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Intraphase Reaction Systems Including Diffusion and Simultaneous Multicomponent Reaction

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Abstract

The system including a multicomponent reaction and simultaneous diffusion exemplified by NH_3 synthesis is investigated with special attention to "effectiveness" and composition change along the direction of mass transfer.

The system in one dimension is represented by the following equations.

$$\frac{d^2 X_i}{dl^2} + \frac{\nu/\nu_i}{1-(\nu/\nu_i)X_i} \left(\frac{dX_i}{dl} \right)^2 = -\frac{\nu_i}{CD_i} \left(1 - \frac{\nu}{\nu_i} X_i \right) R$$

where $i = 1, 2, 3, \dots, n-1$

A unique maximum effectiveness of industrial importance can be obtained by solving the above equations at different initial mole ratios.

Apart from the kinetic effect caused by stoichiometric imbalance, the results indicate, in a qualitative way, the dynamic effect that more diffusive reactant(s) and less diffusive product(s) tend to increase along a diffusion direction, and that the greater the differences among respective diffusivities, the more profound is the effect.

Introduction

In industrial biochemical processes micro-organisms are employed as biological flocs suspended in a fluid or as a film adhering to a mechanical support.

Fig. 1 represents composite models of micro-organisms dispersing uniformly throughout a biochemically inert intercellular gel. This scheme is quite similar to the heterogeneous catalysis shown diagrammatically in Fig. 2 where most reaction species must diffuse through pore paths before reaching "active sites". In fact, the latter can be thought of as a simplified version of the former and it is a common practice to convey the insight obtained from the study of the catalysis to the biochemical process.

There have been many studies, reports, and discussions regarding the behavior of catalyst pores^{1,2,3}), but the chemical reactions treated in them are exclusively the ones consisting of one reactant and one product, and seemingly none has ever mentioned for multicomponent reactions of $\sum \nu_i A_i = 0$ type in which reactants and/or products composition can be varied and differences among their diffusivities can alter the rate behavior of the reaction, and hence, to which the celebrated Thiele modulus cannot be applied.

We set forth mathematical relations which express the effect of the initial mole ratios and differences among the diffusivities upon composition of the reaction

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system along the diffusion path, and draw some general trends therefrom for the effect of diffusivities.

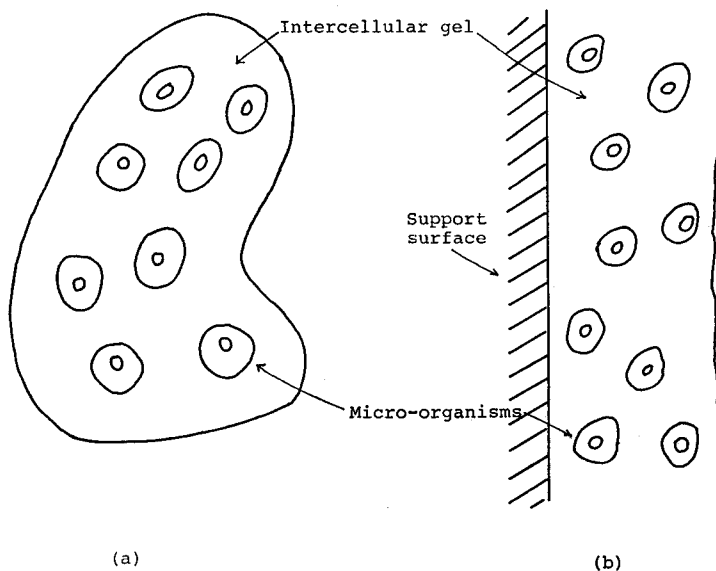


Fig. 1. Model for a microbial mass.
(a) Microbial floc. (b) Microbial film.

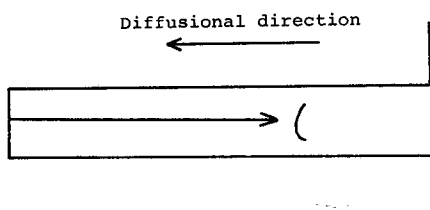


Fig. 2. Schematic representation of a catalyst pore. The direction from the pore entrance toward the bottom is referred to as diffusion direction and the reverse direction, as counter-diffusion direction.

Theoretical Section

Suppose a cylinder along a diffusion direction whose one end is plugged and inside surface has many uniformly distributed active sites, as represented by a catalyst pore (Fig. 2). The cylinder should be narrow enough so that only molecular diffusion prevails within it.

Consider the following reaction occurs at the active sites,

$$\sum_{i=1}^n \nu_i A_i = 0 \quad (1)$$

whose intrinsic reaction velocity can be expressed as

$$R = \frac{1}{\nu_i} \frac{dC_A}{dt} = f(C, X_1, X_2, \dots, X_{n-1}, T) \quad (2)$$

At a steady state, the mole balance for component i is given as

$$\frac{dN_i}{dl} = \nu_i R \quad (3)$$

The molar flux, N_i , can be related to the concentration gradient by

$$N_i = -CD_i \frac{dX_i}{dl} + X_i \sum_{j=1}^n N_j \quad (4)$$

From the stoichiometry, following relations exist among the molar fluxes.

$$N_1/\nu_1 = N_2/\nu_2 = \dots = N_i/\nu_i = \sum_{i=1}^n N_i/\nu \quad (5)$$

By combining Eqs. (3) and (4), and performing some differentiation and manipulation

$$\frac{d^2 X_i}{dl^2} - \frac{\nu/\nu_i}{1-(\nu/\nu_i)X_i} \left(\frac{dX_i}{dl} \right)^2 = - \frac{\nu_i}{CD_i} \left(1 - \frac{\nu}{\nu_i} X_i \right) R \quad (6)$$

where $i=1, 2, 3, \dots, n-1$

The boundary conditions for Eq. (6) are

$$\text{at } l=0; \quad X_i = X_{i0} \quad \text{and} \quad dX_i/dl = 0 \quad (7)$$

If D_i 's do not depend upon concentrations, each equation in Eqs. (6) can be solved independently, and in particular, if all D_i 's are equal to one another and the initial concentrations are in stoichiometrical ratio, the $n-1$ equations become identical, and the Thiele modulus can be applied without problem. However, in cases where D_i 's are different from one another and are the functions of concentrations, Eqs. (6) must be solved simultaneously, and as a matter of course, the Thiele modulus is meaningless. At any rate, whenever diffusivities of chemical species present are not equal, composition variations due merely to diffusion arises along a diffusion path. In reactions at higher pressures where diffusivities of gases are small because of inverse proportionality to pressure, and furthermore in which hydrogen takes part whose diffusivity is rather large, the effect may be significant. The same situation may arise in microbiological processes.

Example Calculation

We take up the time-honored ammonia synthesis reaction,



because (1) its kinetics is comprehensively investigated although its mechanism is not without problem^{4,5}, (2) pore sizes are small enough to prevent turbulence and large enough to permit the use of bulk diffusivities, and (3) it occurs at high pressure in the presence of H_2 .

An expression of the reaction velocity has been given by Dyson *et al.*⁶, which, at 800°K and 300 atm in g-mol/ml, sec, reduces to

$$R = 0.52143 \times 10^{-5} \frac{X_{N_2} X_{H_2}^{1.5}}{X_{NH_3}} - 1.320203 \times 10^{-5} \frac{X_{NH_3}}{X_{H_2}^{1.5}} \quad (9)$$

To estimate the diffusivities of N_2 , H_2 and NH_3 at the reaction condition we start from the values at NTP,

$$D_{N_2-H_2} = 0.784$$

$$D_{N_2-NH_3} = 0.230$$

$$D_{H_2-NH_3} = 0.783$$

which have been obtained experimentally⁷⁾. The values are then adjusted to 800°K and 300 atm by the following theoretical equation⁸⁾.

$$D_{A-B} = \frac{0.001858 T^{1.5} (1/M_A + 1/M_B)^{0.5}}{P \sigma_{AB}^2 \Omega_D} \quad (10)$$

Finally the respective diffusivities in the reaction mixture are calculated from Wilke's equation⁹⁾ which is expressed as

$$D_A = (1 - X_A) / (X_B/D_{A-B} + X_C/D_{A-C}) \quad (11)$$

The Runge-Kutta-Gill method is used for solving the simultaneous differential equations of Eqs. (6). (See Appendix.) Since the number of degrees of freedom of D_i and X_i are both $n-1$, two equations should be solved in the NH_3 synthesis case. However, to emphasize equivalent predictability in guessing the respective diffusivities, three equations are solved and X_i 's obtained are prorated so that they sum up to unity. Fig. 3 depicts an example of composition profile of a catalyst pore of 0.32 cm length in the case where the composition at the bottom is N_2 : 0.2, H_2 : 0.6 and NH_3 : 0.2, and Table 1 denotes the effect of the H_2/N_2 mole ratio under the same NH_3 content at the bottom.

Discussion

In the theory of contact catalysis, Thiele's modulus has long been used for denoting "effectiveness" reduction in a catalyst pore due to diffusional resistance. (Effectiveness means the ratio of the rate of reaction in a pore to the one at which reaction would occur if the concentration and temperature within it were the same as the respective values external to the pore.) Unfortunately, as Thiele's modulus involves only one diffusivity and one reaction rate constant, it can only be applied to reactions having one reactant and one product, *i.e.*, $\nu_1 A_1 \rightleftharpoons \nu_2 A_2$, wherein only one diffusivity needs to be known ($D_{1-2} = D_{2-1}$). In multicomponent reactions where at least two reactants or products are present, the situation is much more involved, because the reaction velocity is not only influenced kinetically by the (initial) mole ratio, but also dynamically by differences among the respective diffusivities, and besides, no single diffusivity can be specified for the modulus.

Effectiveness for a multicomponent reaction depends primarily upon reaction velocity, diffusivities, concentrations and pore geometry. Although, in practice, a chemical reaction and a catalyst are specified, there remains still the component

mole ratio which affects the effectiveness and makes it indefinite. By introducing, for example, the optimization concept further, we can eventually determine unique maximum effectiveness, which is expected to be of industrial importance, through solving the simultaneous equations in Eqs. (6) at different initial mole ratios.

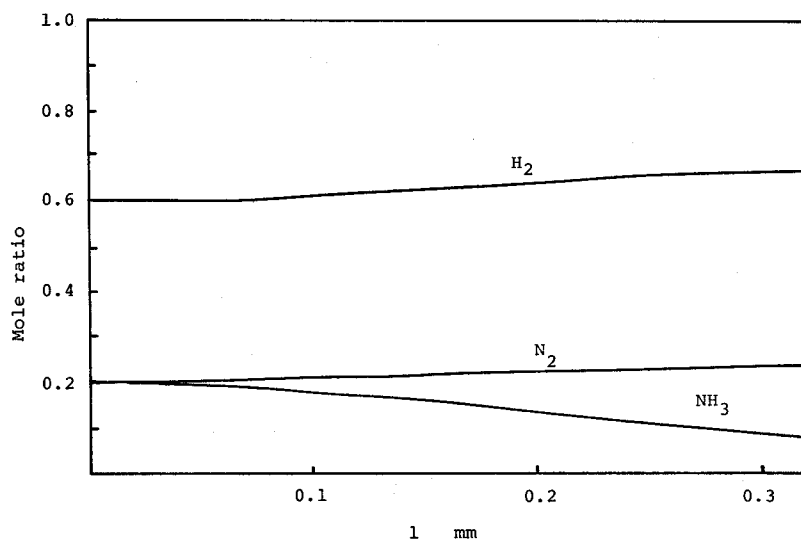


Fig. 3. Concentration profile in a catalyst pore.

Given: Concentration at the bottom in mole fraction,
 N_2 : 0.2, H_2 : 0.6, NH_3 : 0.2; temp., $800^\circ K$; press., 300 atm.

Table 1. NH_3 synthesis in a catalyst pore of 0.32 cm length at $800^\circ K$ and 300 atm.

Entrance				Bottom				Conversion
N_2	H_2	NH_3	H_2/N_2	N_2	H_2	NH_3	H_2/N_2	
0.2361	0.6745	0.0894	2.8569	0.2000	0.6000	0.2000	3.0000	0.1691
0.2459	0.6660	0.0881	2.6854	0.2100	0.5900	0.2000	2.8000	0.1715
0.2558	0.6576	0.0866	2.5712	0.2200	0.5800	0.2000	2.6364	0.1739
0.2657	0.6492	0.0851	2.4432	0.2300	0.5700	0.2000	2.4782	0.1764
0.2757	0.6406	0.0837	2.3217	0.2400	0.5600	0.2000	2.3333	0.1789
0.2857	0.6320	0.0823	2.2121	0.2500	0.5500	0.2000	2.2000	0.1805
0.2958	0.6232	0.0810	2.1068	0.2600	0.5400	0.2000	2.0769	0.1834
0.3058	0.6142	0.0800	2.0085	0.2700	0.5300	0.2000	1.9630	0.1851
0.3158	0.6049	0.0793	1.9154	0.2800	0.5200	0.2000	1.8571	0.1863
0.3257	0.5951	0.0792	1.8271	0.2900	0.5100	0.2000	1.7586	0.1865
0.3355	0.5849	0.0796	1.7434	0.3000	0.5000	0.2000	1.6667	0.1858

Setting aside the problem of determining effectiveness, our next concern is to know to what extent the differences among diffusivities play roles in altering the component concentrations along the pore path. For NH_3 synthesis, this effect can be seen from Table 1 and Fig. 3, which exhibit that the H_2/N_2 ratio is

2.8569 at the entrance of a pore of 3.2 mm length as compared with stoichiometric 3.0000 at the bottom, and the mole ratio which remains approximately constant along the path locates near 2.27. The initial ratio at which maximum conversion is attained, shifts from 1.85, for neglected differences among diffusivities to 1.82.

The situation can be generalized easily to the following expression.

The more diffusive reactant(s) and less diffusive product(s) tend to increase along the diffusion direction (direction toward the bottom), and the less diffusive reactant(s) and more diffusive product(s), along the counterdiffusion direction (direction toward the entrance).

The smaller the diffusivities, and the greater the differences among respective diffusivities, the more profound is the effect.

As Kodama *et al.*¹⁰⁾ pointed out from merely a kinetic viewpoint, the reaction rate expression of Eq. (9) indicates that the maximum conversion can be attained invariably when the H_2/N_2 ratio is less than the stoichiometric value of 3, although at higher conversion the value becomes lower.

Our assertion is that this value shifts to a still different value by the dynamic effect caused by mass transfer. The discussion and procedure developed so far should be applied to the microbiological process in a similar manner.

Nomenclature

- A_i : The i 'th chemical species
- C : Concentration, g-mol/ml
- D : Diffusivity, cm^2/sec
- L : Length of pore, cm
- l : length measured from bottom of a pore toward entrance, cm
- M_i : Molecular weight of component i
- N : Molar flux, g-mol/ cm^2/sec
- n : Number of reaction species
- P : Absolute pressure, atm
- T : Temperature, $^{\circ}\text{K}$
- X_i : Mole fraction of reaction species i
- ν_i : Stoichiometric coefficient of chemical species i , plus for product and minus for reactant
- ν : $\sum \nu_i$
- σ : Lennard-Jones force constant
- Ω_D : Collision integral

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Appendix. Computer Program for Solving the Simultaneous
Differential Equations.

```

DIMENSION D(3), DC(3), CNU(3), A(6), B(4), C(4), YC(3), T(3, 2), R(3, 2),
1 Q (3, 2), Y (3, 2), Z (3,2)
SPEED (X1, X2, X3)=.521433E-5*X1*X2**1.5/X3-1.320203E-5*X3/X2**1.5
CONC (W1, W2, W3)=300./1.987/300./(1.067*W1+1.140*W2+0.96*W3)/1000.
READ (2, 10) H, (YC(I), I=1,3)
10 FORMAT (4F15.5)
WRITE (1,20) H, (YC (I), I=1,3)
20 FORMAT (1H, 10X, 2HH=, E 12.5, 5X, 4HYC 1=, E 12.5, 5X, 4HYC 2=, E 12.5, /,
1 8X, 4HYC3,=E12.5)
CNU(1)=1.0
CNU(2)=3.0
CNU(3)=-2.0
CONST=(300./273.)**1.5/300.
D(3)=0.783*CONST*1.156/0.88665
D(1)=0.784*CONST*0.85680/0.7228
D(2)=0.230*CONST*1.195/0.8827
A(1)=0.0
B(1)=1.0
B(2)=0.2928932
B(3)=1.707107
B(4)=0.3333333
C(1)=0.0
C(4)=0.0
DO 1 IZ=1,3
Y(IZ, 1)=YC(IZ)
Y(IZ, 2)=0.0
Q(IZ, 1)=0.0
Q(IZ, 2)=0.0
1 CONTINUE
DL=0.0
DO 5 N=1,10
A(2)=0.5*H
A(3)=A(2)
A(4)=H
A(5)=H
A(6)=A(2)
C(2)=0.7071068*H
C(3)=-C(2)

```



```

DC(1)=(1.0-YC(1)/(YC(2)/D(1)+YC(3)/D(2) )
DC(2)=(1.0-YC(2)/(YC(1)/D(1)+YC(3)/D(3) )
DC(3)=(1.0-YC(3)/(YC(2)/D(3)+YC(1)/D(2) )
WRITE (1,30) N,(DC (IZ), IZ=1,3)
30 FORMAT (1H ,/, 10X, 2HN=, 18,/, 10X, 4HDC1=, E12.5, 5X, 4HDC2=, E12.5, 15X,
4HDC3=, E12.5)
YT=Y(1,1)+Y(2,1)+Y(3,1)
YC(1)=Y(1,1)/YT
YC(2)=Y(2,1)/YT
YC(3)=Y(3,1)/YT
WRITE (1,40) YT, (YC (I), I=1,30, (Y (IZ, 2), IZ=1, 3)
40 FORMAT (1H , 10X, 3HYT=, E12.5, 4X, 4HYC1=, E12.5, 5X, 4HYC2=, E12.5, /,
1 10X, 4HYC3=, E12.5,/, 10X, 4HYD1=, E12.5, 5X, 4HYD2=, E12.5, 5X, 4HYD3=,
2 E12.5)
PL=DL
DO 2 I2=1, 4
DL=PL+A (I2)
DO 3 IZ=1, 3
Z(IZ, 1)=Y (IZ, 2)
Z(IZ, 2)=-CNU (IZ)/(CONC (YC(1), YC(2), YC(3) )*DC (IZ) )*(1.0-2.0/CNU (IZ))*
1 YC(IZ) )*SPEED(YC(1), YC(2), YC(3) )
2 -2.0/CNU(IZ)/(1.0-2.0/CNU(IZ)*YC(IZ) )*
3 Y(IZ, 2)**2
DO 4 I3=1, 2
T(IZ, I3)=A(I2+2)*Z(IZ, I3)-Q(IZ, I3)
R(IZ, I3)=B(I2)*T(IZ, I3)
Y(IZ, I3)=Y(IZ, 1)+R(IZ, I3)
Q (IZ, I3)=3.0*R(IZ, I3)-T(IZ, I3)+C(I2)*Z(IZ, I3)
4 CONTINUE
3 CONTINUE
2 CONTINUE
H=0.9*H
5 CONTINUE
STOP
END

```

$CNU(1)$, $CNU(2)$, $CNU(3)$ = stoichiometric coefficients for N_2 , H_2 , NH_3 . $D(1) = D_{N_2-H_2}$, $D(2) = D_{N_2-NH_3}$, $D(3) = D_{H_2-NH_3}$;
 $DC(1)$, $DC(2)$, $DC(3)$ = diffusivities of N_2 , H_2 , NH_3 in the gas mixture, respectively.
 $Y(IZ, 1)$ = mole fraction of species IZ ; $Y(IZ, 2)$ = gradient of mole fraction of species IZ ; $YC(IZ)$ = corrected mole fraction of species IZ .