

THE INTERPHASE CATALYTIC EFFECTIVENESS FACTOR: Activity, Yield and Non-isothermality

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An essential component of any course in Chemical Reaction Engineering is the Diffusion-Catalytic Reaction topic. In an introductory course, it is deemed imperative that the student gain an insight into the key features which characterize the behavior of a reaction network in which diffusion of heat and/or mass affects the observed, global rate of catalytic reaction. In sum, how does heat and mass transport intrusions affect:

- activity for various reaction orders?
- Yield/selectivity for multipathed reaction networks?
- Observed reaction order and activation energy? and finally
- how can diffusional intrusions be detected in terms of laboratory observables?

We acknowledge two regions of diffusional transport in the typical porous solid catalyzed reaction:

- 1) Intraphase; diffusion of heat and mass within the porous catalyst with simultaneous reaction.
- 2) Interphase: Diffusion of heat and mass through boundary layers surrounding the catalyst pellet or extrusion. Reaction occurs in series with interphase (external) diffusion.

The global (observed) rate is that phrased in terms of observables. In general, external surface and internal concentrations and temperatures are beyond direct measurement. So a global rate, R_o is

$$R_o = k_x g(C_o)^\alpha$$

where k_x is a rate coefficient based upon observed rate, concentration C_o and order α . The intrinsic, surface catalytic rate is, of course, a complex function of surface concentrations and temperature. Thus the concept of catalytic effectiveness (Thiele) was invoked and elaborated to relate the

intrinsic rate function to the observed functionality.^{1,2,3}

Insofar as one or more steps of a complex, multipathed, reaction network can be altered by diffusion of heat and/or mass, yield/selectivity can be affected. By yield we mean the rate of desired product formation relative to that of key reactive consumption. Selectivity is merely the ratio of two-point yields.

Isothermal Inter-intraphase Effectiveness and Yield

The modern undergraduate readily handles the problems of isothermal first order reaction with both external and internal diffusional events. For a flat plate

$$D \frac{d^2 C}{dx^2} = k_o C \quad (1)$$

with b.c.

$$x = L \quad k_g (C_o - C) = -D \frac{dC}{dx}$$

$$x = 0 \quad dC/dx = 0$$

the solution to which is in terms of overall catalytic effectiveness

$$\eta = \frac{\frac{1}{L} \int_0^L k_o C dx}{k_o C_o} \quad (2)$$

is

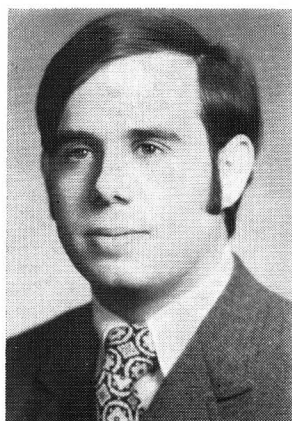
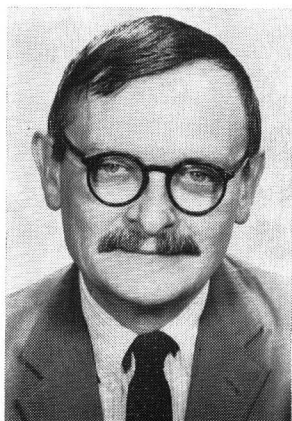
$$\eta = \frac{\tanh \phi}{\phi \left[1 + \frac{\phi \tanh \phi}{(Bi)_m} \right]} \quad (3)$$

where

$$\phi = L \sqrt{\frac{k_o}{D}} = \text{Thiele Modulus}; (Bi)_m = \frac{k_g L}{D} = \text{Mass Biot Number}$$

The diffusion affected yield for consecutive reaction is also readily analyzed by the undergraduate for isothermal conditions.^{2,4}

However, for nonlinear kinetics and non-isothermal environments, analytical solutions are not to be found, and the more sophisticated approximate mathematical treatments are usually beyond the undergraduate, or if within his grasp, the very journey through that mathematical jungle may cause the student to lose sight of the physics of the problem and the engineering consequences. A simple alternative exists requiring no more than the use of a slide rule, whereby key features of the more complex internal diffusion-



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reaction problem become manifest. We simply deal with the external (interphase) problem.

Isothermal External Diffusion-Reaction

In steady state reaction of n th order over a flat nonporous catalytic plate, equating mass transport to surface reaction, we have

$$k_g a (C_o - C) = k_s C^n \quad (4)$$

Dividing by $k_g a C_o$, where $f = C/C_o$

$$1 - f = \left[\frac{k_o C_o^{n-1}}{k_g a} \right] f^n = Da_o f^n \quad (5)$$

where

$$Da_o = \frac{k_o C_o^{n-1}}{k_g a} = \text{Damköhler Number}$$

External isothermal effectiveness is

$$\eta = \frac{\text{Actual Surface rate at } C}{\text{Rate if } C = C_o} \quad (6)$$

or

$$\eta = \frac{k_o C^n}{k_o C_o^n} = \left(\frac{C}{C_o} \right)^n = f^n$$

Equation (5) is easily solved for $n = 1, 1/2, 2$ and -1 . The negative first order reflects abnormal kinetics (i.e. rate increases with conversion). Such a case is found in transition metal

catalyzed oxidation of CO at CO concentrations above 1%.⁵ The solutions are:

$$n = 1 \quad \eta = \frac{1}{1 + Da_o} \quad (7)$$

$$n = 1/2 \quad \eta = \sqrt{\frac{(2 + Da_o^2)}{2} \left[1 - \sqrt{1 - \frac{4}{(2 + Da_o^2)^2}} \right]} \quad (8)$$

$$n = 2 \quad \eta = \left[\frac{\sqrt{1 + 4 Da_o} - 1}{2 Da_o} \right]^2 \quad (9)$$

$$n = -1 \quad \eta = \frac{2}{1 + \sqrt{1 - 4 Da_o}}, \text{ no solution exists for } Da_o > 1/4 \quad (10)$$

These external isothermal effectiveness factors are displayed in Figure 1 on log-log co-ordinates. The similarity to internal effectiveness behavior for linear and nonlinear kinetics is evident. We learn by this simple arithmetic manipulation that

- The greater the reaction order, the greater the diffusional taxation for a given value of Da_o .
- An effectiveness greater than unity is possible if an adsorbable species inhibits the rate.
- At large values of the modulus, all η values approach the reciprocal of the modulus.

Now the global rate is, of course,

$$R_o = \eta k_o C_o^n \quad (11)$$

At large values of Da_o , $\eta \rightarrow 1/Da_o$

$$R_o = \frac{k_o}{\frac{k_o C_o^{n-1}}{k_g a}} \cdot C_o^n = k_g a C_o$$

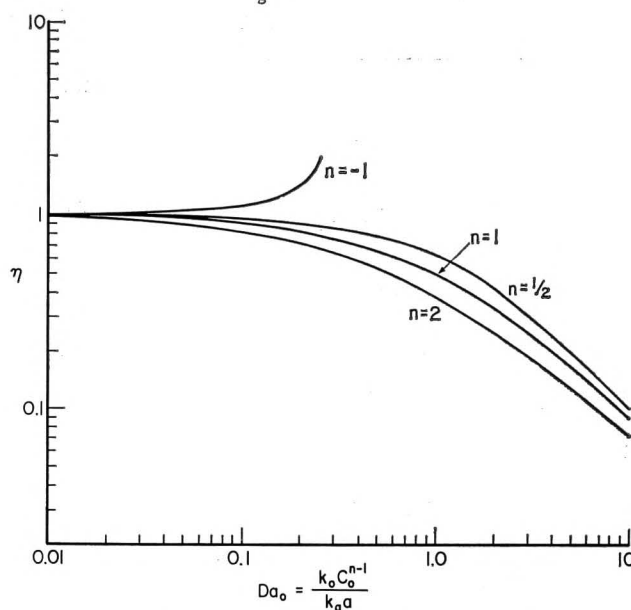


Fig. 1. Isothermal External Catalytic Effectiveness for Reaction Order n

so the experimental rate coefficient k_x is $k_g a$ and the reaction order changes from n to unity. Activation energy changes from its true value when $\eta = 1$ to a small value characteristic of a mass transfer coefficient $k_g a$.

The students readily realize however that Fig. 1, while instructive, is of little use unless k_o is known *a priori* to permit computation of Da_o . They soon learn that Fig. 1 is easily re-expressed in terms of observables. Dividing both sides of equation (11) by $k_g a C_o$

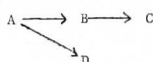
$$\frac{R_o}{k_g a C_o} = \eta \frac{k_o}{k_g a} C_o^{n-1} = \eta Da_o \quad (12)$$

Hence by replotting Fig. 1 in terms of η vs ηDa_o , we secure Fig. 2 which permits determination of η from the observed rate R_o , bulk concentration C_o and a calculatable transport coefficient $k_g a$. Fig. 2 also teaches that the ultimate observed rate is that of bulk mass transport, i.e., at $\eta Da_o = 1$. Aris* points out that by eq's (7-10) and (5) Figure 2 obeys the equation:

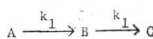
$$\eta = (1 + \eta Da_o)^n$$

Isothermal Yield/Selectivity

A multipathed network, such as



is obviously a combination of consecutive and simultaneous reaction. Consider consecutive reaction



In the absence of mass diffusional limitations, surface concentrations equal those in the bulk stream, so for linear kinetics

$$-R_A = k_1 A_o \quad (13)$$

$$R_B = k_1 A_o - k_2 B_o$$

Dividing, we secure the point yield

$$-\frac{dB}{dA} = Y_B = 1 - \frac{k_2}{k_1} \frac{B_o}{A_o} \quad (14)$$

Anticipating diffusion, then

$$k_g a (A_o - A) = k_1 A \quad (15)$$

$$k_g a (B - B_o) = k_1 A - k_2 B \quad (16)$$

and solving for B, then the ratio of rates (yield)

Solving for A in (15), substituting in (16)

is

$$-\frac{dB}{dA} = Y_B = \frac{1}{1 + Da_2} - \frac{k_2}{k_1} \frac{(1 + Da_1)}{(1 + Da_2)} \frac{B_o}{A_o} \quad (17)$$

or

$$Y_B = \eta_2 - \frac{\eta_2 k_2}{\eta_1 k_1} \frac{B_o}{A_o} \quad (18)$$

*Aris, R. Personal Communication Sept. 1972.

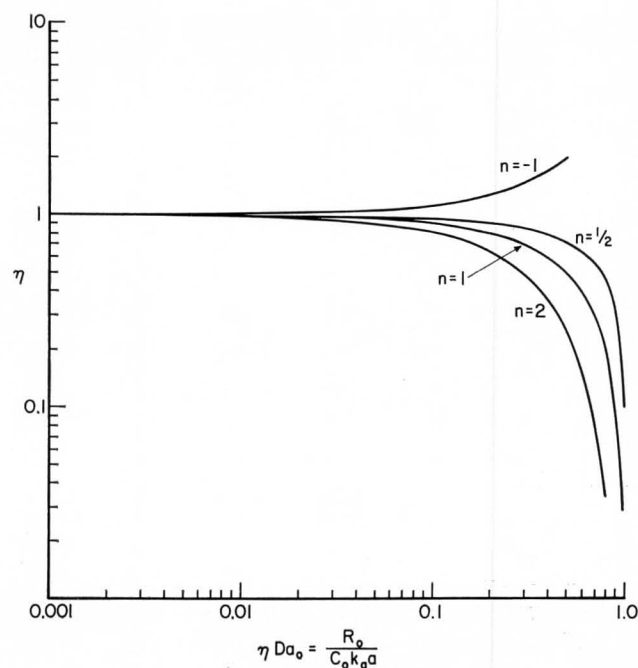


Fig. 2. Isothermal External Catalytic Effectiveness in terms of Observables for orders n

When $B_o = 0$, initial point yield is

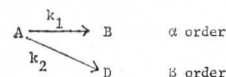
$$-\frac{dB}{dA} = \frac{1}{1 + Da_2} \quad (19)$$

or selectivity is, when $B_o = 0$

$$\frac{dB}{dC} = \frac{1}{Da_2} = \frac{k_g a}{k_2} \quad (20)$$

Thus with mass diffusion, the survival of B depends upon the ratio of the escape rate from the surface to its rate of destruction on the surface.

For simultaneous reaction



Selectivity,
$$s = \frac{dB}{dD} = \frac{k_1}{k_2} A_o^{\alpha-\beta} \quad (21)$$

With no diffusional gradient

$$S_o = \frac{k_1}{k_2} A_o^{\alpha-\beta} \quad (22)$$

OR

$$\frac{S}{S_o} = \frac{k_1/k_2}{(k_1/k_2)_o} \left(\frac{A}{A_o} \right)^{\alpha-\beta} \quad (23)$$

Isothermal selectivity alteration is then

$$s/s_o = \left(\frac{A}{A_o} \right)^{\alpha-\beta} \quad (24)$$

As $A < A_o$, we readily see that when $A < A_o$ (diffusion intrusion)

$\alpha = \beta$ no affect upon selectivity

$\alpha > \beta$ selectivity for B declines

$\alpha < \beta$ selectivity for B improves

This finding follows from Fig. 1: The reaction of highest order is most taxed by mass diffusion.

Non-isothermal Effectiveness and Yield

Here the analysis in terms of external effectiveness is truly fruitful since the corresponding internal problem is only solved rigorously by numerical means even for linear kinetics.^{6,7,8,9}

The non-isothermal external effectiveness is

$$\bar{\eta} = \frac{k}{k_0} \left(\frac{C}{C_0} \right)^n \quad (25)$$

The linear case is quite easily handled in terms of observables as follows:*

*In view of equations (5) and (25), the non-isothermal external effectiveness for any order is

$$\bar{\eta} = \frac{k}{k_0} (1 - \bar{\eta} Da_0)^n$$

k the rate coefficient as the surface temperature is, relative to k_0

$$k = k_0 \exp \left[-\epsilon \left(\frac{1}{t} - 1 \right) \right] \quad (26)$$

where $\epsilon = E/RT_0$ and $t = T/T_0$

$$\text{also } \frac{C}{C_0} = \frac{1}{1 + Da} \text{ and } Da = Da_0 \exp \left[-\epsilon \left(\frac{1}{t} - 1 \right) \right] \quad (27)$$

$$\text{so } \bar{\eta} = \frac{\exp \left[-\epsilon \left(\frac{1}{t} - 1 \right) \right]}{1 + Da_0 \exp \left[-\epsilon \left(\frac{1}{t} - 1 \right) \right]} \quad (28)$$

$$\text{rearranging } \bar{\eta} = (1 - \bar{\eta} Da_0) \exp \left[-\epsilon \left(\frac{1}{t} - 1 \right) \right] \quad (29)$$

Note that $\bar{\eta} Da_0 = \frac{R_0}{C_0 k_0 a}$, is the observable.

We now evaluate t by heat balance

$$ha(T - T_0) = (-\Delta H) R_0$$

we divide both sides by $k_g a C_0 T_0$

$$\frac{h}{k_g C_0} (t-1) = \left(\frac{-\Delta H}{T_0} \right) \frac{R_0}{k_g a C_0} = \left(\frac{-\Delta H}{T_0} \right) \bar{\eta} Da_0$$

Invoking the j factor analogy

$$\frac{k_g}{u} (Sc)^{2/3} = \frac{h}{\rho u C_p} (Pr)^{2/3}$$

then

$$\frac{h}{k_g} = \rho C_p \left(\frac{Sc}{Pr} \right)^{2/3}$$

thus

$$t = 1 + \left[\frac{(-\Delta H) C_0}{\rho C_p T_0} \right] \bar{\eta} Da_0 (Le)^{2/3} \quad (30)$$

or

$$t = 1 + \beta \bar{\eta} Da_0 \text{ where } \beta = \left[\frac{(-\Delta H) C_0}{\rho C_p T_0} \right] (Le)^{2/3}$$

and Le is the Lewis number D/α .

The student now chooses a value of ϵ , and β as fixed. Then for a series of $\bar{\eta} Da_0$ values (say 0.001 to the limiting value of unity), he or she* computes t and by equation (29) the $\bar{\eta}$ - $\bar{\eta} Da_0$ values are obtained. This simple procedure is re-

*Ycs, Virginia, there is a co-ed Notre Dame

peated at other positive (exothermic) and negative (endothermic) value of β for the fixed ϵ . Results are shown in Figs. 3 and 4 for ϵ of 20 and 10, and a range of β values.

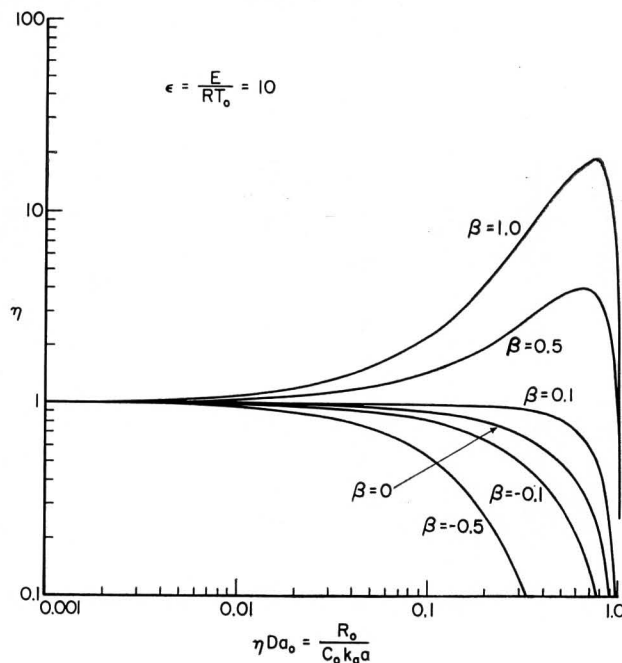


Fig. 3. Non-isothermal External Catalytic Effectiveness in terms of Observables—First Order, $\epsilon = 10$

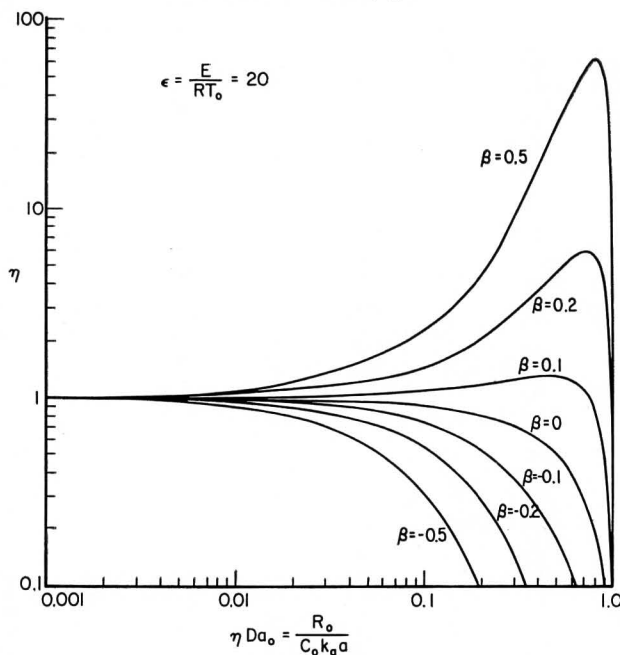


Fig. 4. Non-isothermal External Catalytic Effectiveness in terms of Observables—First Order, $\epsilon = 20$

We see that the chief characteristics of the non-isothermal intraphase (internal) effectiveness factor are displayed by the very easily calculated external effectiveness behaviour:

- (a) $\bar{\eta}$ values much greater than unity are found for exothermic reactions.
- (b) the Arrhenius number, ϵ is more important than β in determining $\bar{\eta}$ and
- (c) at high values of the modulus $\bar{\eta}$ falls well below unity.

Yield/selectivity in a non-isothermal atmosphere is readily treated. In equations (17) and (23), the ratio k_1/k_2 at surface temperature appears. This ratio relative to its value at bulk temperature T_0 , is

$$\frac{(k_1/k_2)_T}{(k_1/k_2)_0} = \exp \left[-\Delta\epsilon \left(\frac{1}{t} - 1 \right) \right]$$

where

$$\Delta\epsilon = \epsilon_1 - \epsilon_2 = \frac{(E_1 - E_2)}{RT_0}$$

A valuable qualitative insight into non-isothermal yield/selectivity trends is secured by the student by consideration of Fig. 5.

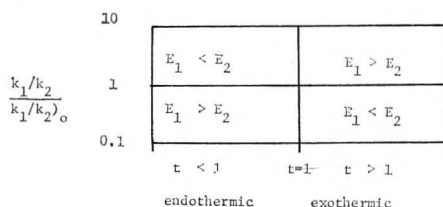


Fig. 5. Yield/Selectivity Trends in Non-Isothermal Atmosphere.

In the light of Fig. 5, consider non-isothermal selectivity in simultaneous reaction, equation (23)

$$\frac{s}{s_0} = \frac{k_1/k_2}{(k_1/k_2)_0} \left(\frac{A}{A_0} \right)^{\alpha-\beta} \quad (23)$$

From a knowledge of the sign of $\Delta\epsilon$ and the thermochemistry of the reactions, the student can predict whether mass and heat transfer limitation will enhance or tax selectivity, or over a range of conditions the heat transport limitation may just compensate the taxation of mass transport.

Transient Isothermal Effectiveness

The analysis of transient external effectiveness is also simple yet instructive. Consider a case where reactant is exposed to the catalytic surface at $\tau = 0$. A first order reaction is assumed under isothermal conditions. What is the $\eta\tau$ relationship?

$$k_g a(C_0 - C) = kC + \frac{dC}{d\tau}$$

or

$$1 - \eta = Da_0 \eta + \frac{d\eta}{d\theta}$$

where

$$\eta = C/C_0 \text{ and } \theta = k_g a \tau$$

the desired solution is

$$\eta = \frac{Da_0 + \exp \theta}{(1 + Da_0) \exp \theta}$$

Which is more conveniently expressed in terms of η at any time relative to η_{ss} at final steady-state.

$$\frac{1 - \eta}{1 - \eta_{ss}} = \frac{\exp \theta - 1}{\exp \theta}$$

This equation teaches that the dimensionless group $k_g a \tau$ determines the rate of approach to steady-state. In the case of the internal effectiveness in transient, approach to steady-state is governed by an analogous dimensionless group

$$\theta^* = \frac{D\tau}{L^2}$$

where D is internal diffusivity and L the pellet dimension¹⁰

Practical Applications

While the primary purpose of the development of external effectiveness is its instructive value in shedding light on the internal problem, it should not be forgotten that there exists some quite important catalytic systems involving gaseous reaction over nonporous catalysts. For example, NH_3 is oxidized to NO and HCN is synthesized from NH_3 , O_2 and methane over platinum alloy wire matrices. Methanol may be oxidized to formaldehyde over nonporous silver. Such systems are susceptible to analyses in terms of the external effectiveness.

Conclusions

The diffusion-reaction problem is profitably viewed in terms of external mass and heat transport affected activity and selectivity in a simple analytical fashion with readily calculated results which bear very fruitful analogy to features revealed by the often much more difficult-to-solve internal diffusion-reaction problems. \square

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