

The purpose of this chapter is to provide a framework for determining the reaction rate given a detailed statement of the reaction chemistry.

We use several concepts from the subject of chemical kinetics to illustrate two key points:

- 1 The stoichiometry of an elementary reaction defines the concentration dependence of the rate expression.
- 2 The quasi-steady-state assumption (QSSA) and the reaction equilibrium assumption allow us to generate reaction-rate expressions that capture the details of the reaction chemistry with a minimum number of rate constants.

The concepts include:

- the elementary reaction
- Tolman's principle of microscopic reversibility
- elementary reaction kinetics
- the quasi-steady-state assumption
- the reaction equilibrium assumption

The goals here are to develop a chemical kinetics basis for the empirical expression, and to show that kinetic analysis can be used to take mechanistic insight and describe reaction rates from first principles.

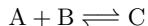
- We also discuss heterogeneous catalytic adsorption and reaction kinetics.
- Catalysis has a significant impact on the United States economy<sup>1</sup> and many important reactions employ catalysts.<sup>2</sup>
- We demonstrate how the concepts for homogeneous reactions apply to heterogeneously catalyzed reactions with the added constraint of surface-site conservation.
- The physical characteristics of catalysts are discussed in Chapter 7.

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<sup>1</sup>Catalysis is at the heart of the chemical industry, with sales in 1990 of \$292 billion and employment of 1.1 million, and the petroleum refining industry, which had sales of \$140 billion and employment of 0.75 million in 1990 [13].

<sup>2</sup>Between 1930 and the 1980s, 63 major products and 34 major process innovations were introduced by the chemical industry. More than 60% of the products and 90% of these processes were based on catalysis[13].

- Stoichiometric statements such as



are used to represent the changes that occur during a chemical reaction. These statements can be interpreted in *two* ways.

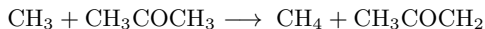
- The reaction statement may represent the change in the relative amounts of species that is observed when the reaction proceeds. **overall stoichiometry**
- Or the reaction statement may represent the actual molecular events that are presumed to occur as the reaction proceeds. **elementary reaction**
- The elementary reaction is characterized by a change from reactants to products that proceeds without identifiable intermediate species forming.

- For an elementary reaction, the reaction rates for the forward and reverse paths are proportional to the concentration of species taking part in the reaction raised to the absolute value of their stoichiometric coefficients.
- The reaction order in all species is determined directly from the stoichiometry.
- Elementary reactions are usually unimolecular or bimolecular because the probability of collision between several species is low and is not observed at appreciable rates.
- For an overall stoichiometry, on the other hand, any correspondence between the stoichiometric coefficients and the reaction order is purely coincidental.

- The first example involves the mechanism proposed for the thermal decomposition of acetone at 900 K to ketene and methyl-ethyl ketone (2-butanone) [17].
- The overall reaction can be represented by



- The reaction is proposed to proceed by the following elementary reactions



- The thermal decomposition of acetone generates four stable molecules that can be removed from the reaction vessel: CO, CH<sub>4</sub>, CH<sub>2</sub>CO and CH<sub>3</sub>COC<sub>2</sub>H<sub>5</sub>.
- Three radicals are formed and consumed during the thermal decomposition of acetone: CH<sub>3</sub>, CH<sub>3</sub>CO and CH<sub>3</sub>COCH<sub>2</sub>.
- These three radicals are reaction intermediates and cannot be isolated outside of the reaction vessel.



# Overall stoichiometry from Mechanism

- Assign the species to the **A** vector as follows

Species	Formula	Name
$A_1$	$\text{CH}_3\text{COCH}_3$	acetone
$A_2$	$\text{CH}_3$	methyl radical
$A_3$	$\text{CH}_3\text{CO}$	acetyl radical
$A_4$	$\text{CO}$	carbon monoxide
$A_5$	$\text{CH}_3\text{COCH}_2$	acetone radical
$A_6$	$\text{CH}_2\text{CO}$	ketene
$A_7$	$\text{CH}_4$	methane
$A_8$	$\text{CH}_3\text{COC}_2\text{H}_5$	methyl ethyl ketone

- The stoichiometric matrix is

$$\nu = \begin{bmatrix} -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 1 & 0 & 0 & 0 & 0 \\ -1 & -1 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & -1 & 0 & 0 & -1 & 0 & 0 & 1 \end{bmatrix}$$

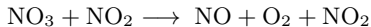
- Multiply  $\nu$  by  $[ 1 \ 1 \ 2 \ 1 \ 1 ]$
- We obtain

$$[ -3 \ 0 \ 0 \ 1 \ 0 \ 1 \ 2 \ 1 ]$$

which is the overall stoichiometry given in Reaction 5.1.

## Example Two — Smog

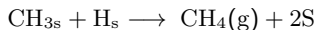
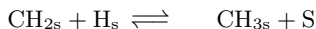
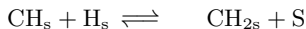
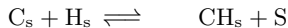
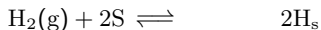
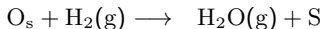
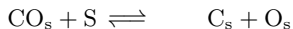
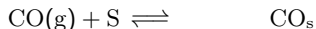
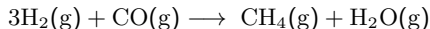
- The second example involves one of the major reactions responsible for the production of photochemical smog.
- The overall reaction and one possible mechanism are



- In this reaction mechanism, nitrogen dioxide is activated by absorbing photons and decomposes to nitric oxide and oxygen radicals (elementary Reaction 5.8).
- Stable molecules are formed: NO and O<sub>2</sub>
- Radicals, O and NO<sub>3</sub>, are generated and consumed during the photochemical reaction.
- Work through the steps to determine the linear combination of the mechanistic steps that produces the overall reaction.

## Example Three — Methane Synthesis

- The third example involves the synthesis of methane from synthesis gas, CO and H<sub>2</sub>, over a ruthenium catalyst [6].
- The overall reaction and one possible mechanism are



- The subscripts g and ads refer to gas phase and adsorbed species, respectively, and S refers to a vacant ruthenium surface site.
- During the overall reaction, the reagents adsorb (elementary Reactions 5.150 and 5.153), and the products form at the surface and desorb (elementary Reactions 5.152 and 5.157).
- Adsorbed CO ( $\text{CO}_s$ ) either occupies surface sites or dissociates to adsorbed carbon and oxygen in elementary Reaction 5.151.

- The adsorbed carbon undergoes a sequential hydrogenation to methyne, methylene, and methyl, all of which are adsorbed on the surface.
- Hydrogenation of methyl leads to methane in elementary Reaction 5.157.
- In this example, the overall reaction is twice the fourth reaction added to the remaining reactions.

- One criterion for a reaction to be elementary is that as the reactants transform into the products they do so without forming intermediate species that are chemically identifiable.
- A second aspect of an elementary reaction is that the reverse reaction also must be possible on energy, symmetry and steric bases, using only the products of the elementary reaction.
- This reversible nature of elementary reactions is the essence of Tolman's principle of microscopic reversibility [19, p. 699].



*This assumption (at equilibrium the number of molecules going in unit time from state 1 to state 2 is equal to the number going in the reverse direction) should be recognized as a distinct postulate and might be called the principle of microscopic reversibility. In the case of a system in thermodynamic equilibrium, the principle requires not only that the total number of molecules leaving a given quantum state in unit time is equal to the number arriving in that state in unit time, but also that the number leaving by any one particular path, is equal to the number arriving by the reverse of that particular path.*

Various models or theories have been postulated to describe the rate of an elementary reaction. Transition state theory (TST) is reviewed briefly in the next section to describe the flow of systems (reactants  $\rightarrow$  products) over potential-energy surfaces. Using Tolman's principle, the most probable path in one direction must be the most probable path in the opposite direction. Furthermore, the Gibbs energy difference in the two directions must be equal to the overall Gibbs energy difference — the ratio of rate constants for an elementary reaction must be equal to the equilibrium constant for the elementary reaction.

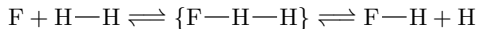
In this section we outline the transition-state theory (TST), which can be used to predict the rate of an elementary reaction. Our purpose is to show how the rate of an elementary reaction is related to the concentration of reactants. The result is

$$r_i = k_i \prod_{j \in \mathcal{R}_i} c_j^{-\nu_{ij}} - k_{-i} \prod_{j \in \mathcal{P}_i} c_j^{\nu_{ij}} \quad (5.22)$$

in which  $j \in \mathcal{R}_i$  and  $j \in \mathcal{P}_i$  represent the reactant species and the product species in the  $i$ th reaction, respectively.

Equation 5.22 forms the basis for predicting reaction rates and is applied to homogeneous and heterogeneous systems. Because of its wide use, much of Chapter 5 describes the concepts and assumptions that underlie Equation 5.22.

We consider a simple reaction to illustrate the ideas



The potential energy  $V(r)$  of the molecule is related to the relative position of the atoms, and for a diatomic molecule the potential energy can be represented with a Morse function

$$V(r) = D \left[ e^{-2\beta r} - 2e^{-\beta r} \right]$$

in which  $D$  is the dissociation energy,  $r$  is the displacement from the equilibrium bond length, and  $\beta$  is related to the vibrational frequency of the molecule. The following figure presents the Morse functions for HF and H<sub>2</sub> molecules.

# Potential energy of HF and H<sub>2</sub> molecules

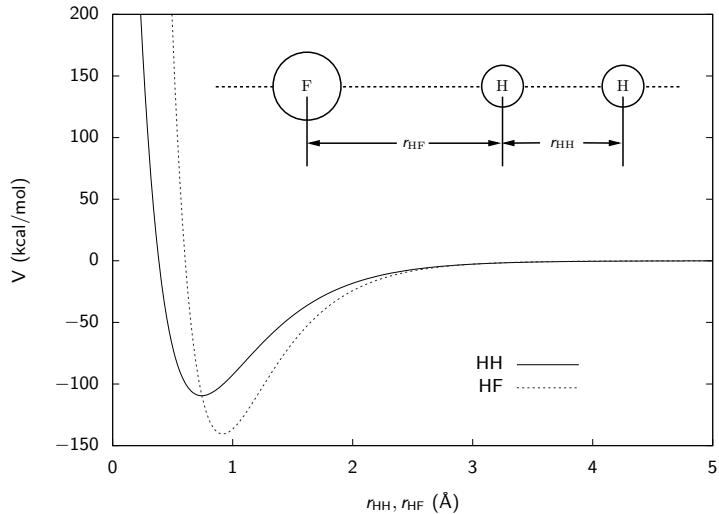
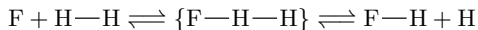


Figure 5.1: Morse potential for H<sub>2</sub> and HF.

- Molecules containing  $N$  atoms require  $3N$  Cartesian coordinates to specify the locations of all the nuclei.
- Consider a molecule of three atoms; we require only three coordinates to describe the internuclear distances.
- We choose the two distances from the center atom and the bond angle as the three coordinates.
- The potential energy is a function of all three coordinate values. A plot of the energy would be a three-dimensional surface, requiring four dimensions to plot the surface.

- We fix the bond angle by choosing a collinear molecule
- Only the two distances relative to a central atom are required to describe the molecule.
- The potential energy can be expressed as a function of these two distances, and we can view this case as a three-dimensional plot.

- Figure 5.2 shows a representative view of such a surface for the collinear collision between F and H<sub>2</sub>.



- Several sources provided the data used to calculate this potential-energy surface [14, 16, 15].
- Moore and Pearson provide a more detailed discussion of computing potential-energy surfaces [12].



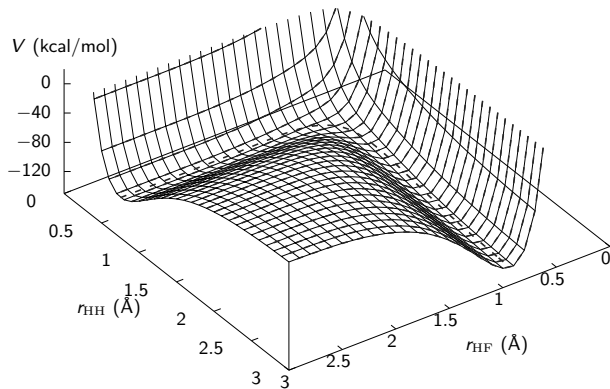


Figure 5.2: Potential-energy surface for the F, H<sub>2</sub> reaction.

## Collinear Approach of HF and H<sub>2</sub> – Energy Contours

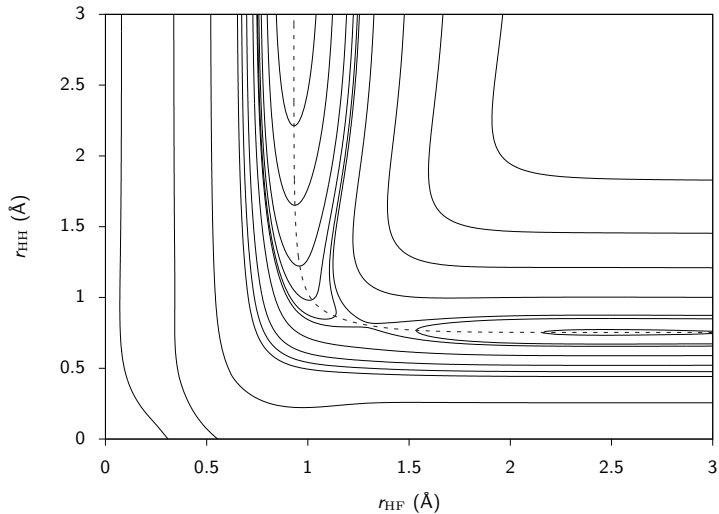


Figure 5.3: Contour representation of the potential-energy surface.

- Large  $r_{\text{HF}}$ . F atoms exist along with  $\text{H}_2$  molecules. Reproduces the  $\text{H}_2$  curve in Figure 5.1.
- Large  $r_{\text{HH}}$ . H atoms exist along with HF molecules. Reproduces the curve for HF in Figure 5.1.
- As the F atom is brought into contact with  $\text{H}_2$  in a collinear fashion, a surface of energies is possible that depends on the values of  $r_{\text{HF}}$  and  $r_{\text{HH}}$ .
- The minimum energy path along the valleys is shown by the dashed line in Figures 5.2 and 5.3.
- The reaction starts in the  $\text{H}_2$  valley at large  $r_{\text{HF}}$ , proceeds along the minimum energy path and ends in the HF valley at large  $r_{\text{HH}}$ .

- The transition state is the saddle point connecting the two valleys. The minimum energy path is a saddle point.
- The dashed line is referred to as the reaction-coordinate pathway, and movement along this path is the reaction coordinate,  $\xi$ .
- Figure 5.4 is a reaction-coordinate diagram, which displays the energy change during this reaction.

## Reaction coordinate diagram

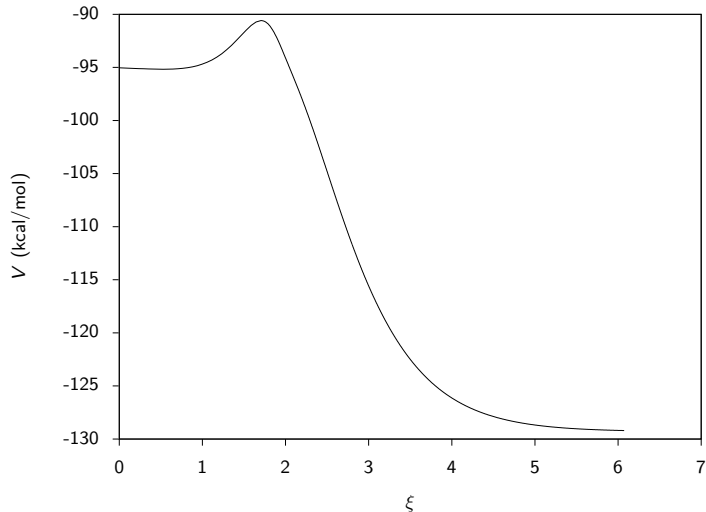


Figure 5.4: Reaction-coordinate diagram.

- The reaction coordinate represents travel along the minimum energy path from reactants to products.
- The difference in energies between reactants and products is the heat of reaction; in this case it is exothermic by 34 kcal/mol.
- The barrier height of 4 kcal/mol between reactants and products is used to calculate the activation energy for the reaction.

## Transition state complex

- The molecular structure (the relative positions of F, and two H's) at the saddle point is called the transition-state complex.
- The principle of microscopic reversibility implies that the same structure at the saddle point must be realized if the reaction started at  $\text{HF} + \text{H}$  and went in reverse.
- The transition-state complex is NOT a chemically identifiable reaction intermediate; it is the arrangement of atoms at the point in energy space between reactants and products.
- Any change of relative positions of F and the two H's for the transition-state complex (as long as the motions are collinear) results in the complex reverting to reactants or proceeding to products.
- Using statistical mechanics and the potential energy diagram, we can calculate the rate constant, i.e. the frequency at which the transition state decomposes to reactants or products.

- One of the characteristic features of many chemically reacting systems is the widely disparate time scales at which reactions occur.
- It is not unusual for complex reaction mechanisms to contain rate constants that differ from each other by several orders of magnitude.
- Moreover, the concentrations of highly reactive intermediates may differ by orders of magnitude from the concentrations of relatively stable reactants and products.
- These widely different time and concentration scales present challenges for accurate estimation of rate constants, measurement of low-concentration species, and even numerical solution of complex models.



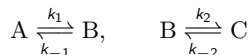
- On the other hand, these disparate scales often allow us to approximate the complete mechanistic description with simpler rate expressions that retain the essential features of the full problem on the time scale or in the concentration range of interest.
- Although these approximations were often used in earlier days to allow easier model solution, that is not their primary purpose today.
- The reduction of complex mechanisms removes from consideration many parameters that would be difficult to estimate from available data.
- The next two sections describe two of the most widely used methods of model simplification: the equilibrium assumption and the quasi-steady-state assumption.

# The Reaction Equilibrium Assumption

- In the reaction equilibrium assumption, we reduce the full mechanism on the basis of fast and slow *reactions*.
- In a given mechanism consisting of multiple reactions, some reactions may be so much faster than others, that they equilibrate after any displacement from their equilibrium condition.
- The remaining, slower reactions then govern the rate at which the amounts of reactants and products change.
- If we take the extreme case in which all reactions except one are assumed at equilibrium, this remaining slow reaction is called the **rate-limiting step**.
- But the equilibrium approximation is more general and flexible than this one case. We may decompose a full set of reactions into two sets consisting of any number of slow and fast reactions, and make the equilibrium assumption on the set of fast reactions.

## The archetype example of fast and slow reactions

- We illustrate the main features with the simple series reaction



- Assume that the rate constants  $k_2, k_{-2}$  are much larger than the rate constants  $k_1, k_{-1}$ , so the second reaction equilibrates quickly.
- By contrast, the first reaction is slow and can remain far from equilibrium for a significant period of time.
- Because the only other reaction in the network is at equilibrium, the slow, first reaction is called the rate-limiting step.
- We show that the rate of this slow reaction does indeed determine or limit the rate at which the concentrations change.

- We start with the full model and demonstrate what happens if  $k_2, k_{-2} \gg k_1, k_{-1}$ .
- Consider the solution to the full model with rate constants  $k_1 = 1, k_{-1} = 0.5, k_2 = k_{-2} = 1$  and initial conditions  $c_A(0) = 1.0, c_B(0) = 0.4, c_C(0) = 0$  shown in Figure 5.6.

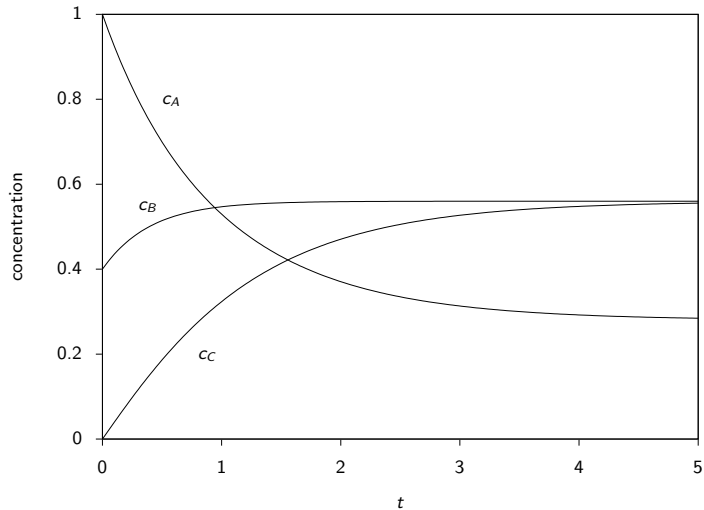


Figure 5.6: Full model solution for  $k_1 = 1, k_{-1} = 0.5, k_2 = k_{-2} = 1$ .

## Turn up the second rate

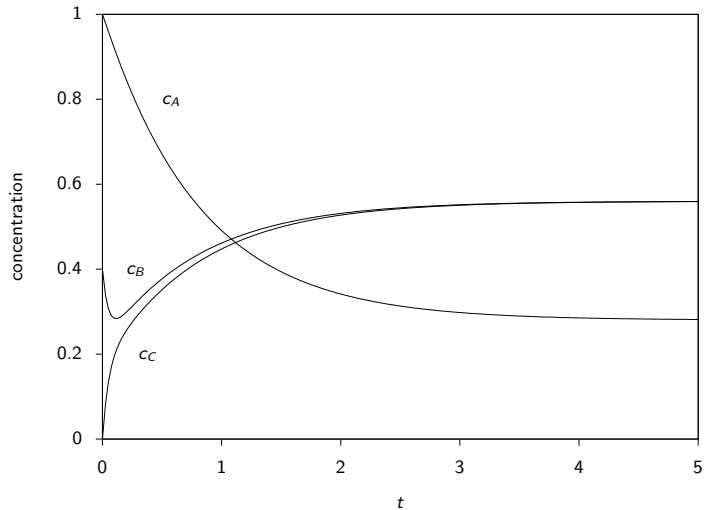


Figure 5.7: Full model solution for  $k_1 = 1$ ,  $k_{-1} = 0.5$ ,  $k_2 = k_{-2} = 10$ .

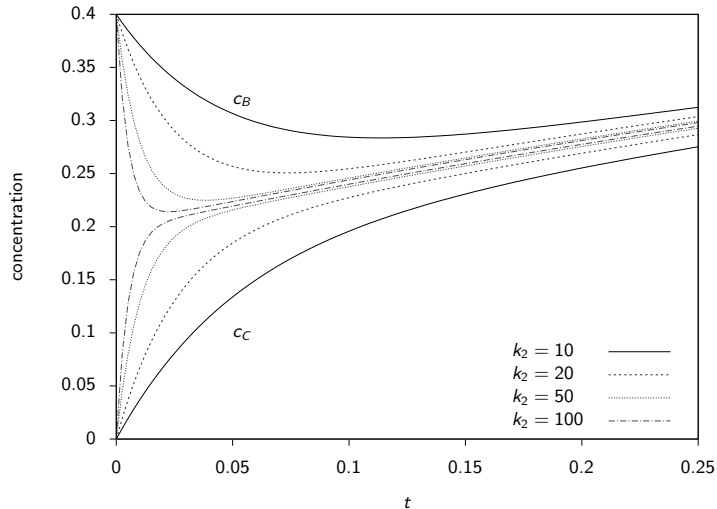


Figure 5.8: Concentrations of B and C versus time for full model with increasing  $k_2$  with  $K_2 = k_2/k_{-2} = 1$ .

- We now analyze the kinetic model. The text shows how to derive models for both the fast and slow time scales. The text also treats models in terms of reaction extent and concentration variables.
- Here I will focus on only the slow time scale model, and only the concentration variables.
- The main thing we are trying to do is enforce the condition that the second reaction is at equilibrium. We therefore set its rate to zero to find the equilibrium relationship between  $c_B$  and  $c_C$ .



- The equilibrium assumption is made by adding the algebraic constraint that  $r_2 = 0$  or  $K_2 c_B - c_C = 0$ .

$$r_2 = 0 = k_2 c_B - k_{-2} c_C$$

$$0 = K_2 c_B - c_C, \quad K_2 = \frac{k_2}{k_{-2}}$$

- The mole balances for the full model are

$$\frac{dc_A}{dt} = -r_1, \quad \frac{dc_B}{dt} = r_1 - r_2, \quad \frac{dc_C}{dt} = r_2$$

- We can add the mole balances for components B and C to *eliminate*  $r_2$

$$\frac{d(c_B + c_C)}{dt} = r_1 \tag{5.45}$$

Notice we have *not* set  $r_2 = 0$  to obtain this result. Equation 5.45 involves no approximation.

- If we differentiate the equilibrium condition, we obtain a second relation,  $K_2 dc_B/dt - dc_C/dt = 0$ , which allows us to solve for both  $dc_B/dt$  and  $dc_C/dt$ ,

$$\frac{dc_B}{dt} = \frac{1}{1 + K_2} r_1 \quad \frac{dc_C}{dt} = \frac{K_2}{1 + K_2} r_1 \quad (*)$$

Equations	Fast Time Scale( $\tau = k_{-2}t$ )	Slow Time Scale( $t$ )
ODEs	$\frac{dc_A}{d\tau} = 0, \quad c_A(0) = c_{A0}$ $\frac{dc_B}{d\tau} = -(K_2c_B - c_C), \quad c_B(0) = c_{B0}$ $\frac{dc_C}{d\tau} = K_2c_B - c_C, \quad c_C(0) = c_{C0}$	$\frac{dc_A}{dt} = -r_1, \quad c_A(0) = c_{A0}$ $\frac{dc_B}{dt} = \frac{1}{1+K_2}r_1, \quad c_B(0) = c_{Bs}$ $\frac{dc_C}{dt} = \frac{K_2}{1+K_2}r_1, \quad c_C(0) = c_{Cs}$
DAEs	$c_A = c_{A0}$ $\frac{dc_B}{d\tau} = -(K_2c_B - c_C), \quad c_B(0) = c_{B0}$ $0 = c_A - c_{A0} + c_B - c_{B0} + c_C - c_{C0}$	$\frac{dc_A}{dt} = -r_1, \quad c_A(0) = c_{A0}$ $0 = K_2c_B - c_C$ $0 = c_A - c_{A0} + c_B - c_{B0} + c_C - c_{C0}$
	$c_{Bs} = \frac{1}{1+K_2}(c_{B0} + c_{C0}), \quad c_{Cs} = \frac{K_2}{1+K_2}(c_{B0} + c_{C0})$	

## Full model and equilibrium assumption

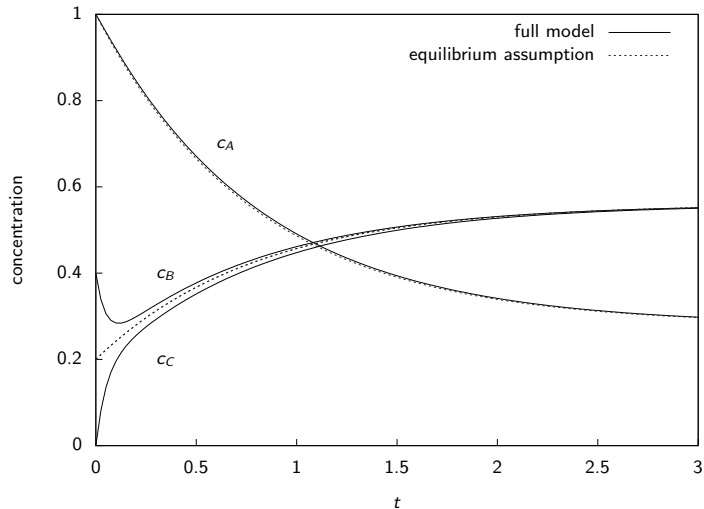


Figure 5.9: Comparison of equilibrium assumption to full model for  $k_1 = 1, k_{-1} = 0.5, k_2 = k_{-2} = 10$ .

- Critique your colleague's proposal.

“Look, you want to enforce  $c_C = K_2 c_B$ , right? Well, that means  $r_2 = 0$ , so just set it to zero, and be done with it. I get the following result.”

$$\frac{dc_A}{dt} = -r_1 \quad \frac{dc_B}{dt} = r_1 - \boxed{r_2} \quad \frac{dc_C}{dt} = \boxed{r_2} \quad \text{full model}$$

$$\frac{dc_A}{dt} = -r_1 \quad \frac{dc_B}{dt} = r_1 \quad \frac{dc_C}{dt} = 0 \quad \text{reduced model}$$

- The result for B and C doesn't agree with Equation (\*). What went wrong?

- Let's look at C's mass balance again

$$\begin{aligned}\frac{dc_C}{dt} &= k_2 c_B - k_{-2} c_C \\ &= k_{-2} (K_2 c_B - c_C)\end{aligned}$$

- Your colleague is suggesting this product is zero because the second term is zero, but what did we do to make the full model approach equilibrium?
- We made  $k_2, k_{-2}$  large!

- So here's the flaw.

$$\frac{dc_C}{dt} = \underbrace{k_{-2}}_{\text{goes to } \infty!} \underbrace{(K_2 c_B - c_C)}_{\text{goes to 0}} \neq 0$$

- The product does *not* go to zero. In fact we just showed

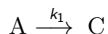
$$\frac{dc_C}{dt} = \frac{K_2}{1 + K_2} r_1$$

- This fact is far from obvious without the analysis that we did.

- We start with the slow time-scale model given in the table and take the limit as  $K_2 \rightarrow \infty$  giving

$$\begin{aligned}\frac{dc_A}{dt} &= -r_1, & c_A(0) &= c_{A0} \\ \frac{dc_B}{dt} &= 0, & c_B(0) &= 0 \\ \frac{dc_C}{dt} &= r_1, & c_C(0) &= c_{B0} + c_{C0}\end{aligned}$$

- In this limit the B disappears,  $c_B(t) = 0$ , and  $r_1 = k_1 c_A$ , which describes the irreversible reaction of A directly to C with rate constant  $k_1$



- We see in the next section that this case is well described also by making the quasi-steady-state assumption on species B.



## Second reaction irreversible in other direction

- Take the second reaction as irreversible in the backward direction,  $K_2 = 0$ . We obtain from the table

$$\begin{aligned}\frac{dc_A}{dt} &= -r_1, & c_A(0) &= c_{A0} \\ \frac{dc_B}{dt} &= r_1, & c_B(0) &= c_{B0} + c_{C0} \\ \frac{dc_C}{dt} &= 0, & c_C(0) &= 0\end{aligned}$$

- This describes the reversible reaction between A and B with no second reaction,  $c_C(t) = 0$ ,



- Under the equilibrium assumption, we see that the two series reactions in Equation 5.41 may reduce to A going directly and irreversibly to C, Equation 5.46, or A going reversibly to B, Equation 5.47, depending on the magnitude of the equilibrium constant of the second, fast reaction.

# The Quasi-Steady-State Assumption

- In the quasi-steady-state assumption, we reduce the full mechanism on the basis of rapidly equilibrating *species* rather than reactions as in the reaction equilibrium assumption.
- Highly reactive intermediate species are usually present only in small concentrations.
- Examples of these transitory species include atoms, radicals, ions and molecules in excited states.

# The Quasi-Steady-State Assumption

- We set the production rate of these species equal to zero, which enables their concentration to be determined in terms of reactants and products using algebraic equations.
- After solving for these small concentration species, one is then able to construct reaction-rate expressions for the stable reactants and stable products in terms of reactant and product concentrations only.
- The idea to set the production rate of a reaction intermediate equal to zero has its origins in the early 1900s [2, 4] and has been termed the Bodenstein-steady-state, pseudo-steady-state, or quasi-steady-state assumption.
- The intermediate species are referred to as QSSA species [20].

- To illustrate the QSSA consider the simple elementary reaction



- Let the initial concentration in a constant-volume, isothermal, batch reactor be  $c_A = c_{A0}$ ,  $c_B = c_C = 0$ .
- The exact solution to the set of reactions is

$$\begin{aligned}c_A &= c_{A0} e^{-k_1 t} \\c_B &= c_{A0} \frac{k_1}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) \\c_C &= c_{A0} \frac{1}{k_2 - k_1} \left( k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t}) \right)\end{aligned}\tag{5.52}$$

- We make  $k_2 \gg k_1$  in order for B to be in low concentration. Formation reactions are much slower than consumption reactions.
- Figure 5.10 shows the normalized concentration of C given in Equation 5.52 versus time for different values of  $k_2/k_1$ .
- The curve  $c_C/c_{A0} = (1 - e^{-k_1 t})$  is shown also (the condition where  $k_2/k_1 = \infty$ ).
- Figure 5.10 illustrates that as  $k_2 \gg k_1$ , the exact solution is equivalent to

$$c_C = c_{A0} (1 - e^{-k_1 t}) \quad (5.53)$$

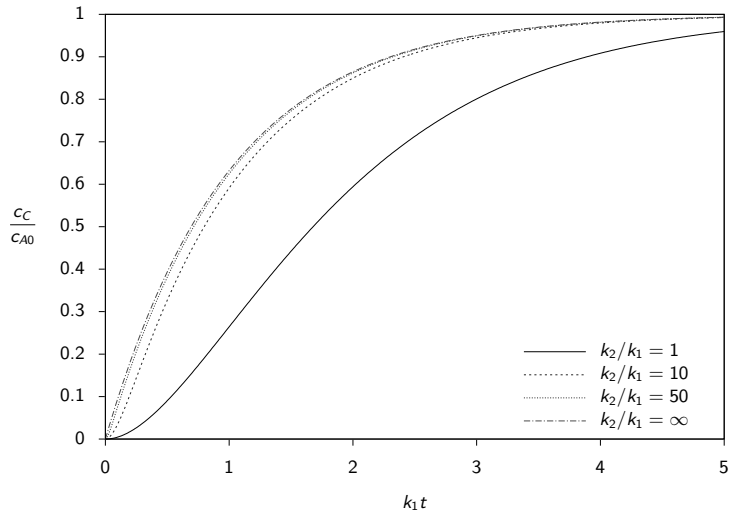


Figure 5.10: Normalized concentration of C versus dimensionless time for the series reaction  $A \rightarrow B \rightarrow C$  for different values of  $k_2/k_1$ .

- Define component B to be a QSSA species. We write

$$\frac{dc_{Bs}}{dt} = 0 = k_1 c_{As} - k_2 c_{Bs}$$

- That leads to

$$c_{Bs} = \frac{k_1}{k_2} c_{As} \tag{5.54}$$

- Note  $c_{Bs}$  is *not* constant; it changes linearly with the concentration of A.
- The issue is not if  $c_B$  is a constant, but whether or not the B equilibrates quickly to its quasi-steady value.

- Substitution of  $c_{Bs}$  into the material balances for components A and C results in

$$\frac{dc_{As}}{dt} = -k_1 c_{As} \quad (5.55)$$

$$\frac{dc_{Cs}}{dt} = k_1 c_{As} \quad (5.56)$$

- The solutions to Equations 5.55 and 5.56 are presented in the following table for the initial condition  $c_{As} = c_{A0}$ ,  $c_{Bs} = c_{Cs} = 0$ .



Scheme I:

Exact Solution

$$c_A = c_{A0} e^{-k_1 t}$$

$$c_B = c_{A0} \frac{k_1}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right)$$

$$c_C = c_{A0} \frac{1}{k_2 - k_1} \left( k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t}) \right) \quad (5.60)$$

QSSA Solution

$$c_{As} = c_{A0} e^{-k_1 t}$$

$$c_{Bs} = c_{A0} \frac{k_1}{k_2} e^{-k_1 t}$$

$$c_{Cs} = c_{A0} \left( 1 - e^{-k_1 t} \right) \quad (5.63)$$

Table: Exact and QSSA solutions for kinetic Scheme I.

## Approximation error in C production

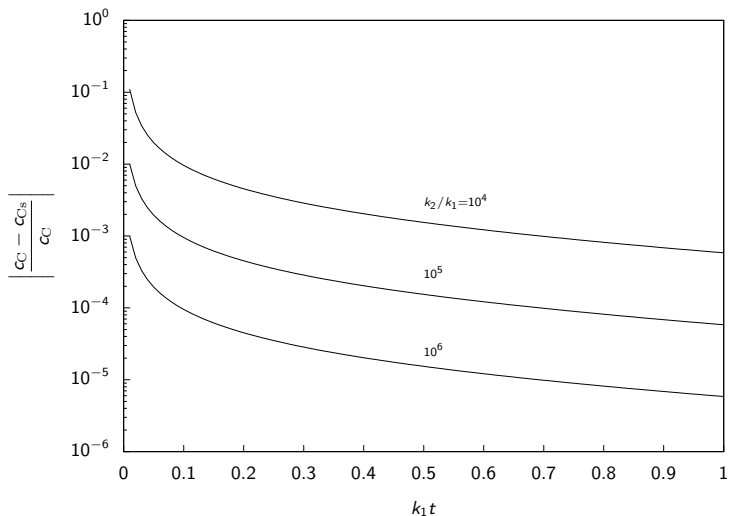


Figure 5.11: Fractional error in the QSSA concentration of C versus dimensionless time for the series reaction  $A \rightarrow B \rightarrow C$  for different values of  $k_2/k_1$ .

- The QSSA is a useful tool in reaction analysis.
- Material balances for batch and plug-flow reactors are ordinary differential equations.
- By setting production rates to zero for components that are QSSA species, their material balances become algebraic equations. These algebraic equations can be used to simplify the reaction expressions and reduce the number of equations that must be solved simultaneously.
- In addition, appropriate use of the QSSA can eliminate the need to know several difficult-to-measure rate constants. The required information can be reduced to ratios of certain rate constants, which can be more easily estimated from data.

# Developing Rate Expressions from Complex Mechanisms

- In this section we develop rate expressions for the mechanistic schemes presented in the introduction.
- The goal is to determine the rate in terms of measurable quantities, such as the concentrations of the reactants and products, and the temperature.
- The following procedure enables one to develop a reaction-rate expression from a set of elementary reactions.

- 1 Identify the species that do not appear in equilibrium reactions and write a statement for the rate of production of these species using Equations 5.38 and 5.39.

$$r_i = k_i \prod_{j \in \mathcal{R}_i} c_j^{-\nu_{ij}} - k_{-i} \prod_{j \in \mathcal{P}_i} c_j^{\nu_{ij}} \quad (5.38)$$

$$R_j = \sum_{i=1}^{n_r} \nu_{ij} r_i \quad (5.39)$$

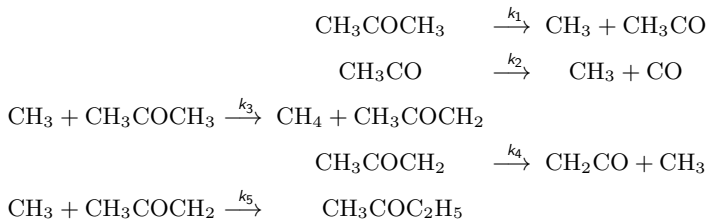
- 2 If the rate of production statement developed in step 1 contains the concentration of reaction intermediates, apply the QSSA to these species.
- 3 Perform the necessary algebraic manipulations and substitute the resulting intermediate concentrations into the rate of production statement from step 1.

## Example 5.2: Production rate of acetone

- The thermal decomposition of acetone is represented by the following stoichiometry



- Use the following mechanism to determine the production rate of acetone [17].
- You may assume the methyl, acetyl and acetone radicals are QSSA species.



## Solution

Let the species be designated as:

<i>Species</i>	<i>Formula</i>	<i>Name</i>
$A_1$	$\text{CH}_3\text{COCH}_3$	<i>acetone</i>
$A_2$	$\text{CH}_3$	<i>methyl radical</i>
$A_3$	$\text{CH}_3\text{CO}$	<i>acetyl radical</i>
$A_4$	$\text{CO}$	<i>carbon monoxide</i>
$A_5$	$\text{CH}_3\text{COCH}_2$	<i>acetone radical</i>
$A_6$	$\text{CH}_2\text{CO}$	<i>ketene</i>
$A_7$	$\text{CH}_4$	<i>methane</i>
$A_8$	$\text{CH}_3\text{COC}_2\text{H}_5$	<i>methyl ethyl ketone</i>



- Write the production rate of acetone using Reactions 5.77 and 5.79

$$R_1 = -k_1 c_1 - k_3 c_1 c_2 \quad (5.82)$$

- Species 2, 3 and 5 are QSSA species. Apply the QSSA to each of these species

$$R_2 = 0 = k_1 c_1 + k_2 c_3 - k_3 c_1 c_2 + k_4 c_5 - k_5 c_2 c_5 \quad (5.83)$$

$$R_3 = 0 = k_1 c_1 - k_2 c_3 \quad (5.84)$$

$$R_5 = 0 = k_3 c_1 c_2 - k_4 c_5 - k_5 c_2 c_5 \quad (5.85)$$

- From Equation 5.84

$$c_3 = \frac{k_1}{k_2} c_1 \quad (5.86)$$

- Adding Equations 5.83, 5.84 and 5.85 gives

$$c_5 = \frac{k_1}{k_5} \frac{c_1}{c_2} \quad (5.87)$$

- Inserting the concentrations shown in Equations 5.86 and 5.87 into Equation 5.83 gives

$$k_3 c_2^2 - k_1 c_2 - \frac{k_1 k_4}{k_5} = 0$$

$$c_2 = \frac{k_1}{2k_3} + \sqrt{\frac{k_1^2}{4k_3^2} + \frac{k_1 k_4}{k_3 k_5}} \quad (5.88)$$

in which the positive sign is chosen to obtain a positive concentration.

- This result can be substituted into Equation 5.82 to give the rate in terms of measurable species.

$$R_1 = - \left( \frac{3}{2} k_1 + \sqrt{\frac{k_1^2}{4} + \frac{k_1 k_3 k_4}{k_5}} \right) c_1 \quad (5.89)$$

- Equation 5.89 can be simplified to

$$R_1 = -k_{\text{eff}} c_1 \quad (5.90)$$

by defining an effective rate constant

$$k_{\text{eff}} = \frac{3}{2} k_1 + \sqrt{\frac{k_1^2}{4} + \frac{k_1 k_3 k_4}{k_5}}$$

- The production rate of acetone is first order in the acetone concentration.
- If, based on kinetic theories, we knew all the individual rate constants, we could calculate the rate of acetone production.
- Alternately, we can use Equation 5.90 as the basis for designing experiments to determine if the rate of production is first order in acetone and to determine the magnitude of the first-order rate constant,  $k_{\text{eff}}$ .

## Example 5.3: Production rate of oxygen

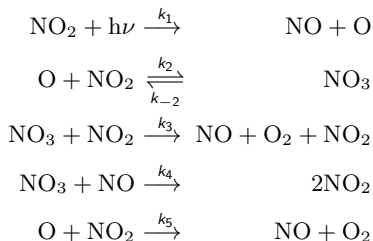
- Given the following mechanism for the overall stoichiometry



derive an expression for the production rate of  $\text{O}_2$ .

- Assume atomic O and  $\text{NO}_3$  radicals are QSSA species. The production rate should be in terms of the reactant,  $\text{NO}_2$ , and products, NO and  $\text{O}_2$ .

□



- Let the species be designated as:

$$A_1 = \text{NO}_2, \quad A_2 = \text{NO}, \quad A_3 = \text{O}, \quad A_4 = \text{NO}_3, \quad A_5 = \text{O}_2$$

- The production rate of molecular oxygen is

$$R_5 = k_3 c_1 c_4 + k_5 c_1 c_3 \quad (5.97)$$

- Species 3 and 4 are QSSA species. Applying the QSSA gives

$$R_3 = 0 = k_1 c_1 - k_2 c_1 c_3 + k_{-2} c_4 - k_5 c_1 c_3 \quad (5.98)$$

$$R_4 = 0 = k_2 c_1 c_3 - k_{-2} c_4 - k_3 c_1 c_4 - k_4 c_2 c_4 \quad (5.99)$$

- Adding Equations 5.98 and 5.99

$$0 = k_1 c_1 - k_3 c_1 c_4 - k_4 c_2 c_4 - k_5 c_1 c_3 \quad (5.100)$$

This result can be used to simplify the rate expression.



- Adding Equations 5.97 and 5.100

$$R_5 = k_1 c_1 - k_4 c_2 c_4 \quad (5.101)$$

- The intermediate  $\text{NO}_3$  concentration is found by solving Equation 5.98 for  $c_3$ .

$$c_3 = \frac{k_1}{k_2 + k_5} + \frac{k_{-2}}{k_2 + k_5} \frac{c_4}{c_1} \quad (5.102)$$

- Substituting Equation 5.102 into Equation 5.99 and rearranging gives

$$c_4 = \frac{k_1 k_2 c_1}{(k_2 k_3 + k_3 k_5) c_1 + (k_2 k_4 + k_4 k_5) c_2 + k_{-2} k_5} \quad (5.103)$$

- The rate expression now can be found using Equations 5.101 and 5.103

$$R_5 = k_1 c_1 - \frac{k_1 k_2 k_4 c_1 c_2}{(k_2 k_3 + k_3 k_5) c_1 + (k_2 k_4 + k_4 k_5) c_2 + k_{-2} k_5} \quad (5.104)$$

- Equation 5.104 is rather complex; but several terms in the denominator may be small leading to simpler power-law reaction-rate expressions.
- One cannot produce forms like Equation 5.104 from simple collision and probability arguments.
- When you see these forms of rate expressions, you conclude that there was a complex, multistep mechanism, which was reduced by the equilibrium assumption or QSSA.

## Example 5.4: Free-radical polymerization kinetics

- Polymers are economically important and many chemical engineers are involved with some aspect of polymer manufacturing during their careers.
- Polymerization reactions raise interesting kinetic issues because of the long chains that are produced.
- Consider free-radical polymerization reaction kinetics as an illustrative example.
- A simple polymerization mechanism is represented by the following set of elementary reactions.

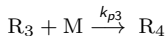
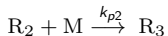
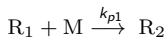


# Free-radical polymerization reactions

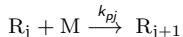
## Initiation:



## Propagation:

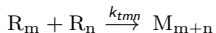


⋮



⋮

## Termination:



- I is initiator
- M is monomer
- $M_j$  is a dead polymer chain of length  $j$
- $R_j$  is a growing polymer chain of length  $j$

- Initiation. In free-radical polymerizations, the initiation reaction generates the free radicals, which initiate the polymerization reactions. An example is the thermal dissociation of benzoyl peroxide as initiator to form a benzyl radical that subsequently reacts with styrene monomer to form the first polymer chain.
- The termination reaction presented here is a termination of two growing polymer chains by a combination reaction.

- Develop an expression for the rate of monomer consumption using the assumptions that  $k_{pj} = k_p$  for all  $j$ , and  $k_{tmn} = k_t$  is independent of the chain lengths of the two terminating chains.
- You may make the QSSA for all growing polymer radicals.

- From the propagation reactions we can see the rate of monomer consumption is given by

$$R_M = - \sum_{j=1}^{\infty} r_{pj} = -k_p c_M \sum_{j=1}^{\infty} c_{Rj} \quad (5.105)$$

- The rate of the  $j$ th propagation reaction is given by

$$r_{pj} = k_p c_M c_{Rj}$$

- Making the QSSA for all polymer radicals, we set their production rates to zero

$$\begin{array}{rcccc}
 r_I & - & k_p c_{R_1} c_M & - & k_t c_{R_1} \sum_{j=1}^{\infty} c_{R_j} & = & 0 \\
 k_p c_{R_1} c_M & - & k_p c_{R_2} c_M & - & k_t c_{R_2} \sum_{j=1}^{\infty} c_{R_j} & = & 0 \\
 k_p c_{R_2} c_M & - & k_p c_{R_3} c_M & - & k_t c_{R_3} \sum_{j=1}^{\infty} c_{R_j} & = & 0 \\
 + & & \vdots & & \vdots & & \vdots \\
 \hline
 r_I & & & - & k_t \sum_{i=1}^{\infty} c_{R_i} \sum_{j=1}^{\infty} c_{R_j} & = & 0
 \end{array} \tag{5.106}$$



- We solve Equation 5.106 for the total growing polymer concentration and obtain

$$\sum_{j=1}^{\infty} c_{Rj} = \sqrt{r_I/k_t}$$

- Substituting this result into Equation 5.105 yields the monomer consumption rate

$$R_M = -k_p c_M \sqrt{r_I/k_t}$$

- From the initiation reaction, the initiation rate is given by  $r_I = k_I c_I$ , which upon substitution gives the final monomer consumption rate

$$\boxed{R_M = -k_p \sqrt{k_I/k_t} \sqrt{c_I} c_M} \quad (5.107)$$

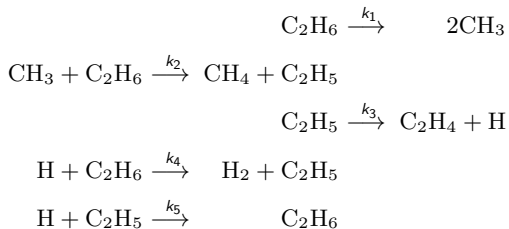
- Consumption rate of monomer is first order in monomer concentration. We can therefore easily calculate the time required to reach a certain conversion.
- Notice that this result also provides a mechanistic justification for the production rate used in Chapter 4 in which monomer consumption rate was assumed linear in monomer concentration.

## Example 5.5: Ethane pyrolysis

- This example illustrates how to apply the QSSA to a flow reactor.
- We are interested in determining the effluent concentration from the reactor and in demonstrating the use of the QSSA to simplify the design calculations.
- Ethane pyrolysis to produce ethylene and hydrogen also generates methane as an unwanted reaction product.



- The following mechanism and kinetics have been proposed for ethane pyrolysis [10]



- The rate constants are listed in the table
- The preexponential factor  $A_0$  has units of  $\text{s}^{-1}$  or  $\text{cm}^3/\text{mol s}$  for first- and second-order reactions, respectively.

Reaction	$A_0$	$E(\text{kJ/mol})$
1	$1.0 \times 10^{17}$	356
2	$2.0 \times 10^{11}$	44
3	$3.0 \times 10^{14}$	165
4	$3.4 \times 10^{12}$	28
5	$1.6 \times 10^{13}$	0

Table 5.6: Ethane pyrolysis kinetics.

- The pyrolysis is performed in a  $100 \text{ cm}^3$  isothermal PFR, operating at a constant pressure of 1.0 atm and at 925 K.
- The feed consists of ethane in a steam diluent.
- The inlet partial pressure of ethane is 50 Torr and the partial pressure of steam is 710 Torr.
- The feed flowrate is  $35 \text{ cm}^3/\text{s}$ .

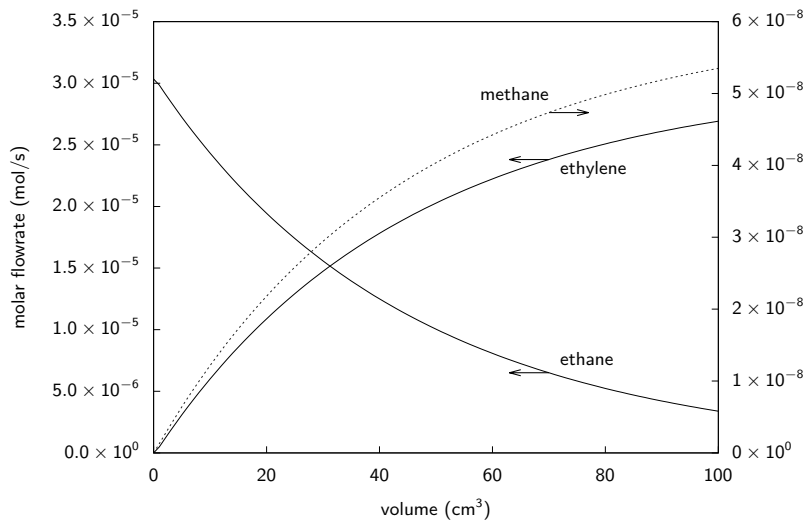
- The exact solution involves solving the set of eight species mass balances

$$\frac{dN_j}{dV} = R_j \quad (5.108)$$

subject to the feed conditions.

- The results for  $C_2H_6$ ,  $C_2H_4$  and  $CH_4$  are plotted in the next figure.
- The  $H_2$  concentration is not shown because it is almost equal to the  $C_2H_4$  concentration.
- Note the molar flowrate of  $CH_4$  is only 0.2% of the molar flowrate of the other products,  $C_2H_4$  and  $H_2$ .
- The concentrations of the radicals,  $CH_3$ ,  $C_2H_5$  and  $H$ , are on the order of  $10^{-6}$  times the ethylene concentration.

# Exact solution





## Find a simplified rate expression

- Assuming the radicals  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  and  $\text{H}$  are QSSA species, develop an expression for the rate of ethylene formation.
- Verify that this approximation is valid.

- The rate of ethylene formation is

$$R_{C_2H_4} = k_3 c_{C_2H_5} \quad (5.109)$$

- Next use the QSSA to relate  $C_2H_5$  to stable reactants and products

$$R_{CH_3} = 0 = 2k_1 c_{C_2H_6} - k_2 c_{CH_3} c_{C_2H_6} \quad (5.110)$$

$$R_H = 0 = k_3 c_{C_2H_5} - k_4 c_H c_{C_2H_6} - k_5 c_H c_{C_2H_5} \quad (5.111)$$

$$R_{C_2H_5} = 0 = k_2 c_{CH_3} c_{C_2H_6} - k_3 c_{C_2H_5} + k_4 c_{C_2H_6} c_H - k_5 c_H c_{C_2H_5} \quad (5.112)$$

- Adding Equations 5.110, 5.111 and 5.112 gives

$$c_H = \frac{k_1}{k_5} \frac{c_{C_2H_6}}{c_{C_2H_5}} \quad (5.113)$$

## Simplified rate expression

- Inserting Equation 5.113 into Equation 5.111 yields

$$0 = k_3 k_5 c_{C_2H_5}^2 - k_4 k_1 c_{C_2H_6}^2 - k_1 k_5 c_{C_2H_6} c_{C_2H_5}$$
$$c_{C_2H_5} = \left( \frac{k_1}{2k_3} + \sqrt{\left( \frac{k_1}{2k_3} \right)^2 + \frac{k_1 k_4}{k_3 k_5}} \right) c_{C_2H_6} \quad (5.114)$$

- Finally

$$R_{C_2H_4} = k_3 \left( \frac{k_1}{2k_3} + \sqrt{\left( \frac{k_1}{2k_3} \right)^2 + \frac{k_1 k_4}{k_3 k_5}} \right) c_{C_2H_6} \quad (5.115)$$

- This can be rewritten as

$$R_{C_2H_4} = k c_{C_2H_6} \quad (5.116)$$

in which

$$k = k_3 \left( \frac{k_1}{2k_3} + \sqrt{\left( \frac{k_1}{2k_3} \right)^2 + \frac{k_1 k_4}{k_3 k_5}} \right)$$

- At 925 K,  $k = 0.797 \text{ s}^{-1}$ .
- Let's show that

$$c_H = \frac{k_1/k_5}{k_1/2k_3 + \sqrt{(k_1/2k_3)^2 + k_1 k_4/k_3 k_5}} \quad (5.117)$$

$$c_{CH_3} = \frac{2k_1}{k} \quad (5.118)_{152}$$

- The validity of the QSSA is established by solving the set of ODEs

$$\begin{aligned} \frac{dN_{C_2H_6}}{dV} &= -r_1 - r_2 - r_4 + r_5 & \frac{dN_{H_2}}{dV} &= r_4 \\ \frac{dN_{CH_4}}{dV} &= r_2 & \frac{dN_{H_2O}}{dV} &= 0 \\ \frac{dN_{C_2H_4}}{dV} &= r_3 \end{aligned}$$

subject to the initial molar flowrates.

- During the numerical solution the concentrations needed in the rate equations are computed using

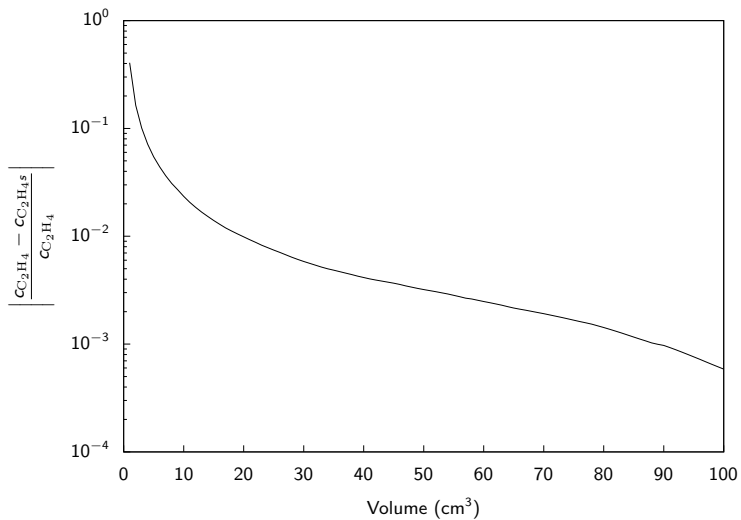
$$c_{C_2H_6} = \left( \frac{N_{C_2H_6}}{N_{C_2H_6} + N_{CH_4} + N_{C_2H_4} + N_{H_2} + N_{H_2O}} \right) \frac{P}{RT} \quad (5.119)$$

and Equations 5.114, 5.117 and 5.118.

- Note we can neglect H, CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> in the molar flowrate balance (Equation 5.119) because these components are present at levels on the order of 10<sup>-6</sup> less than C<sub>2</sub>H<sub>6</sub>.

- The next figure shows the error in the molar flowrate of ethylene that results from the QSSA.
- The error is less than 10% after  $3.1 \text{ cm}^3$  of reactor volume; i.e., it takes about 3% of the volume for the error to be less than 10%.
- Similarly, the error is less than 5% after  $5.9 \text{ cm}^3$  and less than 1% after  $18.6 \text{ cm}^3$ .
- The figure shows that the QSSA is valid for sufficiently large reactors, such as  $100 \text{ cm}^3$ .
- If the reactor volume were very small (a very short residence time), such as  $20 \text{ cm}^3$ , the QSSA would not be appropriate.

# Error in QSSA reduction



- What has been gained in this QSSA example? The full model solution requires the simultaneous solution of eight ODEs and the reduced model requires solving five ODEs.
- Both full and reduced models have five rate constants.
- However, the results for the exact solution demonstrate that  $\text{CH}_4$  is a minor product at this temperature and this also would be found in the experimental data.
- This suggests we can neglect  $\text{CH}_4$  in a species balance when computing mole fractions.

- Therefore the mass action statement



does a reasonable job of accounting for the changes that occur in the PFR during ethane pyrolysis.

- QSSA analysis predicts the ethane pyrolysis rate should be first order in ethane concentration and the rate constant is  $k = 0.797 \text{ s}^{-1}$ .
- Using the reduced model

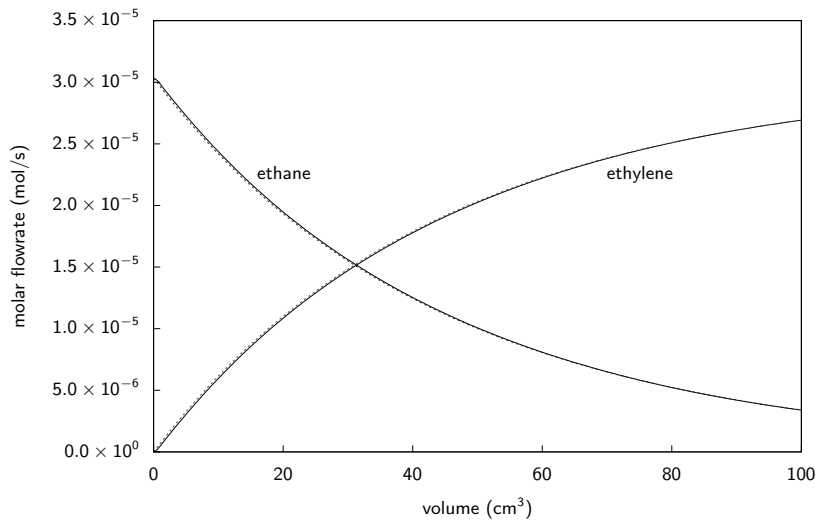
$$R_{\text{C}_2\text{H}_6} = -r \quad R_{\text{H}_2} = r$$

we can solve the model analytically.

- The next figure shows that nearly equivalent predictions are made for the simplified scheme based on the mass action statement, Reaction 5.120 using Equation 5.116 for the rate expression.



# Exact and reduced model

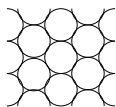


- This simple example demonstrates that when one has all the kinetic parameters the full model can be solved and the QSSA is not useful.
- The reverse situation of knowing a mechanism but not the rate constants could pose a difficult optimization problem when fitting all the rate constants to data.
- The QSSA analysis provides a framework for simplifying the kinetic expressions and removing difficult-to-estimate rate constants.
- In this example, one would expect a first-order expression to describe adequately the appearance of ethylene

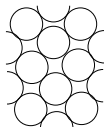
- Our goal is to provide the student with a simple picture of surfaces and to provide a basis for evaluating heterogeneously catalyzed reaction kinetics and reaction-rate expressions.
- Keep in mind the goal is to develop a rate expression from a reaction mechanism. This rate expression can be used to fit model parameters to rate data for a heterogeneously catalyzed reaction.
- We present the elementary steps that comprise a surface reaction — adsorption, surface reaction and desorption.
- To streamline the presentation, the discussion is limited to gas-solid systems and a single chemical isotherm, the Langmuir isotherm.
- The interested student can find a more complete and thorough discussion of adsorption, surface reaction and desorption in numerous textbooks [5, 18, 1, 8, 11, 3].

- A heterogeneously catalyzed reaction takes place at the surface of a catalyst.
- Catalysts, their properties, and the nature of catalytic surfaces are discussed in Chapter 7. For this discussion, we approximate the surface as a single crystal with a known surface order.
- The density of atoms at the low-index planes of transition metals is on the order of  $10^{15} \text{ cm}^{-2}$ . Figure 5.16 presents the atomic arrangement of low-index surfaces for various metals.

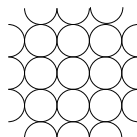
## Some common crystal structures of surfaces I



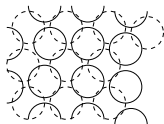
fcc (111)



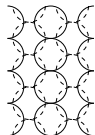
bcc (110)



fcc (100)



bcc (100)

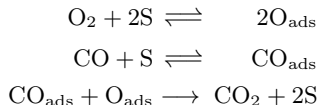


fcc (110)

Figure 5.16: Surface and second-layer (dashed) atom arrangements for several low-index surfaces.

- This figure illustrates the packing arrangement and different combinations of nearest neighbors that can exist at a surface.
- An fcc(111) surface atom has six nearest-surface neighbors
- An fcc(100) surface atom has four nearest-surface neighbors
- An fcc(110) surface atom has two nearest-surface neighbors.
- The interaction between an adsorbing molecule and the surface of a single crystal depends on the surface structure.

- Consider the oxidation of CO on Pd, an fcc metal.
- The following mechanism has been proposed for the oxidation reaction over Pd(111) [7]



in which the subscript *ads* refers to adsorbed species and S refers to vacant surface sites.

- This example illustrates the steps in a catalytic reaction — adsorption of reactants in Reactions 5.121 and 5.122, reaction of adsorbed components in Reaction 5.123, and desorption of products also shown as part of Reaction 5.123.

- Adsorption occurs when an incident atom or molecule sticks to the surface.
- The adsorbing species can be bound weakly to the surface (physical adsorption) or it can be held tightly to the surface (chemical adsorption).
- A number of criteria have been applied to distinguish between physical and chemical adsorption. In some cases the distinction is not clear. Table 5.7 lists several properties that can be used to distinguish between physisorption and chemisorption.



Property	Chemisorption	Physisorption
amount	limited to a monolayer	multilayer possible
specificity	high	none
heat of adsorption	typically $> 10$ kcal/mol	low (2–5 kcal/mol)
activated	possibly	generally not

Table 5.7: Chemisorption and physisorption properties.

The most distinguishing characteristics are the degree of coverage and the specificity.

**Chemisorption:** Chemical adsorption occurs when a chemical bond or a partial chemical bond is formed between the surface (adsorbent) and the adsorbate. The formation of a bond limits the coverage to at most one chemisorbed adsorbate for every surface atom. The upper limit need not have a one-to-one adsorbate to surface atom stoichiometry; for example, saturation can occur after one-third of all sites are occupied.

**Physisorption:** Physical adsorption occurs once the partial pressure of the adsorbate is above its saturation vapor pressure. Physisorption is similar to a condensation process and has practically no dependence on the solid surface and the interaction between the adsorbate and adsorbent. Just as water vapor condenses on any cold surface placed in ambient, humid air, a gas such as  $N_2$  condenses on solids maintained at 77 K.

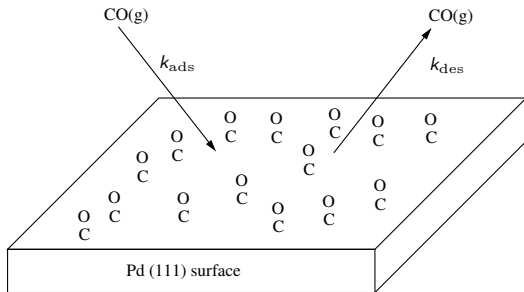


Figure 5.17: Schematic representation of the adsorption/desorption process.

- The Langmuir adsorption model assumes that all surface sites are the same.
- As long as the incident molecules possess the necessary energy, and entropy considerations are satisfied, adsorption proceeds if a vacant site is available.
- The Langmuir process also assumes adsorption is a completely random surface process with no adsorbate-adsorbate interactions.
- Since all sites are equivalent, and adsorbate-adsorbate interactions are neglected, the surface sites can be divided into two groups, vacant and occupied.

- The surface-site balance is therefore

$$\left\{ \begin{array}{l} \text{Total number of} \\ \text{surface sites} \\ \text{per unit area} \end{array} \right\} = \left\{ \begin{array}{l} \text{Number of} \\ \text{vacant sites} \\ \text{per unit area} \end{array} \right\} + \left\{ \begin{array}{l} \text{Number of} \\ \text{occupied sites} \\ \text{per unit area} \end{array} \right\}$$

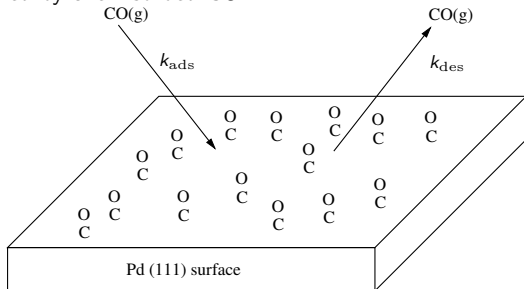
$$\bar{c}_m = \bar{c}_v + \sum_{j=1}^{n_s} \bar{c}_j \quad (5.124)$$

- Dividing by the total number of surface sites leads to the fractional form of the site balance.

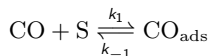
$$1 = \frac{\bar{c}_v}{\bar{c}_m} + \sum_{j=1}^{n_s} \frac{\bar{c}_j}{\bar{c}_m} = \theta_v + \sum_{j=1}^{n_s} \theta_j \quad (5.125)$$

- The units for  $\bar{c}_m$  often are number of sites per gram of catalyst.

- Consider again Figure 5.17 showing the model of a surface consisting of vacant sites and sites covered by chemisorbed CO.



- The CO in the gas phase is adsorbing on the surface and desorbing from the surface.
- The forward rate of adsorption and the reverse rate of desorption, are given by



$$r_{\text{ads}} = k_1 c_{\text{CO}} \bar{c}_v, \quad r_{\text{des}} = k_{-1} \bar{c}_{\text{CO}}$$

- The units of the rate are mol/time·area.
- The rate expressions follow directly from the reaction mechanism because the reactions are treated as elementary steps.

- Equating the adsorption and desorption rates at equilibrium gives

$$k_1 c_{\text{CO}} \bar{c}_v = k_{-1} \bar{c}_{\text{CO}}$$

- Solving for the surface concentration gives

$$\bar{c}_{\text{CO}} = \frac{k_1}{k_{-1}} c_{\text{CO}} \bar{c}_v = K_1 c_{\text{CO}} \bar{c}_v \quad (5.127)$$

- The conservation of sites gives

$$\bar{c}_v = \bar{c}_m - \bar{c}_{\text{CO}} \quad (5.128)$$

- Substituting Equation 5.128 into Equation 5.127 and rearranging leads to the Langmuir isotherm for single-component, associative adsorption

$$\bar{c}_{\text{CO}} = \frac{\bar{c}_m K_1 c_{\text{CO}}}{1 + K_1 c_{\text{CO}}} \quad (5.129)$$



- Dividing both sides of Equation 5.129 by the total concentration of surface sites  $\bar{c}_m$  leads to the fractional form of the single component, associative Langmuir adsorption isotherm.

$$\theta_{\text{CO}} = \frac{K_1 c_{\text{CO}}}{1 + K_1 c_{\text{CO}}} \quad (5.130)$$

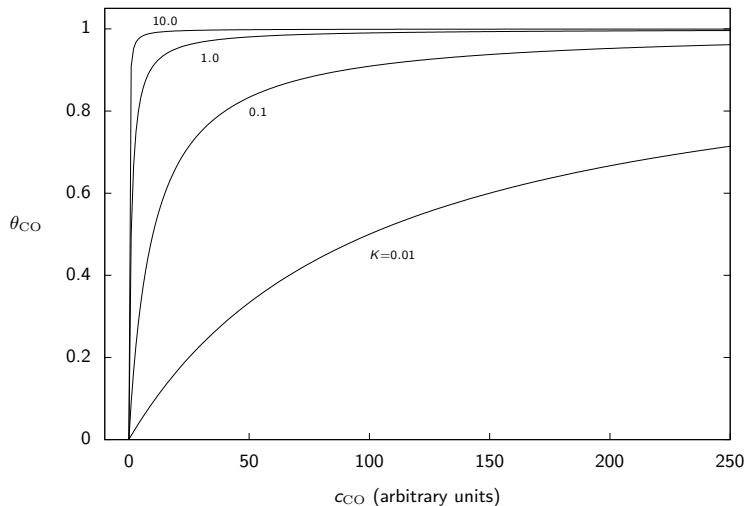


Figure 5.18: Fractional coverage versus adsorbate concentration for different values of the adsorption constant,  $K$ .

- Figure 5.18 presents the general shape of the fractional coverage as a function of pressure for different values of  $K$ .
- In the limit  $K_1 c_{CO} \gg 1$ , Equations 5.129 and 5.130 asymptotically approach  $\bar{c}_m$  and 1.0, respectively.
- Since adsorption is exothermic,  $K_1$  decreases with increasing temperature and higher CO partial pressures are required to reach saturation.
- Figure 5.18 illustrates the effect of  $K$  on the coverage. In all cases the surface saturates with the adsorbate; however, the concentration at which this saturation occurs is a strong function of  $K$ .
- Single component adsorption is used to determine the number of active sites,  $\bar{c}_m$ .

- The adsorption data can be fit to either the Langmuir isotherm (Equation 5.129) or to the “linear” form of the isotherm.
- The linear form is obtained by taking the inverse of Equation 5.129 and multiplying by  $c_{CO}$

$$\frac{c_{CO}}{\bar{c}_{CO}} = \frac{1}{K_1 \bar{c}_m} + \frac{c_{CO}}{\bar{c}_m} \quad (5.131)$$

- A plot of the linear form provides  $1/(K_1 \bar{c}_m)$  for the intercept and  $1/\bar{c}_m$  for the slope.

**Example 5.6: Fitting Langmuir adsorption constants to CO data**

- The active area of supported transition metals can be determined by adsorbing carbon monoxide. Carbon monoxide is known to adsorb associatively on ruthenium at 100°C.
- Use the following uptake data for the adsorption of CO on 10 wt % Ru supported on Al<sub>2</sub>O<sub>3</sub> at 100°C to determine the equilibrium adsorption constant and the number of adsorption sites.

$P_{\text{CO}}$ (Torr)	100	150	200	250	300	400
CO adsorbed ( $\mu\text{mol/g cat}$ )	1.28	1.63	1.77	1.94	2.06	2.21



- The next two figures plot the data for Equations 5.129 and 5.131, respectively.
- From the data for the “linear” model, we can estimate using least squares the slope,  $0.35 \text{ g}/\mu\text{mol}$ , and the zero concentration intercept,  $1.822 \text{ cm}^3/\text{g}$ , and then calculate

$$K_1 = 0.190 \text{ cm}^3/\mu\text{mol}$$

$$\bar{c}_m = 2.89 \mu\text{mol}/\text{g}$$

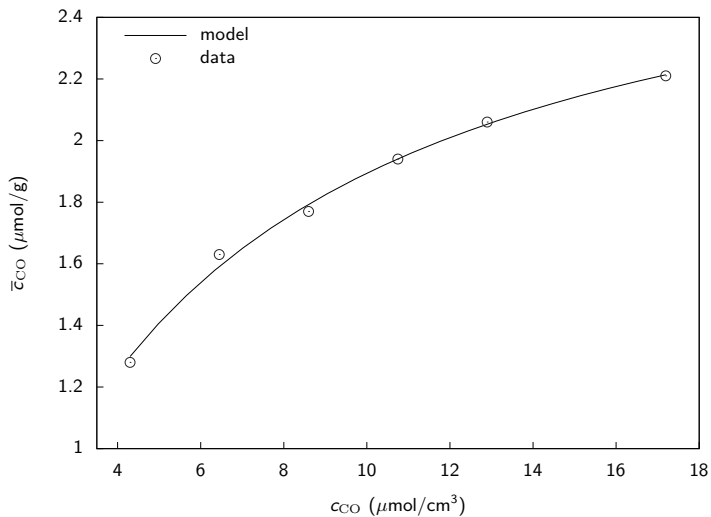


Figure 5.19: Langmuir isotherm for CO uptake on Ru.

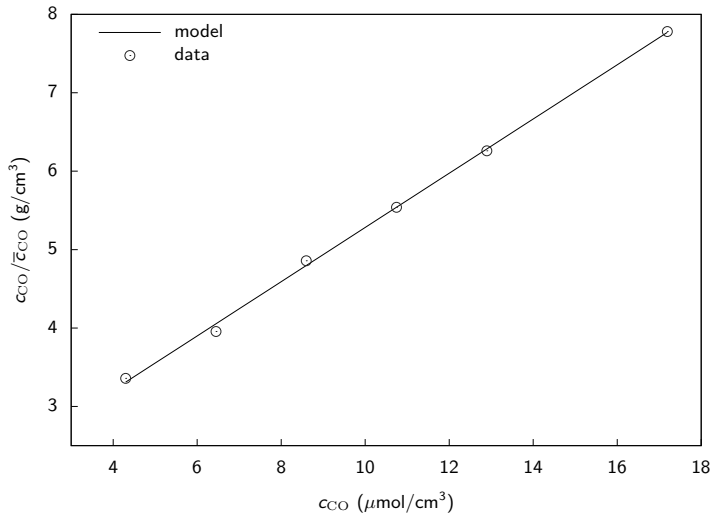
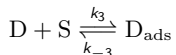
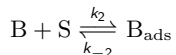


Figure 5.20: Linear form of Langmuir isotherm for CO uptake on Ru.



- We now consider multiple-component adsorption.
- If other components, such as B and D, are assumed to be in adsorption-desorption equilibrium along with CO, we add the following two reactions



- Following the development that led to Equation 5.127, we can show the equilibrium surface concentrations for B and D are given by

$$\bar{c}_B = K_2 c_B \bar{c}_v \quad (5.132)$$

$$\bar{c}_D = K_3 c_D \bar{c}_v$$

- The site balance becomes

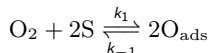
$$\bar{c}_v = \bar{c}_m - \bar{c}_{\text{CO}} - \bar{c}_B - \bar{c}_D \quad (5.134)$$

- Substituting Equation 5.134 into Equation 5.127 and rearranging leads to a different isotherm expression for CO.

$$\bar{c}_{\text{CO}} = \frac{\bar{c}_m K_{\text{CO}} c_{\text{CO}}}{1 + K_1 c_{\text{CO}} + K_2 c_B + K_3 c_D} \quad (5.135)$$

- The terms in the denominator of Equation 5.135 have special significance and the magnitude of the equilibrium adsorption constant, when multiplied by the respective concentration, determines the component or components that occupy most of the sites.
- Each of the terms  $K_i c_j$  accounts for sites occupied by species  $j$ .
- From Chapter 3 we know the equilibrium constant is related to the exponential of the heat of adsorption, which is exothermic. Therefore, the more strongly a component is chemisorbed to the surface, the larger the equilibrium constant.
- Also, if components have very different heats of adsorption, the denominator may be well approximated using only one  $K_i c_j$  term.

- The CO oxidation example also contains a dissociative adsorption step



- Adsorption requires the  $\text{O}_2$  molecule to find a pair of adsorption sites and desorption requires two adsorbed O atoms to be adjacent.
- When a bimolecular surface reaction occurs, such as dissociative adsorption, associative desorption, or a bimolecular surface reaction, the rate in the forward direction depends on the probability of finding pairs of reaction centers.
- This probability, in turn, depends on whether or not the sites are randomly located, and whether or not the adsorbates are mobile on the surface.

- The probability of finding pairs of vacant sites can be seen by considering adsorption onto a checkerboard such as Figure 5.21.

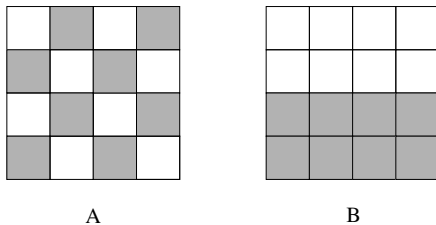
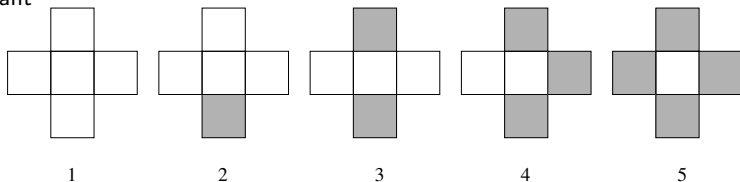


Figure 5.21: Two packing arrangements for a coverage of  $\theta = 1/2$ .

- Let two sites be adjacent if they share a common line segment (i.e., do not count sharing a vertex as being adjacent) and let  $\theta$  equal the fraction of surface covered.
- The checkerboard has a total 24 adjacent site pairs, which can be found by counting the line segments on adjoining squares.

- Figure 5.21 presents two possibilities where half the sites (the shaded squares) are covered.
- For Figure 5.21A the probability an incident gas atom striking this surface in a random location hits a vacant site is  $1 - \theta$  and the probability a gas-phase molecule can dissociate on two adjacent vacant sites is  $p = 0$ .
- Figure 5.21B has 10 *vacant* adjacent site pairs. Therefore, the probability of dissociative adsorption is  $p = 10/24$ . The probability of finding vacant adsorption sites is  $0 \leq p \leq 1/2$  for these two examples because the probability depends on the packing arrangement.

- We next show for *random* or independent packing of the surface, the probability for finding pairs of vacant adjacent sites is  $p = (1 - \theta)^2$ .
- The probability for random packing can be developed by considering five different arrangements for a site and its four nearest neighbors, with the center site always vacant



- The probability of any configuration is  $(1 - \theta)^n \theta^m$ , in which  $n$  is the number of vacant sites and  $m$  is the number of occupied sites.

- Arrangement 1 can happen only one way.
- Arrangement 2 can happen four ways because the covered site can be in four different locations.
- Similarly, arrangement 3 can happen six different ways, 4 can happen four ways, and 5 can happen only one way.
- Therefore, the probability of two adjacent sites being vacant is

$$p_1 + 4p_2 + 6p_3 + 4p_4 + 0p_5 \quad (5.137)$$

- An incoming gas molecule can hit the surface in one of four positions, with one atom in the center and the other pointing either north, south, east or west.
- For random molecule orientations, the probabilities that a molecule hits the arrangement with a correct orientation are:  $p_1$ ,  $(3/4)4p_2$ ,  $(1/2)6p_3$  and  $(1/4)4p_4$ .
- Therefore, the probability of a successful collision is

$$p = p_1 + 3p_2 + 3p_3 + p_4$$



- Use  $(1 - \theta)^n \theta^m$  for  $p_1, p_2, p_3, p_4$

$$p = (1 - \theta)^5 + 3(1 - \theta)^4 \theta + 3(1 - \theta)^3 \theta^2 + (1 - \theta)^2 \theta^3$$

$$p = (1 - \theta)^2 [(1 - \theta)^3 + 3(1 - \theta)^2 \theta + 3(1 - \theta) \theta^2 + \theta^3]$$

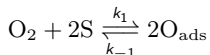
- Using a binomial expansion,  $(x + y)^3 = x^3 + 3x^2y + 3xy^2 + y^3$ , the term in brackets can be written as

$$p = (1 - \theta)^2 [(1 - \theta) + \theta]^3$$

$$p = (1 - \theta)^2$$

- Therefore, we use  $\theta_v \cdot \theta_v$  to represent the probability of finding pairs of vacant sites for dissociative adsorption.
- The probability of finding other pair combinations is the product of the fractional coverage of the two types of sites.

- Returning to Reaction 5.136



- We express the rates of dissociative adsorption and associative desorption of oxygen as

$$r_{\text{ads}} = k_1 \bar{c}_v^2 c_{\text{O}_2} \quad (5.138)$$

$$r_{\text{des}} = k_{-1} \bar{c}_{\text{O}}^2 \quad (5.139)$$

- The units on  $k_1$  are such that  $r_{\text{ads}}$  has the units of mol/time·area.
- At equilibrium, the rate of adsorption equals the rate of desorption leading to

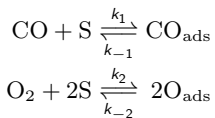
$$\bar{c}_{\text{O}} = \sqrt{K_1 c_{\text{O}_2}} \bar{c}_v \quad (5.140)$$

- Combining Equation 5.140 with the site balance, Equation 5.124, and rearranging leads to the Langmuir form for single-component dissociative adsorption

$$\bar{c}_{\text{O}} = \frac{\bar{c}_m \sqrt{K_1 c_{\text{O}_2}}}{1 + \sqrt{K_1 c_{\text{O}_2}}} \quad (5.141)$$

- The Langmuir isotherms represented in Equations 5.129 and 5.141 are different because each represents a different gas-surface reaction process.
- Both share the asymptotic approach to saturation at sufficiently large gas concentration, however.

- Determine the equilibrium CO and O surface concentrations when O<sub>2</sub> and CO adsorb according to



- At equilibrium adsorption rate equals desorption rate

$$r_1 = 0 = k_1 c_{\text{CO}} \bar{c}_v - k_{-1} \bar{c}_{\text{CO}}$$

$$r_2 = 0 = k_2 c_{\text{O}_2} \bar{c}_v^2 - k_{-2} \bar{c}_{\text{O}}^2$$

- Solving for the surface coverages in terms of the concentration of vacant sites gives

$$\bar{c}_{\text{CO}} = K_1 c_{\text{CO}} \bar{c}_v \quad (5.142)$$

$$\bar{c}_{\text{O}} = \sqrt{K_2 c_{\text{O}_2}} \bar{c}_v \quad (5.143)$$

- The remaining unknown is  $\bar{c}_v$ , which can be found using the site balance

$$\bar{c}_m = \bar{c}_v + \bar{c}_{\text{CO}} + \bar{c}_{\text{O}} \quad (5.144)$$

- Combining Equations 5.142–5.144 yields

$$\bar{c}_v = \frac{\bar{c}_m}{1 + K_1 c_{CO} + \sqrt{K_2 c_{CO_2}}} \quad (5.145)$$

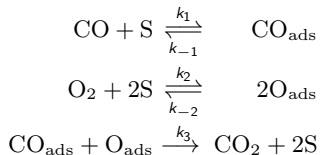
- We next substitute the vacant site concentration into Equations 5.142 and 5.143 to give the surface concentrations in terms of gas-phase concentrations and physical constants

$$\bar{c}_{CO} = \frac{\bar{c}_m K_1 c_{CO}}{1 + K_1 c_{CO} + \sqrt{K_2 c_{CO_2}}}$$

$$\bar{c}_O = \frac{\bar{c}_m \sqrt{K_2 c_{CO_2}}}{1 + K_1 c_{CO} + \sqrt{K_2 c_{CO_2}}}$$

## Example 5.7: Production rate of CO<sub>2</sub>

- Find the rate of CO<sub>2</sub> production using the following reaction mechanism



- Assume the O<sub>2</sub> and CO adsorption steps are at equilibrium.
- Make a log-log plot of the production rate of CO<sub>2</sub> versus gas-phase CO concentration at constant gas-phase O<sub>2</sub> concentration.
- What are the slopes of the production rate at high and low CO concentrations?





- The rate of  $\text{CO}_2$  production is given by

$$R_{\text{CO}_2} = k_3 \bar{c}_{\text{CO}} \bar{c}_{\text{O}} \quad (5.147)$$

- The surface concentrations for CO and O were determined in the preceding example,

$$\bar{c}_{\text{CO}} = \frac{\bar{c}_m K_1 c_{\text{CO}}}{1 + K_1 c_{\text{CO}} + \sqrt{K_2 c_{\text{O}_2}}}$$

$$\bar{c}_{\text{O}} = \frac{\bar{c}_m \sqrt{K_2 c_{\text{O}_2}}}{1 + K_1 c_{\text{CO}} + \sqrt{K_2 c_{\text{O}_2}}}$$

- Substituting these concentrations onto Equation 5.147 gives the rate of CO<sub>2</sub> production

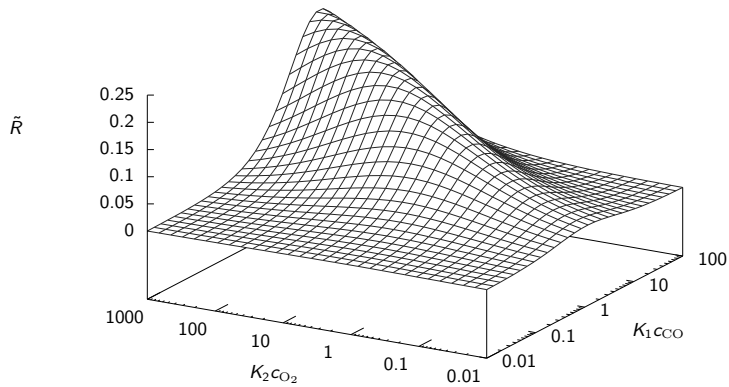
$$R_{\text{CO}_2} = \frac{k_3 \bar{c}_m^2 K_1 c_{\text{CO}} \sqrt{K_2 c_{\text{O}_2}}}{\left(1 + K_1 c_{\text{CO}} + \sqrt{K_2 c_{\text{O}_2}}\right)^2} \quad (5.148)$$

- For ease of visualization, we define a dimensionless production rate

$$\tilde{R} = R_{\text{CO}_2} / (k_3 \bar{c}_m^2)$$

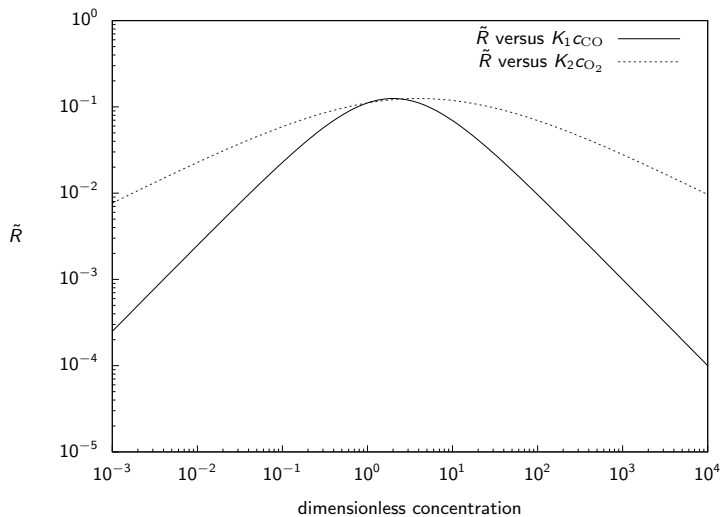
and plot this production rate versus dimensionless concentrations of CO and O<sub>2</sub> in the next figure.

# Production rate of $\text{CO}_2$



- Notice that the production rate goes to zero if either  $\text{CO}$  or  $\text{O}_2$  gas-phase concentration becomes large compared to the other.
- This feature is typical of competitive adsorption processes and second-order reactions. If one gas-phase concentration is large relative to the other, then that species saturates the surface and the other species surface concentration is small, which causes a small reaction rate.
- If we hold one of the gas-phase concentrations constant and vary the other, we are taking a slice through the surface of the figure.
- The next figure shows the result when each of the dimensionless gas-phase concentrations is held fixed at 1.0.

# Production rate of $\text{CO}_2$



- Notice again that increasing the gas-phase concentration of either reactant increases the rate until a maximum is achieved, and then decreases the rate upon further increase in concentration.
- High gas-phase concentration of either reactant inhibits the reaction by crowding the other species off the surface.
- Notice from the figure that  $\log \tilde{R}$  versus  $\log(K_1 c_{\text{CO}})$  changes in slope from 1.0 to  $-1.0$  as  $\text{CO}$  concentration increases.
- As the concentration of  $\text{O}_2$  increases, the slope changes from 0.5 to  $-0.5$ . These values also can be deduced by taking the logarithm of Equation 5.148.

- Rate expressions of the form of Equation 5.148 are known as Hougen-Watson or Langmuir-Hinshelwood kinetics [9].
- This form of kinetic expression is often used to describe the species production rates for heterogeneously catalyzed reactions.

We introduced several concepts in this chapter that are the building blocks for reaction kinetics.

- Most reaction processes consist of more than one elementary reaction.
- The reaction process can be represented by a mass action statement, such as  $\text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_4 + \text{H}_2$  in Example 5.5, but this statement does not describe how the reactants convert into the products.
- The atomistic description of chemical events is found in the elementary reactions.
- First principles calculations can be used to predict the order of these elementary reactions and the values of their rate constants.



- The reaction order for elementary reactions is determined by the stoichiometry of the reaction

$$r_i = k_i \prod_{j \in \mathcal{R}_i} c_j^{-\nu_{ij}} - k_{-i} \prod_{j \in \mathcal{P}_i} c_j^{\nu_{ij}}$$

- Two assumptions are generally invoked when developing simplified kinetic rate expressions:
  - 1 some of the elementary reactions are slow relative to the others; the fast reactions can be assumed to be at equilibrium.  
If only one step is slow, this single reaction determines all production rates, and is called the rate-limiting step;
  - 2 the rate of formation of highly reactive intermediate species can be set to zero; the concentration of these intermediates is found from the resulting algebraic relations rather than differential equations.

- Reactions at surfaces
  - ① The chemical steps involved in heterogeneous reactions (adsorption, desorption, surface reaction) are generally treated as elementary reactions.
  - ② In many cases, one reaction is the slow step and the remaining steps are at equilibrium.
  - ③ For heterogeneous reactions, we add a site balance to account for the vacant and occupied sites that take part in the reaction steps.

# Notation I

$a_j$	activity of species $j$
$c_j$	concentration of species $j$
$c_{js}$	steady-state concentration of $j$
$\bar{c}_j$	concentration of species $j$ on the catalyst surface
$\bar{c}_m$	total active surface concentration (monolayer coverage concentration)
$\bar{c}_v$	concentration of vacant surface sites
$f_j$	fugacity of species $j$
$f_j^\circ$	standard-state fugacity of pure species $j$
$F_j$	flux of species $j$ from the gas phase to the catalyst surface
$g_{ei}$	degeneracy of the $i$ th electronic energy level
$h$	Planck's constant
$I$	moment of inertia for a rigid rotor
$I_i$	moment of inertia about an axis
$k_B$	Boltzmann constant
$K$	reaction equilibrium constant
$m$	mass of a molecule (atom)
$M_j$	molecular weight of species $j$
$n_j$	moles of species $j$
$N_j$	molar flowrate of species $j$
$p$	probability of finding adjacent pairs of sites
$P$	total pressure

## Notation II

$P_j$	partial pressure of species $j$
$\mathcal{P}_i$	product species in reaction $i$
$\left(\frac{q}{V}\right)_j$	molecular partition function of species $j$
$q_{\text{elec}}$	electronic partition function
$q_{\text{rot}}$	rotational partition function
$q_{\text{vib}}$	vibrational partition function
$Q$	partition function
$Q_f$	volumetric flowrate at the reactor inlet
$r_i$	reaction rate for $i$ th reaction
$R$	gas constant
$R_j$	production rate for $j$ th species
$\mathcal{R}_i$	reactant species in reaction $i$
$t$	time
$T$	absolute temperature
$V(r)$	intermolecular potential energy
$V_R$	reactor volume
$z$	compressibility factor
$\epsilon_i$	energy of the $i$ th electronic level
$\epsilon_i$	extent of the $i$ th reaction
$\theta_j$	fractional surface coverage of species $j$
$\theta_v$	fractional surface coverage of vacant sites

$\nu_{ij}$	stoichiometric number for the $j$ th species in the $i$ th reaction
$\sigma$	symmetry number, 1 for a heteronuclear molecule, 2 for homonuclear molecule
$\tau$	lifetime of a component
$\phi_j$	fugacity coefficient for species $j$



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