

CRITERIA FOR THE ESTIMATION OF TRANSPORT EFFECTS IN A NETWORK OF HETEROGENEOUS CATALYTIC REACTIONS

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Abstract

Diagnostic criteria for establishing the absence of heat and mass transport limitations in a porous pellet, in which a complex network of heterogeneous catalytic reactions with Langmuir-Hinshelwood kinetics occur, are given. The dimensionless criteria are derived by means of a perturbation technique. They use only observable quantities and so can be easily estimated. The treatment is readily extended to obtain the diagnostic tests for detecting the relative importance of interphase temperature and concentration gradients. The use of the criteria is illustrated by applying them to several specific cases.

Introduction

The heat and mass transfer steps which affect chemical reactions occurring in porous catalyst pellets have received considerable attention in recent years (Satterfield, 1980; Van Parijs and Froment, 1986; Luss, 1977; Gonzo and Gottifredi, 1983a). Under the conditions normally found in laboratory catalytic reactors, heat and mass fluxes can be large enough to cause finite concentration and temperature gradients both within catalyst particles and in the surrounding fluid film. It has been stated that catalytic data should be free from all transport influences to obtain the intrinsic kinetics of the reactions. A number of useful criteria have been developed in the past to assess whether measured catalytic rates are independent of the influence of these parasitic phenomena (Mears, 1971a; Madon and Boudart, 1982; Gonzo and Gottifredi, 1983 b).

Nevertheless, most of these works have been concerned with a single chemical reaction. In many important processes in the petroleum industry, such as cracking, dehydrogenation, hydrogenation, desulfurization, a large number of reactions occur simultaneously, situation which is also met in laboratory studies of such reactions. Only recently attempts have been made to model the more realistic situation of

multicomponent diffusion combined with multiple chemical reactions (Van Parijs and Froment, 1984; Numaguchi and Kikuchi, 1988; Xu and Froment, 1989). Gonzo et al. (1983, 1988) and Gottifredi et al. (1986) have succeeded in predicting analytically the isothermal effectiveness factors for parallel catalytic reactions taking place in a porous pellet of arbitrary geometry. It is well known that one of the most useful aspects of the engineering concept of the effectiveness factor is its use to obtain diagnostic criteria for the kinetic regime of heterogeneous catalytic reactions.

In this paper, using a perturbation technique previously developed (Gottifredi and Gonzo, 1987), general intraparticle transport criteria are derived for a complex network of catalytic reactions with kinetic expressions commonly encountered in catalysis such as those of Langmuir-Hinshelwood. The criteria for detecting interphase transport limitations, as demonstrated by several authors (Cassiere and Carberry, 1973; Gonzo and Gottifredi, 1983b; Froment, 1984) for a single chemical reaction, will be extended to a general set of heterogeneous reactions in series and/or in parallel. Finally, the use of the criteria will be illustrated by applying them to different experimental cases reported in the literature.

Intraparticle transport limitations

Single Particle Analysis

Consider a set of catalytic reactions occurring in a single catalyst pellet. The mass and energy conservation equations can be expressed in dimensionless form as:

$$x^n \frac{dx^n}{dx} \frac{dC_i}{dx} = \sum_j \lambda_{ij} h_j^2 r_j^* \quad (1)$$

for $i = 1, 2, 3, \dots, I$ (species)
 $j = 1, 2, 3, \dots, J$ (reactions)

and

$$x^n \frac{dx^n}{dx} \frac{dT}{dx} = - \sum_j \beta_j h_j^2 r_j^* \quad (2)$$

Where $n = 0, 1, 2$ is to denote slab, cylindrical or spherical geometry; and:

$$C_i = \frac{C'_i}{C'_{i0}}, \quad T = \frac{T'}{T'_s}$$

$$\lambda_{ij} = - \alpha_{ij} \frac{D_{e,i} C'_{i0}}{D_{e,i} C'_{i0}}, \quad r_j^* = \frac{r_j}{r_{j0}} \quad (3)$$

$$x = \frac{x'}{R_p}, \quad h_j^2 = R_p^2 \frac{r_{j0}}{D_{e,j} C'_{i0}}$$

$$\beta_j = \frac{D_{e,i} C'_{i0} (-\Delta H_j)}{K_r T'_s} \quad (4)$$

The prime denote dimensional values.

Eqs. (1) and (2) are subject to the following boundary conditions:

$$\frac{dC_i}{dx} = \frac{dT}{dx} = 0 \quad x = 0$$

$$C_i = T = 1 \quad x = 1 \quad (5)$$

As can be seen, species 1 ($i = 1$) has been selected as the key component. This selection depends in the first place on the operating conditions, the reactions kinetic and on the availability and precision of the required fundamental information.

Finally, parameter δ_j is defined as:

$$\delta_j = h_j^2 / h_1^2 \leq 1 \quad (6)$$

The highest rate of reaction, under the system conditions, is selected as reference reaction ($j = 1$); since taken into account Eq. (4):

$$\delta_j = r_j / r_{j0} \leq 1 \quad (7)$$

In order to judge whether the kinetic regime is achieved, a general accepted criterion is to consider that the deviation from unity of the corresponding effectiveness factor (η_j) be less than five percent. Then the inequality of Eq. (8) must be satisfied:

$$|1 - \eta_j| \leq 0.05 \quad (8)$$

It is known that as $h_j \rightarrow 0$ (mainly $h_1 \rightarrow 0$) the effectiveness factors approaches unity, indicating that the intraparticle heat and mass transport limitations have a negligible influence on the observed reaction rates. When this situation is met, the presence of a small parameter (h_1^2 in this case) in the nonlinear differential Eqs. (1) and (2) naturally suggests the following perturbation solutions for the concentration and temperature profiles:

$$C_i = 1 + A_i(x) h_1^2 + O(h_1^4) \quad (9)$$

$$T = 1 + B(x) h_1^2 + O(h_1^4) \quad (10)$$

Substitution into Eqs. (1) and (2), and collecting terms of the same order in h_1 , the following set of nonlinear ordinary uncoupled equations is found:

$$\frac{dx^n}{dx} \frac{dA_i(x)}{dx} = x^n \sum_j \delta_j \lambda_{ij} \quad (11)$$

$$\frac{dx^n}{dx} \frac{dB(x)}{dx} = - x^n \sum_j \delta_j \beta_j \quad (12)$$

Eqs. (11) and (12) must be solved subject to:

$$\frac{dA_i(x)}{dx} = \frac{dB(x)}{dx} = 0 \quad x = 0$$

$$A_i(x) = B(x) = 0 \quad x = 1 \quad (13)$$

due to boundary conditions (5).

The dimensionless concentrations and temperature profiles in the pellet are then obtained:

$$C_i = 1 + \frac{\sum_j \delta_j \lambda_{ij}}{2(n+1)} (x^2 - 1) h_i^2 + O(h_i^4) \quad (14)$$

$$T = 1 - \frac{\sum_j \delta_j \beta_j}{2(n+1)} (x^2 - 1) h_i^2 + O(h_i^4) \quad (15)$$

With the aim of determining the criteria, η_j must be calculated. It is given by:

$$\eta_j = r_j(\text{ob})/r_{j\infty} = (n+1) \int_0^1 r_j^* x^n dx \quad (16)$$

To solve Eq. (16) it is necessary to know the kinetic expression of reaction r_j . Since reaction $j = 1$ has the highest rate, Eq. (7), and therefore the highest Thiele modulus, the criteria will be deduced for this reaction. So, a general rate equation is considered

$$r_1 = \frac{k_1^r \prod C_i^{n_i} - k_1^r \prod C_i^{m_i}}{[1 + \sum_i K_i C_i^{m_i}]^a} \quad (17)$$

By taking into account Eqs. (14) and (15), the dimensionless expression for r_1^* , neglecting terms of order higher than h_i^2 , is found

$$r_1^* = 1 + h_i^2 \frac{(x^2 - 1)}{2(n+1)} \cdot \sigma \quad (18)$$

where

$$\begin{aligned} \sigma = Q^{-1} [&k_{1v}^r (\prod C_{iv}^{n_i}) (\gamma_1^r b + \sum_i p_i a_i) - \\ &- k_{1v}^r (\prod C_{iv}^{m_i}) (\gamma_1^r b + \sum_i q_i a_i) - \\ &- \alpha K^{-1} [\sum_i K_{iu} C_{iu}^{m_i} (\gamma_i b + m_i a_i)] \end{aligned} \quad (19)$$

and

$$Q = k_{1v}^r \prod C_{iv}^{n_i} - k_{1v}^r \prod C_{iv}^{m_i} \quad K = 1 + \sum_i K_{iu} C_{iu}^{m_i} \quad (20)$$

$$b = - \sum_j \delta_j \beta_j \quad a_i = \sum_j \delta_j \lambda_{ij} \quad (21)$$

$$\gamma_j = E_j / R T_s \quad \gamma_i = \Delta H_i / R T_s \quad (22)$$

By substitution of Eq. (18) into Eq. (16) the effectiveness factor η_1 is obtained, which introduced in Eq. (8) gives the criterion for kinetic control:

$$\frac{r_1(\text{ob}) R_s^2}{D_{e,i} C_{i\infty}'} \leq \frac{0.05 (n+1) (n+3)}{| \sigma |} \quad (23)$$

The criterion established by Eq. (23) is obeyed only if h_i is small, which is the basic assumption stated.

Since intraparticle mass transfer resistance is normally greater than the corresponding heat transport, it is useful to have separately the criteria for checking mass and heat transport effects; specially when the reacting system is exothermic and compensation effect may arise.

In this case, the denominator of the right hand side of Eq. (23) is σ_m or σ_T for checking absence of mass or heat transport effect respectively; where:

$$\sigma_m = \sigma (\gamma_i = \gamma_i = 0) \quad (24)$$

and

$$\sigma_T = \sigma (a_i = 0) \quad (25)$$

The application of the criteria obtained through Eqs. (24) and (25) is somewhat limited by the fact that, the mass transfer criteria assume uniform temperature and the heat transfer criteria assume negligible concentration gradients.

Interphase transport limitations

When external transport phenomena are analyzed mass and heat balances at the outer pellet surface must be considered. The procedure presented by several investigators (Luss, 1977; Gonzo and Gottifredi, 1983b; Cassiere and Carberry, 1973) for the case of a single reaction is extended to a network of reactions.

The mass and heat balances are:

$$(n+1) \left(\frac{C_{i\infty}'}{C_{i\infty}'} - 1 \right) B_{imj} = \sum_j \lambda_{ij} h_j^2 \eta_j \quad (26)$$

$$(n+1) \left(\frac{T_s}{T_s} - 1 \right) B_{it} = - \sum_j \beta_j h_j^2 \eta_j \quad (27)$$

Taking into account the definitions of η_j and h_j

$$\eta_j h_j^2 = \frac{C_{i\infty}'}{C_{i\infty}'} \eta_{j\infty} h_j^2 \quad (28)$$

Eq. (28) when substituted into Eqs. (26) and (27) gives:

$$\frac{C_{io}'}{C_{io}} = 1 + \frac{R_s P_i (\text{ob})}{(n+1) k_{ci} C_{io}'} = 1 + \varepsilon_i \quad (29)$$

$$\frac{T_s'}{T_s} = 1 + \frac{R_s G (\text{ob})}{(n+1) h_e T_s'} = 1 + \varepsilon_T \quad (30)$$

where

$$P_i (\text{ob}) = \sum_j \alpha_{ij} r_j (\text{ob}) \quad (31)$$

$$G (\text{ob}) = \sum_j (-\Delta H_j) r_j (\text{ob}) \quad (32)$$

Sometimes, the relative difference of concentration or temperature (ε_i or ε_T) is enough to check the absence of interphase transport limitations. Nevertheless, to obtain a correct criterion, this must be related with the kinetics of the reaction network occurring in the pellet.

Defining r_j^{\square} as the relation between the rate of reaction j under external pellet surface conditions ($r_{j\sigma}$) and the rate which would prevail if the conditions were the corresponding to bulk fluid phase ($r_{j\mu}$)

$$r_j^{\square} = r_{j\sigma} / r_{j\mu} \quad (33)$$

Then, the criterion to establish the absence of interphase transport limitations can be expressed as:

$$r_j^{\square} - 1 \leq 0.05 \quad (34)$$

Taking into account that for avoiding interphase limitations, ε_i and ε_T must be small, and considering Eqs. (29), (30) and (17); r_i^{\square} results:

$$r_i^{\square} = 1 + \varphi_i \quad (35)$$

with

$$\begin{aligned} \varphi_i = Q_s^{-1} [&k_{ia}^r (\prod_i C_{io}^{r_i}) (\gamma_{ia}^r \varepsilon_T + p_i \varepsilon_i) - \\ &k_{ia}^s (\prod_i C_{io}^{s_i}) (\gamma_{ia}^s \varepsilon_T + q_i \varepsilon_i)] - \\ &\alpha K^{-1} \sum_i K_{im} C_{io}^{im} (\gamma_{im} \varepsilon_T + m_i \varepsilon_i) \end{aligned} \quad (36)$$

where any neglected terms are of order ε_i^2 , ε_T^2 , $\varepsilon_i \varepsilon_T$ or higher. Then, the dimensionless interphase criterion is:

$$1 \leq \frac{0.05}{|\varphi_i|} \quad (37)$$

which is valid whether heat and mass limitations exist inside the particle or not. As can be seen, the criterion is similar in form to Eq. (23).

In general, the heat transfer resistance of the film adjacent to the particle, can be much larger than the resistance inside the particle. In contrast, the principal mass transfer resistance occurs inside the catalyst pellet. Therefore, the film concentration gradient is usually negligible and the external transport limitation is exclusively due to heat transport (Mears, 1971b). Then, it is interesting to have the criterion discriminated for heat and for mass transport influences, which is specially useful for the case of exothermic reacting system where compensation effect occurs.

To obtain the criteria for checking interphase heat or mass transport effects, the denominator of the right hand side of Eq. (37) must be changed by φ_{iT} or φ_{im} respectively, where:

$$\varphi_{iT} = \varphi_i (\varepsilon_i = 0) \quad (38)$$

and

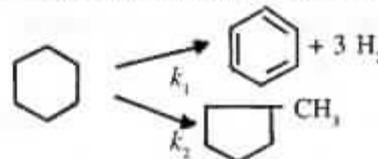
$$\varphi_{im} = \varphi_i (\varepsilon_T = 0) \quad (39)$$

Here, the comment previously done for the use of Eqs. (24) and (25) is also valid.

Examples of use of criteria

I) Allan and Voorhies Jr. (1972) studied the simultaneous dehydrogenation and isomerization of cyclohexane over a halogen free Pt-Al₂O₃ -mordenite catalyst. The experimental runs were made at 686 K, 5.78 atm and 20 mol H₂/mol cyclohexane feed. It was shown experimentally that interphase transport is not rate limiting. When intraparticle effects were checked, by a reduction in catalyst particle size, the data indicated that no internal transport limitations exists for pellets with diameter less than approximately 0.25 mm.

The reaction network can be represented by:



$$\Delta H_1 = 52.5 \text{ Kcal/mol}$$

$$\Delta H_2 = 12.5 \text{ Kcal/mol}$$

Using the information shown in Table 1, the right hand side of inequality in Eq. (23) is found to be 0.626.

Then

The rate equations are:

$$r_1' = k_1 P_c \quad r_2' = k_2 P_c$$

$$\frac{r_1(\text{ob}) R_p^2}{D_{e,c} C_{e1}'} \leq 0.626$$

being P_c the cyclohexane partial pressure in atmospheres.

from which the maximum particle size that can be used, before intraparticle limitations become significant. It is calculated as

Table 1.— Use of criteria

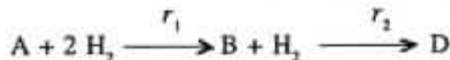
Example (I)		
Catalyst:		
$\rho_p = 0.65 \text{ g/cm}^3$	$S_p = 489 \text{ m}^2/\text{g}$	$\epsilon = 0.75$
$\tau = 2.5$	$K_e = 5.3 \cdot 10 \text{ cal}/(\text{s cm K})$	$\bar{r} = 4.7 \text{ nm}$
Diffusivities:		
$D_c = 1.05 \cdot 10^{-2} \text{ cm}^2/\text{s}$	$D_{K,c} = 1.303 \cdot 10^{-2} \text{ cm}^2/\text{s}$	
$D_{e,c} = 3.15 \cdot 10^{-3} \text{ cm}^2/\text{s}$		
Kinetic parameters:		
$k_1 = 0.04484 \text{ mol}/(\text{g}_{cat} \text{ atm min})$	$E_1 = 14.4 \text{ Kcal/mol}$	
$k_2 = 0.00777 \text{ mol}/(\text{g}_{cat} \text{ atm min})$	$E_2 = 12.5 \text{ Kcal/mol}$	
Example (II)		
Kinetic parameters:		
$k_1 = 9.94 \cdot 10 \text{ min}^{-1}$	$k_2 = 8.38 \cdot 10 \text{ min}^{-1}$	$H = 346.4 \text{ bar} \cdot \text{l/mol}$
$K_p/K_A = 8.68 \cdot 10^2$	$K_D/K_A = 2.89 \cdot 10^2$	$K_{II} = 15.1 \text{ l/mol}$
Effective diffusivities:		
$D_{e,H_2} = 2.84 \cdot 10^{-6} \text{ cm}^2/\text{s}$ $D_{e,A} = D_{e,B} = D_{e,D} = 6.63 \cdot 10^{-7} \text{ cm}^2/\text{s}$		
Example (III)		
Catalyst:		
$\rho_p = 1.4 \text{ g/cm}^3$	$S_p = 57 \text{ m}^2/\text{g}$	$\epsilon = 0.217$
$\tau = 5$	$K_e = 7 \cdot 10^6 \text{ cal}/(\text{s cm K})$	$r = 10^3 \text{ nm}$
Kinetic parameters:		
$\Delta H_1 = 28.2 \text{ Kcal/mol}$	$\Delta H_2 = 4.8 \text{ Kcal/mol}$	$\Delta H_3 = -23.4 \text{ Kcal/mol}$
$K_e = 0.1$		
Effective diffusivities:		
$D_{e,B} = 0.079 \text{ cm}^2/\text{s}$ $D_{e,C} = 0.055 \text{ cm}^2/\text{s}$ $D_{e,D} = 0.346 \text{ cm}^2/\text{s}$		

$$d_p \text{ (max)} = 2 R_0 \text{ (max)} = 0.17 \text{ mm}$$

This value is in close agreement with that experimentally obtained, taking into account the uncertainty involved in the parameter values.

II) The liquid phase hydrogenation of phenolic compounds was studied by Zwicky and Gut (1978); on 5% Pd/C catalyst.

The reaction scheme for the hydrogenation of pure o-cresol (A) to 2-methyl-cyclohexanone (B) and to 2-methyl cyclohexanol (D) is the following:



The kinetic expressions are of the Langmuir-Hinshelwood type, with adsorption of hydrogen and substrate on different active sites of the catalyst

$$r'_1 = \frac{C_T k_1 C'_A}{(C'_A + (K_B/K_A) C'_B + (K_D/K_A) C'_D)(1 + (K_H/H) C'_{H_2})} \quad \frac{(K_H/H) C'_{H_2}}{(K_H/H) C'_{H_2}}$$

$$r'_2 = \frac{C_T k_2 C'_B}{((K_A/K_B) C'_A + C'_B + (K_D/K_B) C'_D)(1 + (K_H/H) C'_{H_2})} \quad \frac{(K_H/H) C'_{H_2}}{(K_H/H) C'_{H_2}}$$

Here r' is the reaction rate in mol/l.min, C_T is the total concentration of phenolic compounds in mol/l. K_A , K_B , K_D and K_H are the adsorption equilibrium constants and H the Henry's law constant for hydrogen solubility.

The reaction was carried out at a constant pressure of 40 bar, a temperature of 393.2 K and a stirrer speed that make the hydrogen liquid absorption resistance negligible. The amount of catalyst used was 1 % by weight with particle of 10^{-4} cm diameter.

The criteria is applied to the system in a point where:

$$C'_{A0} = 0.89 \text{ mol/l} \quad C'_{B0} = 7.12 \text{ mol/l}$$

$$C'_{D0} = 0.89 \text{ mol/l}$$

while

$$C'_{H_2O} = 0.115 \text{ mol/l}$$

Interphase transport

Using the information presented by Zwicky and Gut (1978) and data in Table 1; the relative concen-

trations gradients $\Delta C'/C'_{io}$ in the fluid-solid film result:

$$\epsilon_{H_2} = - 6.03 \cdot 10^{-5} \quad \epsilon_A = - 1.342 \cdot 10^{-5}$$

$$\epsilon_B = 6.94 \cdot 10^{-6} \quad \epsilon_D = 7.86 \cdot 10^{-6}$$

which when compared with the bulk concentrations, indicate that the mass transport effects in the film are negligible.

Applying the criteria, Eq. (37), assuming $\epsilon_T = 0$

$$1 \leq 1.58 \cdot 10^3$$

which tell us that interphase transfer resistances do not affect the experimental results.

Intraparticle transport

By taking the hydrogen as the key component and using the information given in Table 1, a value of 0.259 results for the right side of the criterion Eq. (23), considerably exceeding the value of 0.0012 for the left side.

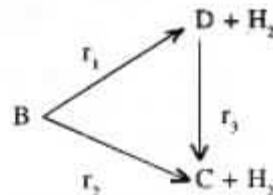
Hence, insignificant intraparticle mass transport limitations are indicated for this case.

The maximum particle diameter that could be used is:

$$2 \cdot R_0 \text{ (max)} = d_p \text{ (max)} = 15 \cdot 10^{-4} \text{ cm}$$

which means that under these experimental conditions, it is possible to use particles of approximately 15 μm diameter before detecting transport influences on the rate data.

III) Finally, the butadiene (D) production by dehydrogenation of 1-butene (B) and the simultaneous coking (C) from butene and butadiene over a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst is studied. The kinetic of this network of reactions was determined by Dumez and Froment (1976).



The set of rate equations are:

$$r_1' = \frac{3.154 \cdot 10^7 \exp(-29236/RT) (P_B - P_B P_D / K_p)}{(1 + 1.727 P_B + 3.593 P_H + 38.028 P_D)^2} \exp(-42.12 C_c)$$

nary mixture of B and *i*. The flux relationships can be easily established by the reaction stoichiometry for a single reaction (Butt, 1963). It is introduced the following expression for the flux relationships in the case of a network of reactions:

$$r_2'' = \frac{3.117 \cdot 10^6 \exp(-32800/RT) P_B^{0.743}}{(1 + 1.695 \sqrt{P_H})^2} \exp(-45.53 C_c)$$

$$N_i/N_B = \frac{\sum_j \delta_j \alpha_{ij}}{\sum_j \delta_j \alpha_{Bj}} \quad (41)$$

The effective diffusivity for species *i* is given by the expression:

$$r_3'' = \frac{1.0216 \cdot 10^4 \exp(-21042/RT) P_B^{0.853}}{(1 + 1.695 \sqrt{P_H})^2} \exp(-45.53 C_c)$$

$$D_{e,i} = \frac{\epsilon}{\tau} \left(\frac{1}{D_{k,i}} + \frac{1}{D_{i,m}} \right)^{-1}$$

The criterion for freedom from intraparticle limitations can be obtained directly from Eq. (23). The dimensionless group of the left of the criterion, for catalyst particle diameter of 0.4 mm is:

Where *P_i* is the partial pressure of component *i* in atm, *C_c* is the coke content of the catalyst in g_{coke}/g_{cat} and activation energy is given in cal/mol. *r₁'* is expressed in mol/g_{cat} · h, *r₂'* and *r₃'* are expressed in g_{coke}/g_{cat} · h.

The catalyst used was a Cr₂O₃-Al₂O₃ catalyst containing 20 wt % Cr₂O₃. The properties of this catalyst as well as value of the different parameters are given in Table 1.

The authors had shown that interphase transport limitations are negligible.

The analysis is carried out after two minutes of reaction at 873K where the conditions are:

$$P_B = 0.204 \text{ atm} \quad P_D = 0.022 \text{ atm}$$

$$P_H = 0.024 \text{ atm}$$

and

$$C_c = 0.76 \cdot 10^{-2} \text{ g}_{\text{coke}}/\text{g}_{\text{cat}}$$

The binary diffusion coefficients were obtained using the Fuller et al. formula (Reid et al., 1987). The mean binary diffusion coefficient *D_{B,m}* of component B in the multicomponent mixture was calculated according to the Stefan-Maxwell equation (Froment and Bischoff, 1979):

$$D_{B,m} = \frac{1 - y_B \sum_{i=1}^I N_i/N_B}{\sum_{i=1}^I \frac{y_i - y_B N_i/N_B}{D_{B,i}}} \quad (40)$$

where *N_i* is the component *i* flux, *y_i* its mole fraction and *D_{B,i}* the molecular diffusion coefficient for bi-

The criterion for freedom from intraparticle limitations can be obtained directly from Eq. (23).

The dimensionless group of the left of the criterion, for catalyst particle diameter of 0.4 mm is:

$$\frac{r_1(\text{ob}) R_*^2}{D_{e,B} C_{B0}} = 2.91 \cdot 10^{-2}$$

and the right hand side:

$$\frac{0.75}{9.8754 + 0.1785} = 7.46 \cdot 10^{-2}$$

where 9.8754 came from the mass transfer contribution and 0.1785 from the heat transport.

As it can be seen the criterion is satisfied and it can be concluded that the reaction system is free of all transport influences.

Also, the limiting particle diameter for which the kinetic regime is ensured can be calculated:

$$2 \cdot R_o(\text{max}) = d_p(\text{max}) = 0.64 \text{ mm}$$

To avoid internal transport influences, catalyst particles of *d_p* = 0.4 mm were used by Dumez and Froment in experiment at 873 K, which is in agreement with the result obtained applying the criterion.

Conclusions

Criteria for evaluating the significance of interphase and intraparticle transport limitations in a complex network of catalytic heterogeneous reac-

tions, have been developed. If the criteria are obeyed, one can be sure that the observed kinetic data are those correspondent to true reaction rates and free of transport artifacts.

In the case of exothermic reacting system, the denominator of the right side of the criteria, Eqs. (23), (37) can be close to or equal to zero. When this occurs, the heat effect compensates for the diffusion effects. For this peculiar case it is better to apply the diagnostic test separately for checking mass and heat transfer effects. For endothermic system, the full criteria must be applied, since both effects add up to each other.

The main disadvantage of theoretical criteria is that they require knowledge of the kinetic expressions and the value of the associated parameters. Nevertheless, the conclusion based on theoretical calculations of the possible role of transport processes are frequently more reliable and less time consuming (Temkin, 1979).

Finally, the philosophy of using these criteria should be conservative and when diagnostic tests are slightly fulfilled more precise parameter estimation is needed before neglecting heat and mass transport effects.

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Nomenclature

B_{ie}	Biot number for heat transport
B_{im}	Biot number for mass transport of species i
$D_{e,i}$, D_i , $D_{k,i}$	effective, molecular and Knudsen diffusivity of component i
d_p	pellet diameter
E	apparent activation energy of reaction j
G (ob)	observed heat generation rate
h_c	heat transfer coefficient in the film
h_j	Thiele modulus for reaction j
k_{ci}	mass transfer coefficient for species i in the film
P_i (ob)	observed production rate of species i
q_i	reaction order for species i , reverse reaction
r_j	rate of reaction j per unit pellet volume
r_j'	rate of reaction j per unit mass of catalyst
\bar{r}	mean pore radius

R_0 characteristic length of the pellet

Greek letters

α_i	stoichiometric coefficient of species i in reaction j
β_j	Prater number for reaction j
γ_j	Arrhenius number
ΔH_j	heat of reaction j
ΔH_i	heat of adsorption of species i
ϵ	catalyst porosity
η_j	catalyst effectiveness factor for reaction j
κ_c	effective thermal conductivity of catalyst pellet
ρ_p	pellet density
τ	tortuosity factor

Subscripts

s	external pellet surface value
o	bulk fluid phase value
ob	observed

Superscripts

f	parameters for the forward reaction
R	parameters for the reverse reaction

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