Note: A tutorial of Polymath can be found in the summary notes of Chapter 1.

(b) Flow system. The stoichiometric table is the same as that for a batch system except that the number of moles of each species, N_i, is replaced by the molar flow rate of that species, F_i. For constant temperature and pressure, the volumetric flow rate is $v = v_0(1 + \varepsilon X)$, and the resulting concentrations of species A and B are

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{1+\varepsilon X} \tag{E3-6.5}$$

$$C_B = \frac{F_B}{v} = \frac{2F_{A0}X}{v_0(1+\varepsilon X)} = \frac{2C_{A0}X}{1+\varepsilon X} \tag{E3-6.6}$$

At equilibrium, $X = X_e$, and we can substitute Equations (E3-6.5) and (E3-6.6) into Equation (E3-6.1) to obtain the expression

$$K_C = \frac{C_{Be}^2}{C_{Ae}} = \frac{[2C_{A0}X_e/(1+\varepsilon X_e)]^2}{C_{A0}(1-X_e)/(1+\varepsilon X_e)}$$

Simplifying gives

$$K_C = \frac{4C_{A0}X_e^2}{(1-X_e)(1+\varepsilon X_e)} \tag{E3-6.7}$$

Rearranging to use Polymath yields

$$X_e = \sqrt{\frac{K_C(1-X_e)(1+\varepsilon X_e)}{4C_{A0}}} \tag{E3-6.8}$$

For a flow system with pure N_2O_4 feed, $\varepsilon = y_{A0}\,\delta = 1(2-1) = 1$.

We shall let Xef represent the equilibrium conversion in a flow system. Equation (E3-6.8) written in the Polymath format becomes

f(Xef) = Xef − [kc*(1 − Xef)*(1 + eps*Xef)/4/cao]^0.5

This solution is also shown in Table E3-6.2 ($X_{ef} = 0.51$).

Note that the equilibrium conversion in a flow reactor (i.e., $X_{ef} = 0.51$), with negligible pressure drop, is greater than the equilibrium conversion in a constant-volume batch reactor ($X_{eb} = 0.44$). Recalling Le Châtelier's principle, can you suggest an explanation for this difference in X_e?

(c) Rate laws. Assuming that the reaction follows an elementary rate law, then

$$-r_A = k_A\left[C_A - \frac{C_B^2}{K_C}\right] \tag{E3-6.9}$$

1. For a constant volume ($V = V_0$) batch system.

Here $C_A = N_A / V_0$ and $C_B = N_B / V_0$. Substituting Equations (E3-6.2) and (E3-6.3) into the rate law, we obtain the rate of disappearance of A as a function of conversion:

$-r_A = f(X)$
for a batch reactor
with $V = V_0$

$$-r_A = k_A\left[C_A - \frac{C_B^2}{K_C}\right] = k_A\left[C_{A0}(1-X) - \frac{4C_{A0}^2 X^2}{K_C}\right] \qquad \text{(E3-6.10)}$$

2. For a flow system.

Here $C_A = F_A/v$ and $C_B = F_B/v$ with $v = v_0(1 + \varepsilon X)$. Consequently, we can substitute Equations (E3-6.5) and (E3-6.6) into Equation (E3-6.9) to obtain

$-r_A = f(X)$ for a
flow reactor

$$-r_A = k_A\left[\frac{C_A(1-X)}{1+\varepsilon X} - \frac{4C_{A0}^2 X^2}{K_C(1+\varepsilon X)^2}\right] \qquad \text{(E3-6.11)}$$

As expected, the dependence of reaction rate on conversion for a constant-volume batch system [i.e., Equation (E3-6.10)] is different than that for a flow system [Equation (E3-6.11)] for gas-phase reactions.

If we substitute the values for C_{A0}, K_C, ε, and $k = 0.5$ min^{-1} in Equation (E3-6.11), we obtain $-r_A$ solely as a function of X for the flow system.

$$-r_A = \frac{0.5}{\min}\left[0.072\frac{\text{mol}}{\text{dm}^3}\frac{(1-X)}{(1+X)} - \frac{4(0.072\text{ mol/dm}^3)^2 X^2}{0.1\text{ mol/dm}^3(1+X)^2}\right]$$

$$-r_A = 0.0036\left[\frac{(1-X)}{(1+X)} - \frac{2.88\ X^2}{(1+X)^2}\right]\frac{\text{mol}}{\text{dm}^3 \cdot \min} \qquad \text{(E3-6.12)}$$

We can now form our Levenspiel plot.

We see $(1/-r_A)$ goes to infinity as X approaches X_e.
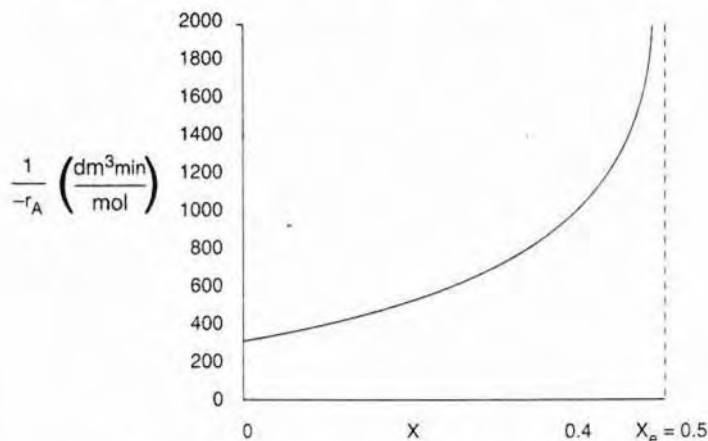

Figure E3-6.1 Levenspiel plot for a flow system.

(d) **CSTR volume**. Just for fun let's calculate the CSTR reactor volume necessary to achieve 80% of the equilibrium conversion of 50% (i.e., $X = 0.8X_e$) $X = 0.4$ for a feed rate of 3 mol/min.

Solution

$$-r_A = 0.0036\left[\frac{(1-0.4)}{(1+0.4)} - \frac{2.88(0.4)^2}{(1+0.4)^2}\right]$$

$$= 0.00070$$

$$V = \frac{F_{A0}X}{-r_A|_X} = \frac{F_{A0}(0.4)}{-r_A|_{0.4}} = \frac{(3 \text{ mol/min})(0.4)}{0.00070 \dfrac{\text{mol}}{\text{dm}^3 \cdot \text{min}}}$$

$$V = 1,714 \text{ dm}^3 = 1.71 \text{ m}^3$$

The CSTR volume necessary to achieve 40% conversion is 1.71 m³.

Closure. Having completed this chapter you should be able to write the rate law in terms of concentration and the Arrhenius temperature dependence. The next step is to use the stoichiometric table to write the concentrations in terms of conversion to finally arrive at a relationship between the rate of reaction and conversion. We have now completed the first three basic building blocks in our algorithm to study isothermal chemical reactions and reactors.

The CRE Algorithm
• Mole Balance, Ch 1
• Rate Law, Ch 3
• Stoichiometry, Ch 3
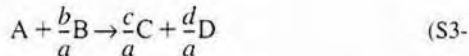• Combine, Ch 4
• Evaluate, Ch 4
• Energy Balance, Ch 8
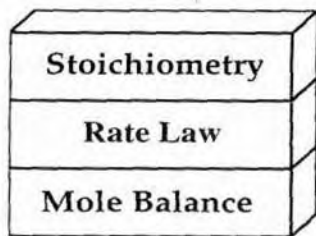
In Chapter 4, we will focus on the **combine** and **evaluation** building blocks which will then complete our algorithm for isothermal chemical reactor design.

SUMMARY

PART 1

1. Relative rates of reaction for the generic reaction:

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D \tag{S3-}$$

The relative rates of reaction can be written either as

$$\boxed{\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}} \text{ or } \boxed{\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}} \tag{S3-}$$

2. *Reaction order* is determined from experimental observation:

$$A + B \longrightarrow C \tag{S3-}$$

$$-r_A = kC_A^\alpha C_B^\beta$$

The reaction in Equation (S3-3) is α order with respect to species A and order with respect to species B, whereas the overall order, n, is $\alpha + \beta$. Rea tion order is determined from experimental observation. If $\alpha = 1$ and $\beta =$ we would say that the reaction is first order with respect to A, second ord with respect to B, and overall third order. We say a reaction follows an el mentary rate law if the reaction orders agree with the stoichiometric coef cients for the reaction as written.

3. The temperature dependence of a specific reaction rate is given by the *Arrh nius equation*,

$$k = Ae^{-E/RT} \tag{S3-}$$

where A is the frequency factor and E the activation energy.

If we know the specific reaction rate, k, at a temperature, T_0, and the act vation energy, we can find k at any temperature, T,

$$k(T) = k(T_0)\exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \tag{S3-}$$

Similarly from Appendix C, Equation (C-9), if we know the equilibrium co stant at a temperature, T_1, and the heat of reaction, we can find the equili rium constant at any other temperature

$$K_P(T) = K_P(T_1)\exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \tag{C-}$$

PART 2

4. The *stoichiometric table* for the reaction given by Equation (S3-1) being carried out in a flow system is

Species	Entering	Change	Leaving
A	F_{A0}	$-F_{A0}X$	$F_{A0}(1 - X)$
B	F_{B0}	$-\left(\dfrac{b}{a}\right) F_{A0}X$	$F_{A0}\left(\Theta_B - \dfrac{b}{a} X\right)$
C	F_{C0}	$\left(\dfrac{c}{a}\right) F_{A0}X$	$F_{A0}\left(\Theta_C + \dfrac{c}{a} X\right)$
D	F_{D0}	$\left(\dfrac{d}{a}\right) F_{A0}X$	$F_{A0}\left(\Theta_D + \dfrac{d}{a} X\right)$
I	$\dfrac{F_{I0}}{F_{T0}}$	—	$\dfrac{F_{I0}}{F_T = F_{T0} + \delta F_{A0}X}$

$$\text{where} \quad \delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

5. In the case of ideal gases, Equations (S3-6) and (S3-7) relate volume and volumetric flow rate to conversion.

Batch constant volume: $\quad V = V_0$ \hfill (S3-6)

Flow systems: Gas: $\quad v = v_0 \left(\dfrac{P_0}{P}\right) (1 + \varepsilon X) \dfrac{T}{T_0}$ \hfill (S3-7)

Liquid: $\quad v = v_0$

For the general reaction given by (S3-1), we have

$$\boxed{\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1}$$ \hfill (S3-8)

$$\delta = \frac{\text{Change in total number of moles}}{\text{Mole of A reacted}}$$

Definitions of δ and ε and

$$\boxed{\varepsilon = y_{A0}\delta}$$ \hfill (S3-9)

$$\varepsilon = \frac{\text{Change in total number of moles for complete conversion}}{\text{Total number of moles fed to the reactor}}$$

6. For gas-phase reactions, we use the definition of concentration ($C_A = F_A/v$) along with the stoichiometric table and Equation (S3-7) to write the concentration of A and C in terms of conversion.

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = C_{A0}\left[\frac{1-X}{1+\varepsilon X}\right]\frac{P}{P_0}\left(\frac{T_0}{T}\right) \quad \text{(S3-10)}$$

$$C_C = \frac{F_C}{v} = C_{A0}\left[\frac{\Theta_C + (c/a)X}{1+\varepsilon X}\right]\frac{P}{P_0}\left(\frac{T_0}{T}\right) \quad \text{(S3-11)}$$

with $\Theta_C = \dfrac{F_{C0}}{F_{A0}} = \dfrac{C_{C0}}{C_{A0}} = \dfrac{y_{C0}}{y_{A0}}$

7. For incompressible liquids, the concentrations of species A and C in the reaction given by Equation (S3-1) can be written as

$$C_A = \frac{F_A}{v} = \frac{F_{A0}}{v_0}(1-X) = C_{A0}(1-X) \quad \text{(S3-12)}$$

$$C_C = C_{A0}\left(\Theta_C + \frac{c}{a}X\right) \quad \text{(S3-13)}$$

Equations (S3-12) and (S3-13) also hold for gas-phase reactions carried out at constant volume in batch systems.

8. In terms of gas-phase molar flow rates, the concentration of species i is

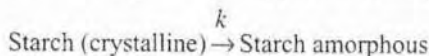$$C_i = C_{T0}\frac{F_i}{F_{T0}}\frac{P}{P_0}\frac{T_0}{T} \quad \text{(S3-14)}$$

CD-ROM MATERIAL

• **Learning Resource**
  1. *Summary Notes for Chapter 3*
  2. *Web Modules*
     A. Cooking a Potato
        The chemical reaction engineering is applied to cooking a potato

$$\text{Starch (crystalline)} \xrightarrow{k} \text{Starch amorphous}$$
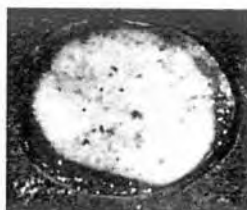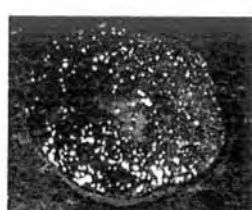
        with

$$k = Ae^{-E/RT}.$$

Summary Notes

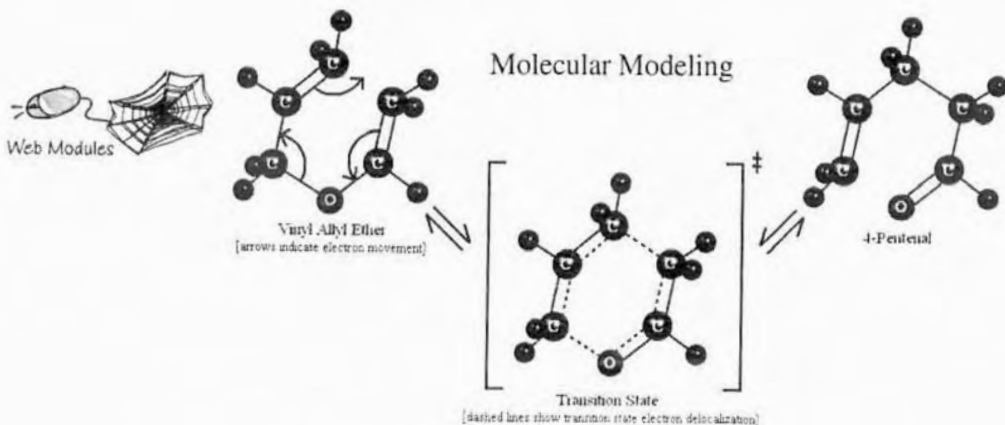8 minutes at 400° F   12 minutes at 400° F   16 minutes at 400° F

B. Molecular Reaction Engineering

Molecular simulators (Spartan, Cerius[2]) are used to make predictions of the activation energy. The fundamentals of density functional are presented along with specific examples.

Web Modules

Molecular Modeling

Vinyl Allyl Ether
[arrows indicate electron movement]

Transition State
[dashed lines show transition state electron delocalization]

4-Pentenal

3. *Interactive Computer Modules*
   A. Quiz Show II

Interactive

Computer Modules

Kinetics Challenge II

For the reaction   A   2D

which is: non-isothermal
irreversible
gas phase with pure A fed to the reactor,

what is the concentration of D? ...

■ 1 $C_D = C_{A0} \dfrac{2X}{(1+X)}$ ■ 3 $C_D = C_{A0} 2X$

■ 2 $C_D = C_{A0} \dfrac{0.5X}{(1-0.5X)}\left[\dfrac{P}{P_0}\right]\left[\dfrac{T}{T_0}\right]$ ☑ 4 $C_D = C_{A0} \dfrac{2X}{(1+X)}\left[\dfrac{P}{P_0}\right]\left[\dfrac{T}{T_0}\right]$

Send Checked Answer   Please check ΔE box to the left of the desired answer and click on "Send Checked Answer"

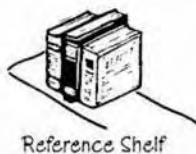Hint   Correct

Main Menu   Continue

D0

4. *Solved Problems*
   A. CDP3-A_B Activation Energy for a Beetle Pushing a Ball of Dung
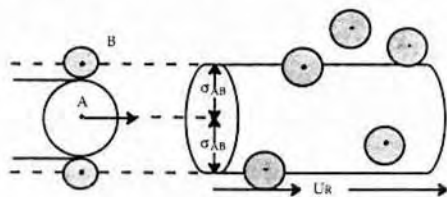   B. CDP3-B_B Microelectronics Industry and the Stoichiometric Table
• **FAQ [Frequently Asked Questions]**—In Updates/FAW icon section
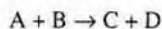
Solved Problems

• **Professional Reference Shelf**

R3.1. *Collision Theory*

In this section, the fundamentals of collision theory

Schematic of collision cross section

are applied to the reaction

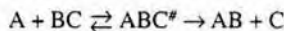$$A + B \rightarrow C + D$$

to arrive at the following rate law

$$-r_A = \underbrace{\pi\sigma_{AB}^2 \left(\frac{8\pi k_B T}{\mu\pi}\right)^{1/2} N_{Avo}}_{A} e^{-E_A/RT} C_A C_B = A e^{-E_A/RT} C_A C_B$$

The activation energy, E_A, can be estimated from the Polanyi equation

$$E_A = E_A^\circ + \gamma_P \Delta H_{Rx}$$

R3.2. *Transition State Theory*

In this section, the rate law and rate law parameters are derived for the reacti

$$A + BC \rightleftarrows ABC^\# \rightarrow AB + C$$

using transition state theory. The Figure P3B-1 shows the energy of the m•
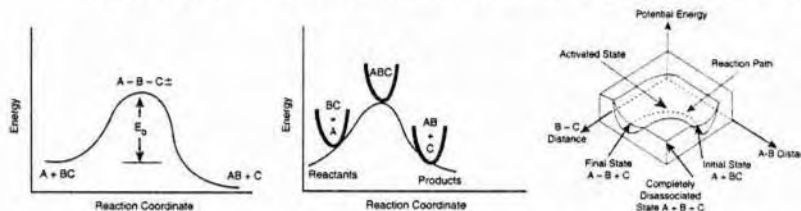ecules along the reaction coordinate which measures the progress of the reacti•

Figure P3B-1   Reaction coordinate for (a) S_{N2} reaction, and (b) generalized reaction. (c) 3-D
energy surface for generalized reaction.

We will now use statistical and quantum mechanics to evaluate $K_C^\#$ to arri•
at the equation

$$-r_A = \left(\frac{k_B T}{h}\right) e^{-\frac{\Delta E_0}{kT}} \frac{(q'_{ABC^\#})}{(q'_A)(q'_{BC})} C_A C_{BC}$$

where q' is overall the partition function per unit volume and is the product of translational, vibration, rotational, and electric partition functions; that is,

$$q' = q'_T q'_V q'_R q'_E$$

The individual partition functions to be evaluated are[5]

Translation

$$q'_T = \frac{(2\pi m k_B T)^{3/2}}{h^3} = \left(\frac{9.88 \times 10^{29}}{m^3}\right)\left(\frac{m_{AB}}{1 \text{ amu}}\right)^{2/3}\left(\frac{T}{300 \text{ K}}\right)^{3/2}$$

Vibration

$$q_V = \frac{1}{1 - \exp\left(-\dfrac{hv}{k_B T}\right)}$$

$$\frac{hv}{k_B T} = \frac{hcv}{k_B T} = 4.8 \times 10^{-3}\left(\frac{\tilde{v}}{1 \text{ cm}^{-1}}\right)\left(\frac{300 \text{ K}}{T}\right)$$

Rotation

$$q_R = \frac{8\pi^2 I k_B T}{S_y h^2} = 12.4\left(\frac{T}{300 \text{ K}}\right)\left(\frac{I_{AB}}{1 \cdot \text{amu} \cdot \text{Å}^2}\right)\left(\frac{1}{S_y}\right)$$
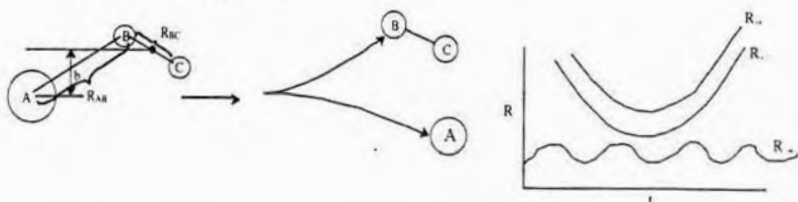
The Eyring Equation

$$k = \left(\frac{k_B T}{h}\right)\frac{e^{\Delta S^\#/R} e^{-\Delta H^\#/RT}}{K_\gamma C_{T0}}$$

R3.3. *Molecular Dynamics*

The reaction trajectories are calculated to determine the reaction cross section of the reacting molecules. The reaction probability is found by counting up the number of reactive trajectories after Karplus.[6]
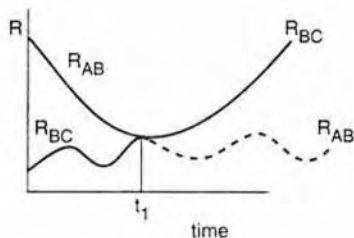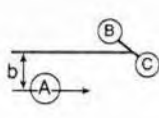
Nonreactive Trajectory

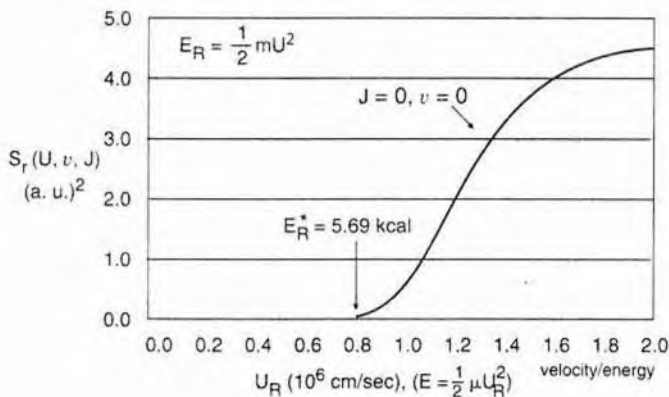[5] R. Masel, *Chemical Kinetics*: (New York McGraw Hill, 2002), p. 594.
[6] M. Karplus, R.N. Porter, and R.D. Sharma, *J. Chem. Phys.*, *43* (9), 3259 (1965).

Reactive Trajectory

Reference Shelf

From these trajectories, one can calculate the following reaction cross section, S_r, shown for the case where both the vibrational and rotational quantum numbers are zero:

The specific reaction rate can then be calculated from first principle for simple molecules.

R3.4. *Measures Other Than Conversion*
Gas Phase
(*Note:* This topic will be covered in Chapter 4 but for those who want to use it now, look on the CD-ROM.) For membrane reactors and gas-phase multiple reactions, it is much more convenient to work in terms of the number of moles (N_A, N_B) or molar flow rates (F_A, F_B, etc.) rather than conversion.

R3.5. *Reactions with Condensation*
We now consider a gas-phase reaction in which condensation occurs. An example of this class of reactions is

$$C_2H_6(g) + 2Br_2(g) \rightarrow C_2H_4Br_2(g, l) + 2HBr(g)$$
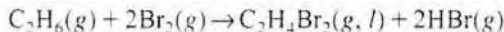
Here we will develop our stoichiometric table for reactions with phase change. When one of the products condenses during the course of a reaction, calculation of the change in volume or volumetric flow rate must be undertaken in a slightly different manner. Plots of the molar flow rates of condensate D and the total, together with the reciprocal rate, are shown here as a function of conversion.

QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

Homework Problems

Web Hint

Creative Thinking

P3-1$_C$ (a) List the important concepts that you learned from this chapter. What concepts are you not clear about?

(b) Explain the strategy to evaluate reactor design equations and how this chapter expands on Chapter 2.

(c) Choose a FAQ from Chapters 1 through 3 and say why it was the most helpful.

(d) Listen to the audios 🔊 on the CD. Select a topic and explain it.

(e) Read through the Self Tests and Self Assessments for Lectures 1 through 4 on the CD-ROM. Select one and critique it. (See Preface.)

(f) Which example on the CD-ROM Lecture notes for Chapters 1 through 3 was most helpful?

(g) Which of the ICMs for the first three chapters was the most fun?

P3-2$_A$ (a) **Example 3-1.** Make a plot of k versus T. On this plot also sketch k versus $(1/T)$ for $E = 240$ kJ/mol, for $E = 60$ kJ/mol. Write a couple of sentences describing what you find. Next write a paragraph describing the activation, how it affects chemical reaction rates, and what its origins are?

(b) **Example 3-2.** Would the example be correct if water was considered an inert?

(c) **Example 3-3.** How would the answer change if the initial concentration or glyceryl sterate were 3 mol/dm^3?

(d) **Example 3-4.** What is the smallest value of $\Theta_B = (N_{B0}/N_{A0})$ for which the concentration of B will *not* become the limiting reactant?

(e) **Example 3-5.** Under what conditions will the concentration of the inert nitrogen be constant? Plot Equation (E3-5.2) of $(1/-r_A)$ as a function of X up to value of $X = 0.99$. What did you find?

(f) **Example 3-6.** Why is the equilibrium conversion lower for the batch system than the flow system? Will this always be the case for constant volume batch systems? For the case in which the total concentration C_{T0} is to remain constant as the inerts are varied, plot the equilibrium conversion as a function of mole fraction of inerts for both a PFR and a constant-volume batch reactor. The pressure and temperature are constant at 2 atm and 340 K. Only N_2O_4 and inert I are to be fed.

(g) **Collision Theory**—Professional Reference Shelf. Make an outline of the steps that were used to derive

$$-r_A = Ae^{-E/RT}C_A C_B$$

(h) The rate law for the reaction $(2A + B \rightarrow C)$ is $-r_A = k_A C_A^2 C_B$ with $k_A = 25(\text{dm}^3/\text{mol})^2/\text{s}$. What are k_B and k_C?

(i) At low temperatures the rate law for the reaction $\left(\frac{1}{2}A + \frac{3}{2}B \rightarrow C\right)$ is $-r_A = k_A C_A C_B$. If the reaction is reversible at high temperatures, what is the rate law?

Kinetics Challenge II

Rate	Law	Stoich
100	100	100
200	200	200
300	300	300

P3-3$_A$ Load the Interactive Computer Module (ICM) Kinetic Challenge from the CD-ROM. Run the module, and then record your performance number for the module which indicates your mastering of the material. Your professor has

the key to decode your performance number. ICM Kinetics Challeng
Performance # _____.

P3-4$_A$ The frequency of flashing of fireflies and the frequency of chirping of cricket
as a function of temperature follow [*J. Chem. Educ.*, 5, 343 (1972) Reprinte
by permission.].

For fireflies:

T (°C)	21.0	25.00	30.0
Flashes/min	9.0	12.16	16.2

For crickets:

T (°C)	14.2	20.3	27.0
Chirps/min	80	126	200

The running speed of ants and the flight speed of honeybees as a function c
temperature are given below [Source: B. Heinrich, *The Hot-Blooded Insect*
(Cambridge, Mass.: Harvard University Press, 1993)].

For ants:

T (°C)	10	20	30	38
V (cm/s)	0.5	2	3.4	6.5

For honeybees:

T (°C)	25	30	35	40
V (cm/s)	0.7	1.8	3	?

(a) What do the firefly and cricket have in common? What are their differ
ences?
(b) What is the velocity of the honeybee at 40°C? At –5°C?
(c) Do the bees, ants, crickets, and fireflies have anything in common? If sc
what is it? You may also do a pairwise comparison.
(d) Would more data help clarify the relationships among frequency, speec
and temperature? If so, in what temperature should the data be obtained
Pick an insect, and explain how you would carry out the experiment t
obtain more data. [For an alternative to this problem, see CDP3-A$_B$.]

P3-5$_B$ **Troubleshooting.** Corrosion of high-nickel stainless steel plates was found t
occur in a distillation column used at DuPont to separate HCN and water. Su
furic acid is always added at the top of the column to prevent polymerizatio
of HCN. Water collects at the bottom of the column and HCN at the top. Th
amount of corrosion on each tray is shown in Figure P3-5 as a function c
plate location in the column.

The bottom-most temperature of the column is approximately 125°(
and the topmost is 100°C. The corrosion rate is a function of temperature an
the concentration of an HCN–H$_2$SO$_4$ complex. Suggest an explanation for th
observed corrosion plate profile in the column. What effect would the colum
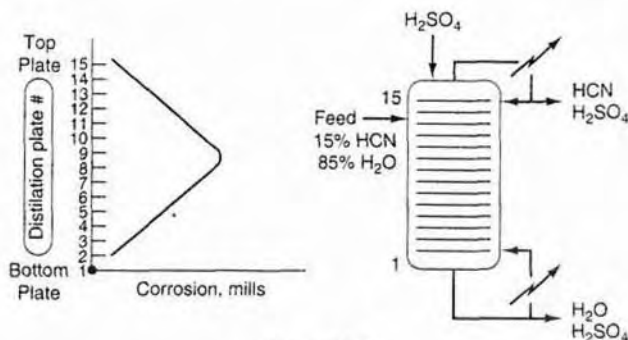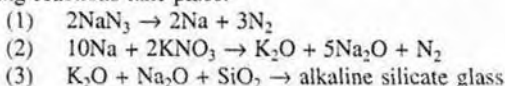operating conditions have on the corrosion profile?

Figure P3-5

P3-6$_B$ **Inspector Sgt. Ambercromby of Scotland Yard.** It is believed, although never proven, that Bonnie murdered her first husband, Lefty, by poisoning the tepid brandy they drank together on their first anniversary. Lefty was unware she had coated her glass with an antidote before she filled both glasses with the poisoned brandy. Bonnie married her second husband, Clyde, and some years later when she had tired of him, she called him one day to tell him of her new promotion at work and to suggest that they celebrate with a glass of brandy that evening. She had the fatal end in mind for Clyde. However, Clyde suggested that instead of brandy, they celebrate with ice cold Russian vodka and they down it Cossack style, in one gulp. She agreed and decided to follow her previously successful plan and to put the poison in the vodka and the antidote in her glass. The next day, both were found dead. Sgt. Ambercromby arrives. What were the first three questions he asks? What are two possible explanations? Based on what you learned from this chapter, what do you feel Sgt. Ambercromby suggested as the most logical explanation?

[Professor Flavio Marin Flores, ITESM, Monterrey, Mexico]

P3-7$_B$ (a) The rule of thumb that the rate of reaction doubles for a 10°C increase in temperature occurs only at a specific temperature for a given activation energy. Develop a relationship between the temperature and activation energy for which the rule of thumb holds. Neglect any variation of concentration with temperature.

(b) Determine the activation energy and frequency factor from the following data:

k (min^{-1})	0.001	0.050
T (°C)	00.0	100.0

(c) Write a paragraph explaining activation energy, E, and how it affects the chemical reaction rate. Refer to Section 3.3 and especially the Professional Reference Shelf sections R3.1, R3.2, and R3.3 if necessary.

P3-8$_C$ **Air bags** contain a mixture of NaN$_3$, KNO$_3$, and SiO$_2$. When ignited, the following reactions take place:

(1) $2NaN_3 \rightarrow 2Na + 3N_2$

(2) $10Na + 2KNO_3 \rightarrow K_2O + 5Na_2O + N_2$

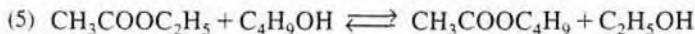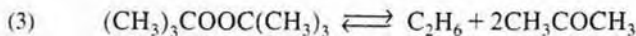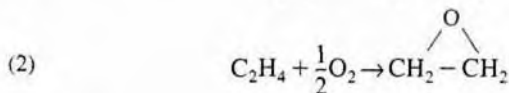(3) $K_2O + Na_2O + SiO_2 \rightarrow$ alkaline silicate glass

Reactions (2) and (3) are necessary to handle the toxic sodium reaction product from detonation. Set up a stoichiometric table solely in terms of NaN_3 (A), KNO_3 (B), etc., and the number of moles initially. If 150 g of sodium azide are present in each air bag, how many grams of KNO_3 and SiO_2 must be added to make the reaction products safe in the form of alkaline silicate glass after the bag has inflated. The sodium azide is in itself toxic. How would you propose to handle all the undetonated air bags in cars piling up in the nation's junkyards.

P3-9$_A$ **Hot Potato.** Review the "Cooking a Potato" web module on the CD-ROM or on the web.

(a) It took the potato described on the web 1 hour to cook at 350°F. Builder Bob suggests that the potato can be cooked in half that time if the oven temperature is raised to 600°F. What do you think?

(b) Buzz Lightyear says, "No Bob," and suggests that it would be quicker to boil the potato in water at 100°C because the heat transfer coefficient is 20 times greater. What are the tradeoffs of oven versus boiling?

(c) Ore Ida Tater Tots is a favorite of one of the Proctors/Graders in the class, Adam Cole. Tater Tots are 1/12 the size of a whole potato but approximately the same shape. Estimate how long it would take to cook a Tater Tot at 400°F? At what time would it be cooked half way through? ($r/R = 0.5$)?

P3-10$_A$ (a) Write the rate law for the following reactions assuming each reaction follows an elementary rate law.

(1)
$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

(2)
$$C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_2 \overset{\displaystyle O}{\overset{\displaystyle \diagup\diagdown}{-}} CH_2$$

(3)
$$(CH_3)_3COOC(CH_3)_3 \rightleftarrows C_2H_6 + 2CH_3COCH_3$$

(4)
$$nC_4H_{10} \rightleftarrows iC_4H_{10}$$

(5) $CH_3COOC_2H_5 + C_4H_9OH \rightleftarrows CH_3COOC_4H_9 + C_2H_5OH$

(b) Write the rate law for the reaction

$$2A + B \rightarrow C$$

if the reaction (1) is second order in B and overall third order, (2) is zero order in A and first order in B, (3) is zero order in both A and B, and (4) is first order in A and overall zero order.

(c) Find and write the rate laws for the following reactions

(1) $H_2 + Br_2 \rightarrow 2HBr$

(2) $H_2 + I_2 \rightarrow 2HI$
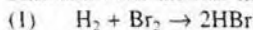
P3-11$_A$ Set up a stoichiometric table for each of the following reactions and express the concentration of each species in the reaction as a function of conversion

evaluating all constants (e.g., ε, Θ). Then, assume the reaction follows an elementary rate law, and write the reaction rate solely as a function of conversion, i.e., $-r_A = f(X)$.

(a) For the liquid-phase reaction

$$\underset{CH_2-CH_2}{\overset{O}{\triangle}} + H_2O \xrightarrow{H_2SO_4} \underset{CH_2-OH}{\overset{CH_2-OH}{|}}$$
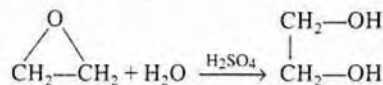
the initial concentrations of ethylene oxide and water are 1 lb-mol/ft^3 and 3.47 lb-mol/ft^3 (62.41 lb/ft$^3 \div 18$), respectively. If $k = 0.1$ dm^3/mol · s at 300 K with $E = 12,500$ cal/mol, calculate the space-time volume for 90% conversion at 300 K and at 350 K.

(b) For the isothermal, isobaric gas-phase pyrolysis

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

pure ethane enters the flow reactor at 6 atm and 1100 K. How would your equation for the concentration and reaction rate change if the reaction were to be carried out in a constant-volume batch reactor?

(c) For the isothermal, isobaric, catalytic gas-phase oxidation

$$C_2H_4 + \tfrac{1}{2}O_2 \longrightarrow \underset{CH_2-CH_2}{\overset{O}{\triangle}}$$

the feed enters a PBR at 6 atm and 260°C and is a stoichiometric mixture of only oxygen and ethylene.

(d) For the isothermal, isobaric, catalytic gas-phase reaction is carried out in a PBR
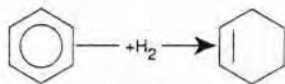
the feed enters a PBR at 6 atm and 170°C and is a stoichiometric mixture. What catalyst weight is required to reach 80% conversion in a fluidized CSTR at 170°C and 270°C? The rate constant is defined wrt benzene and $v_0 = 50$ dm^3/min.

$$k_B = \frac{53 \text{ mol}}{\text{kgcat} \cdot \text{min} \cdot \text{atm}^3} \text{ at 300 K with } E = 80 \text{ kJ/mol}$$

P3-12$_B$ There were 5430 million pounds of ethylene oxide produced in the United States in 1995. The flowsheet for the commercial production of ethylene oxide (EO) by oxidation of ethylene is shown in Figure P3-12. We note that the process essentially consists of two systems, a reaction system and a separation system. Discuss the flowsheet and how your answers to P3-11 (c) would change if air is used in a stoichiometric feed. This reaction is studied further in Chapter 4.
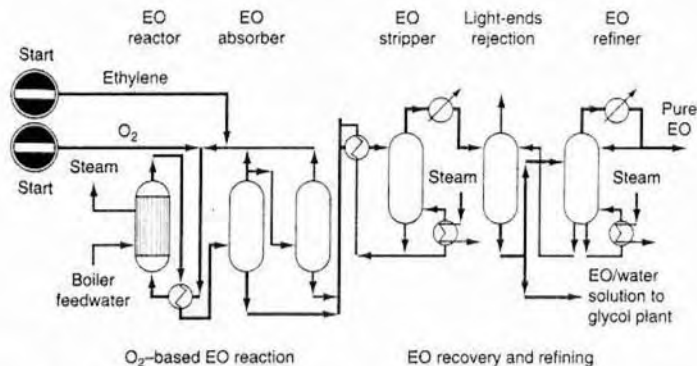
Figure P3-12 EO plant flowsheet. [Adapted from R. A. Meyers, ed.. *Handbook of Chemical Production Processes, Chemical Process Technology Handbook Series,* New York: McGraw-Hill, 1983, p. 1.5-5. ISBN 0-67-041-765-2.]

P3-13$_B$ The formation of nitroanalyine (an important intermediate in dyes—calle fast orange) is formed from the reaction of orthonitrochlorobenzene (ONCB and aqueous ammonia. (See Table 3-1 and Example 9-2.)
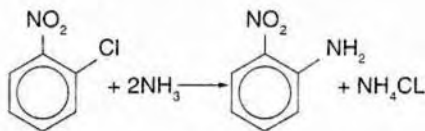
The liquid-phase reaction is first order in both ONCB and ammonia with $k = 0.0017$ m^3/kmol · min at 188°C with $E = 11,273$ cal/mol. The initia entering concentrations of ONCB and ammonia are 1.8 kmol/m^3 and 6.(kmol/m^3, respectively (more on this reaction in Chapter 9).

(a) Write the rate law for the rate of disappearance of ONCB in terms o concentration.

(b) Set up a stoichiometric table for this reaction for a flow system.

(c) Explain how part (a) would be different for a batch system.

(d) Write $-r_A$ solely as a function of conversion. $-r_A =$ _____

(e) What is the initial rate of reaction ($X = 0$)   at 188°C? $-r_A =$ _____
at 25°C? $-r_A =$ _____
at 288°C? $-r_A =$ _____

(f) What is the rate of reaction when $X = 0.90$ at 188°C? $-r_A =$ _____
at 25°C? $-r_A =$ _____
at 288°C? $-r_A =$ _____

(g) What would be the corresponding CSTR reactor volume at 25°C t achieve 90% conversion at 25°C and at 288°C for a molar feed rate of 2 mol/min

at 25°C? $V =$ _____
at 288°C? $V =$ _____

P3-14$_B$ Adapted from M. L. Shuler and F. Kargi, *Bioprocess Engineering*, Prentice Hall (2002). Cell growth takes place in bioreactors called chemostats.
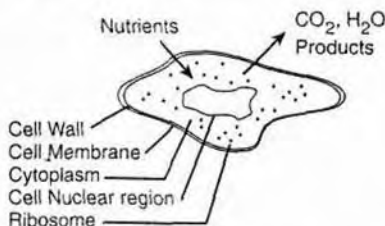
A substrate such as glucose is used to grow cells and produce a product.

$$\text{Substrate} \xrightarrow{\text{Cells}} \text{More Cells (biomass)} + \text{Product}$$

A generic molecule formula for the biomass is $C_{4.4}H_{7.3}N_{0.86}O_{1.2}$. Consider the growth of a generic organism on glucose

$$C_6H_{12}O_6 + aO_2 + bNH_3 \rightarrow c(C_{4.4}H_{7.3}N_{0.86}O_{1.2}) + dH_2O + eCO_2$$

Experimentally, it was shown that for this organism, the cells convert 2/3 of carbon substrate to biomass.

(a) Calculate the stoichiometric coefficients a, b, c, d, and e (*Hint:* carry out atom balances [*Ans:* c = 0.91]).

(b) Calculate the yield coefficients $Y_{C/S}$ (g cells/g substrate) and Y_{C/O_2} (g cells/g O_2). The gram of cells are dry weight (no water—gdw) (*Ans:* Y_{C/O_2} = 1.77 gdw cells/g O_2) (gdw = grams dry weight).

P3-15$_B$ The gas-phase reaction

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \longrightarrow NH_3$$

is to be carried out isothermally. The molar feed is 50% H_2 and 50% N_2, at a pressure of 16.4 atm and 227°C.

(a) Construct a complete stoichiometric table.

(b) What are C_{A0}, δ, and ε? Calculate the concentrations of ammonia and hydrogen when the conversion of H_2 is 60%. (*Ans:* C_{H_2} = 0.1 mol/dm^3)

(c) Suppose by chance the reaction is elementary with k_{N_2} = 40 dm^3/mol/s. Write the rate of reaction *solely* as a function of conversion for (1) a flow system and (2) a constant volume batch system.

P3-16$_B$ Calculate the equilibrium conversion and concentrations for each of the following reactions.

(a) The liquid-phase reaction

$$A + B \rightleftharpoons C$$
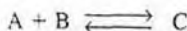
with $C_{A0} = C_{B0} = 2$ mol/dm^3 and $K_C = 10$ dm^3/mol.

(b) The gas-phase reaction

$$A \rightleftharpoons 3C$$

carried out in a flow reactor with no pressure drop. Pure A enters at a temperature of 400 K and 10 atm. At this temperature, $K_C = 0.25$(dm^3/mol)^2.

(c) The gas-phase reaction in part (b) carried out in a constant-volume batch reactor.

(d) The gas-phase reaction in part (b) carried out in a constant-pressure batch reaction.

P3-17$_B$ Consider a *cylindrical batch reactor* that has one end fitted with a frictionless piston attached to a spring (Figure P3-17). The reaction

$$A + B \longrightarrow 8C$$

with the rate expression

$$-r_A = k_1 C_A^2 C_B$$

is taking place in this type of reactor.
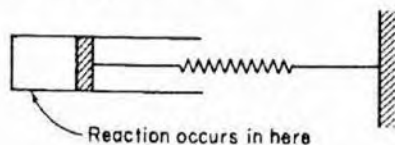

Reaction occurs in here

Figure P3-17

(a) Write the rate law solely as a function of conversion, numerically evaluating all possible symbols. (*Ans.:* $-r_A = 5.03 \times 10^{-9} [(1 - X)^3/(1 + 3X)^{3/2}]$ lb mol/ft$^3 \cdot$s.)

(b) What is the conversion and rate of reaction when $V = 0.2$ ft^3? (*Ans.:* $X = 0.259$, $-r_A = 8.63 \times 10^{-10}$ lb mol/ft$^3 \cdot$s.)

Additional information:

Equal moles of A and B are present at $t = 0$
Initial volume: 0.15 ft^3
Value of k_1: 1.0 (ft^3/lb mol)$^2 \cdot$s^{-1}
The relationship between the volume of the reactor and pressure within the reactor is

$$V = (0.1)(P) \qquad (V \text{ in ft}^3, P \text{ in atm})$$

Temperature of system (considered constant): 140°F
Gas constant: 0.73 ft$^3 \cdot$atm/lb mol$\cdot$°R

P3-18$_C$ Read the sections on Collision Theory, Transition State Theory, and Molecular Dynamics in the Professional Reference Shelf on the CD-ROM.

(a) Use collision theory to outline the derivation of the Polanyi–Semenov equation, which can be used to estimate activation energies from the heats of reaction, ΔH_R, according to the equation

$$E = C - \alpha(-\Delta H_R) \qquad (P3-18.1)$$

(b) Why is this a reasonable correlation? (*Hint:* See Professional Reference Shelf 3R.1: *Collision Theory.*)

(c) Consider the following family of reactions:

	E (kcal/mol)	$-\Delta H_R$ (kcal/mol)
H + RBr $\longrightarrow$ HBr + R	6.8	17.5
H + R'Br $\longrightarrow$ HBr + R'	6.0	20.0

Estimate the activation energy for the reaction

$$CH_3 \bullet + RBr \longrightarrow CH_3Br + R \bullet$$

which has an exothermic heat of reaction of 6 kcal/mol (i.e., $\Delta H_R = -6$ kcal/mol).

(d) What parameters vary over the widest range in calculating the reaction rate constant using transition state theory (i.e., which ones do you need to focus your attention on to get a good approximation of the specific reaction rate)? (See Professional Reference Shelf R3.2.)

(e) List the assumptions made in the molecular dynamics simulation R3.3 used to calculate the activation energy for the hydrogen exchange reaction.

(f) The volume of the box used to calculate the translational partition function for the activated complex was taken as 1 dm³. True or False?

(g) Suppose the distance between two atoms of a linear molecule in the transition state was set at half the true value. Would the rate constant increase or decrease over that of the true value and by how much (i.e., what factor)?

(h) List the parameters you can obtain from Cerius² to calculate the molecular partition functions.

P3-19_D Use Spartan, CACHE, Cerius², Gaussian, or some other chemical computational software package to calculate the heats of formation of the reactants, products, and transition state and the activation barrier, E_B, for the following reactions:

(a) $CH_3OH + O \longrightarrow CH_3O + OH$

(b) $CH_3Br + OH \longrightarrow CH_3OH + Br$

(c) $Cl + H_2 \longrightarrow HCl + H$

(d) $Br + CH_4 \longrightarrow HBr + CH_3$

P3-20_B It is proposed to produce ethanol by one of two reactions:

$$C_2H_5Cl + OH^- \longleftrightarrow C_2H_5OH + Cl^- \tag{1}$$

$$C_2H_5Br + OH^- \longrightarrow C_2H_5OH + Br^- \tag{2}$$
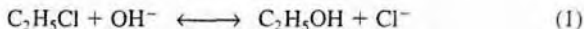
Use Spartan (see Appendix J) or some other software package to answer the following:

(a) What is the ratio of the rates of reaction at 25°C? 100°C? 500°C?

(b) Which reaction scheme would you choose to make ethanol? (*Hint*: Consult *Chemical Marketing Reporter* or *www.chemweek.com* for chemical prices).

[Professor R. Baldwin, Colorado School of Mines]

- **Additional Homework Problems on CD-ROM**

Temperature Effects

CDP3-A_B   Estimate how fast a Tenebrionid Beetle can push a ball of dung at 41.5°C. **(Solution included.)**

CDP3-B_B   Use the Polanyi equation to calculate activation energies. [3rd Ed. P3-20_B]

CDP3-C_B   Given the irreversible rate law at low temperature, write the reversible rate law at high temperature. [3rd Ed. P3-10_B]

Web Hint

Solved Problems

Stoichiometry

CDP3-D$_B$ Set up a stoichiometric table for

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

in terms of molar flow rates. **(Solution included.)**

CDP3-E$_B$ Set up a stoichiometric table for the reaction

$$C_6H_5COCH + 2NH_3 \longrightarrow C_6H_5ONH_2 + NH_2Cl$$

[2nd Ed. P3-10$_B$]

CDP3-F$_B$ The elementary reaction $A(g) + B(l) \longrightarrow C(g)$ takes place in square duct containing liquid B, which evaporates into the gas react ing with A. [2nd Ed. P3-20$_B$]

Hall of Fame

Reactions with Phase Change

CDP3-G$_B$ Silicon is used in the manufacture of microelectronics devices. Set up a stochiometric table for the reaction **(Solution included.)**

$$Si\,HCl_3(g) + H_2(g) \longrightarrow Si(s) + HCl(g) + Si_xH_yCl_z(g)$$
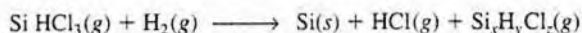
[2nd Ed. P3-16$_B$]

CDP3-H$_B$ Reactions with condensation between chlorine and methane. [3rd Ed P3-21$_B$].

CDP3-I$_B$ Reactions with condensation

$$C_2H_6(g) + 2Br(g) \longrightarrow C_2H_4Br_2(l,\,g) + 2HBr(g)$$
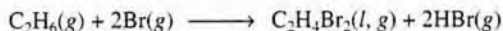
[3rd Ed. P3-22$_B$]

CDP3-J$_B$ Chemical vapor deposition

$$3SiH_4(g) + 4NH_3(g) \longrightarrow SiN_4(s) + 12H_2(g)$$

[3rd Ed. P3-23$_B$]

CDP3-K$_B$ Condensation occurs in the gas-phase reaction:

$$C_2H_4(g) + 2Cl(g) \longrightarrow CH_2Cl_2(g,\,l) + 2HCl(g)$$

[2nd Ed. P3-17$_B$]

New Problems on the Web

CDP3-New   From time to time new problems relating Chapter 3 material to every day interests or emerging technologies will be placed on the web Solutions to these problems can be obtained by emailing the author.

SUPPLEMENTARY READING

1. Two references relating to the discussion of activation energy have already been cited in this chapter. Activation energy is usually discussed in terms of either collision theory or transition-state theory. A concise and readable account of these two theories can be found in

> Masel, R., *Chemical Kinetics*, New York: McGraw Hill, 2002, p. 594.
>
> LAIDLER, K. J. *Chemical Kinetics*. New York: Harper & Row, 1987, Chap. 3.

An expanded but still elementary presentation can be found in

> MOORE, J. W., and R. G. PEARSON, *Kinetics and Mechanism*, 3rd ed. New York: Wiley, 1981, Chaps. 4 and 5.

A more advanced treatise of activation energies and collision and transition-state theories is

> BENSON, S. W., *The Foundations of Chemical Kinetics*. New York: McGraw-Hill, 1960.
>
> STEINFELD, J. I., J. S. FRANCISCO, W. L. HASE, *Chemical Kinetics and Dynamics*, 2nd ed. New Jersey: Prentice Hall, 1999.

2. The books listed above also give the rate laws and activation energies for a number of reactions; in addition, as mentioned earlier in this chapter, an extensive listing of rate laws and activation energies can be found in NBS circulars:

> Kinetic data for larger number of reactions can be obtained on Floppy Disks and CD-ROMs provided by National Institute of Standards and Technology (NIST). Standard Reference Data 221/A320 Gaithersburg, MD 20899; ph: (301) 975-2208 Additional sources are Tables of Chemical Kinetics: Homogeneous Reactions. National Bureau of Standards Circular 510 (Sept. 28, 1951); Suppl. 1 (Nov. 14, 1956); Suppl. 2 (Aug. 5, 1960); Suppl. 3 (Sept. 15, 1961) (Washington, D.C.: U.S. Government Printing Office). Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluate No. 10, JPL Publication 92-20, Aug. 15, 1992, Jet Propulsion Laboratories, Pasadena, Calif.

3. Also consult the current chemistry literature for the appropriate algebraic form of the rate law for a given reaction. For example, check the *Journal of Physical Chemistry* in addition to the journals listed in Section 4 of the Supplementary Reading section in Chapter 4.