

Interfacial Reactions

(Part II)

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7.2.1 Internal transport processes

- ◆ The transport of the reactants from the bulk to the surface of the catalyst was discussed in Lecture 1 of this module. The next step is the diffusional transport of the reactant inside the pores of the catalyst as depicted in Fig. 7.2.1.

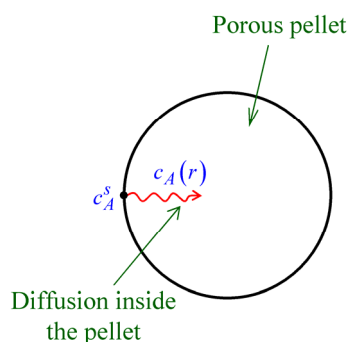


Fig. 7.2.1 Transport inside the catalyst pores.

- ◆ This is a very important step because the majority of the active sites of a catalyst can stay inside the pellet. The pores are not straight, but have tortuous structure distributed randomly inside the pellet.
- ◆ Let us consider the first-order reaction: $A \rightarrow B$ occurring at steady state. The equimolal counterdiffusion model is applicable here, i.e., for every mole of A that diffuses from the surface into the pore, one mole of B diffuses back in the opposite direction. The mass transport occurs by both bulk and Knudsen diffusion. The combined diffusivity, D_c , is given by,

$$D_c = \frac{1}{\frac{1}{D_{AB}} + \frac{1}{D_K^A}} \quad (7.2.1)$$

where D_{AB} is the bulk diffusivity and D_K is the Knudsen diffusivity.

- ◆ Since the pores are not straight and cylindrical but a series of tortuous paths, an *effective diffusivity*, D_e , is defined as follows.

$$D_e = \frac{\varepsilon_p D_c}{\tau} \quad (7.2.2)$$

where D_e is the effective diffusivity, ε_p is the porosity of the catalyst pellet and τ is the tortuosity factor.

- ◆ If the pellet has a bidisperse pore system (i.e., both macro and microporous regions are present), the effective diffusivity is defined as (Smith, 1981),

$$D_e = \left(\frac{1}{D_{AB}} + \frac{1}{D_K^m} \right)^{-1} \varepsilon_m^2 + \left[\frac{\varepsilon_\mu^2 (1 + 3\varepsilon_m)}{1 - \varepsilon_m} \right] \left(\frac{1}{D_{AB}} + \frac{1}{D_K^\mu} \right)^{-1} \quad (7.2.3)$$

where ε_m is the void fraction in the macroporous regions and ε_μ is the void fraction of the microporous regions.

- ◆ Transport in the pellet is assumed to occur by a combination of diffusion through both the regions. Note that there is no tortuosity factor involved in Eq. (7.2.3).
- ◆ The relative importance of diffusion and reaction is expressed by the *effectiveness factor*. It is defined as,

$$\eta = \frac{\text{actual rate for the whole pellet}}{\text{rate evaluated at outer surface conditions}} \quad (7.2.4)$$

If the actual rate is expressed by r_p and the rate evaluated at the outer surface conditions is expressed by r_s , then for the first-order reaction: $A \rightarrow B$ we have,

$$r_p = \eta r_s = \eta k c_A^s \quad (7.2.5)$$

The effectiveness factor can be expressed in terms of the effective diffusivity and reaction rate constant as shown later in this section. The concentration profile of reactant A inside the catalyst pellet is required for this purpose.

- ◆ Let us perform a material balance over the spherical-shell of the pellet of inner radius, r , and outer radius, $(r + \Delta r)$, as shown in Fig. 7.2.2. At steady state, the rate of diffusion into the element minus the rate of diffusion out of the element must equal the rate of disappearance by reaction within the element. Therefore, we can write the following balance equation.

$$\left[-4\pi r^2 D_e \frac{dc_A}{dr} \right]_r - \left[-4\pi r^2 D_e \frac{dc_A}{dr} \right]_{r+\Delta r} = 4\pi r^2 \Delta r \rho_p k c_A \quad (7.2.6)$$

where ρ_p is the density of the pellet.

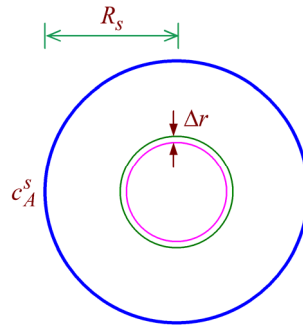


Fig. 7.2.2 Shell balance on a porous catalyst pellet.

- ◆ Taking the limit $\Delta r \rightarrow 0$, we obtain the following second-order differential equation.

$$\frac{d^2 c_A}{dr^2} + \frac{2}{r} \frac{dc_A}{dr} - \frac{k \rho_p c_A}{D_e} = 0 \quad (7.2.7)$$

- ◆ The boundary conditions are,

$$\text{At } r = 0: \frac{dc_A}{dr} = 0 \quad (7.2.8)$$

$$\text{At } r = R_s: c_A = c_A^s \quad (7.2.9)$$

- ◆ The solution of Eq. (7.2.7) with the boundary conditions given by Eqs. (7.2.8) and (7.2.9) is given by,

$$\frac{c_A}{c_A^s} = \frac{R_s \sinh(3\Phi r/R_s)}{r \sinh(3\Phi)} \quad (7.2.10)$$

where Φ is known as *Thiele modulus*, which is defined as,

$$\Phi = \frac{R_s}{3} \left(\frac{k \rho_p}{D_e} \right)^{1/2} \quad (7.2.11)$$

- ◆ The Thiele modulus gives the relative magnitude of reaction rate and diffusion rate. If the Thiele modulus is small, the reaction is the rate-limiting step. On the other hand, if the Thiele modulus is large, diffusion limits the overall rate of reaction.
- ◆ The rate of reaction for the whole pellet is given by,

$$r_p = \frac{4\pi R_s^2 D_e \left(\frac{dc_A}{dr} \right)_{r=R_s}}{\frac{4}{3}\pi R_s^3 \rho_p} = \frac{3D_e \left(\frac{dc_A}{dr} \right)_{r=R_s}}{R_s \rho_p} \quad (7.2.12)$$

Therefore, the effectiveness factor is given by,

$$\eta = \frac{3D_e \left(\frac{dc_A}{dr} \right)_{r=R_s}}{R_s \rho_p k c_A^s} \quad (7.2.13)$$

- ◆ The effectiveness factor can be expressed in terms of the Thiele modulus as,

$$\eta = \frac{1}{\Phi} \left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right] \quad (7.2.14)$$

The variation of effectiveness factor, η , with Thiele modulus is shown in Fig. 7.2.3.

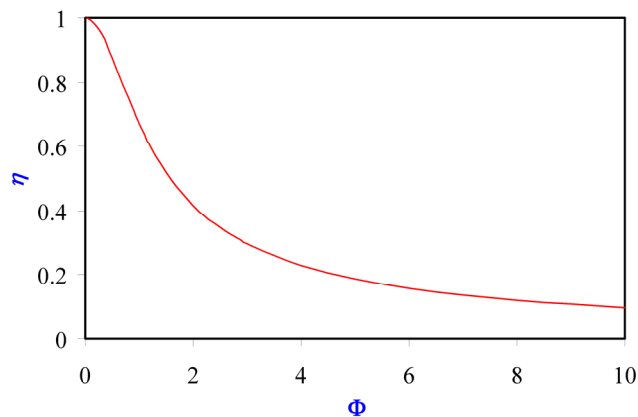


Fig. 7.2.3 Variation of effectiveness factor with Thiele modulus for a first-order reaction on a spherical catalyst.

- ◆ From this figure, it is observed that the effectiveness factor approaches unity for small values of Φ , which indicates that the rate for the whole pellet is same as the rate that would result if the entire interior surface were exposed to the reactant at concentration, c_A^s . In other words, the entire surface is fully effective up to the center of the pellet.
- ◆ On the other hand, if the value of η is much less than unity, only that part of the interior surface which lies close to the outer periphery of the pellet is effective,

and the central part of the pellet is not utilized. Such a situation can be caused by a large value of the Thiele modulus, which may be due to large size of the pellet, low diffusivity, or high rate of reaction.

- ◆ From the η versus Φ diagram, it is observed that η is close to unity if $\Phi \leq 1/3$. If this condition is satisfied, it is possible to ignore the effects of intrapellet mass transfer. This is often called *Weisz criterion*.
- ◆ Therefore, we can write this condition as,

$$R_s \left(\frac{k \rho_p}{D_e} \right)^{1/2} \leq 1 \quad (7.2.15)$$

Therefore,

$$R_s^2 \left(\frac{k \rho_p}{D_e} \right) \leq 1 \quad (7.2.16)$$

- ◆ As $\eta \rightarrow 1$ when the above condition is valid, from Eq. (7.2.5) we can write,

$$k \approx r_p / c_A^s \quad (7.2.17)$$

- ◆ From Eqs. (7.2.16) and (7.2.17) we can write,

$$R_s^2 \left(\frac{r_p \rho_p}{c_A^s D_e} \right) \leq 1 \quad (7.2.18)$$

Example 7.2.1: A first-order reaction: $P \rightarrow Q$ is carried out using 2 mm diameter spherical catalyst pellets in a packed bed. The effective diffusivity of P is $5 \times 10^{-6} \text{ m}^2/\text{s}$, the measured rate of reaction is $0.5 \text{ mol (kg catalyst)}^{-1} \text{ s}^{-1}$, the estimated concentration of reactant, P , on the surface of the catalyst is 10 mol/m^3 , and the density of the pellet is 1200 kg/m^3 . Calculate the effectiveness factor.

Solution: From Eqs. (7.2.5) and (7.2.11) we get,

$$\Phi = \frac{R_s}{3} \left(\frac{k \rho_p}{D_e} \right)^{1/2} = \frac{R_s}{3} \left(\frac{r_p \rho_p}{\eta c_P^s D_e} \right)^{1/2} = \left(\frac{1 \times 10^{-3}}{3} \right) \left(\frac{0.5 \times 1200}{\eta \times 10 \times 5 \times 10^{-6}} \right)^{1/2} = \frac{1.155}{\sqrt{\eta}}$$

Substituting Φ in Eq. (7.2.14) we get,

$$\eta = \frac{\sqrt{\eta}}{1.155} \left[\frac{1}{\tanh\left(3.465/\sqrt{\eta}\right)} - \frac{\sqrt{\eta}}{3.465} \right]$$

Solving the above transcendental equation, we get, $\eta = 0.48$.

7.2.2 Interfacial polycondensation

- ◆ Interfacial polycondensation involves polymerization of two monomers which are dissolved in two immiscible phases. Typical monomers are diacid chloride and diamine. The acid chloride is dissolved in an organic solvent such as xylene, carbon tetrachloride, hexane or dichloro methane. The diamine is dissolved in water. The polymerization reaction takes place at the interface.
- ◆ To illustrate, the reaction between sebacyl chloride and hexamethylene diamine, which produces Nylon 6–10, can be represented as,

$$x\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2 + x\text{ClCO}(\text{CH}_2)_8\text{COCl} \rightarrow [-\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_8\text{CO-}]_x + 2x\text{HCl} \quad (7.2.19)$$
- ◆ The HCl liberated in the reaction is neutralized by an alkali (e.g., NaHCO_3) added to the aqueous phase. The reaction does not take place in the acid phase due to the susceptibility of the acid chloride to hydrolysis. The polycondensation reaction can occur in the aqueous phase for situations where the diacid chloride has substantial solubility in the aqueous phase and good hydrolytic stability.
- ◆ The rate constant for the reaction between diacyl chlorides and diamines is large, $\sim 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, or higher (Doraiswamy and Sharma, 1984).
- ◆ A major application of interfacial polymerization is in the preparation of thin film composite reverse osmosis membranes (e.g., FT-30). The structure of a thin film composite membrane is schematically shown in Fig. 7.2.4.

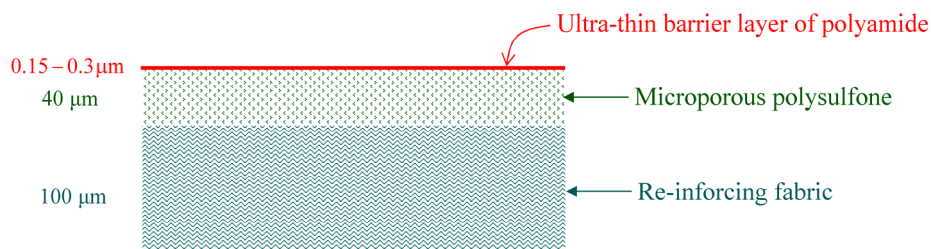


Fig. 7.2.4 Thin film composite reverse osmosis membrane.

- ◆ The topmost thin layer is responsible for the separation of ions. This layer is made by interfacial polycondensation between tri-mesoyl chloride [$\text{C}_6\text{H}_3(\text{COCl})_3$] and *m*-phenylene diamine [$\text{C}_6\text{H}_4(\text{NH}_2)_2$]. The reaction occurs by first soaking the polysulfone support with aqueous solution of *m*-phenylene diamine, and then spreading the hexane solution of tri-mesoyl chloride over it.
- ◆ In the general interfacial polycondensation reaction, three steps are considered, viz. (i) mass transfer of both monomers from the bulk to the interface, (ii) diffusion of diamine through the polymer film, and (iii) second-order reaction. These steps are illustrated in Fig. 7.2.5.

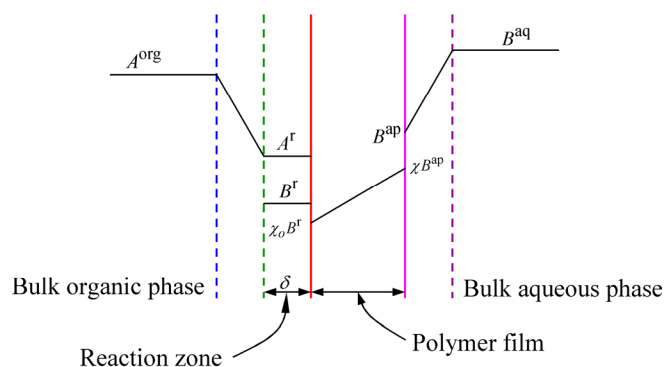


Fig. 7.2.5 Schematic of interfacial polycondensation.

- ◆ The partition coefficient of A between aqueous phase and polymer film is represented by χ , and the same between the polymer film and the organic solvent is represented by χ_o . The superscript 'ap' indicates the interface between the aqueous phase and the polymer film, and the superscript 'r' indicates the reaction zone.
- ◆ The diamine partitions into the organic phase to initiate the polymerization reaction. It encounters excess of diacid chloride in the reaction zone of volume, $a_i \delta$, where δ is the thickness of the reaction zone and a_i is the interfacial area.
- ◆ The approximate thickness of the reaction zone is ~ 10 nm. The reaction produces an oligomeric species which has terminal amine and acid chloride groups. This immediately reacts with the surrounding excess diacid chloride to form a larger oligomer which is acylated at both the ends.

- ◆ The overall reaction is an irreversible coupling of the acid chloride with the incoming diamine. The polymerization reaction scheme is summarized in Table 7.2.1.

Table 7.2.1 Interfacial polycondensation between diamine and diacid chloride

Symbol	Monomer/polymeric species
A	$\text{H}_2\text{N}-\text{R}_1-\text{NH}_2$
B_n	$\text{Cl}-(\text{OC}-\text{R}_2-\text{CONH}-\text{R}_1-\text{NH})_n-\text{OC}-\text{R}_2-\text{COCl}$
C_n	$\text{H}-(\text{NH}-\text{R}_1-\text{NHCO}-\text{R}_2-\text{CO})_n-\text{Cl}$
$A + B_n \rightarrow C_{n+1} + \text{HCl}, \text{ rate} = 4k_p AB_n$	
$C_{n+1} + B_m \rightarrow B_{n+m+1} + \text{HCl}, \text{ rate} = 2k_p C_{n+1} B_m$	

- ◆ The rate constant, k_p , is for the reaction between one $-\text{NH}_2$ group and one $-\text{COCl}$ group. Flory's equal-reactivity hypothesis is assumed to hold for all the reactions. The growth of polymer film as a function of time for the polymerization of Nylon 6-10 under unstirred conditions is depicted in Fig. 7.2.6.

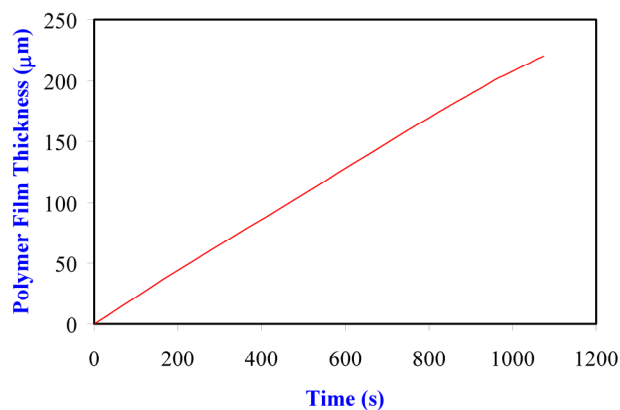


Fig. 7.2.6 Growth of Nylon 6-10 film by interfacial polycondensation in methylene chloride (Karode *et al.*, 1997) [adapted by permission from Elsevier Ltd., © 1997].

7.2.3 Microencapsulation

- ♦ Microencapsulation has been found to be effective for encapsulating water-insoluble pesticides and biological species. These microcapsules are used for controlled or sustained release of the encapsulated material. The performance of these microcapsules depends on the morphology and surface characteristics of the polymeric shell and their size. Both of these characteristics depend on the materials and process conditions.
- ♦ If the polymer is highly cross-linked, the permeability of the encapsulated substance will be very low. Another important parameter is the time required for encapsulation, which is necessary for designing the encapsulator.
- ♦ The hydrophobic substance to be encapsulated and a hydrophobic monomer (e.g., diisocyanate) is dispersed in an aqueous medium stabilized by a surfactant. The aqueous phase contains a hydrophilic monomer (e.g., a diamine). The reaction starts at the surface of the drops and a shell of the polymer forms at the surface. At subsequent times, the monomer, B , has to diffuse through the growing shell before it can react with the other monomer, A , which is present in the organic phase. The polymer swells as it forms. The monomer in the aqueous phase (B) is usually the limiting reactant. The reaction ceases when B is exhausted. The formation of the microcapsule is depicted in Fig. 7.2.7.

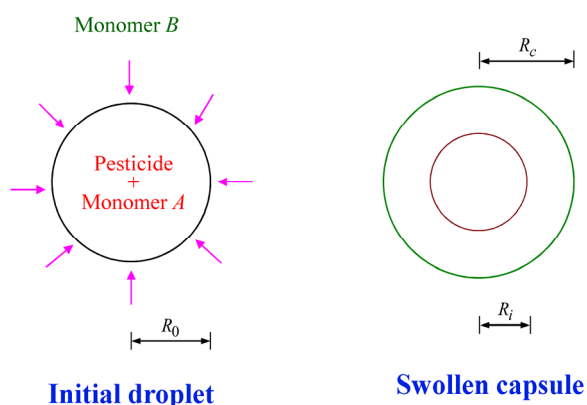


Fig. 7.2.7 Formation of microcapsule by interfacial polycondensation.

- ◆ Let us consider the interfacial polycondensation between hexamethylene-1,6-diamine and hexamethylene-1,6-diisocyanate to encapsulate butachlor (a pesticide). A few assumptions are made to model the process as follows.
- ◆ All the drops are assumed to have the same radius, R_0 , at $t = 0$. If the dispersion has drops having a wide range of size, the surface-to-volume mean radius can be used to perform the calculation instead of R_0 .
- ◆ The dispersion is agitated, and therefore, the rate of external mass transfer is expected to be rapid. Thus, only the diffusion of B through the polymer shell and the reaction at the interface are considered. The diffusion of A within the drop is assumed to be rapid and not rate-limiting. The monomer, B , can diffuse through the polymer as well as through the micropores of the shell. Therefore, an *effective diffusivity* (D_e) is used to describe the diffusion of B . D_e is assumed to be independent of the thickness of the polymeric shell.
- ◆ The rate of movement of the inner boundary due to the growth of the polymer shell is assumed to be small in comparison with the rate of diffusion of B . The pseudo-steady-state approximation is assumed to be applicable for the transport of B through the polymer wall. The interfacial kinetics is expressed as,

$$\left(\frac{1}{4\pi R_i^2} \right) \frac{dn_A}{dt} = k_e c_{Ae} c_{Be} \quad (7.2.20)$$

where n_A is the moles of A in the drop at any time t , and c_{Ae} and c_{Be} are volumetric concentrations at the inner radius of the shell R_i .

- ◆ The diffusion of monomer B through the polymeric shell obeys the following equation under the pseudo-steady-state assumption.

$$\frac{D_e}{r^2} \frac{d}{dr} \left(r^2 \frac{dc_B}{dr} \right) = 0 \quad (7.2.21)$$

$$\text{At } r = R_c: \quad c_B = \chi c_{Bs} \quad (7.2.22)$$

$$\text{At } r = R_i: \quad D_e \frac{dc_B}{dr} = k_e c_{Ae} c_{Be} \quad (7.2.23)$$

where c_B is the concentration of monomer B in the polymer shell, c_{Bs} is the concentration of monomer B in the continuous phase, χ is the partition coefficient for monomer B between the continuous and polymer phases, and R_c is the outer radius of the developing microcapsule. It differs from R_0 (the original radius of the drop) because of swelling.

$$R_c = \left[R_i^3 + \alpha (R_0^3 - R_i^3) \right]^{1/3} \quad (7.2.24)$$

where α is a swelling factor.

- ◆ The concentrations of A and B are referred to the phase in which they are present. The instantaneous concentration profile of B in the polymeric shell is given by,

$$c_B = \chi c_{Bs} \frac{\left[\left(\frac{4\pi R_i D_e}{3k_e n_A} \right) + \frac{1}{R_i} - \frac{1}{r} \right]}{\left[\left(\frac{4\pi R_i D_e}{3k_e n_A} \right) + \frac{1}{R_i} - \frac{1}{R_c} \right]} \quad (7.2.25)$$

The conversion of B is defined as,

$$x_B = 1 - \frac{c_{Bs}}{c_{B0}} \quad (7.2.26)$$

where c_{B0} is the concentration of monomer B in the bulk solution at $t = 0$.

- ◆ If the thickness of the polymeric shell is small relative to the radius of the capsule, the following relation between time and conversion is obtained (Yadav *et al.*, 1990).

$$t = -\frac{2}{\beta} x_B - \frac{3\phi/\beta}{(1-a)(3+ab)} \ln \left(\frac{a-x_B}{a} \right) - \frac{3\phi + (3+2b)(a-1)}{\beta(a-1)(3+b)} \ln(1-x_B) \\ + \frac{3}{b\beta} \left[\frac{\phi b^2 + 3(3+ab)}{(3+b)(3+ab)} \right] \ln \left(1 + \frac{bx_B}{3} \right) \quad (7.2.27)$$

where a , b and ϕ are dimensionless parameters which are defined as follows.

$$a = \frac{N n_{A0}}{V c_{B0}} \quad (7.2.28)$$

$$b = \frac{V_{cB0}(M_A + M_B)}{V_d \rho_s} \quad (7.2.29)$$

$$\phi = \frac{3D_e \rho_s V_d^2}{\alpha R_0 (M_A + M_B) k_e (V_{cB0})^2} \quad (7.2.30)$$

where V_d is the volume of the dispersed organic phase, N is the number of droplets in the system, V is the volume of the aqueous phase, ρ_s is the density of the polymer formed, M_A is the molecular weight of monomer A , M_B is the molecular weight of monomer B , and n_{A0} is the moles of monomer A in the drop at $t = 0$.

- ◆ The parameter, β , is defined as,

$$\beta = \frac{9\chi D_e \rho_s V_d^2}{\alpha R_0^2 (M_A + M_B) V^2 c_{B0}} \quad (7.2.31)$$

- ◆ Let us now consider two limiting situations, viz. (i) kinetic control, and (ii) diffusion control. When the rate of chemical reaction is much smaller than that of diffusion, the kinetic control prevails. The interfacial polycondensation is kinetically controlled if the following criterion is satisfied.

$$\phi \gg [x_B(a - x_B)(1 + 2bx_B/3)] \quad (7.2.32)$$

- ◆ The conversion–time relationship in this case is given by,

$$t = \frac{R_0}{\chi k_e c_{B0}} \left[\frac{1}{(a-1)(3+ab)} \ln \left(\frac{a-x_B}{a} \right) - \frac{1}{(a-1)(3+b)} \ln(1-x_B) + \frac{b}{(3+b)(3+ab)} \ln \left(1 + \frac{bx_B}{3} \right) \right] \quad (7.2.33)$$

The encapsulation process is kinetically controlled at $t = 0$ because no polymer shell exists in the beginning which can offer a diffusional resistance. The process may subsequently become diffusion-controlled after a certain conversion is reached.

- ◆ The condition for diffusion control is,

$$\phi \ll [x_B(a - x_B)(1 + 2bx_B/3)] \quad (7.2.34)$$

The conversion–time relationship in this case is given by,

$$t = \frac{1}{\beta} \left[-2(x_B - x_B^0) + \left(\frac{3+2b}{3+b} \right) \ln \left(\frac{1-x_B^0}{1-x_B} \right) + \frac{9}{(3+b)b} \ln \left\{ \frac{1+bx_B/3}{1+bx_B^0/3} \right\} \right] \quad (7.2.35)$$

where x_B^0 is the conversion after which the control shifts from kinetic at the beginning to diffusion.

- ◆ Equations (7.2.33) and (7.2.35) indicate that the time required for a definite conversion is proportional to R_0 for kinetic control. On the other hand, $t \propto R_0^2$ in the case of diffusion control.

Exercise

Exercise 7.2.1: Derive the equation: $\eta = \frac{1}{\Phi} \left(\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right)$.

Exercise 7.2.2: The bulk diffusivity of a gas is $7.5 \times 10^{-9} \text{ m}^2/\text{s}$ and its Knudsen diffusivity is $1.5 \times 10^{-10} \text{ m}^2/\text{s}$ at 300 K and atmospheric pressure. If the tortuosity factor is 1.2 and the porosity of the pellet is 0.5, compute the effective diffusivity.

Exercise 7.2.3: For a first-order gaseous chemical reaction (rate constant = $2 \times 10^{-5} \text{ m}^3 (\text{kg catalyst})^{-1} \text{ s}^{-1}$), compute the effectiveness factor if the density of the pellet is 2500 kg/m^3 . The effective diffusivity of the gaseous reactant is $2.7 \times 10^{-9} \text{ m}^2/\text{s}$ and the radius of the pellet is 1 mm.

Exercise 7.2.4: Consider the interfacial polycondensation between hexamethylene-1,6-diisocyanate and hexamethylene-1,6-diamine to form polyurea microcapsules. The amount of diisocyanate present in the organic phase is $4.5 \times 10^{-4} \text{ kg}$. The organic phase is dispersed in the aqueous phase by an emulsifier which prevents coalescence between the droplets. The volumes of the aqueous and organic phases are 100 cm^3 and 75 cm^3 , respectively. Calculate the time required to achieve 75% conversion after $3.5 \times 10^{-4} \text{ kg}$ of diamine is added to the aqueous phase. The dispersion is mechanically agitated and the mean diameter of the droplets is $7 \text{ }\mu\text{m}$. The density of the polymer is 1000 kg/m^3 , rate constant for the reaction is $1.5 \times 10^{-6} \text{ m}^4 \text{ kmol}^{-1} \text{ s}^{-1}$, partition coefficient of the diamine between the aqueous and polymer phases is 0.5, effective diffusivity of the diamine through the polymer is $1 \times 10^{-13} \text{ m}^2/\text{s}$, and the swelling factor is 1.6.

Exercise 7.2.5: Answer the following questions clearly.

- 1) What is effective diffusivity?
- 2) What is tortuosity? Why is it used?

- 3) Define effectiveness factor.
- 4) Explain the significance of Thiele modulus.
- 5) Explain how the effectiveness factor varies with Thiele modulus for a first-order catalytic reaction taking place in a spherical catalyst pellet.
- 6) Explain Weisz criterion.
- 7) Under what conditions does the effectiveness factor become close to unity?
- 8) Explain the microencapsulation process by interfacial polycondensation.
- 9) Explain why the interfacial polycondensation reaction between diamine and diacid chloride does not take place in the aqueous phase.

Suggested reading

Textbooks

- ♦ J. M. Smith, *Chemical Engineering Kinetics*, McGraw-Hill, Singapore, 1981, Chapter 11.
- ♦ P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapter 12.

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- ♦ H. S. Fogler, *Elements of Chemical Reaction Engineering*, Prentice-Hall of India, New Delhi, 2008, Chapter 12.
- ♦ L. K. Doraiswamy and M. M. Sharma, *Heterogeneous Reactions: Analysis, Examples, and Reactor Design (Vol. 2)*, John Wiley, New York, 1984, Chapter 3.

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- ♦ S. K. Yadav, A. K. Suresh, and K. C. Khilar, *AIChE J.*, **36**, 431 (1990).