CHAPTER III

DERIVATION OF KINETICS EQUATIONS

3.1. Formulation of Reaction Kinetics Equations

In an adiabatic batch reactor, when A is the limiting reactant:

Mole Balance:
$$N_{A_0} \frac{dX}{dt} = -r_A V \qquad (3.1)$$

    where N_{A0} = initial number of mole of the limiting reactant in the solution

    X = conversion of the limiting reactant

    t = time (min).

    V = total volume of the solution (100 ml).

    r_A = rate of appearance of the limiting reactant ($mol/dm^3 \times s$)

For initial period, V can be assumed constant; hence, the mole balance becomes:

$$C_{A_0} \frac{dX}{dt} = -r_A \qquad (3.2)$$

    where C_{A0} is the initial concentration of the limiting reactant.

Energy Balance:
$$T = T_0 + \frac{[-\Delta H_{rx}(T_0)]X}{C_{ps} + X\Delta Cp} \qquad (3.3)$$

    where T = temperature of the solution (K)

    $\Delta H_{rx}(T_0)$ = heat of reaction at temperature T_0 (kcal/mole A reacted)

    Cp_s = heat capacity of the solution with respect to the limiting reactant (kcal/mole A×K)

    ΔCp = overall change in the heat capacity (kcal/mole A×K)

Since $X\Delta C_p \ll C_{ps}$, the above equation can be written as:

$$T = T_0 + \frac{[-\Delta H_{rx}(T_0)]X}{C_{ps}} \qquad (3.4)$$

Therefore: $$\frac{dT}{dt} = \frac{-\Delta H_{rx}(T_0)}{C_{ps}}\frac{dX}{dt}$$ (3.5)

or: $$\frac{dT}{dt} = \frac{-\Delta H_{rx}(T_0)}{C_{ps}}\left(\frac{-r_A}{C_{A_0}}\right)$$ (3.6)

Rate Law: $$- r_A = kC_A^{\alpha} C_B^{\beta}$$ (3.7)

where C_A = concentration of reactant A in the solution

C_B = concentration of reactant B in the solution

k = rate constant

α, β = exothermic reaction order

Combining: $$\frac{dT}{dt} = \frac{-\Delta H_{rx}(T_0)}{C_{ps}}\left(\frac{kC_A^{\alpha}C_B^{\beta}}{C_{A_0}}\right)$$ (3.8)

Initial rate method: $$\left(\frac{dT}{dt}\right)_{t=0} = \frac{k_{t=0}[-\Delta H_{rx}(T_0)]}{C_{ps}}\left(\frac{C_{A_0}^{\alpha}C_{B_o}^{\beta}}{C_{A_0}}\right)$$ (3.9)

or $$\left(\frac{dT}{dt}\right)_{t=0} = \frac{k_{t=0}[-\Delta H_{rx}(T_0)]}{C_{ps}}\left(\frac{C_{A_0}^{\alpha}C_{B_o}^{\beta}}{C_{A_0}}\right)$$ (3.10)

or $$\left(\frac{dT}{dt}\right)_{t=0} = \frac{k_{t=0}[-\Delta H_{rx}(T_0)]}{C_{ps}}C_{A_o}^{\alpha-1}C_{B_o}^{\beta}$$ (3.11)

Similarly, if B is the limiting reactant:

$$\left(\frac{dT}{dt}\right)_{t=0} = \frac{k_{t=0}[-\Delta H_{rx}(T_0)]}{C_{ps}}C_{A_o}^{\alpha}C_{B_o}^{\beta-1}$$ (3.12)

Moreover, k for oxidation-reduction reactions is typically expressed as:

$$k = k_0 + k_1 * [H^+]^m + \frac{k_2}{[H^+]^n}$$ (3.13)

where $[H^+]$ = concentration of proton in the solution

m, n = proton concentration orders

$$k_0 = k_{00} * e^{\frac{-E_0}{RT}}$$ (3.14)

$$k_1 = k_{01} * e^{\frac{-E_1}{RT}}$$ (3.15)

$$k_2 = k_{02} * e^{\frac{-E_2}{RT}} \qquad (3.16)$$

in which k_{00}, k_{01}, k_{02} = rate constants of the medium, low, and high pH regions, respectively

E_0, E_1, and E_2 = activation energies of the medium, low, and high pH regions, respectively.

Using formulas (3.11) and (3.12), one can study the effect of each reactant and find out the orders of the reaction regarding to each reactant. Once the orders are known, initial rate constants ($k_{t=0}$) at different pH and temperature can be calculated using formulas (3.13) to (3.16) and thus the rate constant expression, or namely, values of k_0, k_1, k_2, E_0, E_1, and E_2, can be determined by using nonlinear regression in Excel, Matlab, or MathCad.

3.2. Model for Controlled Release of Catalyst

3.2.1. Dissolution Model

In controlled release devices employing dissolution as the rate-limiting step, the release of a pH-reducing reagent is controlled by dissolution of the coating polymer. The devices studied in this research are polymer-coated hard gelatin capsules filled with a pH-reducing reagent (e.g. an acid). Once the polymeric coat has dissolved, the hard gelatin capsule is exposed to the aqueous reactive solution. Since the gelatin capsule layer dissolves rapidly in aqueous solutions, the pH-reducing reagent is then immediately available for dissolution and disassociation to reduce the pH of the reactive system and catalyze the exothermic reaction. However, due to the uneven thickness of the coat, the reagent can only be released through a small area of the capsule where the thickness is the smallest. The time taken for all of the reagent to release, dissolve and disassociate to reduce the pH of the solution to a stabilized value is called the release time while the time taken for the coat and gelatin to dissolve is called the lag time. The process is conceptually shown in Figure 3.1.
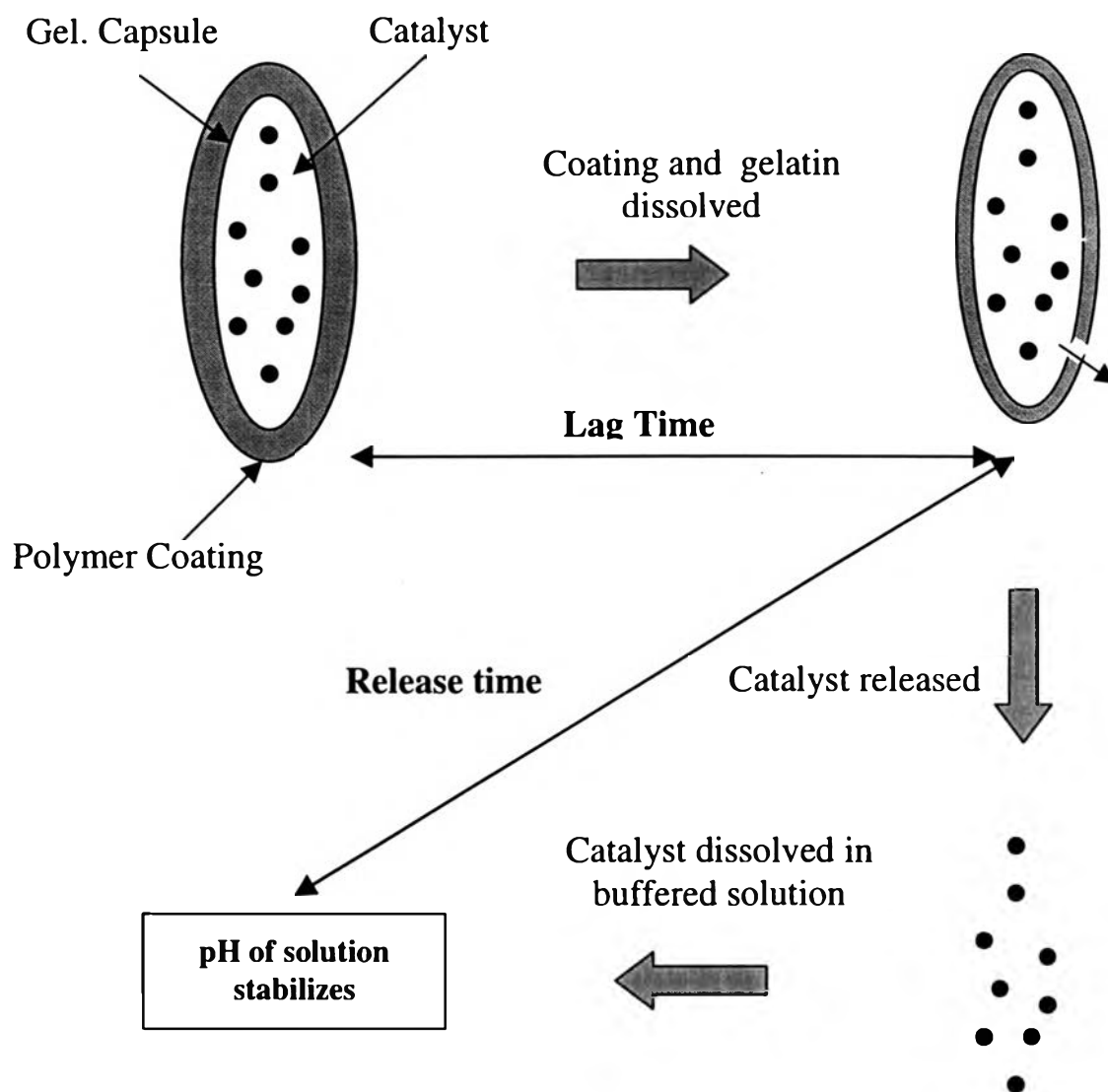
Figure 3.1 Steps of catalyst release from polymer-coated gelatin capsules.

Polymer dissolution is a heterogeneous process, occurring only on the surface of the material. There, the polymer is adjacent to an aqueous phase of high dielectric constant, and the acid dissociation constant is that normally measured in aqueous media. A model for the dissolution of polymer by ionization is shown in Figure 3.2.
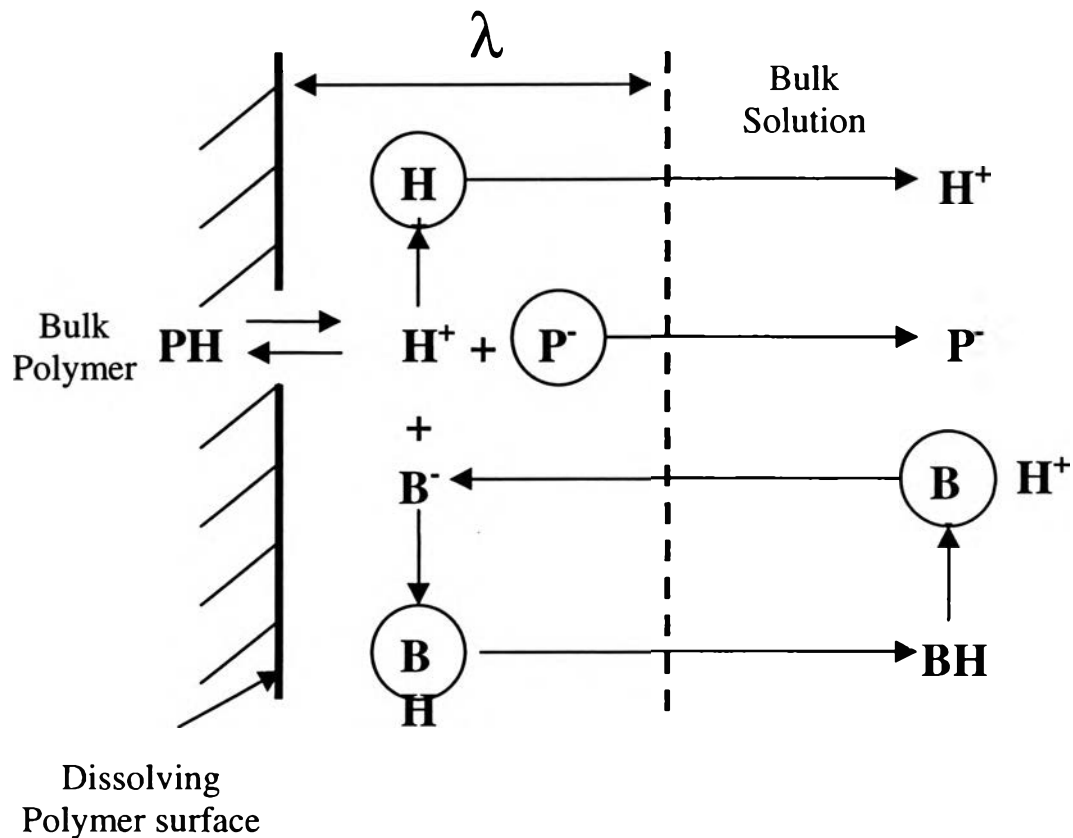
**Figure 3.2 Model for the dissolution of a polymer by ionization.**

3.2.2. Dissolution Governing Mechanisms

Polymer dissolution thus occurs through the dissociation of polymer molecules at the surface followed by diffusion of ionized polymer along with its associated counterions (i.e., hydrogen ions) through the aqueous boundary layer surrounding the polymer matrix. As a result, the dissolution of polymer can occur following two possible mechanisms:

1. Reaction limited

2. External mass transfer limited

3.2.2.1. Reaction Limited

At a class, the polymer represents a series of weak polyacids. In their unionized form, these polyacids are known to be hydrophobic and water insoluble but in the ionized state it is water-soluble. The ionization process can be represented as follows:
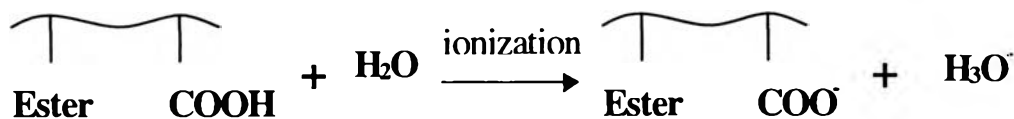
Hence, in the rate limited regime, the rate of dissolution is dominated by the rate of ionization, which is essentially a function of temperature, pH of the solution, and the concentration of polymer on the surface. From the ionization reaction above, it is obvious that in the rate limited regime, the rate of dissolution will directly proportional to the concentration of OH⁻ (or indirectly proportional to the concentration of H⁺), and directly proportional to the concentration of polymer on the surface. A model for the dissolution kinetics presented here is consistent with experimental observations:

$$\text{dissolution rate} \quad (\gamma) = -\frac{dl}{dt} = kp[H^+]^{-q}[P]^r \qquad (3.17)$$

where q and r are reaction orders (positive)

and:
$$kp = kp_0 e^{-\frac{Ep}{RT}} \qquad (3.18)$$

in which kp_0 = frequency factor for the polymer dissolution (mm/h)

Ep = activation energy for the polymer dissolution (kcal/mole)

3.2.2.2. External Mass Transfer Limited

The polymer dissolution will depend on the flow regime, temperature, pH of the solution, thickness of the polymer film, and the amount of polymer used per unit volume of the solution. Parameters for the polymer dissolution can be obtained from Frossling correlation:

$$Sh = 2 + 0.6\, Re^{0.5}\, Sc^{0.33} \qquad (3.19)$$

where Sh = Sherwood number

Re = Renold number

Sc = Schmidt number

3.3. Equations for Numerical Modeling

3.3.1. For a Well-mixed Batch Reactor

Mole Balance: $\qquad N_{A0}\dfrac{dX}{dt} = -r_A V$ (3.20)

or $\qquad \dfrac{dX}{dt} = -\dfrac{r_A V}{N_{A0}}$ (3.21)

Energy Balance: $\qquad \dfrac{dT}{dt} = \dfrac{UA(T_a - T) + (r_A V)[\Delta H_{rx}(T)]}{N_{A0}(Cp_s + \Delta CpX)}$ (3.22)

Where A = heat transfer area of the reactor (m^2)

U = overall heat transfer coefficient of the reactor (kcal/min×K×m^2)

Since $X\Delta C_p \ll C_{ps}$, the above equation can be written as:

$$\dfrac{dT}{dt} = \dfrac{UA(T_a - T) + (r_A V)[\Delta H_{rx}(T)]}{N_{A0}C_{ps}}$$ (3.23)

3.3.2. For a Pipeline (Modeled as a Plug-flow Reactor) Steady State

Mole Balance: $\qquad \dfrac{-dF_i}{dV} + v_i(-r_A) = 0$ (3.24)

or $\qquad \dfrac{1}{\pi r^2}\dfrac{-dF_i}{dl} + v_i(-r_A) = \dfrac{-dC_i}{dt}$ (3.25)

where F_i = molar flowrate of species i.

C_i = Concentration of species i.

v_i = stoichiometric coefficient of species i.

V = volume in the pipeline.

l = length in the pipeline.

r = radius of the pipeline.

Energy Balance:

$$Ua(T_a - T) - \left(\sum_{i=1}^{n} F_i C_{p_i}\right)\dfrac{dT}{dV} + (-r_A)[-\Delta H_{Rx}(T)] = 0$$ (3.26)

where a = heat exchange area per unit volume (m^2/m^3)

Cp_i = heat capacity of species i.

3.3.3. Common Equations

Reaction Kinetics: equations (5.1) and (5.2) and Table 5.1.

Polymer Dissolution Kinetics: equations (5.4) and (5.5)

Catalyst concentration:
$$C_{catalyst} = \begin{cases} 0 & if \ \ l \geq 0 \ \ (t \leq t_l) \\ \dfrac{n_c N_0}{V} \dfrac{t - t_l}{t_r} & if \ \ t_l < t < t_l + t_r \ \ (mol/dm^3) \ \ (3.27) \\ \dfrac{n_c N_0}{V} & if \ \ t \geq t_l + t_r \end{cases}$$

where l = thickness of the polymeric coat (mm)

n_c = number of capsules introduced into the reactive solution

N_0 = number of moles of catalyst encapsulated in one capsule

t_l = lag time (min)

t_r = release time (min)

pH of the solution: $\text{pH} = f\left(C_{NaNO_2}, C_{NH_4Cl}, C_{NaCl}, C_{NaOH}, C_{Catalyst}\right)$ 　　　　(3.28)

where C_{NaNO_2}, C_{NH_4Cl}, C_{NaCl}, C_{NaOH}, and $C_{Catalyst}$ are concentration of those chemicals respectively.

Ionic strength: 　　　　$I = \dfrac{1}{2} \sum CI_i z_i^2$ 　　　　(3.29)

where CI_i = Concentration of each ion

z_i = charge of each ion

Salts effect to pK_a (for $H_x A^{(n-1)-} / H_{x-1} A^{n-}$):

$$pK_a' = pK_a - (2n-1)\left(\dfrac{0.5\sqrt{I}}{1+\sqrt{I}} - 0.1I \right)$$ 　　　　(3.30)

where pK_a = equilibrium constant without salt effects

pK'_a = equilibrium constant with salt effects

n = charge of acidic ion

I = ionic strength

Activity coefficient: $\qquad a_i = C_i.f_i$ $\qquad\qquad$ (3.31)

where f_i = salt effect on H^+ or OH^-

$$-\log f_{H^+} = \frac{0.5\sqrt{I}}{1+3\sqrt{I}}$$ $\qquad\qquad$ (3.32)

$$-\log f_{OH^-} = \frac{0.5\sqrt{I}}{1+\dfrac{10.5}{9}\sqrt{I}}$$ $\qquad\qquad$ (3.33)

Electroneutral equation: $\sum a_i\left[A_i^{a_i+}\right]+\left[H^+\right]=\sum b_i\left[B_i^{b_i-}\right]+\left[OH^-\right]$ $\qquad$ (3.34)

where $\left[A_i^{a_i+}\right]$ = concentration of cation i having a charge of $a_i +$

$\left[B_i^{b_i-}\right]$ = concentration of anion i having a charge of $b_i -$

$[OH^-]$ = concentration of OH^- in the solution

Concentration of each ion (for a multiacid: $H_nA/H_{n-1}A^-/.../A^{n-}$):

$$[H_nA]=\frac{C_{total}}{1+10^{(pH-pKa_1)}+10^{(2pH-pKa_1-pKa_2)}+...+10^{(npH-pKa_1-pKa_2-...-pKa_n)}}$$ $\quad$ (3.35)

$$\left[H_{n-1}A^-\right]=10^{(pH-pKa_1)}[H_nA]$$ $\qquad\qquad$ (3.36)

....

$$\left[A^{n-}\right]=10^{(n\cdot pH-pKa_1-pKa_2-...-pKa_n)}[H_nA]$$ $\qquad\qquad$ (3.37)

Solving those simultaneous equations, one obtains:

$$pH =-\log(h)=-\log\left(\left[H^+\right]f_{H^-}\right)$$ $\qquad\qquad$ (3.38)

where pH is pH of the solution at the given conditions