

Chemical Kinetics

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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

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.

Reactions at Surfaces

- We also discuss heterogeneous catalytic adsorption and reaction kinetics.
- Catalysis has a significant impact on the United States economy¹ and many important reactions employ catalysts.²
- 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.

¹Catalysis 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].

²Between 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].

Elementary Reactions and Microscopic Reversibility

- 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.

Elementary Reactions and Rate Expressions

- 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.

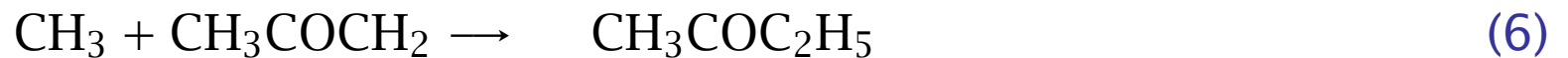
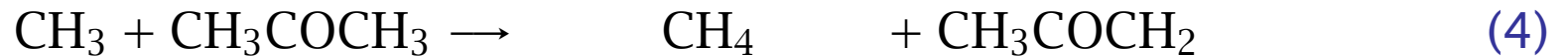
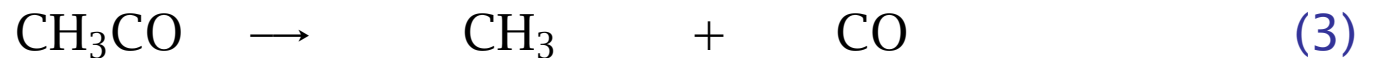
Some Examples — Acetone decomposition

- 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



Acetone decomposition

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



Acetone decomposition

- The thermal decomposition of acetone generates four stable molecules that can be removed from the reaction vessel: CO, CH₄, CH₂CO and CH₃COC₂H₅.
- Three radicals are formed and consumed during the thermal decomposition of acetone: CH₃, CH₃CO and CH₃COCH₂.
- 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	CH_3COCH_3	acetone
A_2	CH_3	methyl radical
A_3	CH_3CO	acetyl radical
A_4	CO	carbon monoxide
A_5	CH_3COCH_2	acetone radical
A_6	CH_2CO	ketene
A_7	CH_4	methane
A_8	$\text{CH}_3\text{COC}_2\text{H}_5$	methyl ethyl ketone

- The stoichiometric matrix is

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

Overall stoichiometry from Mechanism

- Multiply ν by $\begin{bmatrix} 1 & 1 & 2 & 1 & 1 \end{bmatrix}$

- We obtain

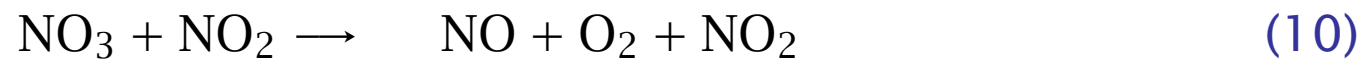
$$\begin{bmatrix} -3 & 0 & 0 & 1 & 0 & 1 & 2 & 1 \end{bmatrix}$$

which is the overall stoichiometry given in Reaction 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





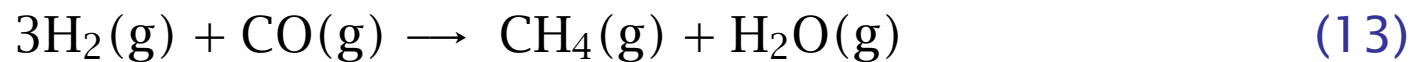
Smog

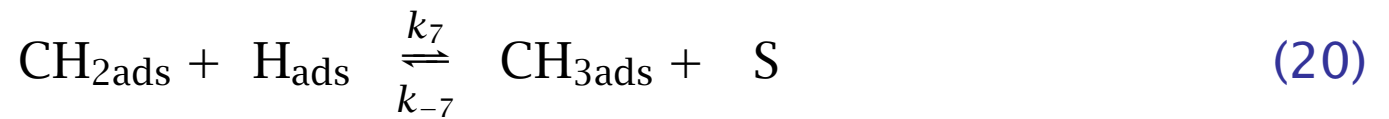
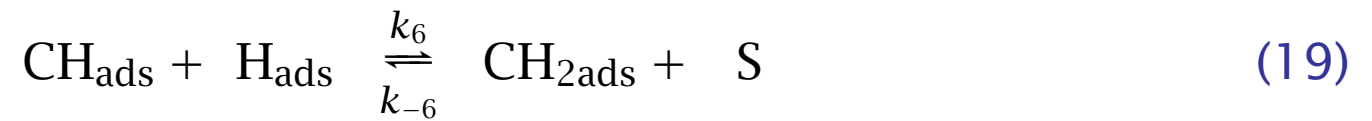
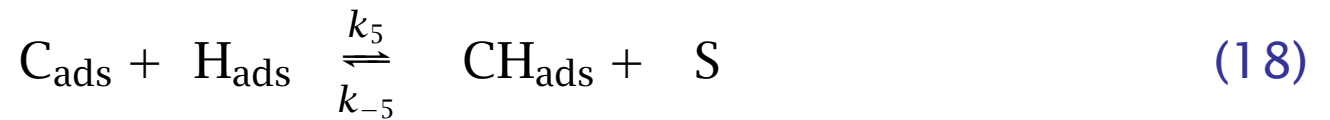
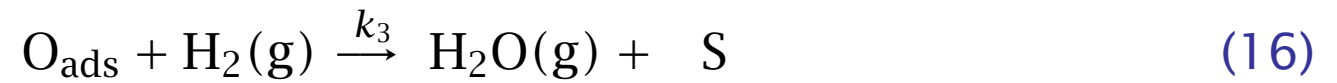
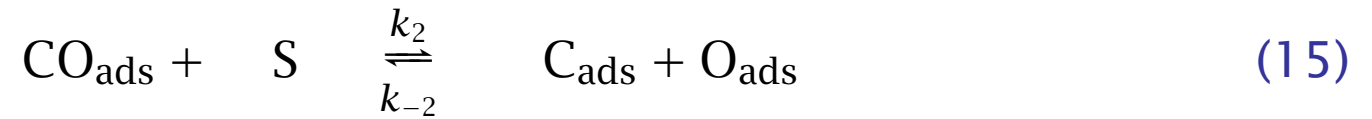
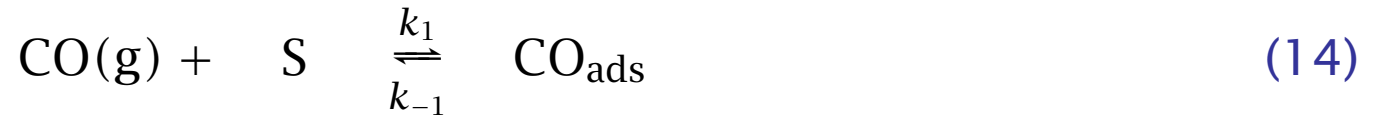
- In this reaction mechanism, nitrogen dioxide is activated by absorbing photons and decomposes to nitric oxide and oxygen radicals (elementary Reaction 8).
- Stable molecules are formed: NO and O₂
- Radicals, O and NO₃, are generated and consumed during the photochemical reaction.
- Work through the 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 H₂, over a ruthenium catalyst [6].

- The overall reaction and one possible mechanism are





Methane Synthesis

- 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 14 and 17), and the products form at the surface and desorb (elementary Reactions 16 and 21).
- Adsorbed CO (CO_s) either occupies surface sites or dissociates to adsorbed carbon and oxygen in elementary Reaction 15.

Methane Synthesis

- 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 21.
- In this example, the overall reaction is twice the fourth reaction added to the remaining reactions.

Elementary Reactions — Characteristics

- 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].

Microscopic Reversibility

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.

Transition State Theory

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.

Elementary Reaction Kinetics

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

$$r_i = k_i \prod_{j \in \mathcal{R}_i} c_j^{-\nu_{ij}} - k_{-i} \prod_{j \in \mathcal{P}_i} c_j^{\nu_{ij}} \quad (22)$$

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 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 22.

Potential Energy Diagrams

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 β is related to the vibrational frequency of the molecule. The following figure presents the Morse functions for HF and H₂ molecules.

Potential energy of HF and H₂ molecules

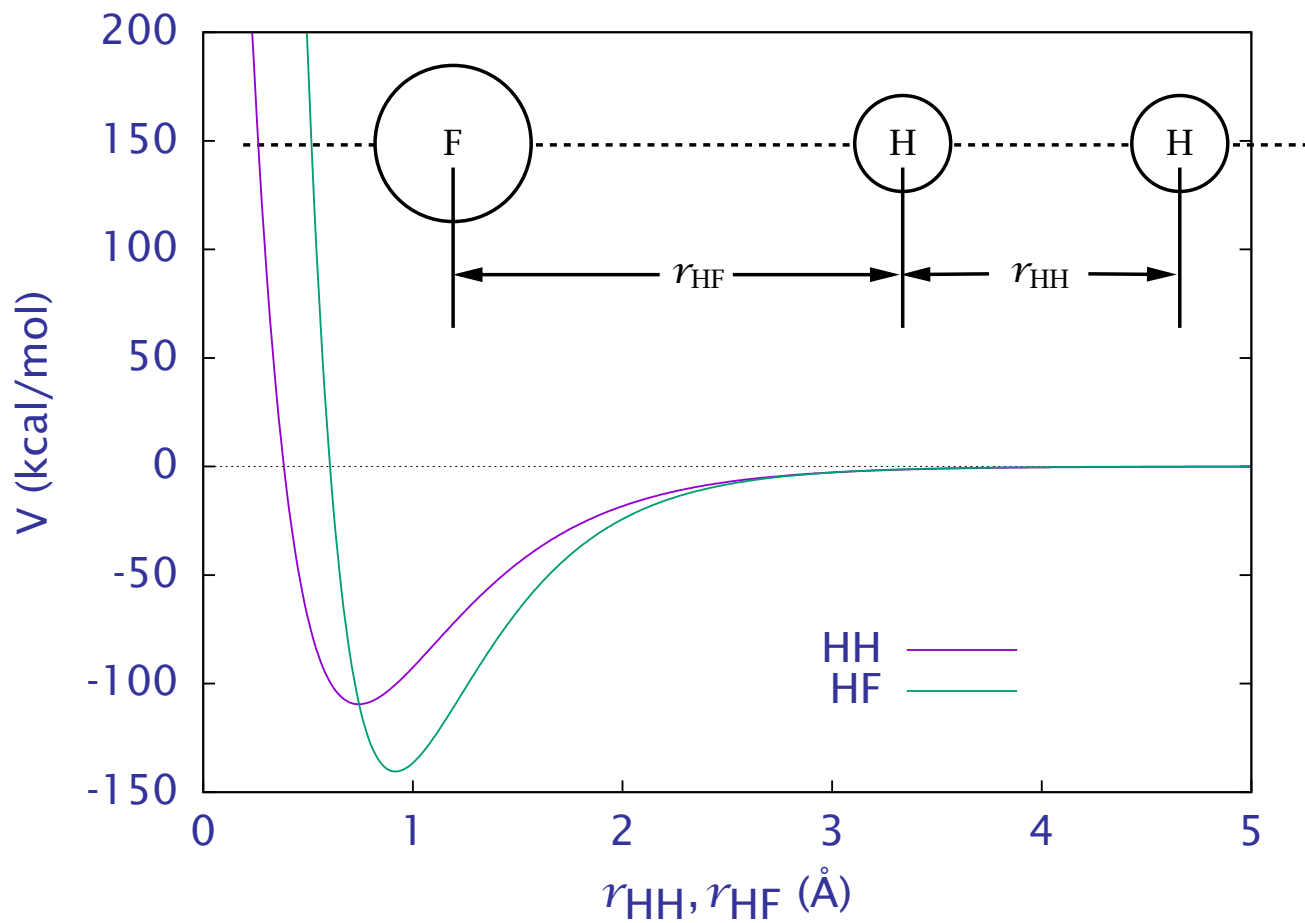


Figure 1: Morse potential for H_2 and HF .

Coordinate system for multi-atom molecules

- 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.

Coordinate system

- 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.

Collinear Approach of HF and H₂

- Figure 2 shows a representative view of such a surface for the collinear collision between F and H₂.



- 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].

Collinear Approach of HF and H₂

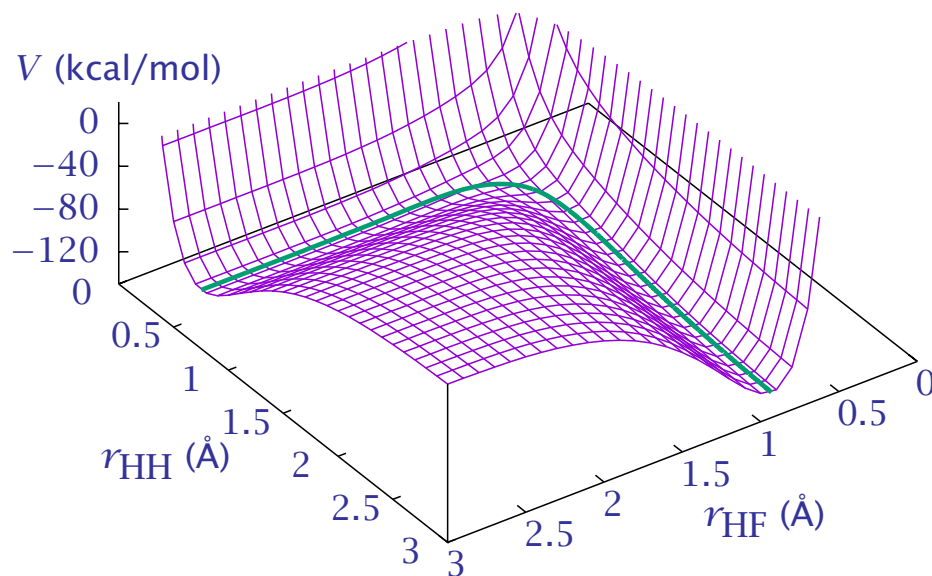


Figure 2: Potential-energy surface for the F, H₂ reaction.

Collinear Approach of HF and H₂ - Energy Contours

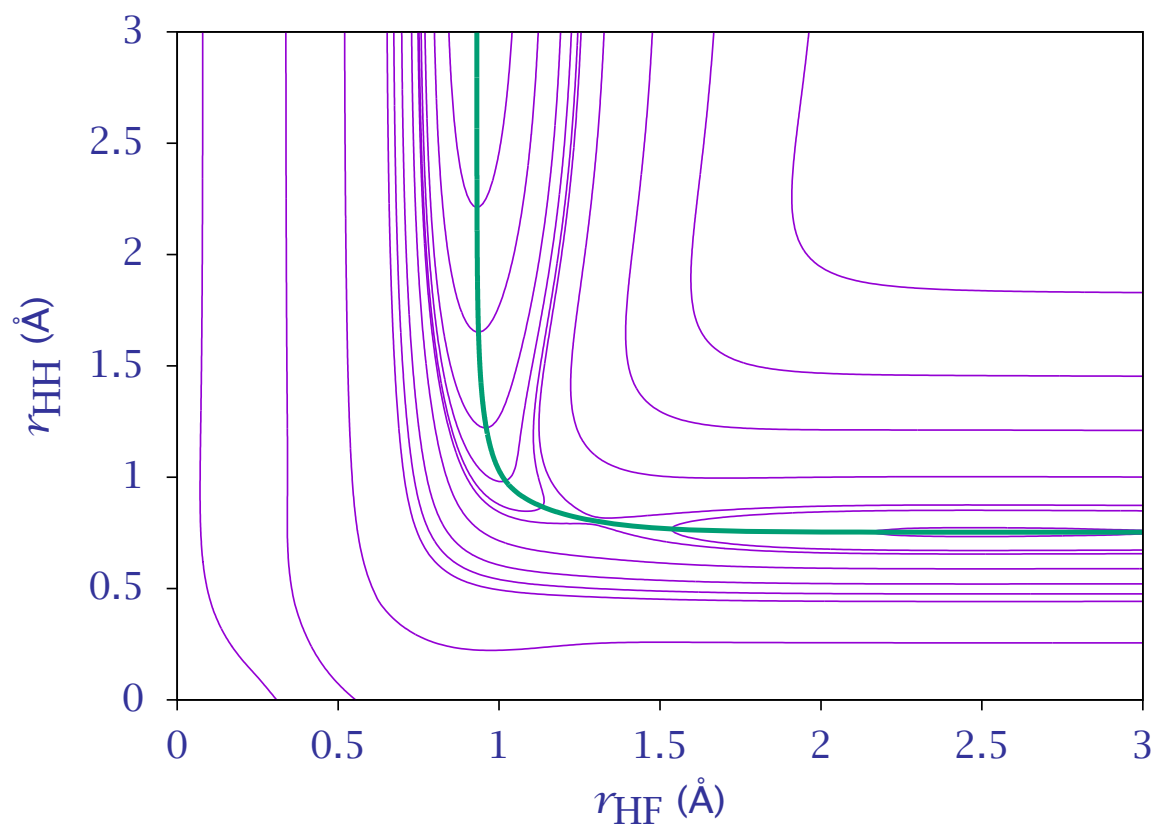


Figure 3: Contour representation of the potential-energy surface.

The energy surface

- Large r_{HF} . F atoms exist along with H_2 molecules. Reproduces the H_2 curve in Figure 1.
- Large r_{HH} . H atoms exist along with HF molecules. Reproduces the curve for HF in Figure 1.
- As the F atom is brought into contact with H_2 in a collinear fashion, a surface of energies is possible that depends on the values of r_{HF} and r_{HH} .
- The minimum energy path along the valleys is shown by the dashed line in Figures 2 and 3.

- The reaction starts in the H₂ valley at large r_{HF} , proceeds along the minimum energy path and ends in the HF valley at large r_{HH} .

The energy surface

- 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, ξ .
- Figure 4 is a reaction-coordinate diagram, which displays the energy change during this reaction.

Reaction coordinate diagram

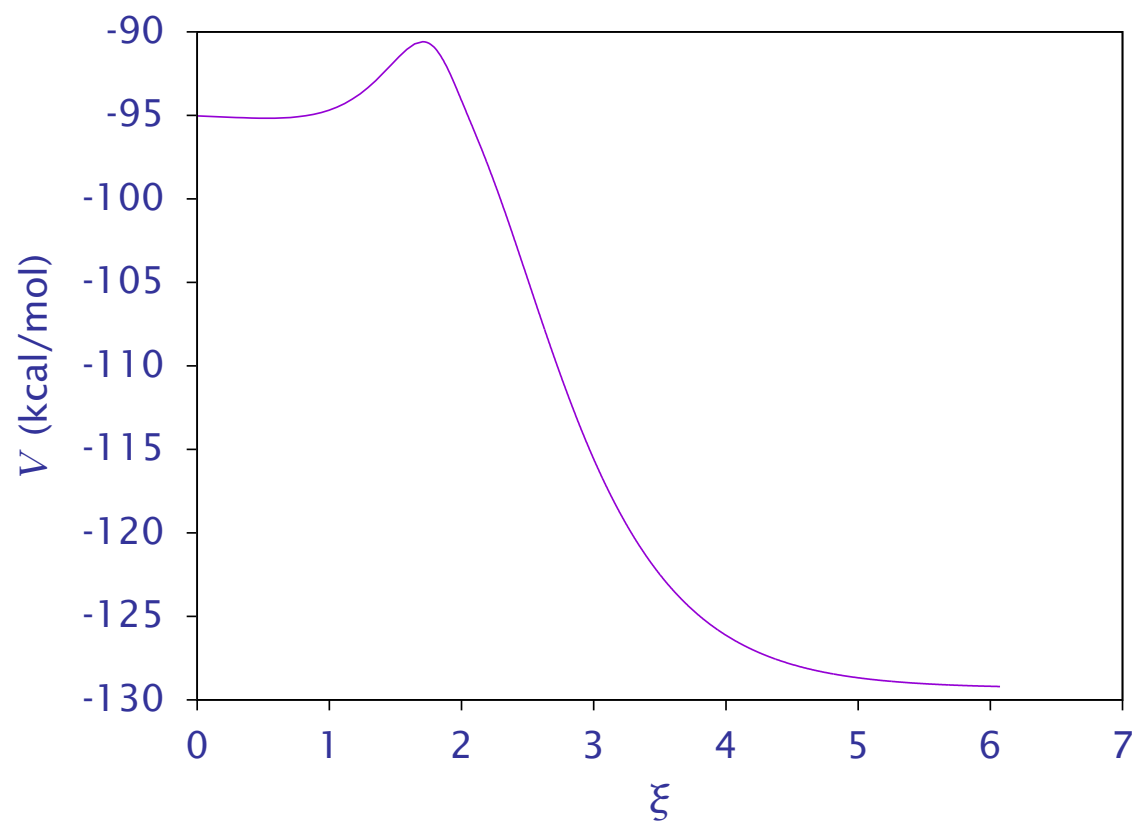


Figure 4: Reaction-coordinate diagram.

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 HF + 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.

Fast and Slow Time Scales

- 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.

Fast and Slow Time Scales

- 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.

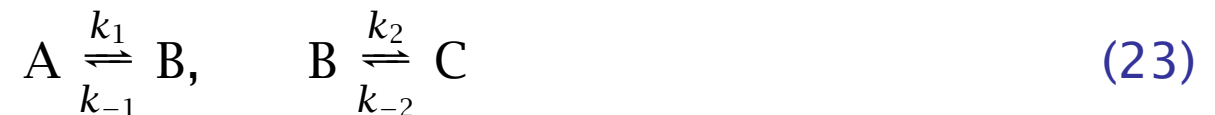
The Reaction Equilibrium Assumption

- 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.

The complete case

- 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.

Full model, rates about the same

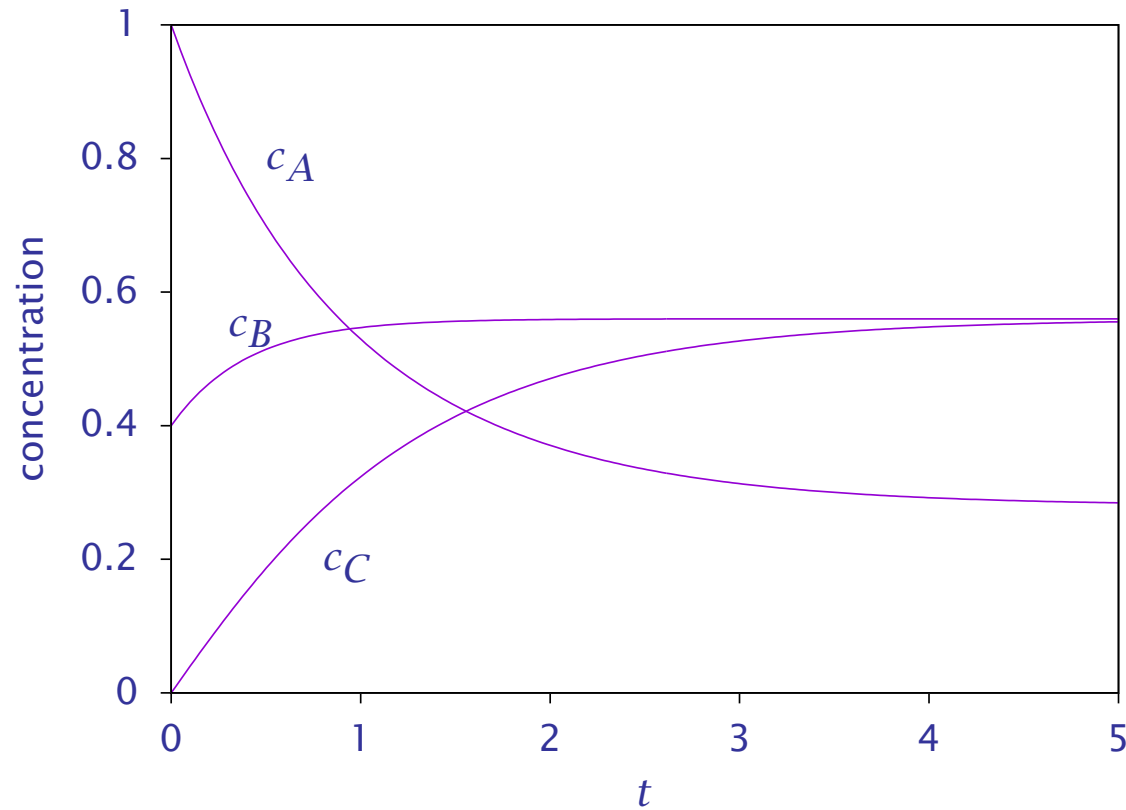


Figure 5: Full model solution for $k_1 = 1, k_{-1} = 0.5, k_2 = k_{-2} = 1$.

Turn up the second rate

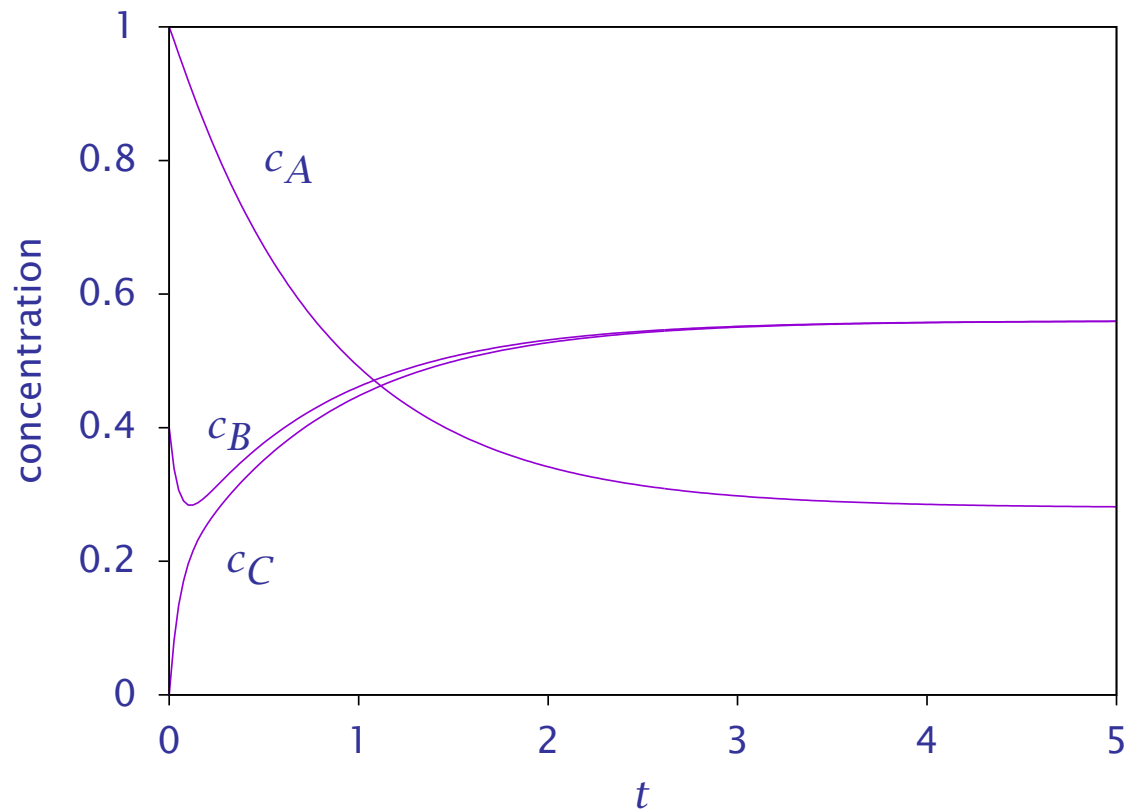


Figure 6: Full model solution for $k_1 = 1, k_{-1} = 0.5, k_2 = k_{-2} = 10$.

Turn it way up

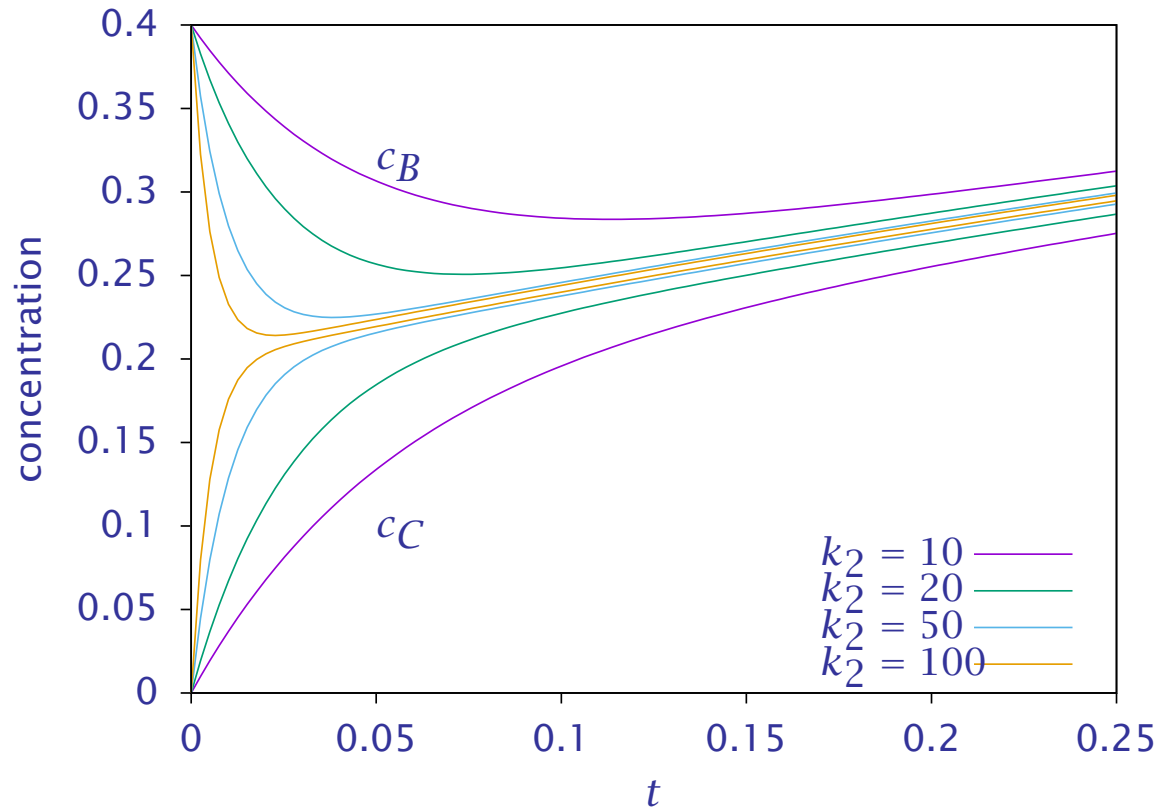


Figure 7: Concentrations of B and C versus time for full model with increasing k_2 with $K_2 = k_2/k_{-2} = 1$.

Now let's do some analysis

- 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 .

Equilibrium constraint

- 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

$$\frac{d(c_B + c_C)}{dt} = r_1 \quad (24)$$

Notice we have *not* set $r_2 = 0$ to obtain this result. Equation 24 involves no approximation.

Getting back to ODEs

- 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 ,

$$\frac{dc_B}{dt} = \frac{1}{1 + K_2} r_1, \quad \frac{dc_C}{dt} = \frac{K_2}{1 + K_2} r_1 \quad (25)$$

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

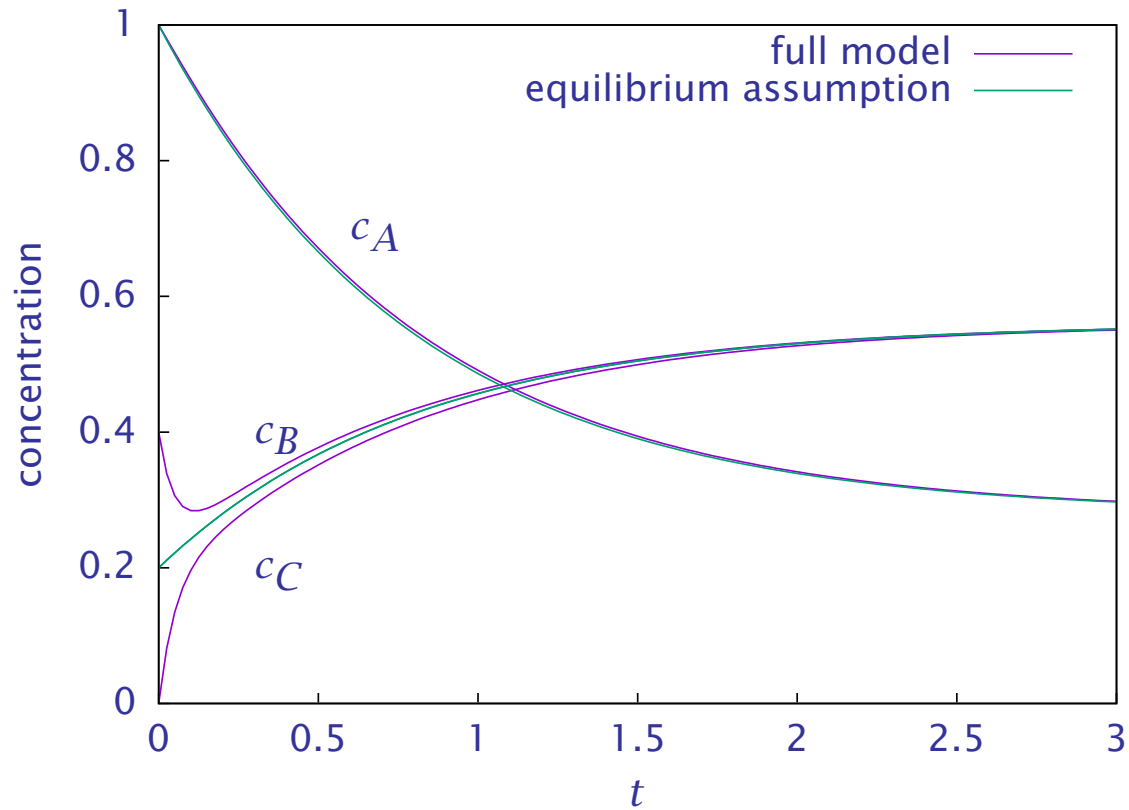


Figure 8: Comparison of equilibrium assumption to full model for $k_1 = 1, k_{-1} = 0.5, k_2 = k_{-2} = 10$.

A trap to avoid

- 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 25. What went wrong?

Paradox lost

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

$$\begin{aligned}\frac{dc_C}{dt} &= k_2c_B - k_{-2}c_C \\ &= k_{-2}(K_2c_B - c_C)\end{aligned}$$

- 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!

Paradox lost

- 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 we did.

Further special cases – second reaction irreversible

- 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 reac-

tion, $c_C(t) = 0$,



- Under the equilibrium assumption, we see that the two series reactions in Equation 23 may reduce to A going directly and irreversibly to C, Equation 26, or A going reversibly to B, Equation 27, 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].

QSSA Example

- 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

$$c_A = c_{A0}e^{-k_1t} \quad (28)$$

$$c_B = c_{A0} \frac{k_1}{k_2 - k_1} (e^{-k_1t} - e^{-k_2t}) \quad (29)$$

$$c_C = c_{A0} \frac{1}{k_2 - k_1} (k_2(1 - e^{-k_1t}) - k_1(1 - e^{-k_2t})) \quad (30)$$

Making B a highly reactive intermediate species

- 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 9 shows the normalized concentration of C given in Equation 30 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 9 illustrates that as $k_2 \gg k_1$, the exact solution is equivalent to

$$c_C = c_{A0} (1 - e^{-k_1 t}) \quad (31)$$

Full model

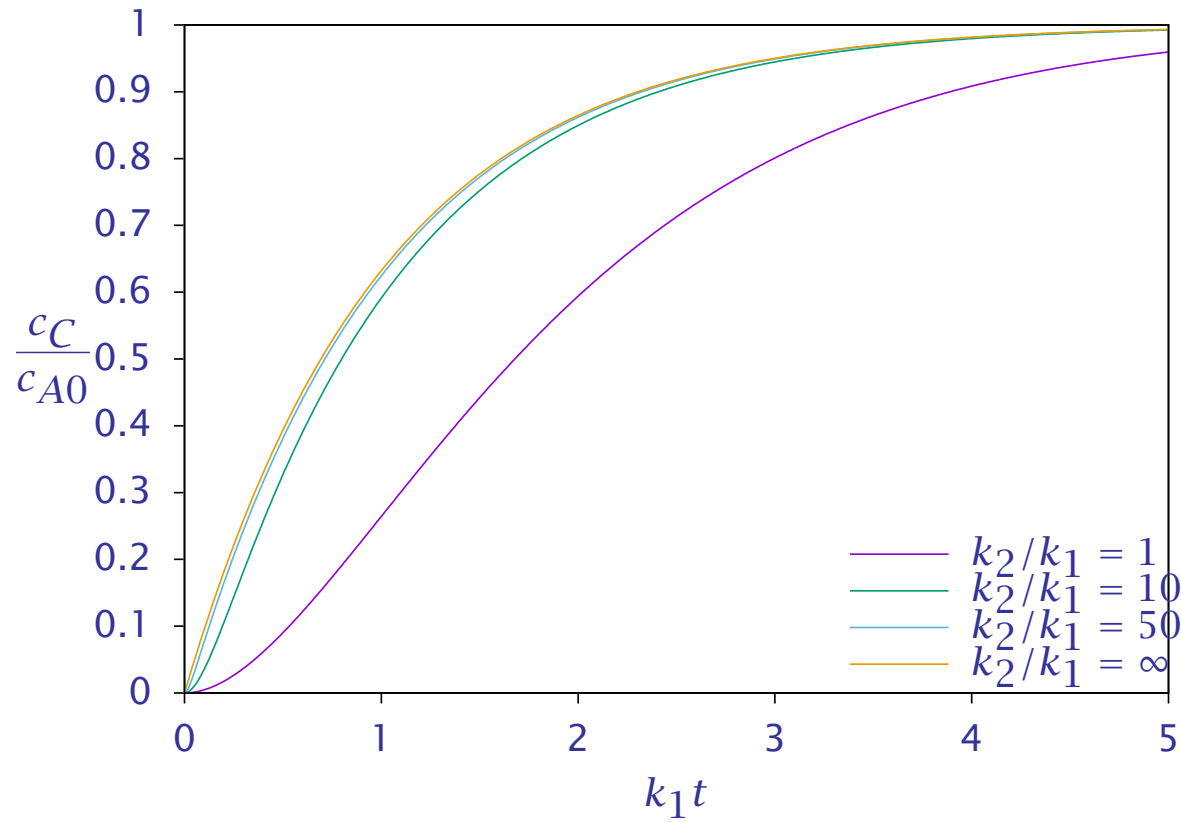


Figure 9: Normalized concentration of C versus dimensionless time for the series reaction $A \rightarrow B \rightarrow C$ for different values of k_2/k_1 .

Applying the QSSA

- 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

$$c_{Bs} = \frac{k_1}{k_2} c_{As} \quad (32)$$

- 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.

Applying the QSSA

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

$$\frac{dc_{As}}{dt} = -k_1 c_{As} \quad (33)$$

$$\frac{dc_{Cs}}{dt} = k_1 c_{As} \quad (34)$$

- The solutions to Equations 33 and 34 are presented in the following table for the initial condition $c_{As} = c_{A0}$, $c_{Bs} = c_{Cs} = 0$.

Results of QSSA

Scheme I:	$A \xrightarrow{k_1} B \xrightarrow{k_2} C$	(35)
<u>Exact Solution</u>		<u>QSSA Solution</u>
$c_A = c_{A0}e^{-k_1t}$	(36)	$c_{As} = c_{A0}e^{-k_1t}$ (39)
$c_B = c_{A0}\frac{k_1}{k_2 - k_1} (e^{-k_1t} - e^{-k_2t})$	(37)	$c_{Bs} = c_{A0}\frac{k_1}{k_2}e^{-k_1t}$ (40)
$c_C = c_{A0}\frac{1}{k_2 - k_1} (k_2(1 - e^{-k_1t}) - k_1(1 - e^{-k_2t}))$	(38)	$c_{Cs} = c_{A0} (1 - e^{-k_1t})$ (41)

Table 1: Exact and QSSA solutions for kinetic Scheme I.

Approximation error in C production

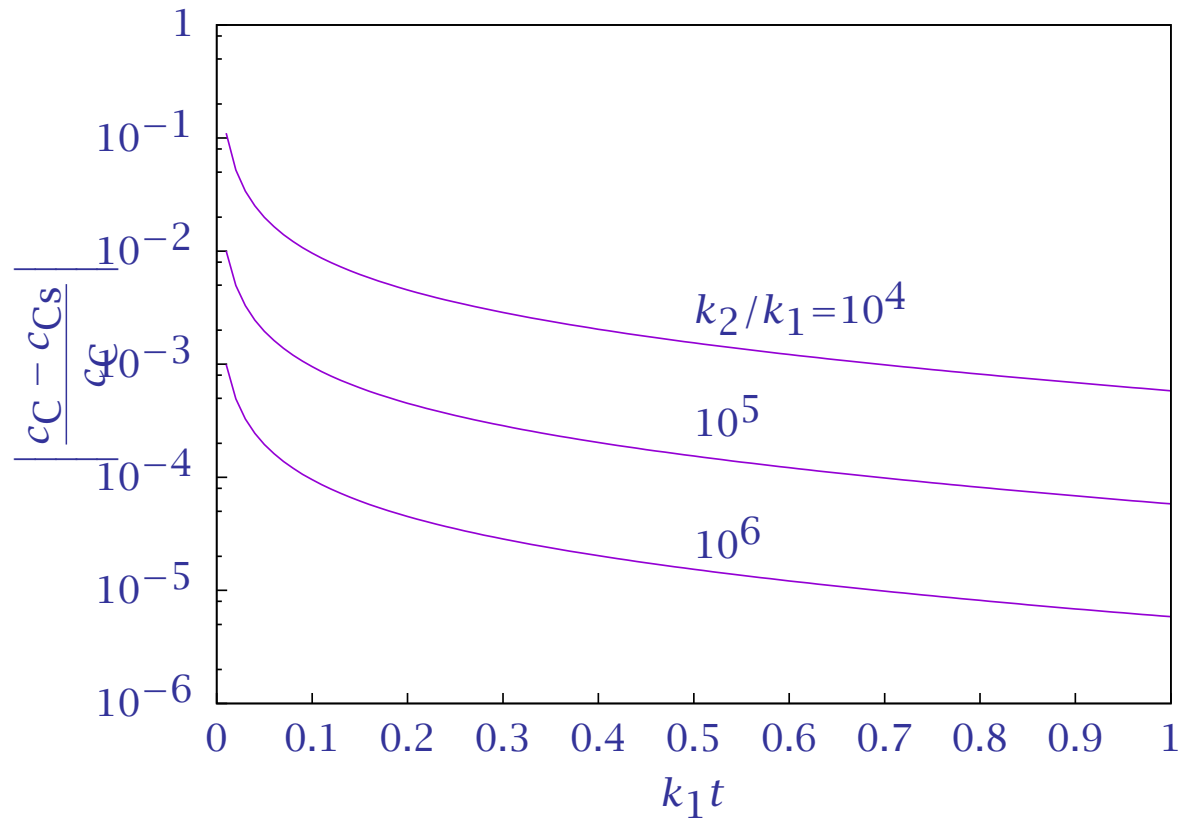


Figure 10: Fractional error in the QSSA concentration of C versus dimensionless time for the series reaction $A \rightarrow B \rightarrow C$ for different values of k_2/k_1 .

QSSA — Summary

- 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.

Procedure

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 42 and 43.

$$r_i = k_i \prod_{j \in \mathcal{R}_i} c_j^{-\nu_{ij}} - k_{-i} \prod_{j \in \mathcal{P}_i} c_j^{\nu_{ij}} \quad (42)$$

$$R_j = \sum_{i=1}^{n_r} \nu_{ij} r_i \quad (43)$$

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.

Production rate of acetone

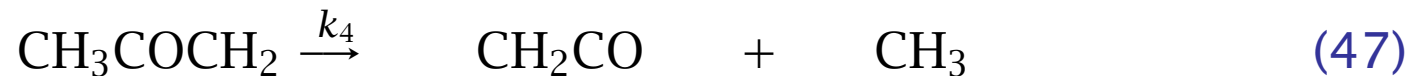
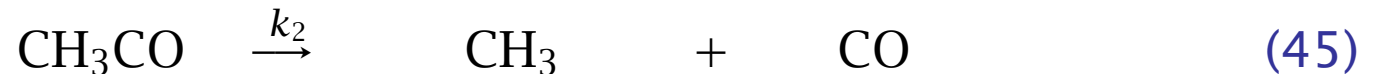
Example 5.1: Production rate of acetone

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



Production rate of acetone

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



Production rate of acetone

Solution

Let the species be designated as:

Species	Formula	Name
A_1	CH_3COCH_3	acetone
A_2	CH_3	methyl radical
A_3	CH_3CO	acetyl radical
A_4	CO	carbon monoxide
A_5	CH_3COCH_2	acetone radical
A_6	CH_2CO	ketene
A_7	CH_4	methane
A_8	$\text{CH}_3\text{COC}_2\text{H}_5$	methyl ethyl ketone

Production rate of acetone — QSSA

- Write the production rate of acetone using Reactions 44 and 46

$$R_1 = -k_1c_1 - k_3c_1c_2 \quad (49)$$

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

$$R_2 = 0 = k_1c_1 + k_2c_3 - k_3c_1c_2 + k_4c_5 - k_5c_2c_5 \quad (50)$$

$$R_3 = 0 = k_1c_1 - k_2c_3 \quad (51)$$

$$R_5 = 0 = k_3c_1c_2 - k_4c_5 - k_5c_2c_5 \quad (52)$$

Production rate of acetone — QSSA

- From Equation 51

$$c_3 = \frac{k_1}{k_2} c_1 \quad (53)$$

- Adding Equations 50, 51 and 52 gives

$$c_5 = \frac{k_1 c_1}{k_5 c_2} \quad (54)$$

Production rate of acetone — QSSA

- Inserting the concentrations shown in Equations 53 and 54 into Equation 50 gives

$$k_3 c_2^2 - k_1 c_2 - \frac{k_1 k_4}{k_5} = 0$$
$$c_2 = \frac{k_1}{2k_3} + \sqrt{\frac{k_1^2}{4k_3^2} + \frac{k_1 k_4}{k_3 k_5}} \quad (55)$$

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

- This result can be substituted into Equation 49 to give the rate in terms of measurable species.

$$R_1 = - \left(\frac{3}{2} k_1 + \sqrt{\frac{k_1^2}{4} + \frac{k_1 k_3 k_4}{k_5}} \right) c_1 \quad (56)$$

Production rate of acetone — QSSA

- Equation 56 can be simplified to

$$R_1 = -k_{\text{eff}}C_1 \quad (57)$$

by defining an effective rate constant

$$k_{\text{eff}} = \frac{3}{2}k_1 + \sqrt{\frac{k_1^2}{4} + \frac{k_1k_3k_4}{k_5}}$$

□

Summary of acetone example

- 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 57 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_{eff} .

Nitric oxide example

Example 5.2: Production rate of oxygen

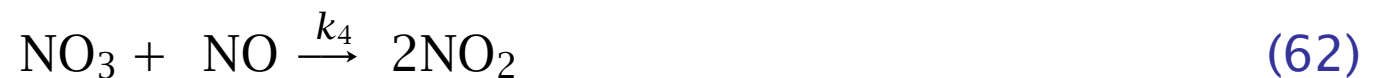
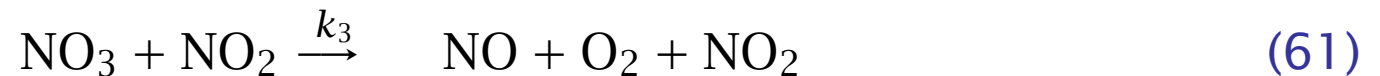
- Given the following mechanism for the overall stoichiometry



derive an expression for the production rate of O_2 .

- Assume atomic O and NO_3 radicals are QSSA species. The production rate should be in terms of the reactant, NO_2 , and products, NO and O_2 .

Nitric oxide example



- Let the species be designated as:

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

Nitric oxide example

- The production rate of molecular oxygen is

$$R_5 = k_3c_1c_4 + k_5c_1c_3 \quad (64)$$

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

$$R_3 = 0 = k_1c_1 - k_2c_1c_3 + k_{-2}c_4 - k_5c_1c_3 \quad (65)$$

$$R_4 = 0 = k_2c_1c_3 - k_{-2}c_4 - k_3c_1c_4 - k_4c_2c_4 \quad (66)$$

- Adding Equations 65 and 66

$$0 = k_1c_1 - k_3c_1c_4 - k_4c_2c_4 - k_5c_1c_3 \quad (67)$$

This result can be used to simplify the rate expression.

Nitric oxide example

- Adding Equations 64 and 67

$$R_5 = k_1c_1 - k_4c_2c_4 \quad (68)$$

- The intermediate NO_3 concentration is found by solving Equation 65 for c_3 .

$$c_3 = \frac{k_1}{k_2 + k_5} + \frac{k_{-2}}{k_2 + k_5} \frac{c_4}{c_1} \quad (69)$$

- Substituting Equation 69 into Equation 66 and rearranging gives

$$c_4 = \frac{k_1k_2c_1}{(k_2k_3 + k_3k_5)c_1 + (k_2k_4 + k_4k_5)c_2 + k_{-2}k_5} \quad (70)$$

- The rate expression now can be found using Equations 68 and 70

$$R_5 = k_1c_1 - \frac{k_1k_2k_4c_1c_2}{(k_2k_3 + k_3k_5)c_1 + (k_2k_4 + k_4k_5)c_2 + k_{-2}k_5} \quad (71)$$

□

Summary of nitric oxide example

- Equation 71 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 71 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.

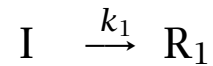
Free-radical polymerization kinetics

Example 5.3: Free-radical polymerization kinetics

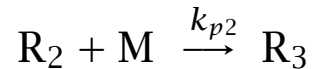
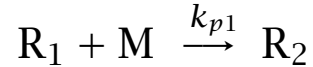
- Polymers are economically important and many chemical engineers are involved with some aspect of polymer manufacturing during their careers.
- Polymerization reactions raise interesting kinetic issues because of the long chains that are produced.
- Consider free-radical polymerization reaction kinetics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

Free-radical polymerization reactions

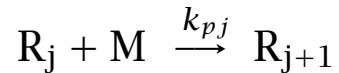
Initiation:



Propagation:



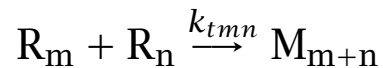
⋮



⋮

- 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

Termination:



Polymerization kinetics

- 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.

Polymerization kinetics

- 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.

Solution

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

$$R_M = - \sum_{j=1}^{\infty} r_{pj} = -k_p c_M \sum_{j=1}^{\infty} c_{Rj} \quad (72)$$

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

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

QSSA

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

$$\begin{array}{rcccc}
 & r_I & - & k_p c_{R_1} c_M & - & k_t c_{R_1} \sum_{j=1}^{\infty} c_{R_j} & = & 0 \\
 & & & \boxed{k_p c_{R_1} c_M} & - & & & \\
 \boxed{k_p c_{R_1} c_M} & - & \boxed{k_p c_{R_2} c_M} & - & k_t c_{R_2} \sum_{j=1}^{\infty} c_{R_j} & = & 0 \\
 \boxed{k_p c_{R_2} c_M} & - & \boxed{k_p c_{R_3} c_M} & - & k_t c_{R_3} \sum_{j=1}^{\infty} c_{R_j} & = & 0 \\
 & + & \vdots & & \vdots & & \\
 \hline
 & r_I & & & - & k_t \sum_{i=1}^{\infty} c_{R_i} \sum_{j=1}^{\infty} c_{R_j} & = & 0
 \end{array} \tag{73}$$

Polymerization kinetics

- We solve Equation 73 for the total growing polymer concentration and obtain

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

- Substituting this result into Equation 72 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

$$R_M = -k_p \sqrt{k_I/k_t} \sqrt{C_I} C_M$$

(74)

Polymerization summary

- 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.



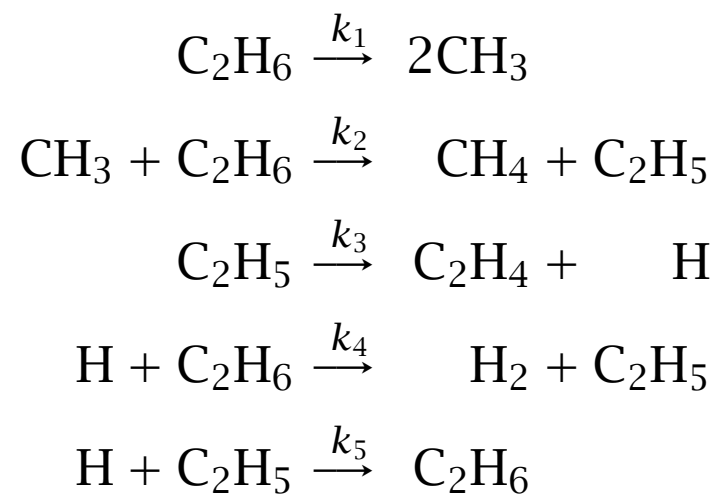
Ethane pyrolysis

Example 5.4: 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.

Ethane pyrolysis

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



Rate constants

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

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

Table 2: Ethane pyrolysis kinetics.

Reactor

- The pyrolysis is performed in a 100 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 $35 \text{ cm}^3/\text{s}$.

Exact solution

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

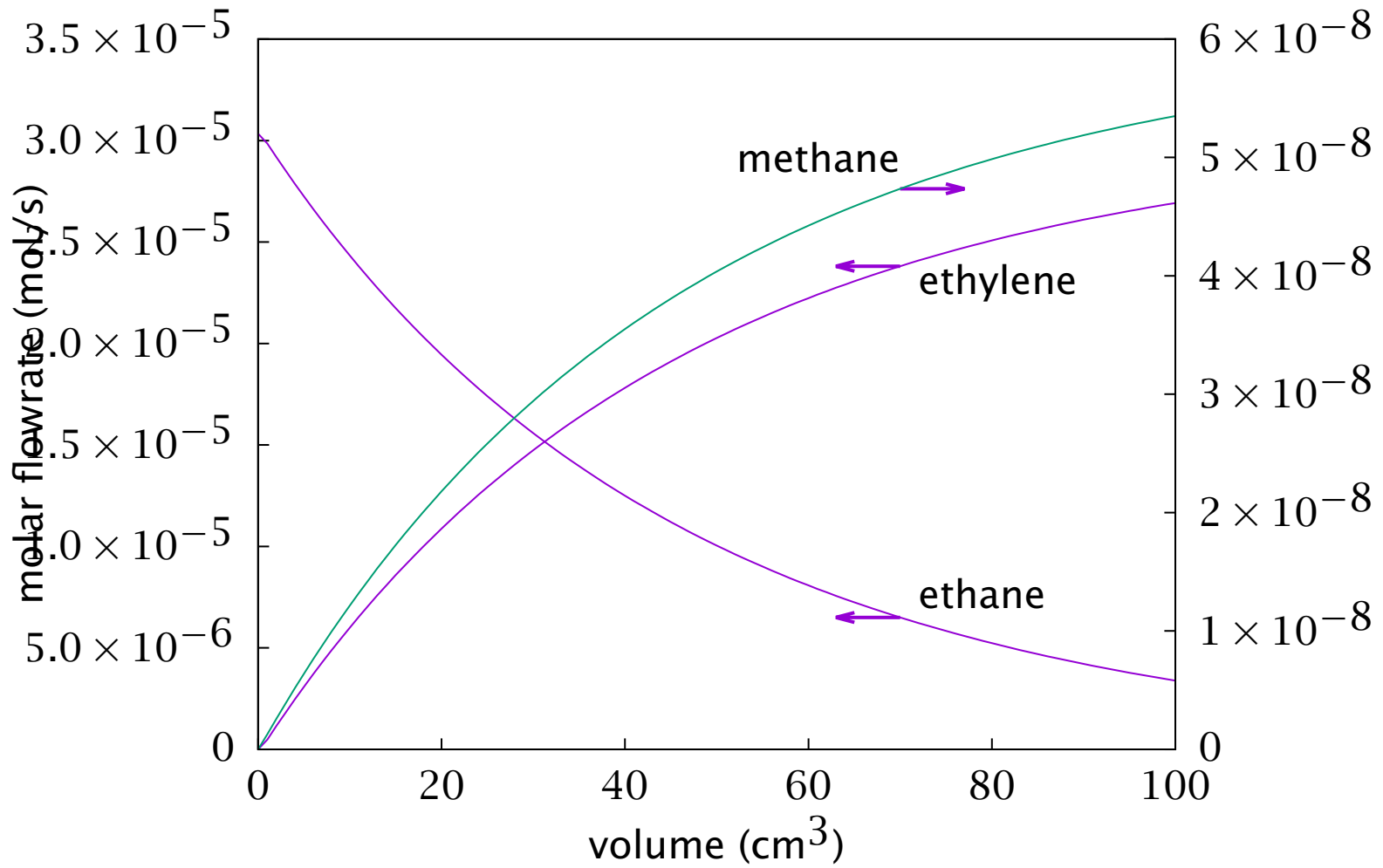
$$\frac{dN_j}{dV} = R_j \quad (75)$$

subject to the feed conditions.

- The results for C₂H₆, C₂H₄ and CH₄ are plotted in the next figure.
- The H₂ concentration is not shown because it is almost equal to the C₂H₄ concentration.
- Note the molar flowrate of CH₄ is only 0.2% of the molar flowrate of the other products, C₂H₄ and H₂.

- 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 CH_3 , C_2H_5 and H are QSSA species, develop an expression for the rate of ethylene formation.
- Verify that this approximation is valid.

Solution

- The rate of ethylene formation is

$$R_{C_2H_4} = k_3 c_{C_2H_5} \quad (76)$$

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

$$R_{CH_3} = 0 = 2k_1 c_{C_2H_6} - k_2 c_{CH_3} c_{C_2H_6} \quad (77)$$

$$R_H = 0 = k_3 c_{C_2H_5} - k_4 c_{CH} c_{C_2H_6} - k_5 c_{CH} c_{C_2H_5} \quad (78)$$

$$R_{C_2H_5} = 0 = k_2 c_{CH_3} c_{C_2H_6} - k_3 c_{C_2H_5} + k_4 c_{C_2H_6} c_{CH} - k_5 c_{CH} c_{C_2H_5} \quad (79)$$

- Adding Equations 77, 78 and 79 gives

$$c_H = \frac{k_1 c_{C_2H_6}}{k_5 c_{C_2H_5}} \quad (80)$$

Simplified rate expression

- Inserting Equation 80 into Equation 78 yields

$$0 = k_3 k_5 c_{\text{C}_2\text{H}_5}^2 - k_4 k_1 c_{\text{C}_2\text{H}_6}^2 - k_1 k_5 c_{\text{C}_2\text{H}_6} c_{\text{C}_2\text{H}_5}$$

$$c_{\text{C}_2\text{H}_5} = \left(\frac{k_1}{2k_3} + \sqrt{\left(\frac{k_1}{2k_3} \right)^2 + \frac{k_1 k_4}{k_3 k_5}} \right) c_{\text{C}_2\text{H}_6} \quad (81)$$

- Finally

$$R_{\text{C}_2\text{H}_4} = k_3 \left(\frac{k_1}{2k_3} + \sqrt{\left(\frac{k_1}{2k_3} \right)^2 + \frac{k_1 k_4}{k_3 k_5}} \right) c_{\text{C}_2\text{H}_6} \quad (82)$$

- This can be rewritten as

$$R_{\text{C}_2\text{H}_4} = k c_{\text{C}_2\text{H}_6} \quad (83)$$

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

$$c_{\text{H}} = \frac{k_1/k_5}{k_1/2k_3 + \sqrt{(k_1/2k_3)^2 + k_1 k_4/k_3 k_5}} \quad (84)$$

$$c_{\text{CH}_3} = \frac{2k_1}{k_2} \quad (85)$$

Verification

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

$$\begin{aligned}\frac{dN_{\text{C}_2\text{H}_6}}{dV} &= -r_1 - r_2 - r_4 + r_5 & \frac{dN_{\text{H}_2}}{dV} &= r_4 \\ \frac{dN_{\text{CH}_4}}{dV} &= r_2 & \frac{dN_{\text{H}_2\text{O}}}{dV} &= 0 \\ \frac{dN_{\text{C}_2\text{H}_4}}{dV} &= r_3\end{aligned}$$

subject to the initial molar flowrates.

- During the numerical solution the concentrations needed in the rate equa-

tions are computed using

$$c_{\text{C}_2\text{H}_6} = \left(\frac{N_{\text{C}_2\text{H}_6}}{N_{\text{C}_2\text{H}_6} + N_{\text{CH}_4} + N_{\text{C}_2\text{H}_4} + N_{\text{H}_2} + N_{\text{H}_2\text{O}}} \right) \frac{P}{RT} \quad (86)$$

and Equations 81, 84 and 85.

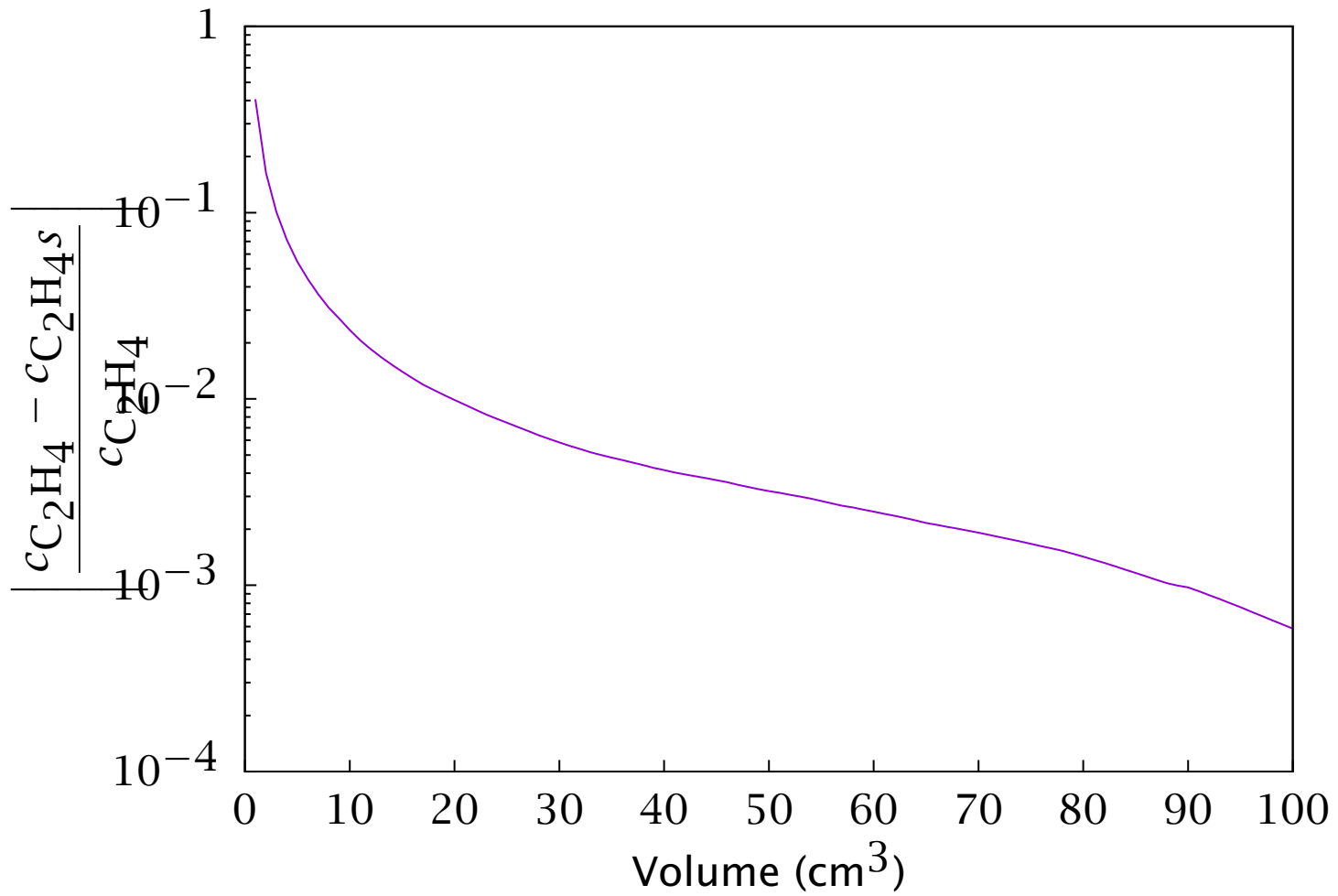
- Note we can neglect H, CH₃ and C₂H₅ in the molar flowrate balance (Equation 86) because these components are present at levels on the order of 10⁻⁶ less than C₂H₆.

Verification

- 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 cm³ 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 cm³ and less than 1% after 18.6 cm³.
- The figure shows that the QSSA is valid for sufficiently large reactors, such as 100 cm³.

- If the reactor volume were very small (a very short residence time), such as 20 cm^3 , the QSSA would not be appropriate.

Error in QSSA reduction



Is QSSA useful here?

- 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 CH_4 is a minor product at this temperature and this also would be found in the experimental data.
- This suggests we can neglect CH_4 in a species balance when computing mole fractions.

Further reduction

- Therefore the mass action statement



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

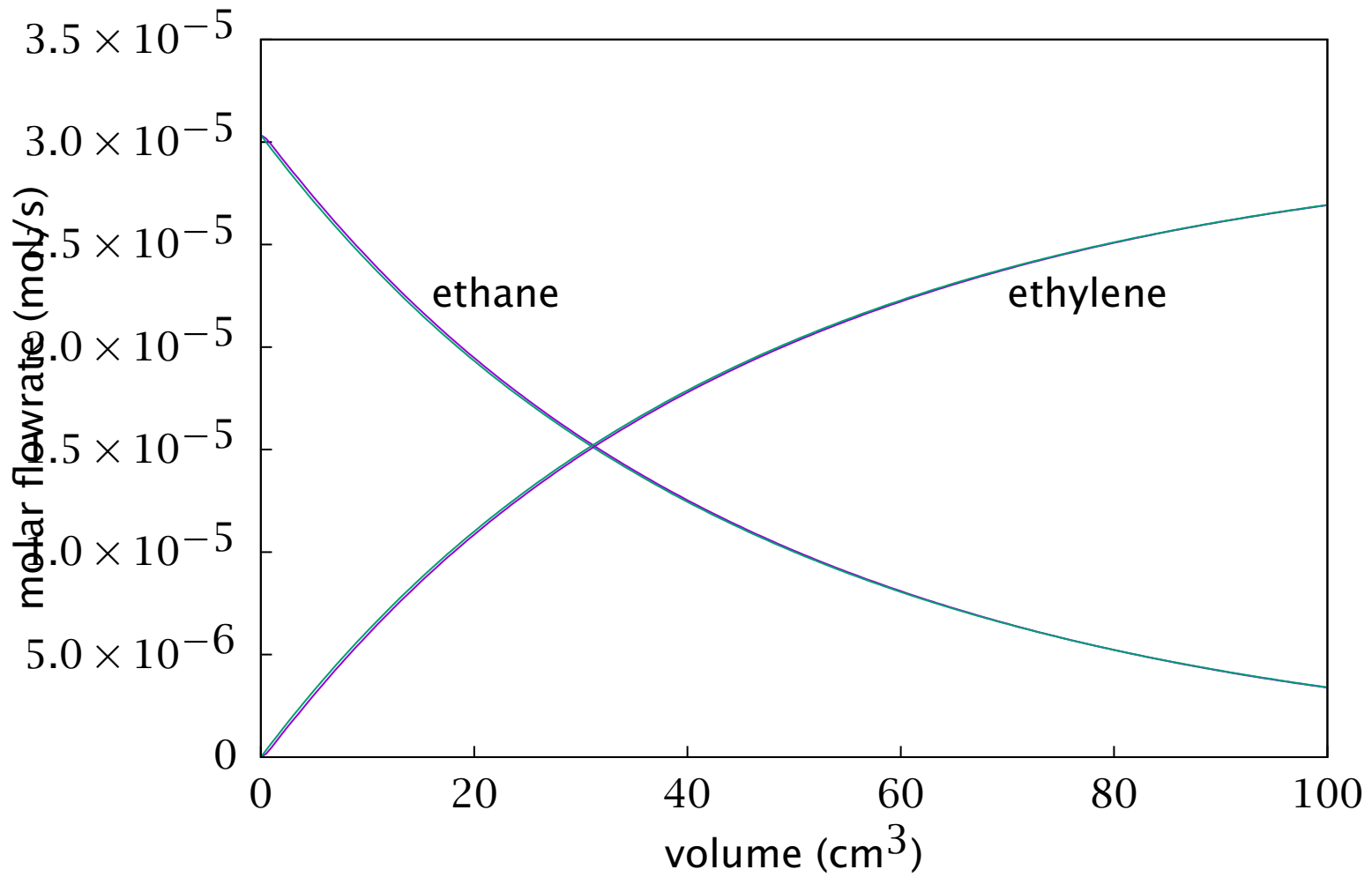
- QSSA analysis predicts the ethane pyrolysis rate should be first order in ethane concentration and the rate constant is $k = 0.797 \text{ s}^{-1}$.
- Using the reduced model

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

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 87 using Equation 83 for the rate expression.

Exact and reduced model



Summary of ethane pyrolysis example

- 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



Reactions at Surfaces

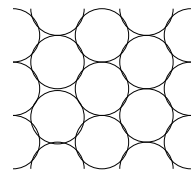
- Our goal is to provide the student with a simple picture of surfaces and to provide a basis for evaluating heterogeneously catalyzed reaction kinetics and reaction-rate expressions.
- Keep in mind the goal is to develop a rate expression from a reaction mechanism. This rate expression can be used to 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].

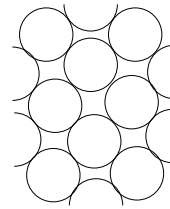
Catalyst surface

- 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} cm^{-2} . Figure 11 presents the atomic arrangement of low-index surfaces for various metals.

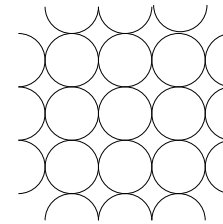
Some common crystal structures of surfaces



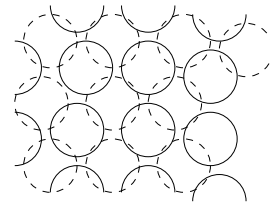
fcc (111)



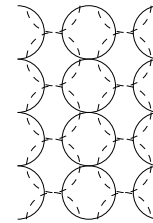
bcc (110)



fcc (100)



bcc (100)



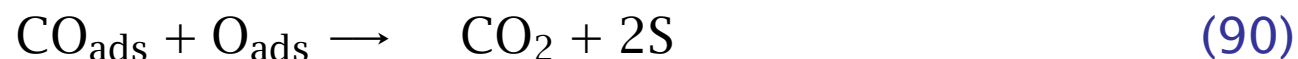
fcc (110)

Figure 11: 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.

CO oxidation example

- 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 88 and 89, reaction of adsorbed components in Reaction 90, and desorption of products also shown as part of Reaction 90.

The adsorption process

- 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 3 lists several properties that can be used to distinguish between physisorption and chemisorption.

Physical and chemical adsorption

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 3: Chemisorption and physisorption properties.

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

Physical and chemical adsorption

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.

CO Adsorption

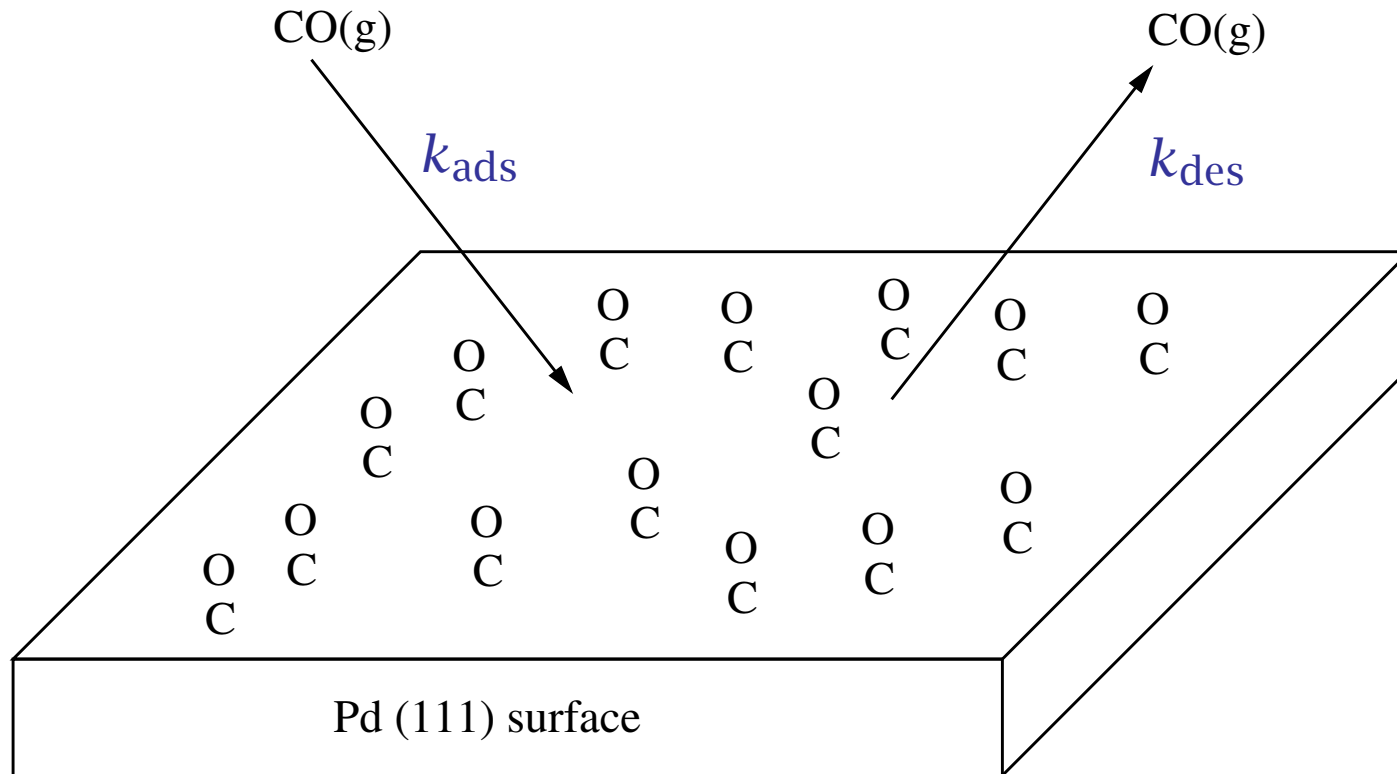


Figure 12: Schematic representation of the adsorption/desorption process.

Langmuir model of adsorption

- 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.

Langmuir model of adsorption

- The surface-site balance is therefore

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

$$\bar{c}_m = \bar{c}_v + \sum_{j=1}^{n_s} \bar{c}_j \quad (91)$$

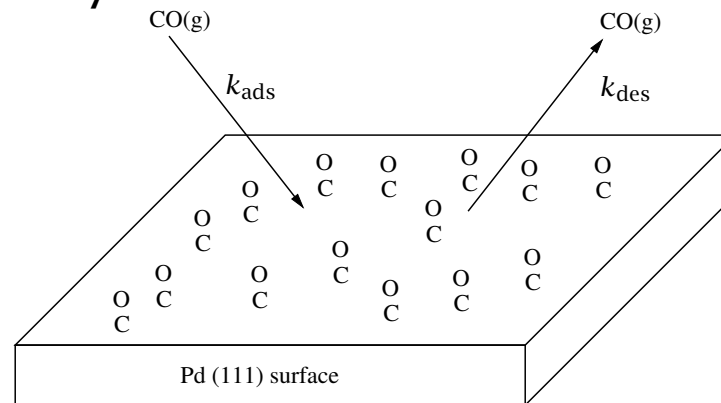
- Dividing by the total number of surface sites leads to the fractional form of the site balance.

$$1 = \frac{\bar{c}_v}{\bar{c}_m} + \sum_{j=1}^{n_s} \frac{\bar{c}_j}{\bar{c}_m} = \theta_v + \sum_{j=1}^{n_s} \theta_j \quad (92)$$

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

Applying the Langmuir model

- Consider again Figure 12 showing the model of a surface consisting of vacant sites and sites covered by chemisorbed CO.



Applying the Langmuir model

- 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.

Adsorption at equilibrium

- 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

$$\bar{c}_{\text{CO}} = \frac{k_1}{k_{-1}} c_{\text{CO}} \bar{c}_v = K_1 c_{\text{CO}} \bar{c}_v \quad (94)$$

- The conservation of sites gives

$$\bar{c}_v = \bar{c}_m - \bar{c}_{\text{CO}} \quad (95)$$

- Substituting Equation 95 into Equation 94 and rearranging leads to the Langmuir isotherm for single-component, associative adsorption

$$\bar{c}_{\text{CO}} = \frac{\bar{c}_m K_1 c_{\text{CO}}}{1 + K_1 c_{\text{CO}}} \quad (96)$$

Langmuir isotherm

- Dividing both sides of Equation 96 by the total concentration of surface sites \bar{c}_m leads to the fractional form of the single component, associative Langmuir adsorption isotherm.

$$\theta_{\text{CO}} = \frac{K_1 c_{\text{CO}}}{1 + K_1 c_{\text{CO}}} \quad (97)$$

Langmuir isotherm

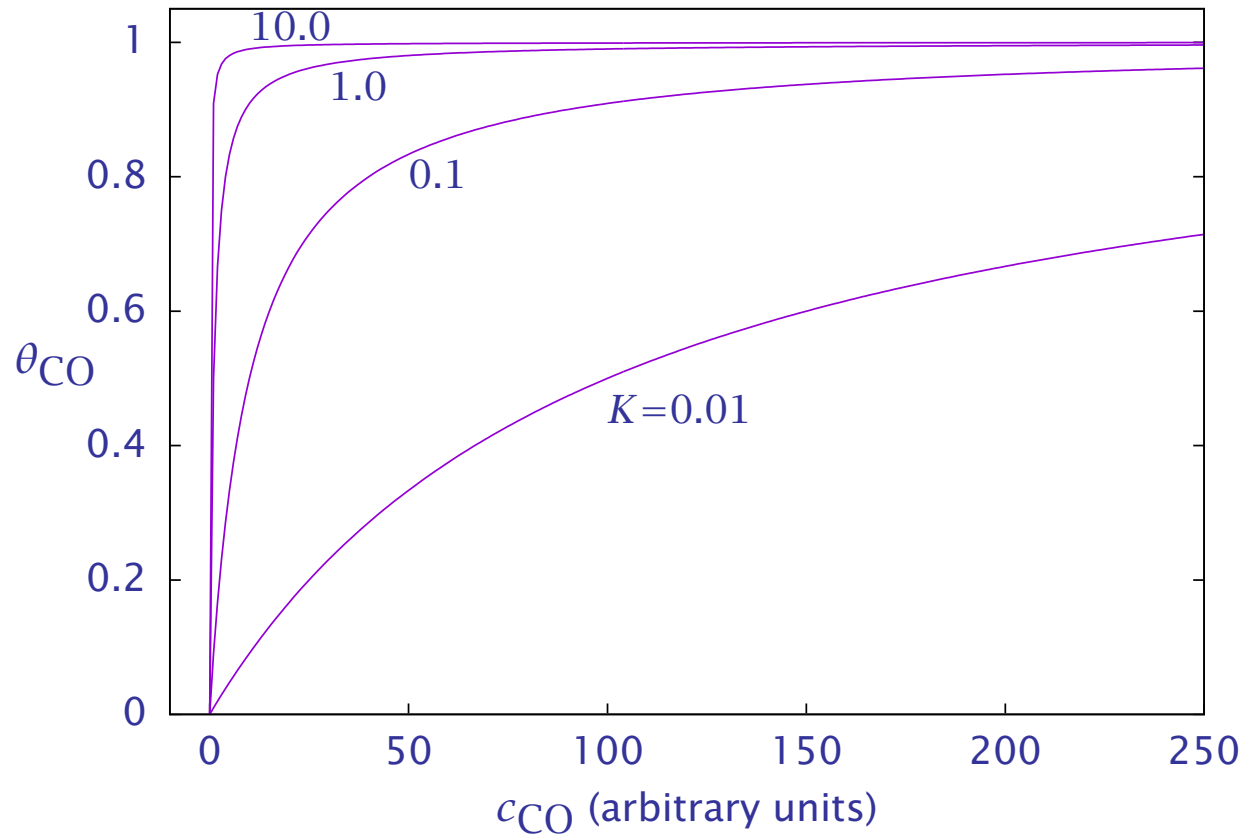


Figure 13: Fractional coverage versus adsorbate concentration for different values of the adsorption constant, K .

- Figure 13 presents the general shape of the fractional coverage as a function of pressure for different values of K .
- In the limit $K_1 c_{\text{CO}} \gg 1$, Equations 96 and 97 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 13 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 .

Fitting parameters to the Langmuir isotherm

- The adsorption data can be fit to either the Langmuir isotherm (Equation 96) or to the “linear” form of the isotherm.
- The linear form is obtained by taking the inverse of Equation 96 and multiplying by c_{CO}

$$\frac{c_{CO}}{\bar{c}_{CO}} = \frac{1}{K_1 \bar{c}_m} + \frac{c_{CO}}{\bar{c}_m} \quad (98)$$

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

CO data example

Example 5.5: 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_2O_3 at 100°C to determine the equilibrium adsorption constant and the number of adsorption sites.

P_{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

Solution

- The next two figures plot the data for Equations 96 and 98, 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

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

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

□

Original model

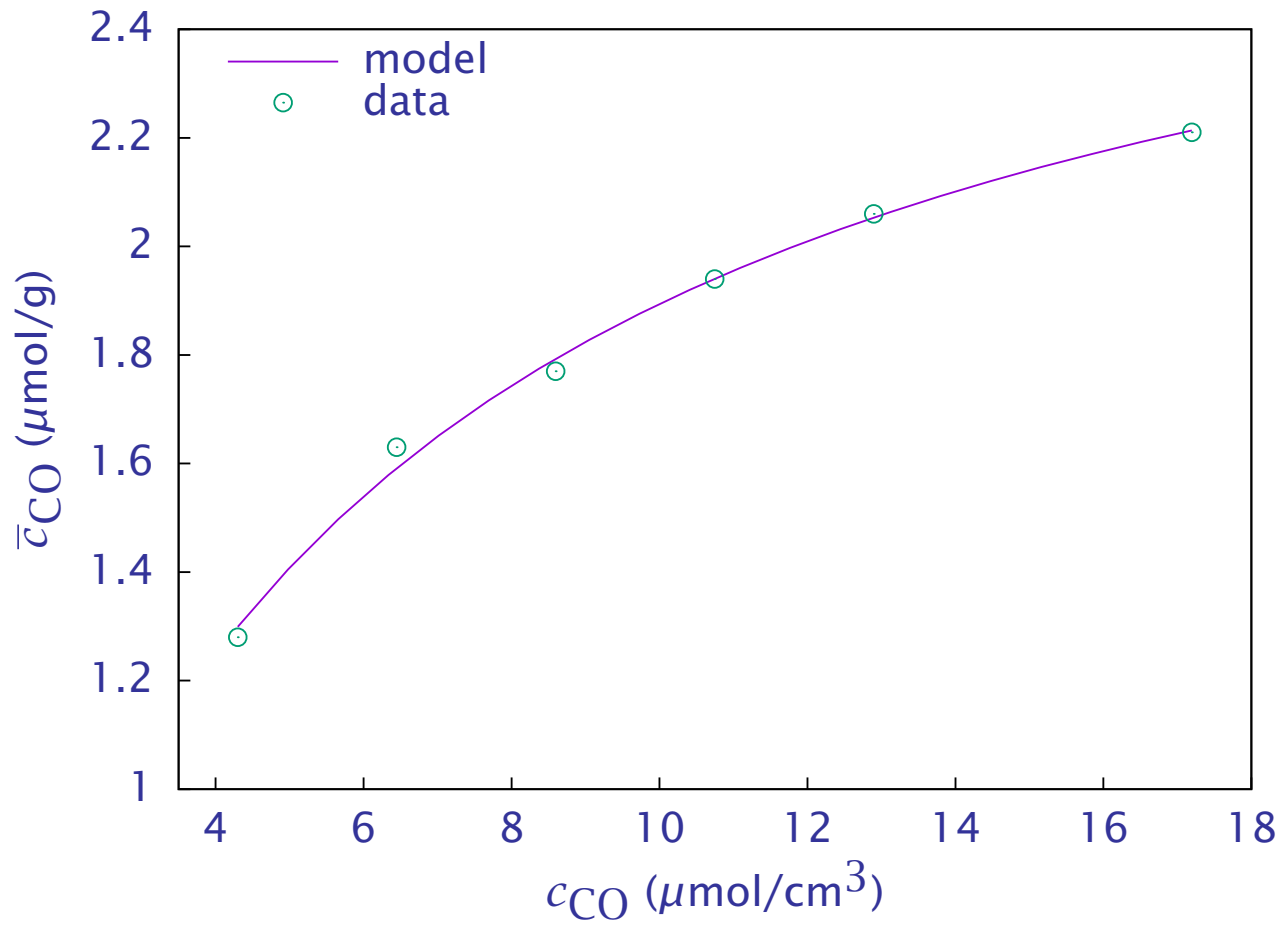


Figure 14: Langmuir isotherm for CO uptake on Ru.

Linear model

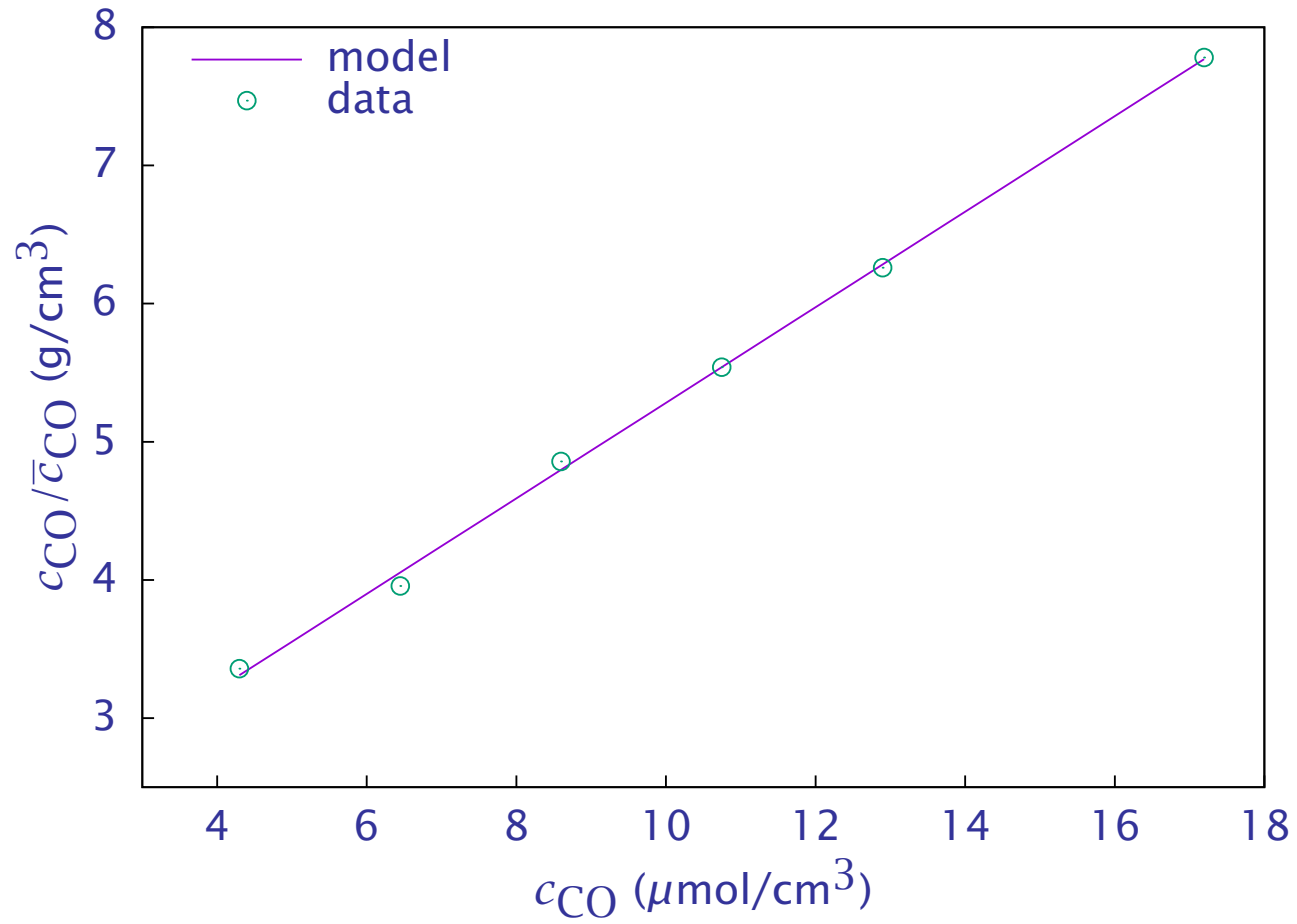
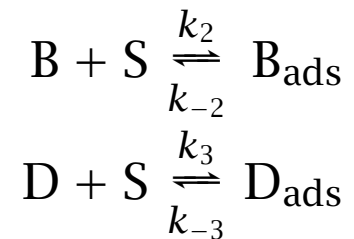


Figure 15: Linear form of Langmuir isotherm for CO uptake on Ru.

Multicomponent adsorption

- 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 94, we can show the equilib-

rium surface concentrations for B and D are given by

$$\bar{c}_B = K_2 c_B \bar{c}_v \quad (99)$$

$$\bar{c}_D = K_3 c_D \bar{c}_v \quad (100)$$

- The site balance becomes

$$\bar{c}_v = \bar{c}_m - \bar{c}_{CO} - \bar{c}_B - \bar{c}_D \quad (101)$$

Multicomponent adsorption

- Substituting Equation 101 into Equation 94 and rearranging leads to a different isotherm expression for CO.

$$\bar{c}_{\text{CO}} = \frac{\bar{c}_m K_{\text{CO}} c_{\text{CO}}}{1 + K_1 c_{\text{CO}} + K_2 c_B + K_3 c_D} \quad (102)$$

- The terms in the denominator of Equation 102 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.

Dissociative adsorption

- The CO oxidation example also contains a dissociative adsorption step

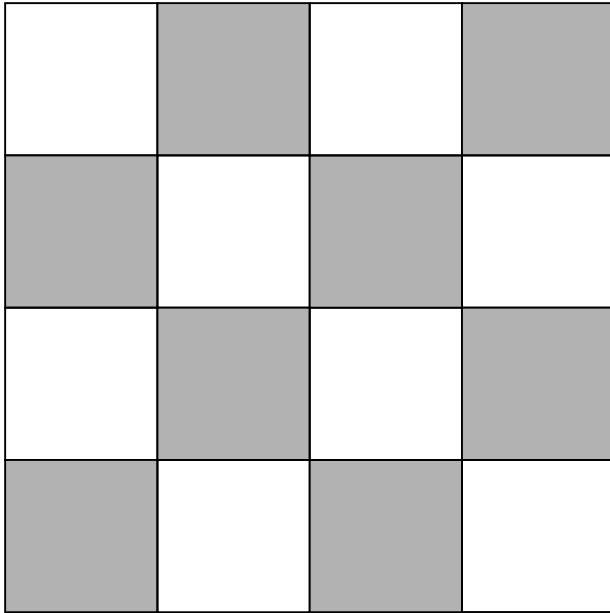


- Adsorption requires the O_2 molecule to find a pair of adsorption sites and desorption requires two adsorbed O atoms to be adjacent.
- When a bimolecular surface reaction occurs, such as dissociative adsorption, associative desorption, or a bimolecular surface reaction, the rate in the forward direction depends on the probability of finding pairs of reaction centers.

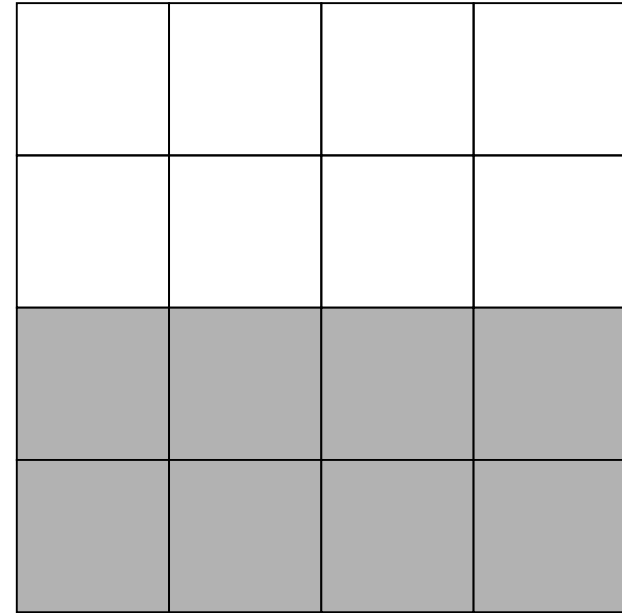
- This probability, in turn, depends on whether or not the sites are randomly located, and whether or not the adsorbates are mobile on the surface.

Pairs of vacant sites

- The probability of finding pairs of vacant sites can be seen by considering adsorption onto a checkerboard such as Figure 16.



A



B

Figure 16: 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 θ equal the fraction of sur-

face covered.

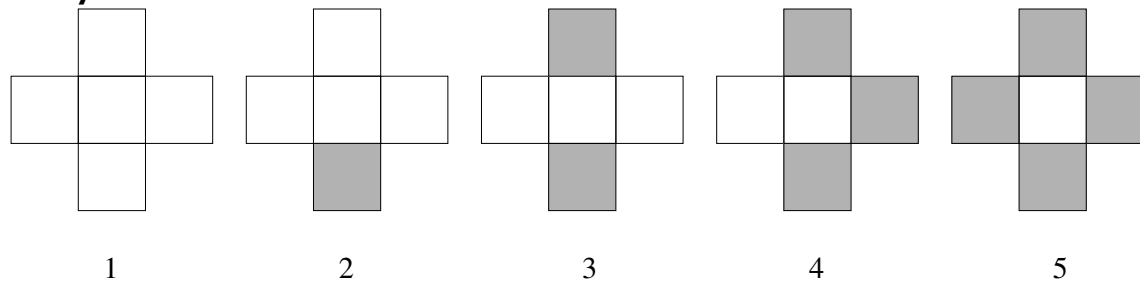
- The checkerboard has a total 24 adjacent site pairs, which can be found by counting the line segments on adjoining squares.

Pairs of vacant sites

- Figure 16 presents two possibilities where half the sites (the shaded squares) are covered.
- For Figure 16A 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 16B 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.

Random packing

- 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.

Random packing

- 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

$$p_1 + 4p_2 + 6p_3 + 4p_4 + 0p_5 \quad (104)$$

Random packing

- 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

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

Random packing

- 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

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

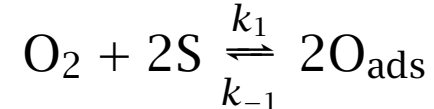
$$p = (1 - \theta)^2$$

Random packing — summary

- 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.

Dissociative adsorption

- Returning to Reaction 103



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

$$r_{\text{ads}} = k_1 \bar{c}_v^2 c_{\text{O}_2} \quad (105)$$

$$r_{\text{des}} = k_{-1} \bar{c}_\text{O}^2 \quad (106)$$

- The units on k_1 are such that r_{ads} has the units of mol/time·area.

- At equilibrium, the rate of adsorption equals the rate of desorption leading to

$$\bar{c}_O = \sqrt{K_1 c_{O_2}} \bar{c}_v \quad (107)$$

- Combining Equation 107 with the site balance, Equation 91, and rearranging leads to the Langmuir form for single-component dissociative adsorption

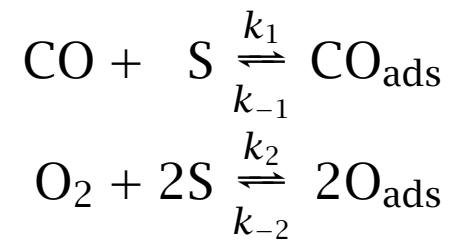
$$\bar{c}_O = \frac{\bar{c}_m \sqrt{K_1 c_{O_2}}}{1 + \sqrt{K_1 c_{O_2}}} \quad (108)$$

Langmuir isotherm for dissociative adsorption

- The Langmuir isotherms represented in Equations 96 and 108 are different because each represents a different gas-surface reaction process.
- Both share the asymptotic approach to saturation at sufficiently large gas concentration, however.

Equilibrium CO and O surface concentrations

- Determine the equilibrium CO and O surface concentrations when O₂ and CO adsorb according to



Solution

- 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

$$\bar{c}_{\text{CO}} = K_1 c_{\text{CO}} \bar{c}_v \quad (109)$$

$$\bar{c}_{\text{O}} = \sqrt{K_2 c_{\text{O}_2} \bar{c}_v} \quad (110)$$

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

$$\bar{c}_m = \bar{c}_v + \bar{c}_{CO} + \bar{c}_O \quad (111)$$

Solution

- Combining Equations 109–111 yields

$$\bar{c}_v = \frac{\bar{c}_m}{1 + K_1 c_{\text{CO}} + \sqrt{K_2 c_{\text{O}_2}}} \quad (112)$$

- We next substitute the vacant site concentration into Equations 109 and 110 to give the surface concentrations in terms of gas-phase concentrations and

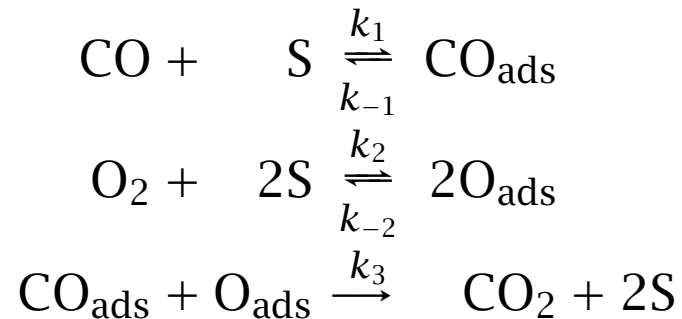
physical constants

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

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

Production rate of CO₂

- Find the rate of CO₂ production using the following reaction mechanism



- Assume the O₂ and CO adsorption steps are at equilibrium.
- Make a log-log plot of the production rate of CO₂ versus gas-phase CO concentration at constant gas-phase O₂ concentration.
- What are the slopes of the production rate at high and low CO concentrations?

Solution

- The rate of CO₂ production is given by

$$R_{\text{CO}_2} = k_3 \bar{c}_{\text{CO}} \bar{c}_{\text{O}} \quad (113)$$

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

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

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

Solution

- Substituting these concentrations onto Equation 113 gives the rate of CO₂ production

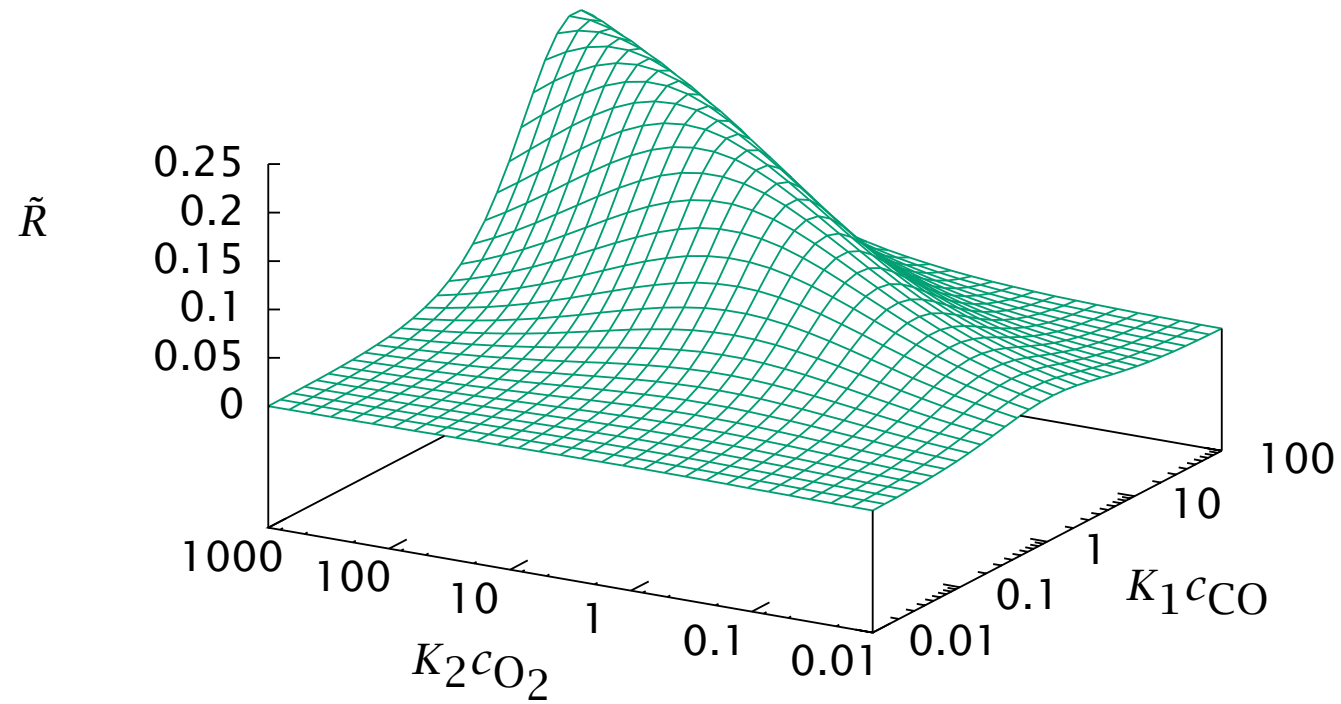
$$R_{\text{CO}_2} = \frac{k_3 \bar{c}_m^2 K_1 c_{\text{CO}} \sqrt{K_2 c_{\text{O}_2}}}{\left(1 + K_1 c_{\text{CO}} + \sqrt{K_2 c_{\text{O}_2}}\right)^2} \quad (114)$$

- 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 O₂ in the next figure.

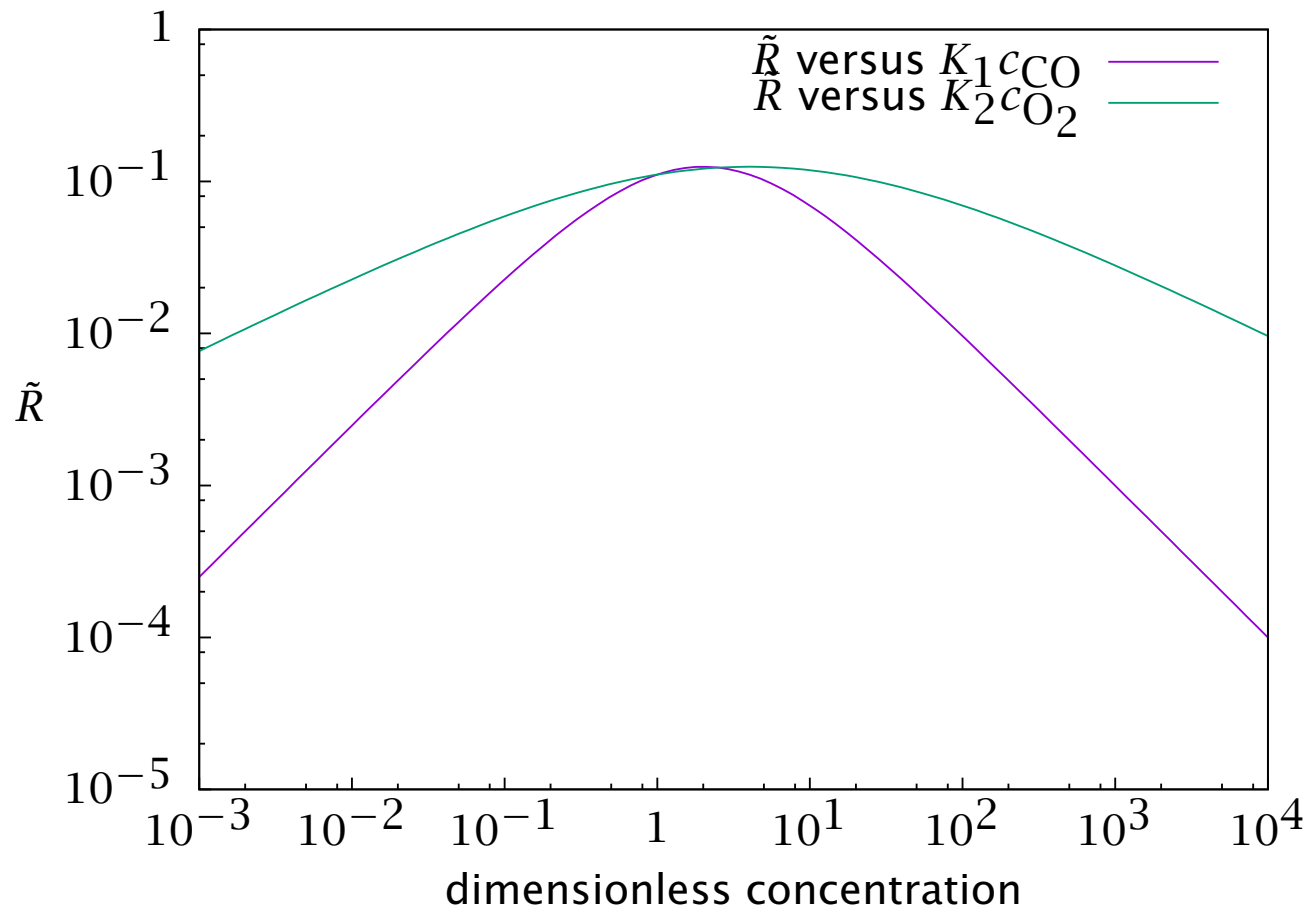
Production rate of CO₂



Production rate of CO₂

- Notice that the production rate goes to zero if either CO or O₂ 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 CO₂



Production rate of CO₂

- 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 $\log(K_1 c_{CO})$ changes in slope from 1.0 to -1.0 as CO concentration increases.
- As the concentration of O₂ increases, the slope changes from 0.5 to -0.5 . These values also can be deduced by taking the logarithm of Equation 114.

Hougen-Watson Kinetics

- Rate expressions of the form of Equation 114 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.

Summary

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 $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ in Example 5.4, 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.

Summary

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

$$r_i = k_i \prod_{j \in \mathcal{R}_i} c_j^{-\nu_{ij}} - k_{-i} \prod_{j \in \mathcal{P}_i} c_j^{\nu_{ij}} \quad (115)$$

- 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.

Summary

- 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

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°	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
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_{elec}	electronic partition function
q_{rot}	rotational partition function
q_{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
ϵ_i	energy of the i th electronic level
ε_i	extent of the i th reaction
θ_j	fractional surface coverage of species j
θ_v	fractional surface coverage of vacant sites
ν_{ij}	stoichiometric number for the j th species in the i th reaction
σ	symmetry number, 1 for a heteronuclear molecule, 2 for homonuclear molecule
τ	lifetime of a component
ϕ_j	fugacity coefficient for species j

References

- [1] A. W. Adamson. *Physical Chemistry of Surfaces*. John Wiley & Sons, New York, fifth edition, 1990.
- [2] M. Bodenstein. Eine Theorie der photochemischen Reaktionsgeschwindigkeiten. *Zeit. physik. Chemie*, 85:329–397, 1913.
- [3] M. Boudart and G. Djega-Mariadassou. *Kinetics of Heterogenous Catalytic Reactions*. Princeton University Press, Princeton, NJ, 1984.
- [4] D. L. Chapman and L. K. Underhill. The interaction of chlorine and hydrogen. The influence of mass. *J. Chem. Soc. Trans.*, 103:496–508, 1913.
- [5] A. Clark. *Theory of Adsorption and Catalysis*. Academic Press, New York, 1970.

- [6] J. G. Ekerdt and A. T. Bell. Synthesis of hydrocarbons from CO and H₂ over silica-supported Ru: Reaction rate measurements and infrared spectra of adsorbed species. *J. Catal.*, 58:170, 1979.
- [7] T. Engel and G. Ertl. In D. P. Woodruff, editor, *The Physics of Solid Surfaces and Heterogeneous Catalysis*, volume four, page 73. Elsevier, Amsterdam, 1982.
- [8] D. O. Hayward and B. M. W. Trapnell. *Chemisorption*. Butterworths, Washington, D.C., second edition, 1964.
- [9] O. A. Hougen and K. M. Watson. Solid catalysts and reaction rates. *Ind. Eng. Chem.*, 35(5):529–541, 1943.
- [10] K. J. Laidler and B. W. Wojciechowski. Kinetics and mechanisms of the thermal decomposition of ethane. I. The uninhibited reaction. *Proceedings of the Royal Society of London, Math and Physics*, 260A(1300):91–102, 1961.

- [11] S. J. Lombardo and A. T. Bell. A review of theoretical models of adsorption, diffusion, desorption, and reaction of gases on metal surfaces. *Surf. Sci. Rep.*, 13:1, 1991.
- [12] J. W. Moore and R. G. Pearson. *Kinetics and Mechanism*. John Wiley & Sons, New York, third edition, 1981.
- [13] Catalysis looks to the future. National Research Council, National Academy Press, Washington, D.C., 1992.
- [14] L. Pedersen and R. N. Porter. Modified semiempirical approach to the H₃ potential-energy surface. *J. Chem. Phys.*, 47(11):4751–4757, 1967.
- [15] J. C. Polanyi and J. L. Schreiber. Distribution of reaction products (theory). Investigation of an ab initio energy-surface for $F + H_2 \rightarrow HF + H$. *Chem. Phys. Lett.*, 29(3):319–322, 1974.

- [16] L. M. Raff, L. Stivers, R. N. Porter, D. L. Thompson, and L. B. Sims. Semiempirical VB calculation of the (H_2I_2) interaction potential. *J. Chem. Phys.*, 52(7):3449–3457, 1970.
- [17] F. O. Rice and K. F. Herzfeld. The thermal decomposition of organic compounds from the standpoint of free radicals. VI. The mechanism of some chain reactions. *J. Am. Chem. Soc.*, 56:284–289, 1934.
- [18] G. A. Somorjai. *Chemistry in Two Dimensions, Surfaces*. Cornell University Press, Ithaca, New York, 1981.
- [19] R. C. Tolman. Duration of molecules in upper quantum states. *J. Phys. Rev.*, 23:693, 1924.
- [20] T. Turányi, A. S. Tomlin, and M. J. Pilling. On the error of the quasi-steady-state approximation. *J. Phys. Chem.*, 97:163, 1993.