and some

* See footnote on page 517.

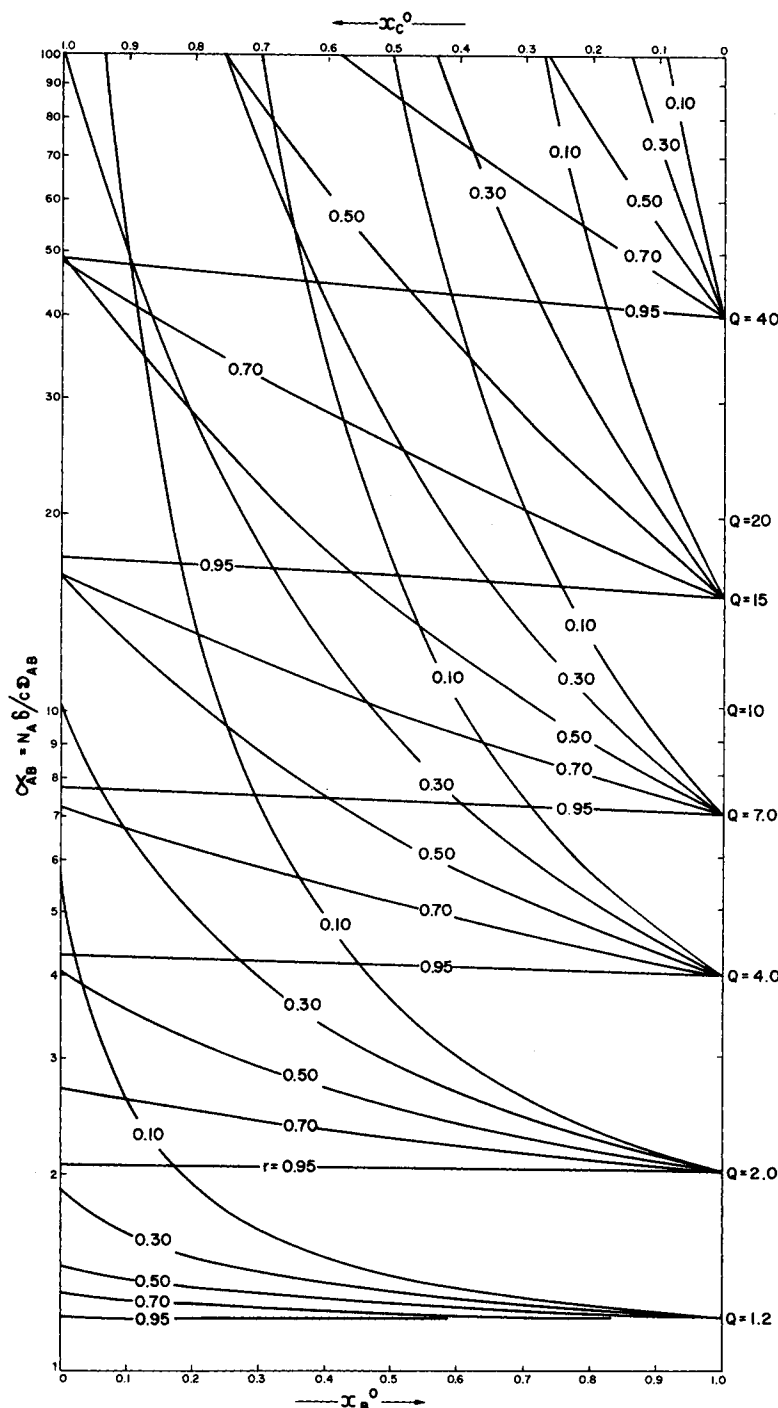


Fig. 2. The calculated values of $\alpha_{AB} = \exp [N_A \delta / c D_{AB}]$ for the problem of diffusion of A through stagnant B and C. These curves were calculated from Equation (7). To find a value of α_{AB} , first select the value of Q at the right of the chart and the curve appropriate for a given value of r . Then move along this curve to the left until the value of x_B^0 is located. For example for $Q = 2$, $r = 0.3$, $x_B^0 = 0.5$, one finds that $\alpha_{AB} = 2.95$.

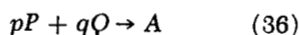
of the characteristic results are plotted in Figure 4. The tabulated data are reported to four significant figures with the following parameters:

$$\begin{aligned} p, q &= 1, 2 \\ r_p, r_q &= 1.0, 1.5, 3.0, 4.5, 6.0 \\ x_{p0} &= 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 \\ x_{q0} &= 0.2, 0.3, 0.4 \end{aligned}$$

In Figure 4 the values of ν_{PQ} are plotted against r_q for the following cases: $p = 1, q = 1, r_p = 1.5, x_{q0} = 0.2$; for various values of x_{p0} ; $p = 1, q = 1, x_{p0} = 0.2, x_{q0} = 0.2$; for various values of x_p ; $x_{p0} = 0.2, x_{q0} = 0.2, r_p = 6.0$; for various values of p and q .

DIFFUSION-CONTROLLED CATALYTIC COMBINING WITH $pP + qQ \rightarrow A$

Species P and Q are diffusing through a gas film of thickness δ , containing P and Q and the reaction product, toward a catalytic surface on which the $(h_p + h_q)$ order irreversible chemical reaction occurs, as shown in Figure 1d:



Thus the Stefan-Maxwell equations for components P and Q with the stoichiometric requirements and the boundary conditions are exactly the same as the problem of $A \rightarrow pP + qQ$ discussed previously [that is, the Stefan-Maxwell equations are Equations (20) and (21), and the boundary conditions are $x_p = x_{p0}$ and $x_q = x_{q0}$ at $\zeta = 0$]. Therefore the solutions of $x_p(\zeta)$ and $x_q(\zeta)$ are exactly the same as $A \rightarrow pP + qQ$ problem. Similarly, there are also three cases which have to be considered, namely $s_+ \neq s_-$, $s_+ = s_- = s_e$, and $s_+ = s_0$ when $s_- = 0$.

Case I

Unequal roots, $s_+ \neq s_-$

In this case $x_p(\zeta)$ can be rewritten from Equation (25):

$$x_p(\zeta) = \frac{1}{s_+ - s_-}$$

$$\begin{aligned} & \{ [X_p s_+ + Y_p + Z_p s_+^{-1}] \exp(s_+ \nu_{PQ} \zeta) \\ & - [X_p s_- + Y_p + Z_p s_-^{-1}] \exp(s_- \nu_{PQ} \zeta) \} \end{aligned}$$

$$+ \frac{Z_p}{s_+ s_-} \quad (37)$$

in which

$$X_p = x_{p0} \quad (38)$$

$$\begin{aligned} & h_p \ln \left[\frac{1}{s_+ - s_-} \left\{ \begin{aligned} & [X_p s_+ + Y_p + Z_p s_+^{-1}] \exp(s_+ \nu_{PQ}) \\ & - [X_p s_- + Y_p + Z_p s_-^{-1}] \exp(s_- \nu_{PQ}) \end{aligned} \right\} + \frac{Z_p}{s_+ s_-} \right] \\ & + h_q \ln \left[\frac{1}{s_+ - s_-} \left\{ \begin{aligned} & [X_q s_+ + Y_q + Z_q s_+^{-1}] \exp(s_+ \nu_{PQ}) \\ & - [X_q s_- + Y_q + Z_q s_-^{-1}] \exp(s_- \nu_{PQ}) \end{aligned} \right\} + \frac{Z_q}{s_+ s_-} \right] \\ & - \ln[-\nu_{PQ}/K_s] = 0 \end{aligned} \quad (42)$$

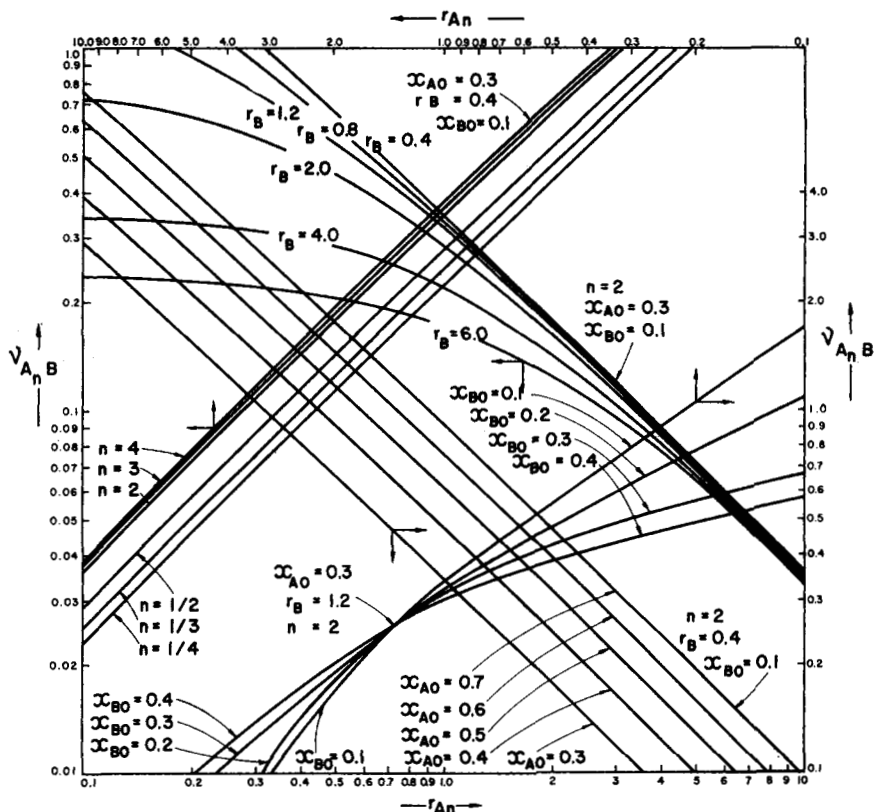


Fig. 3. The calculated values of $\nu_{A_n B} = [N_A \delta / (c D_{A_n B})]$ for the problem of diffusion of A through a stagnant film of B to form A_n at a catalytic surface. These curves were calculated from Equations (15), (16), and (18) for $K = \infty$.

$$\begin{aligned} Y_p &= [p - (1 - q)r_q]x_{p0} \\ &+ p(1 - r_p)x_{q0} + pr_p \quad (39) \end{aligned}$$

$$\begin{aligned} Z_p &= pq(1 - r_p)r_q \\ &- pr_p[(1 - q)r_q - p] \quad (40) \end{aligned}$$

s_+ is defined in Equation (31) with a similar expression for $x_q(\zeta)$ by interchanging all p and q and all P and Q .

One may see that

$$\text{Equation (28)} \quad X = X_p + X_q$$

$$\text{Equation (29)} \quad Y = Y_p + Y_q$$

$$\text{Equation (30)} \quad Z = Z_p + Z_q$$

The kinetic equation at the catalytic surface ($\zeta = 1$) for this problem is

$$\begin{aligned} -N_A &= k_h x_p^{h_p} x_q^{h_q} \\ \text{or } -\frac{\nu_{PQ}}{K_h} &= x_p^{h_p} x_q^{h_q} \quad (41) \end{aligned}$$

in which $k_h = k_p/p = k_q/q$ and $K_h = [k_h \delta / (c D_{PQ})]$. Thus one will get the following transcendental equation of ν_{PQ} at the catalytic surface:

Case II

Equal roots, $s_+ = s_- = s_e$

In this case $x_p(\zeta)$ may also be rewritten from Equation (32):

$$\begin{aligned} x_p(\zeta) &= [X_p - Z_p s_e^{-2}] \exp(s_e \nu_{PQ} \zeta) \\ &+ Z_p s_e^{-2} + [X_p + Y_p s_e^{-1} + Z_p s_e^{-2}] \\ &\cdot s_e \nu_{PQ} \zeta \exp(s_e \nu_{PQ} \zeta) \quad (43) \end{aligned}$$

with a similar expression for $x_q(\zeta)$. Thus at the catalytic surface one gets

$$\begin{aligned} & h_p \ln \left\{ \begin{aligned} & [X_p - Z_p s_e^{-2}] \exp(s_e \nu_{PQ}) \\ & + Z_p s_e^{-2} \\ & + [X_p + Y_p s_e^{-1} + Z_p s_e^{-2}] \\ & \cdot s_e \nu_{PQ} \exp(s_e \nu_{PQ}) \end{aligned} \right\} \\ & + h_q \ln \left\{ \begin{aligned} & [X_q - Z_q s_e^{-2}] \exp(s_e \nu_{PQ}) \\ & + Z_q s_e^{-2} \\ & + [X_q + Y_q s_e^{-1} + Z_q s_e^{-2}] \\ & \cdot s_e \nu_{PQ} \exp(s_e \nu_{PQ}) \end{aligned} \right\} \\ & - \ln[-\nu_{PQ}/K_h] = 0 \quad (44) \end{aligned}$$

in which X_p, X_q, Y_p, Y_q, Z_p , and Z_q are defined in Equations (38) to (40), and $s_e = (1/2)[(1 - p)r_p + (1 - q)r_q - (p + q)]$.

Case III

One root is zero, $s_+ = s_0$ when $s_- = 0$

In this case $x_p(\zeta)$ is rewritten from Equation (34):

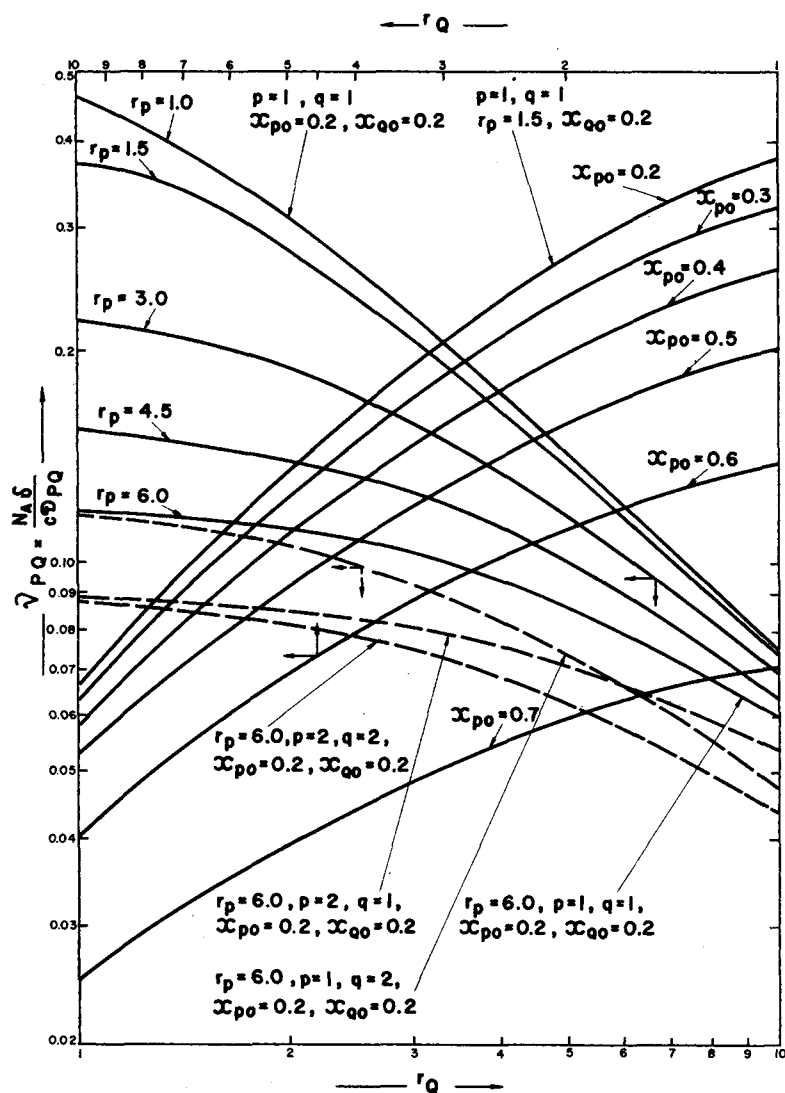


Fig. 4. The calculated values of $\nu_{PQ} = [N_A \delta / c D_{PQ}]$ for the problem of diffusion-controlled catalytic cracking with $A \rightarrow pP + qQ$. These curves were calculated from Equations (27), (33), and (35) for $K = \infty$.

$$x_P(\zeta) = [X_P + Y_P s_0^{-1} + Z_P s_0^{-2}] \exp(s_0 \nu_{PQ} \zeta) - Z_P s_0^{-1} \nu_{PQ} \zeta - Y_P s_0^{-1} - Z_P s_0^{-2} \quad (45)$$

with a similar expression for $x_Q(\zeta)$. Then at the catalytic surface one obtains

$$h_P \ln \left[\frac{[X_P + Y_P s_0^{-1} + Z_P s_0^{-2}] \exp(s_0 \nu_{PQ})}{-Z_P s_0^{-1} \nu_{PQ} - Y_P s_0^{-1} - Z_P s_0^{-2}} \right] + h_Q \ln \left[\frac{[X_Q + Y_Q s_0^{-1} + Z_Q s_0^{-2}] \exp(s_0 \nu_{PQ})}{-Z_Q s_0^{-1} \nu_{PQ} - Y_Q s_0^{-1} - Z_Q s_0^{-2}} \right] - \ln [-\nu_{PQ}/K_A] = 0 \quad (46)$$

in which $X_P, X_Q, Y_P, Y_Q, Z_P,$ and Z_Q are defined in Equations (38) to (40), and $s_0 = (1-p)r_P + (1-q)r_Q - (p+q)$.

Equation (42), (44), and (46) are to be used for the calculation of ν_{PQ} for the various values of $p, q,$ and $x_{P0}, x_{Q0}, r_P, r_Q,$ and K_A .

It is important to note that the values of $x_P(\delta)$ and $x_Q(\delta)$ can be evaluated from the value of ν_{PQ} . These values of $x_P(\delta)$ and $x_Q(\delta)$ determine which of the following conditions holds at the catalytic surface:

- (i) $qx_{Ps} - px_{Qs} = 0$
no excess reactant at the catalytic surface
- (ii) $qx_{Ps} - px_{Qs} > 0$
 xP is the excess reactant at the catalytic surface
- (iii) $qx_{Ps} - px_{Qs} < 0$
 xQ is the excess reactant at the catalytic surface

When $K_A = \infty$, Equations (42), (44), and (46) do not hold. For this case a special consideration has to be made for the calculation of ν_{PQ} because Equation (41) becomes

$$x_P^{h_P} x_Q^{h_Q} = 0 \quad (47)$$

Hence one cannot tell whether $x_P = 0$ or $x_Q = 0$ at the catalytic surface. In

this case one may arbitrarily select $x_P(\delta) = 0$ and proceed with the calculation of ν_{PQ} . Then after the calculation one has to substitute this ν_{PQ} into the expression for $x_Q(\delta)$ to verify its sign, for $x_Q(\delta)$ cannot be a negative value. If by using the ν_{PQ} obtained from $x_P(\delta) = 0$ one gets $x_Q(\delta) < 0$, then it is obvious that the assumption made (that is $x_P(\delta) = 0$) is incorrect and that instead one has to use $x_Q(\delta) = 0$ for the calculation of ν_{PQ} .

In other words if one obtained $x_Q(\delta) = 0$ by use of the ν_{PQ} calculated from $x_P(\delta) = 0$, it is seen that this is case (i), in which there is no excess reactant at the catalytic surface. If $x_Q(\delta) > 0$, this is the case (iii), where x_Q is the excess reactant at the catalytic surface. If $x_Q(\delta) < 0$, this is the case (ii). It is obvious that x_Q is the limiting reactant; thus one has to use $x_Q(\delta) = 0$ for the calculation of ν_{PQ} .

There are also three cases, the same as previous ones, which have to be considered when $K_A = \infty$, namely,

$s_+ \neq s_-$, $s_+ = s_- = s_s$, and $s_+ = s_- = s_0$ when $s_+ = 0$.

Case I

Unequal roots, $s_+ \neq s_-$

The transcendental equation of ν_{PQ} at the catalytic surface is

$$[X_P s_+ + Y_P + Z_P s_+^{-1}] \exp(s_+ \nu_{PQ}) + Z_P (s_+ - s_-) s_+^{-1} s_-^{-1} = [X_P s_- + Y_P + Z_P s_-^{-1}] \exp(s_- \nu_{PQ}) \quad (48)$$

Case II

Equal roots, $s_+ = s_- = s_s$

In this case at the catalytic surface one obtains

$$[X_P - Z_P s_s^{-2}] \exp(s_s \nu_{PQ}) + Z_P s_s^{-2} + [X_P + Y_P s_s^{-1} + Z_P s_s^{-2}] \cdot s_s \nu_{PQ} \exp(s_s \nu_{PQ}) = 0 \quad (49)$$

Case III

One root is zero, $s_+ = s_- = s_0$ when $s_+ = 0$

In this case at the catalytic surface one will obtain

$$[X_P + Y_P s_0^{-1} + Z_P s_0^{-2}] \exp(s_0 \nu_{PQ}) - Z_P s_0^{-1} \nu_{PQ} = [Y_P + Z_P s_0^{-1}] s_0^{-1} \quad (50)$$

Equations (48), (49), and (50) hold only with the condition that the substitution of ν_{PQ} , which is calculated from one of these equations, to $x_Q(\delta)$ gives $x_Q(\delta) \geq 0$. Otherwise, with similar expressions for the above three equations obtained by interchanging, all p and q and all P and Q have to be used for the calculation of ν_{PQ} .

METHODS OF USING EFFECTIVE DIFFUSIVITY

In this section the authors compare the results of diffusion-controlled cata-

lytic cracking with $A \rightarrow pP + qQ$ with those obtained by using an effective diffusivity and the usual binary formulas. Such methods have previously been proposed by Hougen and Watson (6), Wilke (11), and Stewart (9). The method used here is essentially that of Stewart but written up in a form similar to the development given by Hougen and Watson so that comparison between the various ap-

$$N_A = -(c \mathcal{D}_{Am})(1 - \Xi_A x_A)^{-1} \frac{dx_A}{dz} \quad (54)$$

In this expression

$$\Xi_A = [N_A + N_B + N_P + N_Q] N_A^{-1} = \frac{a + b - p - q}{a} \quad (55)$$

and \mathcal{D}_{Am} is an effective diffusivity for A diffusing into the mixture, given by

$$\mathcal{D}_{Am} = \frac{1 - \Xi_A}{\left[\frac{x_B}{\mathcal{D}_{AB}} + \frac{x_P}{\mathcal{D}_{AP}} + \frac{x_Q}{\mathcal{D}_{AQ}} + \frac{x_I}{\mathcal{D}_{AI}} - \frac{x_A}{a} \left(\frac{b}{\mathcal{D}_{AB}} - \frac{p}{\mathcal{D}_{AP}} - \frac{q}{\mathcal{D}_{AQ}} \right) \right]} \quad (56)$$

proaches can be made. The authors suggest a method of modifying the effective-diffusivity approach by allowing the effective diffusivity to vary linearly with either composition or distance.

Assumption of Constant Effective Diffusivity

For the general gaseous reaction $aA + bB \rightleftharpoons pP + qQ$ proceeding in contact with a solid catalyst in the presence of an inert gas I the stoichiometric requirements are

$$N_B = (b/a)N_A, \quad N_P = -(p/a)N_A, \quad \text{and}$$

$$N_Q = -(q/a)N_A \quad (51 a, b, c)$$

Hence the Stefan-Maxwell equation for component A is

$$-\frac{dx_A}{dz} = \frac{N_A}{c} \left[\frac{x_B}{\mathcal{D}_{AB}} + \frac{x_P}{\mathcal{D}_{AP}} + \frac{x_Q}{\mathcal{D}_{AQ}} + \frac{x_I}{\mathcal{D}_{AI}} - \frac{x_A}{a} \left(\frac{b}{\mathcal{D}_{AB}} - \frac{p}{\mathcal{D}_{AP}} - \frac{q}{\mathcal{D}_{AQ}} \right) \right] \quad (52)$$

Thus the expression for N_A becomes

$$N_A = -c \left[\frac{x_B}{\mathcal{D}_{AB}} + \frac{x_P}{\mathcal{D}_{AP}} + \frac{x_Q}{\mathcal{D}_{AQ}} + \frac{x_I}{\mathcal{D}_{AI}} - \frac{x_A}{a} \left(\frac{b}{\mathcal{D}_{AB}} - \frac{p}{\mathcal{D}_{AP}} - \frac{q}{\mathcal{D}_{AQ}} \right) \right]^{-1} \frac{dx_A}{dz} \quad (53)$$

Thus far no assumptions have been made, except that the system consists of ideal gases at constant temperature and pressure.

Next Equation (53) can be rewritten in an alternative form simply for the purpose of obtaining a relation which resembles the expression for binary diffusion of A into stagnant I in a two-component system:

It should be emphasized that the step from Equation (53) to (54) is nothing more than a rearrangement.

Equation (54) is next integrated with respect to z to give

$$\nu_{PQ} = \frac{N_A \delta}{c \mathcal{D}_{PQ}} = \frac{[1 - \Xi_A x_A] \ln[(1 - \Xi_A x_{A0}) / (1 - \Xi_A x_{A\delta})]}{\Xi_A [(x_P + p x_A) r_P + (x_Q + q x_A) r_Q]} \quad (60)$$

$$N_A = (c \mathcal{D}_{Am}) \delta^{-1} (x_{A0} - x_{A\delta}) (x_I)_A^{-1} \quad (57)$$

in which x_I for component A is defined as

$$(x_I)_A = \Xi_A (x_{A0} - x_{A\delta}) \cdot \left\{ \ln \frac{1 - \Xi_A x_{A\delta}}{1 - \Xi_A x_{A0}} \right\}^{-1} \quad (58)$$

The integration of Equation (54) was performed by assuming that \mathcal{D}_{Am} is independent of composition and hence of position. This assumption is clearly made just to effect a simplification.

Equation (57) is the same result which Stewart has given. For B, P, and

Q stationary Equation (57) reduces to the result of Wilke; also Equation (56) is then his expression for effective diffusivity. Note, however, that Wilke's expression for diffusivity is the same as that in equation (17) of Hougen and Watson if all their \mathcal{D}_{ij} are replaced by \mathcal{D}_{ij}^{-1} . Equation (57) is the same as that given by Hougen and Watson, but the \mathcal{D}_{Am} used here are different from theirs.

The solution of the $A \rightarrow pP + qQ$ problem by Equations (56), (57), and (58) is now compared with the exact solution obtained previously. For this problem the \mathcal{D}_{Am} of Equation (56) can be written as

$$\mathcal{D}_{Am} = \frac{(1 - \Xi_A) \mathcal{D}_{PQ}}{(x_P + p x_A) r_P + (x_Q + q x_A) r_Q} \quad (59)$$

Then from Equations (57), (58), and (59) ν_{PQ} can be obtained:

In order to use Equation (60) the quantities x_A , x_P , and x_Q are to be taken as the arithmetic mean of the mole fraction of A, P, and Q at the inner and outer edges of the film. Hence for instantaneous surface reaction one

takes x_A to be $\frac{1}{2} x_{A0}$. Further one takes

x_P to be $\frac{1}{2} [x_{P0} + \{x_{P0} / (x_{P0} + x_{Q0})\}]$

and an analogous expression for x_Q ; this is tantamount to assuming that the ratio of concentrations of P and Q at $z = \delta$ is exactly the same as that at $z = 0$.

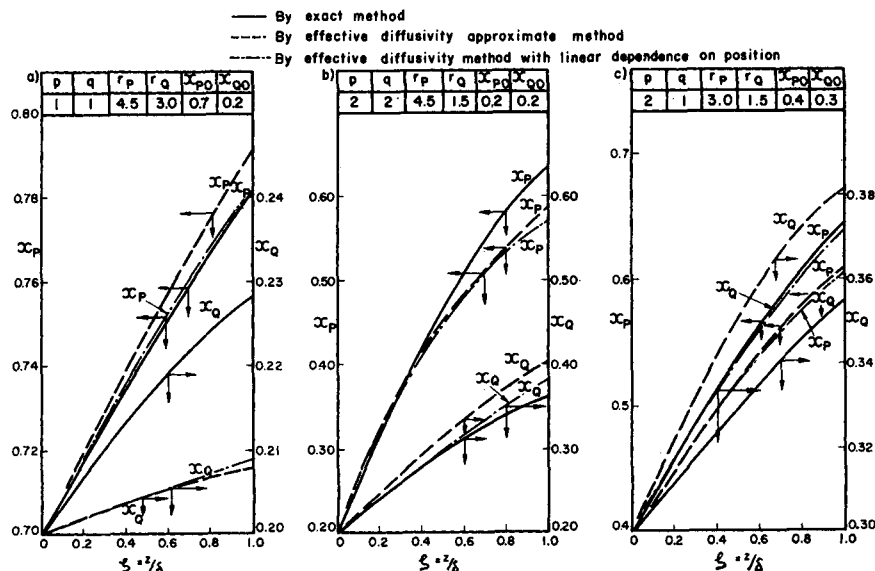


Fig. 5. Comparison of the concentration profiles for the $A \rightarrow pP + qQ$ problem (for $K = \infty$) as calculated by the exact method and by two effective diffusivity methods.

Assumption of Linear Effective Diffusivity

From Equation (56) it is known that the effective diffusivity \mathcal{D}_{Am} is dependent on composition and hence on position. Hence the authors suggest a

$$\nu_{PQ} = \frac{N_A \delta}{c \mathcal{D}_{PQ}} = \frac{1 - x_{A0} (1 - p - q)}{[r_P (x_{P0} + p x_{A0}) + r_Q (x_{Q0} + q x_{A0})] (1 - p - q)} \cdot \frac{\beta}{\ln (1 + \beta)}$$

method for modifying the effective-diffusivity approach so as to make the effective diffusivity linearly dependent on either composition or distance.

Method I

\mathcal{D}_{Am} linearly dependent on distance

In this case Equation (54) for the $A \rightarrow pP + qQ$ problem can be written as

$$N_A = -c \mathcal{D}_{Am0} \left[1 + \beta \left(\frac{z}{\delta} \right) \right] \cdot [1 - x_A (1 - p - q)]^{-1} \frac{dx_A}{dz} \quad (61)$$

In this expression \mathcal{D}_{Am0} is \mathcal{D}_{Am} evaluated at $z = 0$ and is obtained from Equation (59) by replacing x_A , x_P , and x_Q by their corresponding values at $z = 0$, namely x_{A0} , x_{P0} , and x_{Q0} . The quantity β is a constant and can be expressed as follows by use of Equation (59):

$$\beta = \frac{1 - x_{A0} (1 - p - q)}{1 - x_{A0} (1 - p - q)}$$

$$\frac{r_P (x_{P0} + p x_{A0}) + r_Q (x_{Q0} + q x_{A0})}{r_P (x_{P0} + p x_{A0}) + r_Q (x_{Q0} + q x_{A0})} - 1 \quad (62)$$

Equation (61) is next integrated with respect to z to give

$$\ln \left[\frac{1 - x_{A0} (1 - p - q)}{1 - x_A (1 - p - q)} \right] \quad (63)$$

When $K_h = \infty$, $x_{A0} = 0$, and Equation (62) becomes

$$\nu_{PQ} = \frac{N_A \delta}{c \mathcal{D}_{PQ}} = \frac{1 - x_{A0} (1 - p - q)}{[r_P (x_{P0} + p x_{A0}) + r_Q (x_{Q0} + q x_{A0})] (1 - p - q)}$$

$$\beta = \frac{1}{1 - x_{A0} (1 - p - q)}$$

$$\frac{r_P (x_{P0} + p x_{A0}) + r_Q (x_{Q0} + q x_{A0})}{x_{P0} (r_P - r_Q) + r_Q} - 1 \quad (64)$$

In order to make use of Equation (64)

one takes $x_{P0} = \frac{1}{2} \cdot [x_{P0} + \{x_{P0}/(x_{P0} + x_{Q0})\}]$ provided $r_P - r_Q < 0$; when $r_P - r_Q > 0$, Equation (64) must be modified by interchanging all p and q and all P and Q . When $r_P = r_Q$, Equation (64) reduces to $\beta = 0$, and hence $\mathcal{D}_{Am} = \mathcal{D}_{Am0}$.

Method II

\mathcal{D}_{Am} linearly dependent on composition

In this case an expression similar to Equation (61) can be written as

$$N_A = -c \mathcal{D}_{Am0} \left[1 + \beta \left(\frac{x_{A0} - x_A}{x_{A0}} \right) \right] [1 - x_A (1 - p - q)]^{-1} \frac{dx_A}{dz} \quad (65)$$

\mathcal{D}_{Am0} and β are exactly the same as defined in Method I for the case $K_h = \infty$.

Integration of Equation (65) with respect to z gives

$$\left[\left(1 - \frac{\beta}{x_{A0} (1 - p - q)} \right) \cdot \ln \left[\frac{1 - x_{A0} (1 - p - q)}{1 - x_A (1 - p - q)} \right] - \beta \left(\frac{x_{A0} - x_A}{x_{A0}} \right) \right] \quad (66)$$

When $\beta = 0$, Equations (63) and (66) reduce to Equation (60) which is the method of assuming constant effective diffusivity.

Discussion of Results

A few values of ν_{PQ} , calculated from Equations (60), (63), and (66), along with the corresponding exact values from Table 3, are summarized for the $A \rightarrow pP + qQ$ problem (with infinitely fast surface reaction) in Table 1. Additional comparisons are given in Table 4*.

From Table 1 one sees that an effective-diffusivity approach to a multicomponent diffusion problem gives acceptable results. The method is simple, and the formula is similar to that of the binary case. In this method the authors suggest that when the ratio of r_P to r_Q is close to unity, the constant effective-diffusivity approach is preferable; when the ratio of r_P to r_Q is far from unity, the modified effective-diffusivity approach (either linearly dependent on position or linearly dependent on concentration) should be used.

It is important to note that although good agreement for ν_{PQ} is obtained by the effective-diffusivity method, there is quite a discrepancy between the exact concentration profile and that obtained by this method. A few concentration profiles obtained by the exact method, by the constant effective-diffusivity method, and by the method of

* See footnote on page 517.

TABLE 1. SAMPLE COMPARISON OF THE VALUES OF $\nu_{PQ} = N_A \delta / c \mathcal{D}_{PQ}$ BY THE EFFECTIVE DIFFUSIVITY METHODS WITH THOSE FROM THE EXACT SOLUTION, FOR THE $A \rightarrow pP + qQ$ PROBLEM (WITH $K = \infty$)

(In each square the first number is the exact value, the second number is the value calculated from the constant effective diffusivity method [by Equation (60)], the third number is the value calculated from the linearly position-dependent effective-diffusivity method [by Equation (63)], and the fourth number is the value calculated from the linearly concentration-dependent effective-diffusivity method [by Equation (66)].

$r_P \backslash r_Q$		1.0	1.5	3.0	4.5	6.0
$p = 2$ $q = 1$ $x_{P0} = 0.7$ $x_{Q0} = 0.2$	1.0		0.0801	0.0597	0.0474	0.0396
			0.0815	0.0618	0.0498	0.0417
			0.0810	0.0604	0.0476	0.0401
			0.0808	0.0603	0.0481	0.0400
	1.5	0.0647	0.0603	0.0485	0.0402	0.0343
		0.0660	0.0608	0.0491	0.0412	0.0355
		0.0658	0.0608	0.0486	0.0402	0.0344
		0.0659	0.0608	0.0484	0.0402	0.0344
	3.0	0.0361	0.0346	0.0307	0.0271	0.0243
		0.0361	0.0345	0.0304	0.0272	0.0246
		0.0359	0.0343	0.0304	0.0270	0.0242
		0.0359	0.0343	0.0304	0.0270	0.0244
	4.5	0.0248	0.0240	0.0220	0.0203	0.0187
		0.0248	0.0241	0.0220	0.0203	0.0188
		0.0243	0.0239	0.0219	0.0203	0.0187
		0.0246	0.0239	0.0221	0.0203	0.0187
	6.0	0.0188	0.0184	0.0172	0.0162	0.0152
		0.0189	0.0185	0.0172	0.0164	0.0152
		0.0186	0.0184	0.0172	0.0162	0.0152
		0.0190	0.0184	0.0172	0.0161	0.0152

TABLE 2. COMPARISON OF THE CONCENTRATION PROFILE BY THE EFFECTIVE DIFFUSIVITY METHODS AND THAT BY THE EXACT METHOD FOR THE $A \rightarrow pP + qQ$ PROBLEM FOR $K = \infty$

$p = 1$ $q = 1$ $r_p = 4.5$ $r_q = 3.0$ $x_{p0} = 0.7$ $x_{q0} = 0.2$	by the exact method: $x_p(\zeta) = 0.9998 + 0.3793 \exp(0.038\zeta) - 0.6791 \exp(-0.084\zeta)$ $x_q(\zeta) = 0.9998 - 0.2865 \exp(0.038\zeta) - 0.5133 \exp(-0.086\zeta)$ by the constant effective diffusivity method: $x_p(\zeta) = 1.0000 - 0.3000 \exp(-0.316\zeta)$ $x_q(\zeta) = 1.0000 - 0.8000 \exp(-0.012\zeta)$ by the linearly position dependent effective diffusivity method: $x_p(\zeta) = 1.0000 - 0.3000(1 - 0.0221\zeta)^{14.29}$ $x_q(\zeta) = 1.0000 - 0.8000(1 - 0.0221\zeta)^{0.533}$
$p = 2$ $q = 2$ $r_p = 4.5$ $r_q = 1.5$ $x_{p0} = 0.2$ $x_{q0} = 0.2$	by the exact method: $x_p(\zeta) = 0.6665 + 0.4189 \exp(-0.212\zeta) - 0.8854 \exp(-0.871\zeta)$ $x_q(\zeta) = 0.6665 - 0.2715 \exp(-0.212\zeta) - 0.1950 \exp(-0.871\zeta)$ by the constant effective diffusivity method: $x_p(\zeta) = 0.6667 - 0.4667 \exp(-1.544\zeta)$ $x_q(\zeta) = 0.6667 - 0.4667 \exp(-0.515\zeta)$ by the linearly position dependent effective diffusivity method: $x_p(\zeta) = 0.6667 - 0.4667(1 - 0.1304\zeta)^{11.35}$ $x_q(\zeta) = 0.6667 - 0.4667(1 - 0.1304\zeta)^{3.44}$
$p = 2$ $q = 1$ $r_p = 3.0$ $r_q = 1.5$ $x_{p0} = 0.4$ $x_{q0} = 0.3$	by the exact method: $x_p(\zeta) = 1.0000 + 0.1042 \exp(-0.122\zeta) - 0.7042 \exp(-0.453\zeta)$ $x_q(\zeta) = 0.5000 - 0.0711 \exp(-0.122\zeta) - 0.1289 \exp(-0.453\zeta)$ by the constant effective diffusivity method: $x_p(\zeta) = 1.0000 - 0.6000 \exp(-0.448\zeta)$ $x_q(\zeta) = 0.5000 - 0.2000 \exp(-0.565\zeta)$ by the linearly position dependent effective diffusivity method: $x_p(\zeta) = 1.0000 - 0.6000(1 + 0.1081\zeta)^{-4.135}$ $x_q(\zeta) = 0.5000 - 0.2000(1 + 0.1081\zeta)^{-4.370}$

effective diffusivity linearly dependent on position are shown in Table 2. These profiles are plotted in Figure 5. Because profiles calculated by the method of effective diffusivity, linearly dependent on concentration, cannot be expressed explicitly, they are not shown in Table 2.

Certainly the expressions used here for the heterogeneous reaction rates at the wall are idealized expressions. More general expressions should take into account the adsorption and desorption mechanisms which occur at the surface.

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NOTATION

a, b = number of moles
 A_p, B_p, C_p = dimensionless constants defined in Equations (22 a, b, c)

c = molar density (moles cm^{-3});
 $c = p/RT$
 \mathcal{D}_{ij} = binary diffusion coefficient for the gas pair $i-j$ ($\text{cm}^2 \text{sec}^{-1}$)
 \mathcal{D}_{im} = effective binary diffusion coefficient for i into a mixture of the other components (sq. cm. sec^{-1})
 h = order of chemical reaction
 k_h = reaction rate constant for h th order reaction (mole $\text{cm}^{-2} \text{sec}^{-1}$)
 K = dimensionless quantity defined in Equation (14) = $k_h \delta / c \mathcal{D}_{A,p}$
 K_h = dimensionless quantity defined in Equation (26) = $k_h \delta / c \mathcal{D}_{p,q}$
 M, N, R = dimensionless constants defined in Equations (13 a, b, c)
 N_A = mass transfer rate
 N_i = mole flux of the i component with respect to stationary axes (mole $\text{cm}^{-2} \text{sec}^{-1}$)
 n = number of moles
 p = total pressure
 p, q = number of moles
 P, Q = components P and Q
 Q = dimensionless quantity = $(1 - x_{A0}) / (1 - x_{A0})$
 r_i = ratio of binary diffusivity defined in each case
 R = gas constant
 s_i = dimensionless constants defined in Equations (24) and (31)
 T = absolute temperature

X, Y, Z = dimensionless constants defined in Equations (28), (29), and (30)

x_i = mole fraction of the i th component
 z = distance into film, (cm.)

Greek Letters

α_i = dimensionless quantity = $\exp \nu_i$
 β = constant defined in Equation (62)
 δ = thickness of gas film
 Ξ_i = constant defined in Equation (40)
 ζ = z/δ = dimensionless distance coordinate
 ν = total number of chemically distinct species in a multi-component gas mixture
 ν_i = dimensionless quantity = $N_A \delta / c \mathcal{D}_{i,j}$

Subscripts

A, A_n, B, C, P, Q = quantities pertaining to components in multicomponent mixture
 i = quantity pertaining to the i th species in multicomponent mixture
 0 = quantity evaluated at $z = 0$
 δ = quantity evaluated at $z = \delta$
 0 = zero root (with s)
 e = equal root (with s)
 $+$ = positive root (with s)
 $-$ = negative root (with s)

Superscript

0 = the known average quantity

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