

On the Relative Importance of External-Internal Temperature Gradients in Heterogeneous Catalysis

The fraction of the total temperature difference, between bulk fluid and center of a porous catalyst, which resides in the external fluid film is set forth simply in terms of the *observed* global rate parameter and the *ratio* of the mass to thermal Biot numbers. The derived theoretical relationship compares quite favorably with the experimental data of Kehoe and Butt.

Introduction and Background

Following Hutchings' revelation (1966), which declared unequivocally that in a gas-solid catalyzed reaction, the major seat of temperature difference will most likely be external (fluid film), while concentration gradients can be expected to prevail primarily within the porous catalyst, a number of workers have focused attention upon this problem. The most telling analysis has been developed by Lee and Luss (1969), who justly refined the rather primitive quantitative assessment of the relative magnitude of external/internal temperature gradient ratio suggested by Carberry (1966), for the approach of Lee and Luss is marked by rigor and a respect for observables.

The problem is meaningfully reviewed as follows. Catalytic reaction under nonisothermal conditions within a porous flat plate is governed by mass

$$D \frac{d^2C}{dx^2} = kC^n \tag{1a}$$

heat

$$\lambda \frac{d^2T}{dx^2} = kC^n(-\Delta H) \tag{1b}$$

Subject to boundary conditions which anticipate external temperature and concentration gradients, which boundary conditions are: pellet center,  $dc/dx = dT/dx = 0$ ; surface,  $x = L$ ; mass

$$k_g(C_0 - C) = -D \left. \frac{dc}{dx} \right|_{x=L} \tag{2a}$$

heat

$$h(T - T_0) = -\lambda \left. \frac{dT}{dx} \right|_{x=L} \tag{2b}$$

Casting eq 2 in dimensionless terms where  $f = C/C_0$ ,  $z = x/L$ ,  $t = T/T_0$ , we obtain

$$\frac{k_g L}{D} = \frac{-df/dz}{1-f} = \text{mass Biot Number} \tag{3}$$

$$\frac{hL}{\lambda} = \frac{-dt/dz}{t-1} = \text{thermal Biot number}$$

or

$$\text{Biot} = \frac{\text{internal gradient}}{\text{external gradient}} \tag{4}$$

Thus it was that Hutchings (1966) was the first to appreciate that the ratio of mass to thermal Biot numbers should grant us an indication as to where we might expect that the major seat of temperature/concentration gradient should be expected to exist. Assessing the ratio  $(Bi)_m/(Bi)_h$  for gas-porous solid systems, it became evident that that ratio  $r$  assumes values of from about 10 to  $10^5$ , so we

declared in a joint voice apparently inaudible to certain Anglo-Saxon ears, that (a) the major  $\Delta T$  could be expected to be external (interphase) while (b) the concentration gradient can be assumed to be focused largely in the internal (intrapphase) region.

Lee and Luss (1969), being equipped with sound ears and minds, carried the matter further by a fine quantitative analysis which resulted in an equation relating external  $\Delta T_x$  relative to the total  $\Delta T_0$ , phrased in terms of the heat and mass Biot numbers and the observable (Weisz) parameter,  $\phi$ , for a sphere

$$\frac{\Delta T_x}{\Delta T_0} = \frac{\phi/3 (Bi)_h}{\left(1 + \frac{\phi}{3} \left(\frac{1}{(Bi)_h} - \frac{1}{(Bi)_m}\right)\right)} \tag{5}$$

where

$$\phi = \frac{R^2 R_0}{DC_0}$$

and  $R$  = sphere radius;  $D$ , intraphase diffusivity and  $R_0$ , the observed rate.

Present Analysis

Telling as the Lee-Luss analysis is, it requires knowledge of  $\phi$ ,  $(Bi)_m$ , and  $(Bi)_h$  for its implementation. We present herein a treatment developed in the spirit of the Lee-Luss work, yet yielding a  $\Delta T_x/\Delta T_0$  result coined solely in terms of an observable and the *ratio* of Biot numbers.

As Wheeler (1951) and Prater (1958) have shown, the internal  $\Delta T_i$  is secured by eliminating the species chemical generation terms in eq 1a and 1b, so

$$\Delta T_i = \frac{(-\Delta H)D(C_s - C_m)}{\lambda}$$

or

$$\frac{\Delta T_i}{T_s} = \beta \text{ (the Prater number)} \tag{6}$$

which is the maximum  $\Delta T_i$  when  $C_m = 0$  at the pellet center.

The external  $\Delta T_x$  is obtained by a heat balance across the fluid film

$$h_a(T_s - T_0) = R_0(-\Delta H) \tag{7}$$

where  $R_0$  is the observed reaction rate. Dividing (7) by  $k_g a C_0$

$$\Delta T_x = \left[ \frac{R_0}{k_g a C_0} \right] (-\Delta H) C_0 \left( \frac{k_g}{h} \right) \tag{8}$$

But by the heat-mass transport analogy

$$\frac{k_g}{h} = \frac{1}{\rho C_p Le^{2/3}}$$

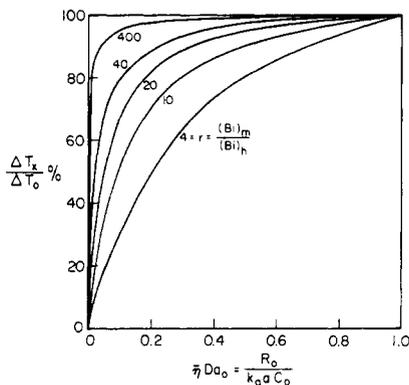


Figure 1. % of total inter-intraphase temperature difference which resides in the external gas film for various values of  $r$ .

where  $Le$  is the Lewis number for the fluid, equal to  $Sc/Pr$ . Equation 8 then assumes the form

$$\frac{\Delta T_x}{T_0} = \left[ \frac{R_0}{k_g a C_0} \right] \frac{(-\Delta H) C_0}{\rho C_p Le^{2/3} C_0} = \bar{\eta} Da \cdot \bar{\beta} \quad (9)$$

where

$$R_0/k_g a C_0 =$$

$\bar{\eta} Da$ , an *observable* (Cassiere, 1973), where  $\bar{\eta}$  is an inter-intraphase effectiveness and

$$Da = \left[ \frac{k_0 C_0^{n-1}}{k_g a} \right]$$

while

$$\bar{\beta} = \frac{(-\Delta H) C_0}{\rho C_p Le^{2/3}} \quad (10)$$

The total (internal-external)  $\Delta T_0$  is given by the sum of eq 6 and 9, once eq 6 is expressed in terms of  $C_0$  rather than  $C_s$ . Equating local mass transport to reaction

$$k_g a (C_0 - C_s) = \eta_i k_s C_s = R_0$$

Dividing by  $k_g a$  and recalling the definition of the observable, then

$$C_s = C_0(1 - \bar{\eta} Da) \quad (11)$$

and so eq 6 becomes ( $C_m = 0$ )

$$\Delta T_i = \frac{(-\Delta H) DC_0}{\lambda} (1 - \bar{\eta} Da)$$

or

$$\frac{\Delta T_i}{T_0} = \beta_0 (1 - \bar{\eta} Da) \quad (12)$$

where

$$\beta_0 = \frac{(-\Delta H) DC_0}{\lambda T_0}$$

and so the overall  $\Delta T_0$  is then the sum of eq 9 and 12

$$\frac{\Delta T_0}{T_0} = \frac{\Delta T_x + \Delta T_i}{T_0} = \bar{\eta} Da \cdot \bar{\beta} + \beta_0 (1 - \bar{\eta} Da) \quad (13)$$

Now  $\beta_0$  is related to  $\bar{\beta}$  by the relation

$$\frac{\bar{\beta}}{\beta_0} = \frac{\lambda}{D \rho C_p Le^{2/3}} \quad (14)$$

or by eq 9, 3, and 4

$$\frac{\bar{\beta}}{\beta_0} = \frac{(Bi)_m}{(Bi)_h} = r \quad (15)$$

So it is that the external gradient  $\Delta T_x$ , relative to the total (external + internal) gradient  $\Delta T_0$ , is given by division of eq 9 by eq 13 with the result, utilizing eq 15

Table I. Comparison of Predictions of Theory (Eq 16) with Experimental Data of Kehoe and Butt (1972)

Run no.	$r^a$	$\eta Da \times 10^3$	$\Delta T_0$ °C	$(\Delta T_x / \Delta T_0)_{pred}$	$(\Delta T_x / \Delta T_0)_{exp}$
8	20	2.45	8	0.05	0.07
9	20	3.75	9	0.07	0.11
10	20	2.17	0	0.04	nil
20	20	12.0	22	0.20	0.3
21	20	8.25	13	0.14	0.15
22	20	7.0	10	0.10	nil
23	20	17.5	37	0.26	0.27
24	20	7.2	30	0.13	0.13
25	20	47.0	30	0.085	0.07
26	20	25.6	100	0.33	0.37
27	20	8.7	51	0.15	0.14
28	20	4.35	40	0.08	0.1

<sup>a</sup> For  $r = 300$  all runs indicate  $(\Delta T_x / \Delta T_0)_{exp}$  of about 100% in accord with eq 16.

$$\frac{\Delta T_x}{\Delta T_0} = \frac{r(\bar{\eta} Da)}{(1 + (\bar{\eta} Da)(r - 1))} \quad (16)$$

Hence the importance of the external temperature gradient is related to the parameters: (1) the ratio of mass to thermal Biot numbers, eq 15, and (2) an observable phrased solely in terms of the observed global rate, bulk concentration, and a readily computed bulk mass transport coefficient,  $k_g a$ .

Equation 16 is displayed in Figure 1. The relationship between our finding (eq 16) and that of Lee and Luss, must, of course, be consistent. The Lee-Luss  $\Delta T_x / \Delta T_0$  functionality is (eq 5)

$$\frac{\Delta T_x}{\Delta T_0} = \frac{\phi/3(Bi)_h}{\left(1 + \frac{\phi}{3} \left(\frac{1}{(Bi)_h} - \frac{1}{(Bi)_m}\right)\right)} \quad (5)$$

which was derived for a sphere. As noted by Goldstein (1973), when the characteristic pellet dimension is defined as  $L = 1/a$ , volume/external surface, then

$$\frac{\phi_L}{(Bi)_m} = \bar{\eta} Da = \frac{R_0}{k_g a C_0} \quad (17)$$

The Lee-Luss observable,  $\phi$ , is defined in terms of the Weisz number for a sphere

$$\phi = \frac{R^3 R_0}{DC_0}$$

thus

$$\phi_L = \phi/3 \quad (18)$$

and multiplying both numerator and denominator of eq 5 by  $(Bi)_m$  and invoking eq 17 we readily transform the Lee-Luss equation (5), originally phrased in terms of  $\phi$ ,  $(Bi)_m$ ,  $(Bi)_h$  into that presented here in terms of  $\bar{\eta} Da$ , and  $r$

$$\frac{\Delta T_x}{\Delta T_0} = \frac{r \bar{\eta} Da}{(1 + \eta Da (r - 1))} \quad (16)$$

### Comparison of Theory and Data

Kehoe and Butt (1972) present inter-intraphase temperature distribution data for a large single pellet in the Ni-kieselguhr catalyzed hydrogenation of benzene.

In their study, pellet no. 1 is characterized by an  $r$  value of 20 while pellet no. 2, of higher thermal conductivity, has an  $r$  value of 300. These values assume a Lewis number of unity. In agreement with eq 16 and its display in Figure 1, Kehoe and Butt observe both internal and exter-

nal temperature gradients for pellet no. 1, while their data for the pellet of high  $r$  value indicate that the total  $\Delta T$  is external.

Since Kehoe and Butt present observed rate,  $R_0$ , the mass Biot number and intraphase diffusivity (and therefore  $k_g a$ ) and bulk concentration data for each of their runs, we readily compute our observable  $\eta Da$  (eq 9). As  $r$  is also known  $\Delta T_x/\Delta T_0$  can be computed by eq 16. This comparison of theory and experimental data is set forth in Table I.

## Conclusions

A most conservative estimate of the importance of the external  $\Delta T_x$  is secured solely in terms of observed rate and the ratio of the Biot numbers. Given the fact that for gas-porous solid systems the Biot number ratio is indeed large ( $10-10^4$ ), the assumption implicitly set forth in Hutchings' work, that external temperature gradients can be far more important than internal (intrapphase) gradients, is surely verified for anticipated values of  $r$  in most gas-solid systems. We may, then, with some confidence invoke a model of an isothermal catalyst pellet operative at a temperature dictated by external heat transport in catalytic-reactor simulation (Minhas, 1969; White, 1969). Comparison of the theoretical relation herein derived with experimental data proves to be rather satisfying.

## Nomenclature

$a$  = external surface to volume ratio,  $1/L$   
 $(Bi)_m$  = mass Biot number  
 $(Bi)_h$  = thermal Biot number  
 $C$  = species concentration  
 $C_p$  = heat capacity  
 $D$  = intraparticle diffusivity  
 $Da$  = Damkohler number  
 $f$  = reduced concentration,  $C/C_0$   
 $h$  = interphase heat transfer coefficient  
 $\Delta H$  = reaction enthalpy change

$k$  = chemical rate coefficient  
 $k_g$  = bulk mass transport coefficient  
 $L$  = volume to external surface ratio,  $1/a$   
 $Le$  = Lewis number  $Sc/Pr$   
 $Pr$  = Prandtl number  
 $r$  = ratio of mass to thermal Biot numbers  
 $R$  = pellet radius  
 $R_0$  = observed, global, reaction rate  
 $Sc$  = Schmidt number  
 $t$  = reduced temperature,  $T/T_0$   
 $T$  = temperature  
 $z$  = reduced length,  $x/L$

## Greek Letters

$\beta$  = Prater number based on  $C_s$   
 $\beta_0$  = Prater number based on  $C_0$   
 $\bar{\beta}$  = interphase adiabatic temperature change  
 $\bar{\eta}$  = overall effectiveness factor  
 $\eta_i$  = internal effectiveness  
 $\lambda$  = pellet thermal conductivity  
 $\phi$  = Weisz number

## Subscripts

0 = bulk fluid condition  
s = surface condition

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## Coalescence and Conductivity in Dynamic Foam

Prehumidified nitrogen was bubbled through aqueous solutions of anionic, cationic, and nonionic surfactant to form foam that ascended continuously through a vertical glass column, 5.1 cm in diameter and 1 m in height, which was equipped with electrical conductivity cells to measure foam density at various levels *in situ*. For residence times of several minutes there was generally only a small change in foam density and a moderate shift in bubble size distribution as a result of interbubble gas diffusion, and there was no apparent rupture-induced coalescence, provided an adequate concentration of surfactant was present.

## Introduction

**Purpose.** When employing the technique of foam fractionation, an important consideration is the rate at which the overflowing column of foam delivers liquid. This rate depends in part on coalescence within the rising foam before it overflows. Furthermore, such coalescence furnishes induced internal reflux which further enriches the overflowing foam with the surface active components. Overflow and coalescence are also pertinent to other situations involving foam. Accordingly, the present study was conducted primarily to investigate the nature and extent of coalescence in steadily ascending foam. Also, as an addendum, the relationship obtained between the volumetric density and the electrical conductivity of foam was com-

pared with the corresponding determinations that were employed in earlier studies.

**Instability.** Coalescence stems from instability which is of two general types. The first is the growth of large bubbles at the expense of smaller bubbles. This is caused by higher pressure in the smaller bubbles which forces gas to diffuse from these smaller bubbles to the larger bubbles. Small bubbles may even shrink to the point of disappearance. By making certain convenient assumptions, de Vries (1957) derived equations for approximately predicting the rate of diffusion-induced coalescence among bubbles the sizes of which are distributed unimodally.

The second type of instability is the rupture of the films [lamellae] which separate bubbles. In foams of sufficient stability, such as were employed in the present investiga-