

NOTE

MULTICOMPONENT DIFFUSION IN A NETWORK OF
HETEROGENEOUS CATALYTIC REACTIONS

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INTRODUCTION

Usually more than one single reaction take place in a reacting system. In this case, we have to deal with a multicomponent mixture in a reaction network. Particularly in heterogeneous catalysis, it is important to establish and combine the rate of the transport steps with the chemical reactions; especially, the transport of reactants and products inside the porous solid. In the last case the calculation of the diffusion coefficients of different species in the multicomponent system is needed.

The aim of this communication is to describe a procedure for the calculation of the bulk diffusion coefficient of a species diffusing through a multicomponent mixture in a system where several reactions are carried out in a porous pellet.

ANALYSIS

Consider the set of reactions

$$\sum_j \alpha_{ij} \cdot S_j = 0 \quad , \quad \text{with} \quad \begin{array}{l} i = 1, 2, \dots, I \text{ Species} \\ j = 1, 2, \dots, J \text{ Reactions} \end{array} \quad (1)$$

occurring inside a porous catalyst particle.

The pseudo-binary molecular diffusivity for species i diffusing through the multicomponent ideal gas mixture, for unidimensional flux, is given by the modified Stefan - Maxwell equation (Bird et al., 1960; Cunningham and Williams, 1980; Froment and Bischoff, 1990; Whitaker, 1986)

$$D_{i,m} = \frac{1 - y_i \sum_k (N_k/N_i)}{\sum_k \frac{y_k - y_i (N_k/N_i)}{D_{i,k}}} \quad , \quad (2)$$

where $D_{i,k}$ are the usual binary diffusivities and y_i and N_i the mole fraction and the flux of species i , respectively.

For a single reaction, steady state flux relationships can be easily established by the reaction stoichiometry (Butt, 1963).

If

$$\sum_i \alpha_i \cdot S_i = 0 \quad , \quad i = 1, 2, 3, \dots, I \quad (3)$$

the relation

$$N_i/\alpha_i = \text{constant} \quad ,$$

and the flux ratios :

$$(N_i/N_k) = (\alpha_i/\alpha_k) \quad . \quad (4)$$

For a reaction network however the steady state flux ratios can not be obtained directly, since the species can participate in several reactions and as reactant or product. In this case, it is necessary to take into account the magnitude of each reaction rate as well as the reaction network stoichiometry.

The magnitude δ_j for reaction j can be defined as :

$$\delta_j = r_j / \sum_j r_j \quad , \quad (5)$$

where r_j is the value of reaction rate j .

Thus, δ_j can be used as the weighing factor in considering the contribution on the net flux of a species due to its participation in reaction j . Therefore, the steady state flux relationships can be calculated as :

$$N_i/N_k = \sum_j \delta_j \cdot \alpha_{i,j} / \sum_j \delta_j \cdot \alpha_{k,j} \quad (6)$$

Equation (6) reduces to Eq.(4) for the case of a single reaction.

For the calculation of the diffusion coefficient of "i" in the mixture, it is better to use equation (7a), to avoid the problem that arises when the net flux of a species is zero due to a particular combination of δ_j and α_{ij} .

$$D_{i,m} = \frac{N_i - y_i \sum_k N_k}{\sum_k \frac{N_i \cdot y_k - y_i \cdot N_k}{D_{i,k}}} \quad (7a)$$

which in function of parameter δ_j is :

$$D_{i,m} = \frac{\sum_j \delta_j \cdot \alpha_{i,j} - y_i \cdot \sum_k (\sum_j \delta_j \cdot \alpha_{k,j})}{\sum_k \frac{y_k \cdot \sum_j \delta_j \cdot \alpha_{i,j} - y_i \cdot \sum_j \delta_j \cdot \alpha_{k,j}}{D_{i,k}}} \quad (7b)$$

As can be seen, Eq.(7a) reduces to the well known Wilke equation for diffusion of species i through a solution of stagnant k (Sherwood et al., 1975) :

$$D_{i,m} = \frac{1 - y_i}{\sum_{k \neq i} y_k / D_{i,k}} \quad (8)$$

which is strictly valid at infinite dilution.

Kubota et al. (1969) have deduced an expression for the diffusivity relative to the fixed solid :

$$D_{i,m} = \left[\sum_k \frac{y_k - y_i \cdot N_k / N_i}{D_{k,i}} \right]^{-1} \quad (9)$$

which with the modification for a network of reactions introduced in this work results into :

$$D_{i,m} = \frac{\sum_j \delta_j \cdot \alpha_{i,j}}{\sum_k \frac{y_k \cdot \sum_j \delta_j \cdot \alpha_{i,j} - y_i \cdot \sum_j \delta_j \cdot \alpha_{k,j}}{D_{i,k}}} \quad (10)$$

Kubota et al. stated that Eq.(9) supplies a better prediction of the multicomponent diffusion coefficient than Eq.(8). Equation(10) agrees with Eq.(7b) when there is no change in number of moles in each reaction of the system.

Sometime from experimental data, as in the numerical example presented, it is not possible to calculate the reaction rate r_j from the net production rates of species i , R_i . This problem is met in any kinetic network in which not all the reactions are independent. However, the steady state flux ratio is also given by the ratio of the net production rates :

$$N_i/N_k = R_i/R_k \quad (11)$$

Therefore, this procedure can now be used for calculating the

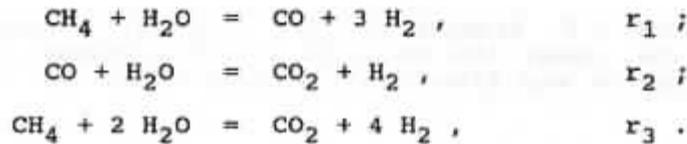
binary molecular diffusivity for species i in the mixture from experimental data, even if the kinetic of the reaction network of the system under investigation is not yet known.

Of course, bulk diffusion coefficient is only one term in the calculation of the effective diffusivity in the porous pellet.

NUMERICAL EXAMPLE

The steam reforming of methane accompanied by water - gas shift on a $\text{Ni/MgAl}_2\text{O}_4$ catalyst will be used to illustrate the method of computation. The intrinsic kinetics of this network of reactions was determined by Xu and Froment (1989).

The reaction scheme is :



Consider a temperature of 823 K, a total pressure of 5 bar and the following partial pressures for the components :

$$\begin{aligned} P_M &= 0.547 \text{ bar}, & P_W &= 3.082 \text{ bar}, & P_H &= 1.259 \text{ bar}, \\ P_D &= 0.1 \text{ bar}, & P_O &= 0.012 \text{ bar}, \end{aligned}$$

using M, W, H, O and D for methane, water, hydrogen, carbon monoxide and carbon dioxide, respectively. The reaction rate values in ($\text{mol/g}_{\text{catal.}}\text{h}$) are :

$$r_1 = 0.4083, \quad r_2 = 5.927 \cdot 10^{-3}, \quad r_3 = 0.1387.$$

The binary diffusion coefficients were obtained using the Fuller et al. (Reid et al., 1987) formula.

$$\begin{aligned} D_{H,W} &= 1.0756 \text{ cm}^2/\text{s} & D_{H,M} &= 0.8377 \text{ cm}^2/\text{s} & D_{H,O} &= 0.9349 \text{ cm}^2/\text{s} \\ D_{H,D} &= 0.7853 \text{ cm}^2/\text{s} & D_{W,M} &= 0.3109 \text{ cm}^2/\text{s} & D_{W,O} &= 0.3083 \text{ cm}^2/\text{s} \\ D_{W,D} &= 0.2469 \text{ cm}^2/\text{s} & D_{M,O} &= 0.2573 \text{ cm}^2/\text{s} & D_{M,D} &= 0.2103 \text{ cm}^2/\text{s} \\ D_{O,D} &= 0.1938 \text{ cm}^2/\text{s} \\ \delta_1 &= 0.73843 & \delta_2 &= 1.072 \cdot 10^{-2} & \delta_3 &= 0.25085 \end{aligned}$$

The diffusion coefficients calculated following Eq. (7b), Eq. (10) and Wilke equation are shown in Table 1.

TABLE 1
Diffusion Coefficients Values
 $D_{i,m}$ in cm^2/s

Diffusion Coefficient	Equation (7b)	Kubota Eq. (10)	Wilke Equation
$D_{M,m}$	0.43266	0.3552	0.63171
$D_{W,m}$	0.8705	0.4409	0.57111
$D_{O,m}$	0.3548	0.3568	0.35714
$D_{D,m}$	0.24319	0.2865	0.29302
$D_{H,m}$	1.0230	1.2098	1.02406

As can be seen, the differences between diffusion coefficients

calculated through Eq.(7b), Eq.(8) or Eq.(10) are as high as 50 %. Nevertheless, for a dilute compound (carbon monoxide) all the equations predict similar values.

The important point here is that Eqs.(7b) or (10) afford a better representation of multicomponent diffusion in a reaction network, rather than the simple Wilke equation appropriate for dilute mixtures.

However, only Eq.(7b) reduces to the equation for multicomponent diffusion with a single reaction and agrees with the Wilke equation for the diffusion for very dilute solutions, as it is clearly demonstrated by the results in Table 1. Kubota et al. equation is a particular case of Eq.(7b).

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Nomenclature

$D_{i,k}$ usual binary diffusivities.
 $D_{i,m}$ pseudobinary diffusivity of species i in the mixture.
 N_i steady state flux of species i .
 r_j reaction rate j .
 R_i production rate of species i .
 S_i species i .
 Y_i mole fraction of species i .

Greek symbols

α_{ij} stoichiometric coefficient of species i in reaction j .
 δ_j parameter defined by Eq.(5).

REFERENCES

- Bird R., Stewart W. and Lightfoot E., "Transport Phenomena", John Wiley, New York (1960).
 Butt J., "Catalytic Effectiveness in Multicomponent and Variable Diffusivity System", *AIChE J.*, **9**, 707 (1963).
 Cunningham R.E., Williams R.J.J.; "Diffusion in Gases and Porous Media" Plenum Press, New York (1980).
 Froment G.F., Bischoff, K.B., "Chemical Reactor Analysis and Design". 2nd Edition. John Wiley, New York (1990).
 Kubota H., Yamanaka Y., Dalla Lana I.G., "Approximate Estimation of Catalyst Effectiveness Factor", *J.Chem.Eng.Japan*, **2**, 71, (1969).
 Reid R., Prausnitz J.M., Poling B.; "The Properties of Gases and Liquids". Fourth Ed., McGraw-Hill. New York (1987).
 Sherwood T., Pigford R., Wilke C.R.; "Mass Transfer". McGraw-Hill. New York (1975).
 Whitaker S., "Concepts and Design of Chemical Reactors", S. Whitaker & A. Cassano Edts., Gordon and Breach Sc. Publ., New York (1986).
 Xu J., Froment G.F., "Methane Steam Reforming, Methanation and Water-Gas Shift. Intrinsic Kinetics", *AIChE J.*, **35**, 88 (1989).