TEMPERATURE EFFECTS IN HETEROGENEOUS CATALYSIS

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IN THE STUDY of mass and heat transfer effects for a first-order irreversible gas-phase reaction occurring over a bed of catalyst pellets, it is interesting to analyze the effect of temperature on the observed rate of reaction. To a first approximation, it would seem that a graph of effectiveness factor, $\bar{\eta}$, versus Thiele modulus, m_o, could be used to easily calculate the reaction rate, $\bar{R}$, as a function of temperature from the basic relation

$$\bar{R} = k_{vo}\,\bar{\eta} \tag{1}$$

where k_{vo} is the rate constant at the gas-phase temperature T_o. However, such charts (refer to [1], for example) are usually based on constant values of the Arrhenius parameter, $\bar{\gamma}$, the intraparticle thermal parameter, $\bar{\beta}$, and the Biot number for mass transfer, $\mathbf{Bi}_m$. In reality, these three parameters vary appreciably with temperature for a given reaction system, so that the behavior of the system cannot be determined by following $\bar{\eta}$ versus m_o on a single chart. Consequently, in order to analyze the effect of temperature, one must return to the model that was used to generate the charts, developed by Carberry and Kulkarni [2], and solve the model without holding γ, $\bar{\beta}$ and $\mathbf{Bi}_m$ constant.

In this paper, we present an *analytic* solution of the heterogeneous reaction model for the effect of temperature on the system described earlier. Our analytic formulation utilizes a "reference state," or system characteristics at a single temperature, to explicitly determine the behavior of the system at any temperature.

The contribution which we want to make will be more accessible if the derivation of the basic equations of the heterogeneous reaction model is reviewed. We have incorporated the isothermal pellet assumption [2] into our model, realizing that a specific design problem may deserve a more rigorous approach and that our results do not apply to complex kinetics which may show autocatalytic behavior. Although it is the behavior of the system parameters with the bulk gas temperature T_o that is desired, we find that it is convenient to use the surface (*i.e.*, pellet) temperature T_s as the independent variable in our model. For any T_s we calculate the appropriate T_o, but in regions of multiplicity a value of T_o corresponds to three values of T_s at steady state, two of which are stable.

MASS TRANSFER EFFECTS

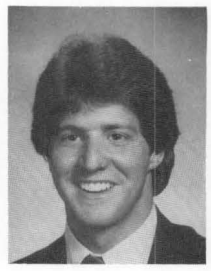
At steady state the rate of reaction in the pellet, $\bar{r}$, equals the rate of interphase mass transfer of reactant A towards the surface,

$$\bar{r} = k_c a\left(C_{Ao} - C_{As}\right) \tag{2}$$

where k_c is the mass transfer coefficient, a is the outside area of the pellet per unit volume, and C_{As} is the concentration of reactant A in the gas at the pellet surface.

Intraphase diffusion occurs with chemical reaction within the pellet and produces a concentration gradient, described in slab geometry by

$$\frac{C_A(z)}{C_{As}} = \frac{\cosh\left(z\sqrt{\dfrac{k_{vs}}{D_e}}\right)}{\cosh\left(L\sqrt{\dfrac{k_{vs}}{D_e}}\right)} \tag{3}$$



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where z is the distance from the center of the slab, L is the half thickness of the slab, k_{vs} is the rate constant at the pellet temperature T_s, and D_e is the effective Knudsen diffusivity. The Thiele modulus at T_s is

$$m_s = L\sqrt{\frac{k_{vs}}{D_e}} \tag{4}$$

The effectiveness factor associated with the pellet at T_s is

$$\eta_s = \frac{\bar{r}}{k_{vs} C_{As}} = \frac{D_e \frac{dC_A}{dz}(L)}{k_{vs} C_{As}} \tag{5}$$

so that one can obtain

$$\eta_s = \frac{\tanh m_s}{m_s} \tag{6}$$

For sufficiently high temperature, the rate increases so that the interphase temperature and concentration differences are important. Thus we need to consider the inter-intraphase (overall) effectiveness factor, $\bar{\eta}$, defined through Eq. (1). The rate $\bar{R}$, or the apparent rate constant $\bar{k}$, can be expressed in several ways, as follows; through Eqs. (1), (2), (5) and

$$\bar{R} = \frac{\bar{r}}{C_{Ao}} = \bar{\eta}\,\mathbf{Da}\,k_c a \tag{7}$$

The Damköhler number **Da** is $k_{vo}/k_c a$, and it is convenient to consider together the product $\bar{\eta}$**Da**. From Eq. (7) is clear that $\bar{\eta}$**Da** is an observable, as defined by Carberry [1]. This group measures the importance of the interphase concentration difference, as shown by combining Eqs. (2) and (7)

$$\bar{\eta}\,\mathbf{Da} = 1 - \frac{C_{As}}{C_{Ao}} \qquad (0 \le \bar{\eta}\,\mathbf{Da} \le 1) \tag{8}$$

It is also useful to express $\bar{\eta}$**Da** in terms of m_s, at conditions in the pellet. By combining Eqs. (5), (6), and (7), we obtain

$$\bar{\eta}\,\mathbf{Da} = \frac{\tanh m_s}{m_s} \cdot \frac{k_{vs}}{k_c a} \cdot \frac{C_{As}}{C_{Ao}} \tag{9}$$

When C_{As}/C_{Ao} is replaced according to Eq. (8), the result is

$$\bar{\eta}\,\mathbf{Da} = \frac{m_s \tanh m_s}{m_s \tanh m_s + \frac{m_s^2 k_c a}{k_{vs}}} \tag{10}$$

Now $\mathbf{Bi}_m = d_p k_c / D_e$ and is used with Eq. (4), along with the relation for spherical pellets of diameter d_p, $L = 1/a = d_p/6$ following a common approximation [3], to replace the second term in the denominator of Eq. (10). The result is an equation for $\bar{\eta}$**Da** in terms of m_s and $\mathbf{Bi}_m$,

$$\bar{\eta}\,\mathbf{Da} = \frac{m_s \tanh m_s}{m_s \tanh m_s + \frac{\mathbf{Bi}_m}{6}} \tag{11}$$

In this paper, we present an analytic solution of the heterogeneous reaction model for the effect of temperature on the system described earlier. Our analytic formulation utilizes a "reference state," or system characteristics at a single temperature . . .

Although this equation permits the calculation of $\bar{\eta}$**Da** for a given T_s, we still need to find the corresponding T_o and k_{vo} in order to calculate $\bar{\eta}$.

HEAT TRANSFER EFFECTS

The interphase temperature difference is determined by equating the rates of heat generation and removal for the pellet.

$$\bar{r}(-\Delta H) = h a (T_o - T_s) \tag{12}$$

where $(-\Delta H)$ is the reaction enthalpy difference and h is the heat transfer coefficient. Substituting Eq. (7) into Eq. (12) gives

$$\bar{\eta}\,\mathbf{Da}(-\Delta H) k_c C_{Ao} = h(T_o - T_s) \tag{13}$$

This equation can be rearranged to

$$\frac{T_s}{T_o} = 1 + \frac{k_c(-\Delta H) C_{Ao}}{h T_o} \bar{\eta}\,\mathbf{Da} \tag{14}$$

According to the Chilton-Colburn analogy [4], $j_M = j_H$, so that we can derive

$$\frac{h}{k_c} = (\mathbf{Le})^{2/3} \rho C_p \tag{15}$$

where **Le** = **Sc/Pr** and write the temperature-effect equation as

$$T_s - T_o = \bar{\beta}\,\bar{\eta}\,\mathbf{Da}\,T_o \tag{16}$$

where

$$\bar{\beta} = \frac{(-\Delta H) C_{Ao}}{(\mathbf{Le})^{2/3} \rho C_p T_o} \tag{17}$$

REFERENCE STATE

In order to follow the effect of temperature easily, a reference temperature T_r is defined at which the rate constant k_{vr} is known. Usually T_r would be a suitable low temperature. In the example we shall give, T_r is 600 K. The appropriate k_{vs} can then be calculated by

$$k_{vs} = k_{vr} \exp\left[-\gamma_r\left(\frac{T_r}{T_s} - 1\right)\right] \tag{18}$$

where the Arrhenius parameter $\gamma_r = E/RT_r$ is a constant.

Clearly Eq. (18) can be used to calculate k_{vo} at T_o. We also need D_e at T_s. We assume Knudsen diffusion, so that

$$D_e = D_{er}\left(\frac{T_s}{T_r}\right)^{\frac{1}{2}} \tag{19}$$

Now m_s can be computed at the chosen T_s. In Eq. (11), which we need to calculate $\bar{\eta}\mathbf{Da}$, the parameter $\mathbf{Bi}_m$ must be found. We write

$$\mathbf{Bi}_m = \mathbf{Sh}\frac{D_{AB}}{D_e} = j_M \mathbf{Re}\,\mathbf{Sc}^{\frac{1}{3}}\frac{D_{AB}}{D_e} \tag{20}$$

where $\mathbf{Re} = d_pG/\mu$, G is the gas mass velocity, μ is the viscosity of gas, and D_{AB} is the diffusivity of gas A thru B. Among many possibilities, we choose the following correlation for j_M in a packed bed [4]:

$$j_M = 2.25\,\mathbf{Re}^{-\frac{1}{2}} \tag{21}$$

so that

$$\mathbf{Bi}_m = 2.25\,\mathbf{Re}^{\frac{1}{2}}\mathbf{Sc}^{\frac{1}{3}}\frac{D_{AB}}{D_e} \tag{22}$$

As a first approximation we evaluate $\mathbf{Bi}_m$ at T_s; after T_o is estimated, the solution could be iterated with an average of T_o and T_s used for the estimation of μ and D_{AB}. **Sc** is little affected by temperature. If D_{AB} is proportional to $T_s^{3/2}$, and μ to $T_s^{1/2}$, then there results

$$\mathbf{Bi}_m = \mathbf{Bi}_{mr}\left(\frac{T_s}{T_r}\right)^{\frac{3}{4}} \tag{23}$$

For a chosen T_s we now calculate $\mathbf{Bi}_m$ from Eq. (23), m_s from Eq. (4) with Eqs. (18) and (19), and then use Eq. (11) to find $\bar{\eta}\mathbf{Da}$. Before using Eq. (16) to find T_o, it is convenient to define

$$\bar{\beta}_r = \frac{(-\Delta H)C_{Ao}}{(\mathbf{Le})^{\frac{2}{3}}\rho C_p T_r} \tag{24}$$

so that

$$T_s - T_o = \bar{\beta}_r\,\bar{\eta}\,\mathbf{Da}\,T_r \tag{25}$$

For a given mole fraction X_{Ao}, $\bar{\beta}_r$ defined by Eq. (24) is approximately constant; C_{Ao}/ρ is constant, and usually the effects of temperature on $(-\Delta H)/C_p$ and **Le** are small.

For a chosen T_s, we now know $\bar{\eta}\mathbf{Da}$ and T_o. Equation (24) can be used to find k_{vo} at T_o, and m_o is defined by Eq. (3) with k_{vo} replacing k_{vs}. It is interesting to

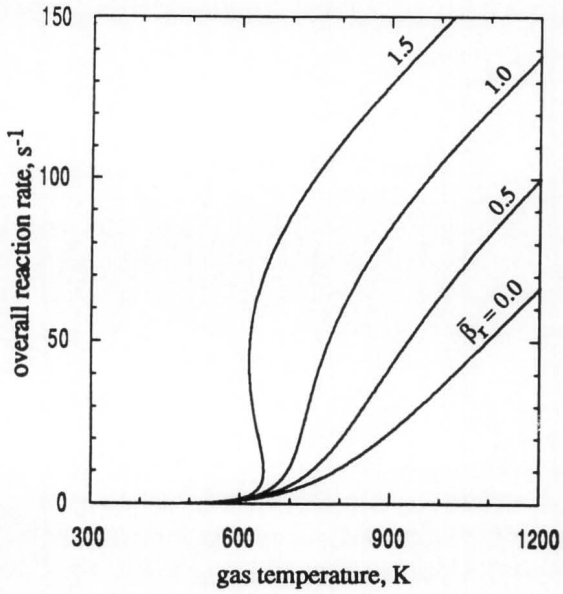

FIGURE 2: Overall reaction rate as a function of gas temperature for the example.

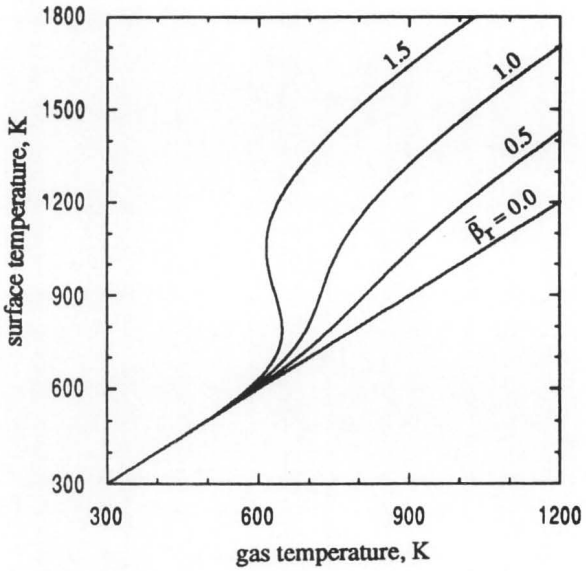

FIGURE 1: Surface temperature as a function of gas temperature for the example pellet-reaction system.

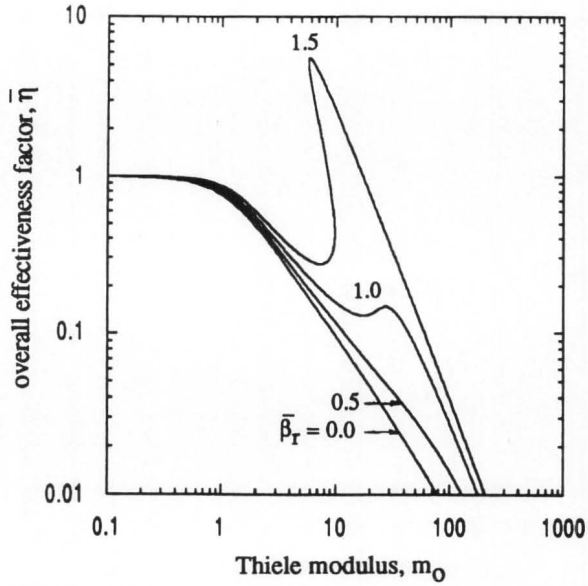

FIGURE 3: Variation of the overall effectiveness factor with the Thiele modulus m_o, for the example.

calculate the rate R, and Eq. (12) gives this quantity once we evaluate $k_c a$. The $\mathbf{Bi}_m$ can be written as

$$k_c a = \frac{\mathbf{Bi}_m D_e}{d_p} \cdot \frac{6}{d_p} \tag{26}$$

Then Eqs. (19) and (23) are used so that

$$k_c a = \frac{6\mathbf{Bi}_m D_{er}}{d_p^2} \cdot \left(\frac{T_s}{T_r}\right)^{\frac{5}{4}} \tag{27}$$

This completes the calculation procedure; for a chosen T_s, we can now calculate $\bar{\eta}\mathbf{Da}$, T_o, m_o, $\bar{R}$ and then $\bar{\eta}$ by Eq. (1).

EXAMPLE

Let us consider the behavior of spherical pellets of 6 mm diameter. Experiments using a powder of 0.3 mm diameter, made by crushing the pellets, give a value for $\bar{k} = \bar{R}$ of 5 s^{-1} at 1 bar and 600 K. For these conditions $\bar{\eta}$ is unity, and $k_v = k_{vs} = k_{vo}$, since $T_s = T_o$. This reaction is first-order and irreversible. Considering T_r to be 600 K, we establish for the 6 mm pellets the values $\gamma_r = 20$, $D_{er} = 2.0 \times 10^{-3}$ cm^2s^{-1}, and $\mathbf{Bi}_{mr} = 1300$, corresponding to $\mathbf{Re} = 50$, $\mathbf{Sc} = 0.6$ and $D_{ABr} = 0.2$ cm^2s^{-1}. Now we can follow the procedure described in the previous section to find the values of interest for this example. A simple computer program with graphics gives the curves discussed below.

Figure 1 shows the surface temperature corresponding to various bulk (gas) temperatures T_o. As T_o is increased, for a large enough $\bar{\beta}_r$, hysteresis loops with multiple steady states are found. Recall that in the actual calculations, T_o is found from T_s. The variation of $\bar{\beta}_r$ can be thought of as arising from changes in C_{Ao}. If $(-\Delta H)$ were varied, this would imply a different reaction with a different γ_r and other parameters. Figure 2 demonstrates how the overall reaction rate (or $\bar{k}$) varies with T_o for the given example.

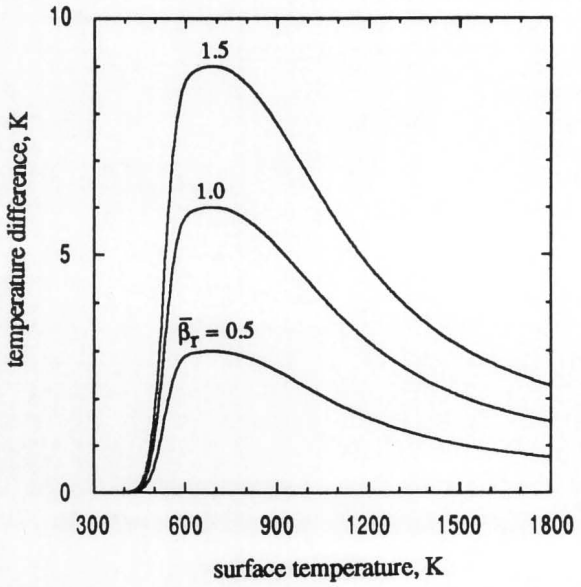

FIGURE 4: Estimation of the difference between the temperatures at the center and at the surface of the example pellet, as a function of surface temperature.

Curves can also be presented in terms of the usual dimensionless parameters, $\bar{\eta}\mathbf{Da}$ or m_o; the variation of $\bar{\eta}$ with m_o is presented in Figure 3. These diagrams have the same general appearance as those of Carberry's text, for example [1]. However, they apply to the chosen particle and reacting system with the parameters already enumerated. Because of the dependence on temperature of k_{vo}, $\mathbf{Bi}_m$, and D_e which are built into the model, somewhat different results for $\bar{\eta}$ would be obtained for a different set of parameters which might lead to the same values of m_o.

It is worth noting that the assumption of a constant pellet temperature is equivalent to choosing a Carberry number [5] of infinity, where

$$\mathbf{Ca} = \frac{\bar{\beta}_r}{\beta_r} = \frac{\mathbf{Bi}_{mr}}{\mathbf{Bi}_{hr}} \tag{28}$$

As the thermal conductivity λ_p of the pellet goes to infinity, $\bar{\beta}_r$ and $\mathbf{Bi}_{hr}$ go to zero and $\mathbf{Ca}$ is infinite, corresponding to an isothermal pellet. If we retain the results already calculated with $\mathbf{Ca} = \infty$, we can set $\mathbf{Ca} = 100$, a reasonable value [1], and estimate the temperature rise inside the pellet. The result for our example is shown in Figure 4. The ΔT's found are low enough so that the isothermal pellet model seems justified.

In the design of a fixed-bed catalytic reactor, the mass and energy balances written in terms of T_o and C_{Ao} are integrated along the bed. The present simple model for heterogeneous effects can easily be incorporated into an algorithm for the simulation of such a reactor. Thus a realistic result can be obtained by simple methods.

ACKNOWLEDGEMENT

The authors wish to thank Professor Robert Rinker for a helpful discussion of the paper.

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