

SECTION **7**

Reaction Kinetics

PERRY'S CHEMICAL ENGINEERS' HANDBOOK

8TH EDITION



TIBERIU M. LEIB
CARMO J. PEREIRA

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0-07-154214-0

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DOI: 10.1036/007151130X

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Reaction Kinetics*

Tiberiu M. Leib, Ph.D. *Principal Consultant, DuPont Engineering Research and Technology, E. I. du Pont de Nemours and Company; Fellow, American Institute of Chemical Engineers*

Carmo J. Pereira, Ph.D., MBA *DuPont Fellow, DuPont Engineering Research and Technology, E. I. du Pont de Nemours and Company; Fellow, American Institute of Chemical Engineers*

REFERENCES

BASIC CONCEPTS

Mechanism	7-5
Reaction Rate	7-5
Classification of Reactions	7-5
Effect of Concentration on Rate	7-6
Law of Mass Action	7-6
Effect of Temperature	7-6
Heat of Reaction	7-6
Chemical Equilibrium	7-7
Conversion, Extent of Reaction, Selectivity, and Yield	7-7
Concentration Types	7-8
Stoichiometric Balances	7-8
Single Reactions	7-8
Reaction Networks	7-9
Catalysis	7-9

IDEAL REACTORS

Ideal Batch Reactor	7-11
Batch Reactor (BR)	7-11
Semibatch Reactor (SBR)	7-12
Ideal Continuous Stirred Tank Reactor (CSTR)	7-12
Plug Flow Reactor (PFR)	7-12
Ideal Recycle Reactor	7-12
Examples for Some Simple Reactions	7-13

KINETICS OF COMPLEX HOMOGENEOUS REACTIONS

Chain Reactions	7-14
Phosgene Synthesis	7-14
Ozone Conversion to Oxygen in Presence of Chlorine	7-14
Hydrogen Bromide Synthesis	7-15
Chain Polymerization	7-15
Nonchain Reactions	7-15
Homogeneous Catalysis	7-15

*The contributions of Stanley M. Walas, Ph.D., Professor Emeritus, Department of Chemical and Petroleum Engineering, University of Kansas (Fellow, American Institute of Chemical Engineers), author of this section in the seventh edition, are acknowledged.

The authors of the present section would like to thank Dennie T. Mah, M.S.Ch.E., Senior Consultant, DuPont Engineering Research and Technology, E. I. du Pont de Nemours and Company (Senior Member, American Institute of Chemical Engineers; Member, Industrial Electrolysis and Electrochemical Engineering; Member, The Electrochemical Society), for his contributions to the "Electrochemical Reactions" subsection; and John Villadsen, Ph.D., Senior Professor, Department of Chemical Engineering, Technical University of Denmark, for his contributions to the "Biochemical Reactions" subsection. We acknowledge comments from Peter Harriott, Ph.D., Fred H. Rhodes Professor of Chemical Engineering (retired), School of Chemical and Biomolecular Engineering, Cornell University, on our original outline and on the subject of heat transfer in packed-bed reactors. The authors also are grateful to the following colleagues for reading the manuscript and for thoughtful comments: Thomas R. Keane, DuPont Fellow (retired), DuPont Engineering Research and Technology, E. I. du Pont de Nemours and Company (Senior Member, American Institute of Chemical Engineers); Güray Tosun, Ph.D., Senior Consultant, DuPont Engineering Research and Technology, E. I. du Pont de Nemours and Company (Senior Member, American Institute of Chemical Engineers); and Nitin H. Kollhapure, Ph.D., Senior Consulting Engineer, DuPont Engineering Research and Technology, E. I. du Pont de Nemours and Company (Senior Member, American Institute of Chemical Engineers).

7-2 REACTION KINETICS

Acid-Catalyzed Isomerization of Butene-1	7-15
Enzyme Kinetics	7-15
Autocatalysis	7-16

INTRINSIC KINETICS FOR FLUID-SOLID CATALYTIC REACTIONS

Adsorption Equilibrium	7-16
Dissociation	7-17
Different Sites	7-17
Change in Number of Moles	7-17
Reactant in the Gas Phase	7-17
Chemical Equilibrium in Gas Phase	7-17
No Rate-Controlling Step	7-18
Liquid-Solid Catalytic Reactions	7-18
Biocatalysis	7-18

FLUID-SOLID REACTIONS WITH MASS AND HEAT TRANSFER

Gas-Solid Catalytic Reactions	7-19
External Mass Transfer	7-19
Intraparticle Diffusion	7-20
Intraparticle Diffusion and External Mass-Transfer Resistance	7-22
Heat-Transfer Resistances	7-22
Catalyst Deactivation	7-22
Gas-Solid Noncatalytic Reactions	7-23
Sharp Interface Model	7-23
Volume Reaction Model	7-25

GAS-LIQUID REACTIONS

Reaction-Diffusion Regimes	7-27
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GAS-LIQUID-SOLID REACTIONS

Gas-Liquid-Solid Catalytic Reactions	7-28
Polymerization Reactions	7-29
Bulk Polymerization	7-29
Bead Polymerization	7-29
Emulsion Polymerization	7-29
Solution Polymerization	7-29
Polymer Characterization	7-29

Chain Homopolymerization Mechanism and Kinetics	7-30
Step Growth Homopolymerization Mechanism and Kinetics	7-30
Copolymerization	7-30
Biochemical Reactions	7-30
Mechanism	7-31
Monod-Type Empirical Kinetics	7-31
Chemostat with Empirical Kinetics	7-32
Electrochemical Reactions	7-32
Kinetic Control	7-32
Mass-Transfer Control	7-33
Ohmic Control	7-33
Multiple Reactions	7-33

.DETERMINATION OF MECHANISM AND KINETICS

Laboratory Reactors	7-33
Batch Reactors	7-34
Flow Reactors	7-35
Multiphase Reactors	7-35
Solid Catalysts	7-35
Bioreactors	7-35
Calorimetry	7-35
Kinetic Parameters	7-35
Data Analysis Methods	7-36
Differential Data Analysis	7-36
Integral Data Analysis	7-36
The Half-Life Method	7-36
Complex Rate Equations	7-37
Parameter Estimation	7-37
Linear Models in Parameters, Single Reaction	7-37
Nonlinear Models in Parameters, Single Reaction	7-38
Network of Reactions	7-38
Theoretical Methods	7-38
Prediction of Mechanism and Kinetics	7-38
Lumping and Mechanism Reduction	7-38
Multiple Steady States, Oscillations, and Chaotic Behavior	7-39
Software Tools	7-39

Nomenclature and Units

The component A is identified by the subscript a . Thus, the number of moles is n_a ; the fractional conversion is X_a ; the extent of reaction is ζ_a ; the partial pressure is p ; the rate of consumption is r_a ; the molar flow rate is N_a ; the volumetric flow rate is q ; reactor volume is V_r or simply V for batch reactors; the volumetric concentration is $C_a = n_a/V$ or $C_a = N_a/q$; the total pressure is P ; and the temperature is T . Throughout this section, equations are presented without specification of units. Use of any consistent unit set is appropriate.

Following is a listing of typical nomenclature expressed in SI and U.S. Customary System units.

Symbol	Definition	SI units	U.S. Customary System units	Symbol	Definition	SI units	U.S. Customary System units
A, B, C, . . .	Names of substances			p_a	Partial pressure of substance A	Pa	psi
A	Free radical, as CH ₃			q	Volumetric flow rate	m ³ /s	ft ³ /s
a	Activity			Q	Electric charge	Coulomb	
BR	Batch reactor			\bar{R}	Radial position, radius, universal gas constant		
b	Estimate of kinetic parameters, vector			Re	Reynolds number		
C_a	Concentration of substance A	kg·mol/m ³	lb·mol/ft ³	RgSS	Regression sum of squares		
CSTR	Continuous stirred tank reactor			RSS	Residual sum of squares		
C_0	Initial concentration	kg·mol/m ³	lb·mol/ft ³	r_a	Rate of reaction of A per unit volume		
c_p	Heat capacity at constant pressure	kJ/(kg·K)	Btu/(lbm·°F)	S	Selectivity, stoichiometric matrix, objective function for parameter estimation		
Δc_p	Heat capacity change in a reaction	kJ/(kg·K)	Btu/(lbm·°F)	SBR	Semibatch reactor		
D	Diffusivity, dispersion coefficient	m ² /s	ft ² /s	Sc	Schmidt number		
D_e	Effective diffusivity	m ² /s	ft ² /s	Sh	Sherwood number		
D_K	Knudsen diffusivity	m ² /s	ft ² /s	ΔS	Entropy change	kJ/(kg·mol·K)	Btu/(lb·mol·R)
DP	Degree of polymerization			s	Estimate of variance		
E	Activation energy, enhancement factor for gas-liquid mass transfer with reaction, electrochemical cell potential			t	Time, t statistic		
F	Faraday constant, F statistic			u	Linear velocity	m/s	ft/s
f	Efficiency of initiation in polymerization			V	Volume of reactor, variance-covariance matrix		
f_a	C_a/C_{a0} or n_a/n_{a0} , fraction of A remaining unconverted			v	Molar volume	m ³ /kg·mol	ft ³ /lb·mol
Ha	Hatta number			WCLD	Weight chain length distribution		
He	Henry constant for absorption of gas in liquid			WMMD	Weight molecular weight distribution		
ΔG	Free energy change	kJ/kg·mol	Btu/lb·mol	X	Linear model matrix for parameter estimation, fractional conversion		
ΔH_r	Heat of reaction	kJ/kg·mol	Btu/lb·mol	X_a	$1 - f_a = 1 - C_a/C_{a0}$ or $1 - n_a/n_{a0}$, fraction of A converted		
I	Initiator for polymerization, modified Bessel functions, electric current			x	Axial position in a reactor, mole fraction in liquid	Variable	
j	Electric current density	A/m ²		Y	Yield; yield coefficient for biochemical reactions		
K_a	Adsorption constant			y	Mole fraction in gas, predicted dependent variable		
K_e	Chemical equilibrium constant			z	x/L , normalized axial position		
k	Specific rate constant of reaction, mass-transfer coefficient			Greek letters			
L	Length of path in reactor	m	ft	α	Fraction of initial catalyst activity, probability of propagation for chain polymerization, confidence level		
LFSS	Lack of fit sum of squares			β	r/R , normalized radial position, fraction of poisoned catalyst, kinetic parameter vector		
M	Average molecular weight in polymers, dead polymer species, monomer			δ	Film thickness or boundary layer thickness, relative change in number of moles by reaction		
m	Number of moles in electrochemical reaction	kg·mol	lb·mol	$\delta(t)$	Unit impulse input, Dirac function		
N	Molar flow rate, molar flux			ϵ	Fraction void space in a packed bed, relative change in number of moles by reaction, residual error, porosity, current efficiency		
NCLD	Number chain length distribution			Φ	Weisz Prater parameter		
NMWD	Number molecular weight distribution			ϕ	Thiele modulus		
n	Number of stages in a CSTR battery, reaction order, number of electrons in electrochemical reaction, number of experiments						
n_a	Number of moles of A present	kg·mol	lb·mol				
n_t	Total number of moles	kg·mol	lb·mol				
P	Total pressure, live polymer species						
PESS	Pure error sum of squares						
PFR	Plug flow reactor						
p	Number of kinetic parameters						

7-4 REACTION KINETICS

Nomenclature and Units (Concluded)

Symbol	Definition	SI units	U.S. Customary System units	Subscripts	
				Subscripts	
Greek letters					
η	Effectiveness factor of porous catalyst, overpotential in electrochemical reactions			d	Deactivation
λ	Parameter for instantaneous gas-liquid reaction, moments in polymer chain length			e	Equilibrium
μ	Viscosity, biomass growth rate, average chain length in polymers			f	Forward reaction, final, formation
ν	μ/ρ , kinematic viscosity, stoichiometric coefficient, fraction of surface covered by adsorbed species			G	Gas
θ	Dimensionless time			i	Component i
ρ	Density	kg/m ³	lbm/ft ³	j	Reaction j
σ	Variance			L	Liquid
τ	Residence time, tortuosity factor			m	Based on mass, mass transfer
ζ	Extent of reaction			max	Maximum biomass growth, maximum extent of reaction
Subscripts					
act	Activation			n	Chain length in polymers
anode	At anode			o	Oxidized
B	Bed			obs	observed
cathode	At cathode			p	Particle
cell	Electrochemical cell			projected	Electrode projected area
current, j	Current, species j			r	Reverse reaction, reduced
D	Diffusion, dispersion			S	Substrate
				Superscripts	
				s	Solid or catalyst, saturation, surface
				surf	Surface
				v	Based on volume
				x	Biomass
				0	At initial or inlet conditions, as in C_{a0}, n_{a0}, V_0 , at reference temperature
				1/2	Half-life
				Superscripts	
				eq	Equilibrium
				o	At reference temperature
				T	Transposed matrix

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Catalysis, Wiley, 2001; Naumann, *Chemical Reactor Design*, Wiley, 1987; Panchenkov and Lebedev, *Chemical Kinetics and Catalysis*, Mir Publishers, 1976; Petersen, *Chemical Reaction Analysis*, Prentice-Hall, 1965; Rase, *Chemical Reactor Design for Process Plants: Principles and Case Studies*, Wiley, 1977; Rose, *Chemical Reactor Design in Practice*, Elsevier, 1981; Satterfield, *Heterogeneous Catalysis in Practice*, McGraw-Hill, 1991; Schmidt, *The Engineering of Chemical Reactions*, Oxford University Press, 1998; Smith, *Chemical Engineering Kinetics*, McGraw-Hill, 1981; Steinfeld, Francisco, and Hasse, *Chemical Kinetics and Dynamics*, Prentice-Hall, 1989; Ulrich, *Guide to Chemical Engineering Reactor Design and Kinetics*, Ulrich, 1993; Van Santen and Neurock, *Molecular Heterogeneous Catalysis: A Conceptual and Computational Approach*, Wiley, 2006; Van Santen and Niemantsverdriet, *Chemical Kinetics and Catalysis, Fundamental and Applied Catalysis*, Plenum Press, New York, 1995; van't Riet and Tramper, *Basic Bioreactor Design*, Dekker, 1991; Walas, *Reaction Kinetics for Chemical Engineers*, McGraw-Hill, 1959; reprint, Butterworths, 1989; Walas, *Chemical Reaction Engineering Handbook of Solved Problems*, Gordon & Breach Publishers, 1995; Westerterp, van Swaaij, and Beenackers, *Chemical Reactor Design and Operation*, Wiley, 1984.

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The mechanism and corresponding kinetics provide the rate at which the chemical or biochemical species in the reactor system react at the prevailing conditions of temperature, pressure, composition, mixing, flow, heat, and mass transfer. Observable kinetics represent the true intrinsic chemical kinetics only when competing phenomena such as transport of mass and heat are not limiting the rates. The intrinsic chemical mechanism and kinetics are unique to the reaction system. Knowledge of the intrinsic kinetics therefore facilitates reactor selection, choice of optimal operating conditions, and reactor scale-up and design, when combined with understanding of the associated physical and transport phenomena for different reactor scales and types.

This section covers the following key aspects of reaction kinetics:

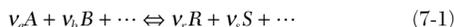
- Chemical mechanism of a reaction system and its relation to kinetics
- Intrinsic rate data using equations that can be correlative, lumped, or based on detailed elementary kinetics
- Catalytic kinetics
- Effect of mass transfer on kinetics in heterogeneous systems
- Intrinsic kinetic rates from experimental data and/or from theoretical calculations
- Kinetic parameter estimation

The use of reaction kinetics for analyzing and designing suitable reactors is discussed in Sec. 19.

BASIC CONCEPTS

MECHANISM

The mechanism describes the reaction steps and the relationship between the reaction rates of the chemical components. A single chemical reaction includes reactants A, B, \dots and products R, S, \dots



where ν_i are the *stoichiometric coefficients* of components A, B, \dots , i.e., the relative number of molecules of A, B, \dots that participate in the reaction. For instance, the HBr synthesis has the global stoichiometry $\text{H}_2 + \text{Br}_2 \rightleftharpoons 2\text{HBr}$.

The *stoichiometry* of the reaction defines the reaction elemental balance (atoms of H and Br, for instance) and therefore relates the number of molecules of reactants and products participating in the reaction. The stoichiometric coefficients are not unique for a given reaction, but their ratios are unique. For instance, for the HBr synthesis above we could have written the stoichiometric equation $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Br}_2 \rightleftharpoons \text{HBr}$ as well.

Often several reactions occur simultaneously, resulting in a *network of reactions*. When the network is broken down into *elementary* or *single-event* steps (such as a single electron transfer), the network represents the *true mechanism* of the chemical transformations leading from initial reactants to final products through intermediates. The intermediates can be molecules, ions, free radicals, transition state complexes, and other moieties. A network of *global reactions*, with each reaction representing the combination of a number of elementary steps, does not represent the true mechanism of the chemical transformation but is still useful for global reaction rate calculations, albeit empirically. The stoichiometry can only be written in a unique manner for elementary reactions, since as shown later, the reaction rate for elementary reactions is determined directly by the stoichiometry through the concept of the law of mass action.

REACTION RATE

The *specific rate* of consumption or production of any reaction species i , r_i , is the rate of change of the number of molecules of species i with time per unit volume of reaction medium:

$$r_i = \frac{1}{V} \frac{dn_i}{dt} \quad (7-2)$$

The rate is negative when i represents a *reactant* (dn_i/dt is negative since n_i is decreasing with time) and positive when i represents a *product*

(dn_i/dt positive since n_i is increasing with time). The specific rate of a reaction, e.g., that in Eq. (7-1) is defined as

$$\begin{aligned} r &= -r_i/\nu_i && \text{for reactants} \\ r &= r_i/\nu_i && \text{for products} \end{aligned} \quad (7-3)$$

By this definition, the specific rate of reaction is uniquely defined, and its sign is always positive. Inversely, the rate of reaction of each component or species participating in the reaction is the specific reaction rate multiplied by the species' stoichiometric coefficient with the corrected sign (negative for reactants, positive for products).

CLASSIFICATION OF REACTIONS

Reactions can be classified in several ways. On the basis of *mechanism* they may be

1. *Irreversible*, i.e., the reverse reaction rate is negligible: $A + B \Rightarrow C + D$, e.g., CO oxidation $\text{CO} + \frac{1}{2}\text{O}_2 \Rightarrow \text{CO}_2$
2. *Reversible*: $A + B \rightleftharpoons C + D$, e.g., the water-gas shift $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
3. *Equilibrium*, a special case with zero net rate, i.e., with the forward and reverse reaction rates of a reversible reaction being equal. All reversible reactions, if left to go to completion, end in equilibrium.
4. *Networks of simultaneous reactions*, i.e., consecutive, parallel, complex (combination of consecutive and parallel reactions):



e.g., two-step hydrogenation of acetylene to ethane



A further classification is from the point of view of the number of reactant molecules participating in the reaction, or the *molecularity*:

1. *Unimolecular*: $A \Rightarrow B$, e.g., isomerization of ortho-xylene to para-xylene, O-xylene to P-xylene, or $A \Rightarrow B + C$, e.g., decomposition $\text{CaCO}_3 \Rightarrow \text{CaO} + \text{CO}_2$
2. *Bimolecular*: $A + B \Rightarrow C$ or $2A \Rightarrow B$ or $A + B \Rightarrow C + D$, e.g., $\text{C}_2\text{H}_4 + \text{H}_2 \Rightarrow \text{C}_2\text{H}_6$
3. *Trimolecular*: $A + B + C \Rightarrow D$ or $3A \Rightarrow B$

This last classification has fundamental meaning only when considering elementary reactions, i.e., reactions that constitute a single chemical transformation or a single event, such as a single electron transfer. For elementary reactions, molecularity is rarely higher than 2. Often elementary reactions are not truly unimolecular, since in order for the reaction to occur, energy is required and it is obtained through collision with other molecules such as an inert solvent or gas.

7-6 REACTION KINETICS

Thus the unimolecular reaction $A \Rightarrow B$ could in reality be represented as a bimolecular reaction $A + X \Rightarrow B + X$, i.e., A collides with X to produce B and X , and thus no net consumption of X occurs.

Reactions can be further classified according to the *phases* present. Examples for the more common cases are

1. *Homogeneous gas*, e.g., methane combustion
2. *Homogeneous liquid*, e.g., acid/base reactions to produce soluble salts
3. *Heterogeneous gas-solid*, e.g., HCN synthesis from NH_3 , CH_4 , and air on a solid catalyst
4. *Heterogeneous gas-liquid*, e.g., absorption of CO_2 in amine solutions
5. *Heterogeneous liquid-liquid*, e.g., reaction in immiscible organic and aqueous phases such as synthesis of adipic acid from cyclohexanone and nitric acid
6. *Heterogeneous liquid-solid*, e.g., reaction of limestone with sulfuric acid to make gypsum
7. *Heterogeneous solid-solid*, e.g., self-propagating, high-temperature synthesis of inorganic pure oxides (SHS)
8. *Heterogeneous gas-liquid-solid*, e.g., catalytic Fischer-Tropsch synthesis of hydrocarbons from CO and H_2
9. *Heterogeneous gas-liquid-liquid*, e.g., oxidations or hydrogenations with phase transfer catalysts

Reactions can also be classified with respect to the *mode of operation* in the reaction system as

1. *Isothermal constant volume* (batch)
2. *Isothermal constant pressure* (continuous)
3. *Adiabatic*
4. *Nonisothermal* temperature-controlled (by cooling or heating), batch or continuous

EFFECT OF CONCENTRATION ON RATE

The *concentration* of the reaction components determines the rate of reaction. For instance, for the irreversible reaction



the rate can be represented *empirically* as a power law function of the reactant concentrations such as

$$r = kC_a^a C_b^b \quad C_i = \frac{n_i}{V} \quad (7-5)$$

The exponents a and b represent the *order of the reaction* with respect to components A and B , and the *sum* $a + b$ represents the *overall order of the reaction*. The order can be a positive, zero, or negative number indicating that the rate increases, is independent of, or decreases with an increase in a species concentration, respectively. The exponents can be whole (integral order) or fraction (fractional order). In Eq. (7-5) k is the *specific rate constant* of the reaction, and it is independent of concentrations for elementary reactions only. For global reactions consisting of several elementary steps, k may still be constant over a narrow range of compositions and operating conditions and therefore can be considered constant for limited practical purposes. A further complexity arises for nonideal chemical solutions where activities have to be used instead of concentrations. In this case the rate constant can be a function of composition even for elementary steps (see, for instance, Froment and Bischoff, *Chemical Reactor Analysis and Design*, Wiley, 1990).

When Eq. (7-4) represents a global reaction combining a number of elementary steps, then rate equation (7-5) represents an empirical correlation of the global or overall reaction rate. In this case exponents a and b have no clear physical meaning other than indicating the overall effect of the various concentrations on rate, and they do not have any obvious relationship to the stoichiometric coefficients p and q . This is not so for elementary reactions, as shown in the next subsection. Also, as shown later, power law and rate expressions other than power law (e.g., hyperbolic) can be developed for specific reactions by starting with the mechanism of the elementary steps and making simplifying assumptions that are valid under certain conditions.

LAW OF MASS ACTION

As indicated above, the dependence of rate on concentration can be shown to be of the general form

$$r = kf(C_a, C_b, \dots) \quad (7-6)$$

For elementary reactions, the *law of mass action* states that the rate is proportional to the concentrations of the reactants raised to the power of their respective molecularity. Thus for an elementary irreversible reaction such as (7-4) the rate equation is

$$r = kC_a^p C_b^q \quad (7-7)$$

Hence, the exponents p and q of Eq. (7-7) are the stoichiometric coefficients when the stoichiometric equation truly represents the mechanism of reaction, i.e., when the reactions are elementary. As discussed above, the exponents a and b in Eq. (7-5) identify the order of the reaction, while the stoichiometric coefficients p and q in Eq. (7-7) also identify the molecularity—for elementary reactions these are the same.

EFFECT OF TEMPERATURE

The *Arrhenius equation* relates the specific rate constant to the absolute temperature

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (7-8)$$

where E is called the *activation energy* and k_0 is the *preexponential factor*. As seen from Eq. (7-8), the rate can be a very strongly increasing (exponential) function of temperature, depending on the magnitude of the activation energy E . This equation works well for elementary reactions, and it also works reasonably well for global reactions over a relatively narrow range of temperatures in the absence of mass-transfer limitations. The Arrhenius form represents an energy barrier on the reaction pathway between reactants and products that has to be overcome by the reactant molecules.

The Arrhenius equation can be derived from theoretical considerations using either of two competing theories, the *collision theory* and the *transition state theory*. A more accurate form of Eq. (7-8) includes an additional temperature factor

$$k = k_0 T^m \exp\left(-\frac{E}{RT}\right) \quad 0 < m < 1 \quad (7-9)$$

but the T^m factor is often neglected because of the usually much stronger dependence on temperature of the exponential factor in Eq. (7-9), as m is usually small. When m is larger, as it can be for complex molecules, then the T^m term has to be taken into consideration. For more details, see Masel, *Chemical Kinetics and Catalysis*, Wiley, 2001; Levenspiel, *Chemical Reaction Engineering*, 3d ed., Wiley, 1999).

HEAT OF REACTION

Chemical reactions are accompanied by evolution or absorption of energy. The enthalpy change (difference between the total enthalpy of formation of the products and that of the reactants) is called the *heat of reaction* ΔH_r :

$$\Delta H_r = (v_r H_{fr} + v_s H_{fs} + \dots) - (v_a H_{fa} + v_b H_{fb} + \dots) \quad (7-10)$$

where H_{fi} are the *enthalpies of formation* of components i . The reaction is *exothermic* if heat is produced by the reaction (negative heat of reaction) and *endothermic* if heat is consumed (positive heat of reaction). The magnitude of the effective heat of reaction depends upon temperature and the phases of the reactants and product. To estimate the dependence of the heat of reaction on temperature relative to a

reference temperature T_0 , the following expression can be used, provided there is no phase change:

$$\Delta H_r(T) = \Delta H_r(T_0) + \int_{T_0}^T \Delta c_p dT \quad (7-11)$$

$$\Delta c_p = (v_a c_{p_a} + v_b c_{p_b} + \dots) - (v_a c_{p_a} + v_b c_{p_b} + \dots)$$

where c_{p_i} are the *heat capacities* of component i . The heat of reaction can be measured by using calorimetry, or it can be calculated by using a variety of thermodynamic methods out of the scope of this chapter (see relevant sections of this handbook, thermodynamic texts, and Bird, Stewart, and Lightfoot, *Transport Phenomena*, 2d ed., John Wiley & Sons, New York, 2002). It is important to accurately capture the energy balance and its relation to the heat of reaction and heat capacities (see also Denn, *Process Modeling*, Langman, New York, 1986, for correct formulations). The coupling of the heat of reaction with the reaction rate through the Arrhenius equation often has a dominating effect on reactor selection and control, and on the laboratory reactor setup required to obtain accurate intrinsic kinetics and mechanism. More on this can be found in Sec. 19.

CHEMICAL EQUILIBRIUM

Often reactions or reaction steps in a network of reactions are at chemical equilibrium; i.e., the rate of the forward reaction equals the rate of the reverse reaction. For instance, for the reversible reaction



with mass action kinetics, the rate may be written as

$$r = r_f - r_r = k_f C_a^v C_b^v - k_r C_r^v C_s^v \quad (7-13)$$

At chemical equilibrium the forward and reverse reaction rates are equal according to the principle of *microscopic reversibility*:

$$r = r_f - r_r = 0 \quad (7-14)$$

The equilibrium constant K_e (based on volumetric concentrations) is defined as the ratio of the forward and reverse rate constants and is related to the composition at equilibrium as follows:

$$K_e = \frac{k_f}{k_r} = \frac{C_r^v C_s^v}{C_a^v C_b^v} \quad (7-15)$$

K_e can be calculated from the free energy change of the reaction. Using the van't Hoff relation, we obtain the dependence of K_e on temperature:

$$\frac{d(\ln K_e)}{dT} = \frac{\Delta H_r}{RT^2} \quad (7-16)$$

Integrating with respect to temperature, we obtain a form similar to the Arrhenius expression of the rate constant for a narrow range of temperature:

$$K_e = K_{e,0} \exp\left(\frac{\Delta H_r}{RT}\right) \quad (7-17)$$

A more general integral form of Eq. (7-16) is

$$\ln K_e(T) = \ln K_e(T_0) + \frac{1}{R} T \int_{T_0}^T \frac{\Delta H_r(T_0) + \int_{T_0}^T \Delta c_p dT}{T^2} dt \quad (7-18)$$

When a reversible reaction is not at equilibrium, knowledge of K_e can be used to eliminate the rate constant of the reverse reaction by using Eq. (7-15) as follows:

$$r = k_f (C_a^v C_b^v - C_r^v C_s^v / K_e) \quad (7-19)$$

When several reversible reactions occur simultaneously, each reaction r_j is characterized by its equilibrium constant K_{e_j} . When the K_{e_j} are known, the composition at equilibrium can be calculated from a set of equations such as Eq. (7-15) for each reaction.

CONVERSION, EXTENT OF REACTION, SELECTIVITY, AND YIELD

Conversion of a reactant is the number of moles converted per initial or feed moles of a reactant. Thus for component A

$$X_a = 1 - \frac{n_a}{n_{a0}} \quad (7-20)$$

A *limiting reactant* is a reactant whose concentration at the start of the reaction is the least of all reactants relative to the required stoichiometric amount needed for complete conversion. For instance, for the single reaction (7-12), A is the limiting reactant if the initial molar ratio of concentrations of A and B is less than the ratio of their stoichiometric coefficients:

$$\frac{n_{a0}}{n_{b0}} < \frac{v_a}{v_b} \quad (7-21)$$

Once the limiting reactant is depleted, the respective reaction stops even though other (nonlimiting) reactants may still be abundant.

For each reaction or each step in a network of reactions, a unique *extent of reaction* ξ that relates the composition of components that participate in the reaction to each other can be defined. For instance, for the single reaction (7-1):

$$\xi = \frac{n_{a0} - n_a}{v_a} = \frac{n_{b0} - n_b}{v_b} = \dots = -\frac{n_{r0} - n_r}{v_r} = -\frac{n_{s0} - n_s}{v_s} = \dots \quad (7-22)$$

The extent of reaction is related to conversion as follows:

$$\xi = \frac{X_a n_{a0}}{v_a} = \frac{X_b n_{b0}}{v_b} = \dots \quad (7-23)$$

When A is the limiting reactant as in Eq. (7-21), the maximum extent of reaction (with A fully converted) is

$$\xi_{\max} = \frac{n_{a0}}{v_a} \quad (7-24)$$

For multiple reactions with reactants participating in more than one reaction, it is more difficult to determine the limiting reactant and often it is necessary to calculate the concentration as the reactions proceed to determine which reactant is consumed first. When the limiting reactant is depleted, all reactions that use this component as reactant stop, and the corresponding rates become zero.

Selectivity S of a product is the ratio of the rate of production of that product to the rate of production of all products combined. For a single reaction selectivity is trivial—if more than one product occurs, then the selectivity of each product is the ratio of the stoichiometric coefficient of that product to the sum of stoichiometric coefficients of all the products. Thus for reaction (7-1)

$$S_r = \frac{v_r}{v_r + v_s + \dots} \quad (7-25)$$

7-8 REACTION KINETICS

The selectivity of product R for a network of reactions, with all the reactions making the various products included, is

$$S_r = \frac{r_r}{\sum_{\text{all products } i} r_i} \quad (7-26)$$

For instance, for the network of reactions $A + B \xrightarrow{1} C + D$
 $C + E \xrightarrow{2} F + G$, the selectivity to product C is

$$S_c = \frac{r_c}{r_c + r_d + r_f + r_g} = \frac{r_1 - r_2}{(r_1 - r_2) + r_1 + r_2 + r_2} = \frac{r_1 - r_2}{2r_1 + r_2}$$

The *yield* Y of a product R with respect to a reactant A is the ratio of the rate of production of R to that of consumption of A :

$$Y_r = \frac{r_r}{-r_a} \quad (7-27)$$

For a single reaction the yield is trivial and Eq. (7-27) simplifies to the ratio of the respective stoichiometric coefficients:

$$Y_r = \frac{v_r}{v_a} \quad (7-28)$$

The yield quantifies the efficiency of the respective reactant utilization to make the desired products.

CONCENTRATION TYPES

Different concentration types are used for different reaction systems. For gas-phase reactions, *volumetric concentration* or *partial pressures* are equally useful and can be related by the thermodynamic equation of state. For instance, for ideal gases (approximation valid for gases at very low pressure)

$$PV = nRT \quad (7-29)$$

When applied to individual components in a constant-volume system,

$$p_i V = n_i RT \quad (7-30)$$

Using Eq. (7-5), we obtain the relationship between the volumetric concentrations and partial pressures:

$$C_i = \frac{p_i}{RT} \quad (7-31)$$

For an ideal gas the total concentration is

$$C = \frac{P}{RT} \quad (7-32)$$

For higher pressure and nonideal gases, a *compressibility factor* z_i can be used:

$$p_i V = z_i n_i RT \quad \text{and} \quad C_i = \frac{p_i}{z_i RT} \quad (7-33)$$

Other relevant equations of state can also be used for both gases and liquids. This aspect is not in the scope of this section, and the reader is referred to the relevant section of this handbook.

Other concentration units include *mole fractions* for liquid x_i :

$$x_i = \frac{n_i}{\sum n_i} = \frac{C_i}{\sum C_i} = \frac{C_i}{C} \quad (7-34)$$

and for gas y_i :

$$y_i = \frac{n_i}{\sum n_i} = \frac{C_i}{\sum C_i} = \frac{C_i}{C} = \frac{p_i}{\sum p_i} = \frac{p_i}{P} \quad (7-35)$$

The last two terms are only valid for an ideal gas.

STOICHIOMETRIC BALANCES

Single Reactions Equation (7-22) shows that for a single reaction, the number of moles and concentration of all other components can be calculated from the extent of reaction ξ or the conversion based on the limiting reactant, say A , X_a . In terms of number of moles n_i ,

$$\begin{aligned} n_a &= n_{a0} - v_a \xi = n_{a0}(1 - X_a) \\ n_b &= n_{b0} - v_b \xi = n_{b0}(1 - X_b) = n_{b0} - \frac{v_b}{v_a} n_{a0} X_a \\ &\dots \\ n_r &= n_{r0} + v_r \xi = n_{r0} - \frac{v_r}{v_a} n_{a0} X_a \\ n_s &= n_{s0} + v_s \xi = n_{s0} - \frac{v_s}{v_a} n_{a0} X_a \\ &\dots \end{aligned} \quad (7-36)$$

Similarly the number of moles of each component in terms of moles of A , n_{a0} , is

$$\begin{aligned} n_b &= n_{b0} - \frac{v_b}{v_a} (n_{a0} - n_a) \\ &\dots \\ n_r &= n_{r0} + \frac{v_r}{v_a} (n_{a0} - n_a) \\ n_s &= n_{s0} + \frac{v_s}{v_a} (n_{a0} - n_a) \\ &\dots \end{aligned} \quad (7-37)$$

Change in number of moles by the reaction and change in temperature, pressure, and density affect the translation of stoichiometric balances from number of moles to volumetric concentrations. These relationships are different for gases and liquids. For instance, for *constant density* systems (such as many liquid-phase isothermal reactions) or for *constant temperature, constant pressure* gas reaction with no change in number of moles, Eqs. (7-36) and (7-37) can be changed to volumetric concentration C_i by dividing each equation by the constant reaction volume V (e.g., in a batch reactor) and using Eq. (7-5). For example, for the single reaction (7-4) with rate (7-5):

$$\begin{aligned} C_b &= C_{b0} - \frac{q}{p} (C_{a0} - C_a) \\ C_r &= C_{r0} + \frac{r}{p} (C_{a0} - C_a) \\ C_s &= C_{s0} + \frac{s}{p} (C_{a0} - C_a) \end{aligned} \quad (7-38)$$

$$r = k C_a^a \left[C_{b0} - \frac{q}{p} (C_{a0} - C_a) \right]^b = k [C_{a0}(1 - X_a)]^a \left(C_{b0} - \frac{q}{p} C_{a0} X_a \right)^b \quad (7-39)$$

It is best to represent all concentrations in terms of that of the limiting reactant.

Often there is a change in total number of moles due to reaction. Taking the general reaction (7-1), in the gas phase the change in

number of moles relative to moles of component A converted, δ_a , and the total number of moles can be calculated as follows:

$$\delta_a = \frac{v_q + v_s + \dots - v_a - v_b - \dots}{v_a}$$

$$n_a = \sum n_{i0} \quad n = \sum n_i \quad (7-40)$$

$$\frac{n}{n_0} = 1 + y_{a0} \delta_a X_a = 1 + \varepsilon_a X_a$$

$$\varepsilon_a = y_{a0} \delta_a$$

Using the ideal gas law, Eq. (7-29), the volume change depends on conversion as follows:

$$\frac{V}{V_0} = \frac{T}{T_0} \frac{P_0}{P} \frac{n}{n_0} = \frac{T}{T_0} \frac{P_0}{P} (1 + \varepsilon_a X_a) \quad (7-41)$$

Hence, for an isothermal constant-pressure ideal gas reaction system,

$$C_a = \frac{n_a}{V} = \frac{C_{a0}(1 - X_a)}{1 + \varepsilon_a X_a}$$

$$C_b = \frac{n_b}{V} = \frac{C_{b0} - \frac{v_b}{v_a} C_{a0} X_a}{1 + \varepsilon_a X_a}$$

$$\dots$$

$$C_r = \frac{n_r}{V} = \frac{C_{r0} - \frac{v_r}{v_a} C_{a0} X_a}{1 + \varepsilon_a X_a}$$

$$C_s = \frac{n_s}{V} = \frac{C_{s0} - \frac{v_s}{v_a} C_{a0} X_a}{1 + \varepsilon_a X_a}$$

$$\dots \quad (7-42)$$

Applying this to reaction (7-4) and rate (7-5) gives

$$r = k \left[\frac{C_{a0}(1 - X_a)}{1 + \varepsilon_a X_a} \right]^a \left[\frac{C_{b0} - (q/p) C_{a0} X_a}{1 + \varepsilon_a X_a} \right]^b \quad (7-43)$$

Compare this to Eq. (7-39) where there is no change in number of moles.

Reaction Networks The analysis for single reactions can be extended to a network of reactions by defining an extent of reaction for each reaction, or by choosing a representative reactant concentration for each reaction step. For a complex network, the number of independent extents of reaction required to calculate the concentration of all components is equal to the number of *independent reactions*, which is less than or equal to the total number of reactions in the network. To calculate the number of independent reactions, and to form a set of independent reactions and corresponding independent set of concentrations or extents of reaction, we need to construct the *stoichiometric matrix* and determine its *rank*. The stoichiometric matrix is used to derive a relationship between the concentrations and the independent extents of reaction similar to that of a single reaction.

The stoichiometric matrix is the matrix of the stoichiometric coefficients of the reaction network with negative signs for reactants and positive signs for products. For instance, the hydrodechlorination of Freon 12 (CF_2Cl_2) can proceed with the following consecutive mechanism [Bonarowska et al., "Hydrodechlorination of CCl_2F_2 (CFC-12) over Silica-Supported Palladium-Gold Catalysts," *Appl. Catal. B: Environmental*, **30**:187–193, 2001]:



The stoichiometric matrix S for this network is

$$S = \begin{pmatrix} -1 & 1 & 0 & -1 & 1 \\ 0 & -1 & 1 & -1 & 1 \end{pmatrix}$$

The first row refers to the first reaction and the second row to the second reaction. The columns (species) are in the following order: 1- CF_2Cl_2 , 2- CF_2ClH , 3- CF_2H_2 , 4- H_2 , and 5- HCl . The rank of a matrix is the largest square submatrix obtained by deleting rows and columns, whose determinant is not zero. The rank equals the number of independent reactions. This is also equivalent to stating that there are reactions in the network that are linear combinations of the independent reactions. The rank of S above is 2, since the *determinant* of the first 2×2 submatrix is not zero (there are other 2×2 submatrices that are not zero as well but it is sufficient to have at least one that is not zero):

$$S_1 = \begin{pmatrix} -1 & 1 \\ 0 & -1 \end{pmatrix} \quad \det(S_1) = 1 \neq 0$$

Hence the two reactions are independent. Now if we add another step, which converts Freon 12 directly into the final hydrofluorocarbon CF_2H_2 : $\text{CF}_2\text{Cl}_2 + 2\text{H}_2 \Rightarrow \text{CF}_2\text{H}_2 + 2\text{HCl}$, then the stoichiometric matrix becomes

$$S = \begin{pmatrix} -1 & 1 & 0 & -1 & 1 \\ 0 & -1 & 1 & -1 & 1 \\ -1 & 0 & 1 & -2 & 2 \end{pmatrix}$$

Since the last reaction is a linear combination of the first two (sum), it can be easily proved that the rank remains unchanged at 2. So to conclude, the concentrations of all components in this network can be expressed in terms of two, say H_2 and Freon 12, and the first two reactions form an independent reaction set. In case of more complicated networks it may be difficult to determine the independent reactions by observation alone. In this case the *Gauss-Jordan decomposition* leads to a set of independent reactions (see, e.g., Amundson, *Mathematical Methods in Chemical Engineering—Matrices and Their Application*, Prentice-Hall International, New York, 1966).

For a network of reactions the general procedure is as follows:

1. Generate the reaction network by including all known reaction steps.
2. Generate the corresponding stoichiometric matrix.
3. Calculate the rank of the stoichiometric matrix which equals the number of independent reactions and independent component concentrations required to calculate all the remaining component concentrations.
4. For relatively simple networks, observation allows selection of reactions that are independent—for more complex systems use the Gauss-Jordan elimination to reduce the network to a set of independent (nonzero rows) reactions.
5. Select the independent concentration variables and independent reactions, and use these to calculate all other concentrations and reaction rates.

CATALYSIS

A catalyst is a material that increases the rate of both the forward and reverse reactions of a reaction step, with no net consumption or generation of catalyst by the reaction. A catalyst does not affect the reaction thermodynamics, i.e., the equilibrium composition or the heat of reaction. It does, however, affect the temperature sensitivity of the reaction rate by lowering the activation energy or the energy barrier on the reaction pathway from reactants to products. This allows the reaction to occur faster than the corresponding uncatalyzed reaction at a given temperature. Alternatively, catalytic reactions can proceed at lower temperatures than the corresponding noncatalytic reactions. For a network of reactions, the catalyst is often used to speed up desired reactions and/or to slow down undesired reactions for improved selectivity. On the basis of catalysis, reactions can be further classified into

1. Noncatalytic reactions, e.g., free-radical gas-phase reactions such as combustion of hydrocarbons.

7-10 REACTION KINETICS

2. Homogeneous catalytic reactions with the catalyst being dissolved in the same phase as the reactants and products in a homogeneous reaction medium. Here the catalyst is uniformly distributed throughout the system, e.g., the hydroformylation of olefins in the presence of dissolved Co or Rh carbonyls.

3. Heterogeneous catalytic reactions, with the catalyst, for instance, being a solid in contact with reactants and products in a gas-solid, gas-liquid-solid, or a liquid-solid reaction system. Here the catalyst is not uniformly distributed, and the reaction occurring on the catalyst surface requires, for instance, adsorption of reactants and desorption of products from the solid surface, e.g., the catalytic cracking of gasoil to gasoline and lighter hydrocarbons.

Table 7-1 illustrates the enhancement of the reaction rates by the catalyst—this enhancement can be of many orders of magnitude.

TABLE 7-1 The Rate of Enhancement of Some Reactions in the Presence of a Catalyst

Reaction	Catalyst	Rate enhancement	Temperature, K
Ortho $H_2 \Rightarrow$ para H_2	Pt (solid)	10^{40}	300
$2NH_3 \Rightarrow N_2 + 3H_2$	Mo (solid)	10^{20}	600
$C_2H_4 + H_2 \Rightarrow C_2H_6$	Pt (solid)	10^{42}	300
$H_2 + Br_2 \Rightarrow 2HBr$	Pt (solid)	1×10^8	300
$2NO + 2H_2 \Rightarrow N_2 + 2H_2O$	Ru (solid)	3×10^{16}	500
$CH_3COH \Rightarrow CH_4 + CO$	I_2 (gas)	4×10^6	500
$CH_3CH_3 \Rightarrow C_2H_4 + H_2$	NO_2 (gas)	1×10^9	750
$(CH_3)_3COH \Rightarrow$ $(CH_3)_2CH_2CH_2 + H_2O$	HBr (gas)	3×10^8	750

SOURCE: Masel, *Chemical Kinetics and Catalysis*, Wiley, 2001, Table 12.1.

IDEAL REACTORS

Reactions occur in reactors, and in addition to the intrinsic kinetics, observed reaction rates depend on the reactor type, scale, geometry, mode of operation, and operating conditions. Similarly, understanding of the reactor system used in the kinetic experiments is required to determine the reaction mechanism and intrinsic kinetics. In this section we address the effect of reactor type on observed rates. In Sec. 19 the effect of reactor type on performance (rates, selectivity, yield) is discussed in greater detail.

Material, energy, and momentum balances are essential to fully describe the performance of reactors, and often simplifying assumptions and phenomenological assumptions are needed especially for energy and momentum terms, as indicated in greater detail in Sec. 19

(see also Bird, Stewart, and Lightfoot, *Transport Phenomena*, 2d ed., John Wiley & Sons, New York, 2002). Ideal reactors allow us to simplify the energy, momentum, and material balances, thus focusing the analysis on intrinsic kinetics. A useful classification of ideal reactor types is in terms of their concentration distributions versus reaction time and space. Three types of ideal reactors are considered in this section:

1. Ideal *batch reactors (BRs)* including *semibatch reactors (SBRs)*
2. Ideal *continuously stirred tank reactor (CSTR)*, including single and multiple stages
3. *Plug flow reactor (PFR)* with and without *recycle*

Figure 7-1 shows these types of ideal reactors. Other types of ideal and nonideal reactors are treated in detail in Sec. 19.

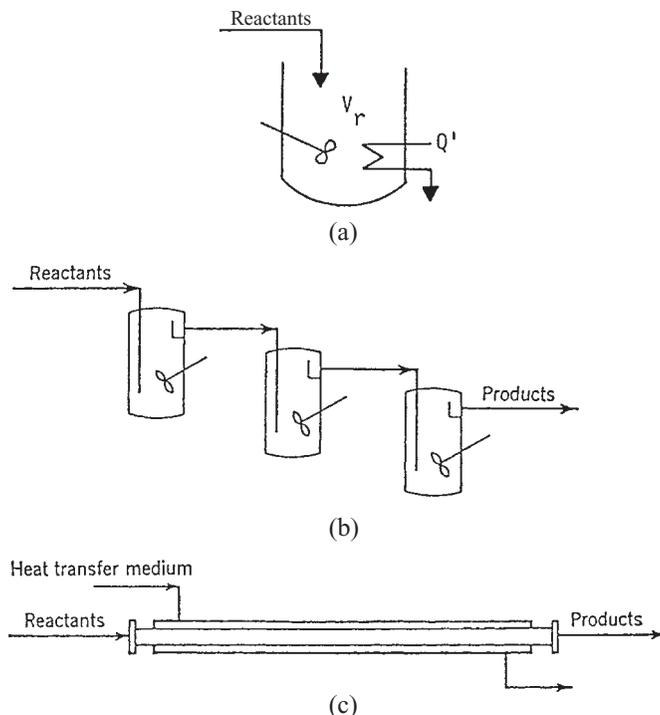


FIG. 7-1 Types of ideal reactors: (a) Batch or semibatch. (b) CSTR or series of CSTRs. (c) Plug flow.

The general form of a balance equation is

$$\text{Input} + \text{sources} - \text{outputs} = \text{accumulation} \quad (7-44)$$

IDEAL BATCH REACTOR

Batch Reactor (BR) Ideal batch reactors (Fig. 7-1a) are tanks provided with agitation for uniform composition and temperature at all times. An ideal batch reactor can be operated under isothermal conditions (constant temperature), temperature-programmed mode (by controlling cooling rate according to a protocol), or adiabatic mode with no heat crossing the reactor boundaries). In adiabatic mode the temperature is increasing, decreasing, or constant as the reaction proceeds for exothermic, endothermic, and thermally neutral reactions, respectively. In the ideal batch reactor, all the reactants are loaded into the reactor and well mixed by agitation before the conditions for reaction initiation (temperature and pressure) are reached; as the reaction proceeds, the concentration varies with time, but at any one time it is uniform throughout due to agitation.

Laboratory batch reactors can be single-phase (e.g., gas or liquid), multiphase (e.g., gas-liquid or gas-liquid-solid), and catalytic or non-catalytic. In this section we limit the discussion to operation at isothermal conditions. This eliminates the need to consider energy, and due to the uniform composition the component material balances are simple ordinary differential equations with time as the independent variable.

An ideal isothermal single-phase batch reactor in which a general reaction network takes place has the following general material balance equation:

$$\frac{dn_i}{dt} = V \sum_j \nu_{ij} r_j \quad n_i = n_{i0} \quad \text{at } t = 0 \quad (7-45)$$

The left-hand side is the accumulation term in moles per second of component i , and the right-hand side is the source term due to chemical reaction also in moles per second, which includes all reactions j that consume or produce component i , and the corresponding stoichiometric coefficients are represented in matrix form as ν_{ij} with a positive sign for products and a negative sign for reactants. This molar

balance is valid for each component since we can multiply each side of the equation by the component molecular weight to obtain the true mass balance equation. In terms of conversion, Eq. (7-45) can be rewritten as

$$\frac{n_{i0} dX_i}{dt} = -V \sum_j \nu_{ij} r_j \quad n_i = n_{i0} \quad \text{at } t = 0 \quad (7-46)$$

and we can integrate this equation to get the *batch reaction time* or *batch residence time* τ_{BR} required to obtain a conversion X_i , starting with initial conversion X_{i0} and ending with final conversion X_{if} :

$$\tau_{BR} = -n_{i0} \int_{X_{i0}}^{X_{if}} \frac{dX_i}{V \sum_j \nu_{ij} r_j} \quad (7-47)$$

To integrate we need to represent all reaction rates r_j in terms of the conversion X_i . For a single reaction this is straightforward [see, e.g., Eq. (7-43)]. However, for a network of reactions, integration of a system of often nonlinear differential equations is required using implicit or semi-implicit integration. For references please see the relevant section of this handbook or any textbook on ordinary differential equations.

A special case of batch reactors is constant-volume or constant-density operation typical of liquid-phase reactions, with volume invariant with time:

$$\frac{dC_i}{dt} = \sum_j \nu_{ij} r_j \quad C_i = C_{i0} \quad \text{at } t = 0 \quad (7-48)$$

A typical concentration profile versus time for a reactant is shown in Fig. 7-2a. Integration of Eq. (7-48) gives the batch residence time

$$\tau_{BR} = \int_{C_{i0}}^{C_{if}} \frac{dC_i}{\sum_j \nu_{ij} r_j} \quad (7-49)$$

For instance, for a single reaction, Eq. (7-43) can be used to describe the reaction rate r_i in terms of one reactant concentration. For reaction networks integration of a system of ordinary differential equations is required.

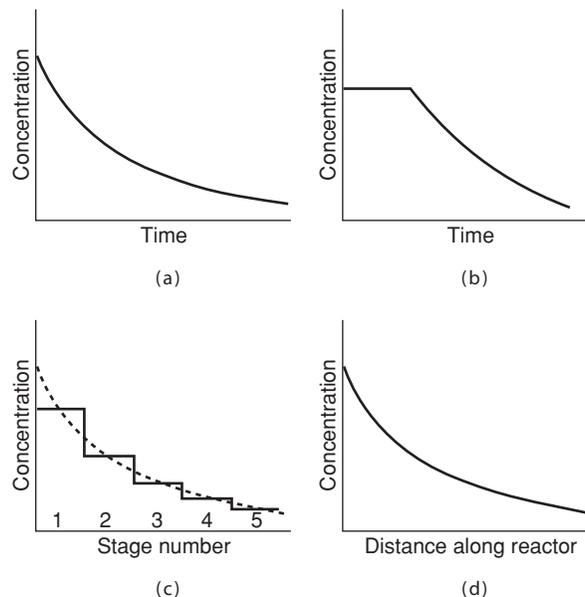


FIG. 7-2 Concentration profiles in batch and continuous flow: (a) Batch time profile. (b) Semibatch time profile. (c) Five-stage CSTRs distance profile. (d) Tubular flow distance profile.

7-12 REACTION KINETICS

Semibatch Reactor (SBR) In semibatch operation, a gas of limited solubility or a liquid reactant may be fed in gradually as it is used up. An ideal isothermal single-phase semibatch reactor in which a general reaction network takes place has the following general material balance equation:

$$\frac{dn_i}{dt} = N_{i0} + V \sum v_{ij} r_j \quad n_i = n_{i0} \quad \text{at } t = 0$$

$$N_{i0} = N_{i0}(t) \quad \text{for } t_{s0i} \leq t \leq t_{s1i} \quad (7-50)$$

The first term on the right-hand side of Eq. (7-50) is the molar feed rate of the components, which can be different for each component, hence the subscript i , and can vary with time. A typical concentration profile versus time for a reactant whose concentration is kept constant initially by controlling the feed rate is shown in Fig. 7-2b. Knowledge of the reaction kinetics allows these ordinary differential equations to be integrated to obtain the reactor composition versus time.

IDEAL CONTINUOUS STIRRED TANK REACTOR (CSTR)

In an ideal continuous stirred tank reactor, composition and temperature are uniform throughout just as in the ideal batch reactor. But this reactor also has a continuous feed of reactants and a continuous withdrawal of products and unconverted reactants, and the effluent composition and temperature are the same as those in the tank (Fig. 7-1b). A CSTR can be operated under transient conditions (due to variation in feed composition, temperature, cooling rate, etc., with time), or it can be operated under steady-state conditions. In this section we limit the discussion to isothermal conditions. This eliminates the need to consider energy balance equations, and due to the uniform composition the component material balances are simple ordinary differential equations with time as the independent variable:

$$\frac{dn_i}{dt} = N_{i0} - N_i + V \sum v_{ij} r_j \quad n_i = n_{i0} \quad \text{at } t = 0 \quad (7-51)$$

At steady state the differential equations simplify to algebraic equations as indicated below:

$$V = - \frac{N_{i0} - N_i}{\sum v_{ij} r_j} \quad (7-52)$$

Equation (7-52) can be expressed in terms of volumetric concentration or in terms of conversions just as we did with the batch reactor. An *apparent residence time* based on feed conditions can be defined for a single-phase CSTR as follows:

$$\tau_{\text{CSTR}} = \frac{V}{q_0} \quad N_{i0} = q_0 C_{i0} \quad N_i = q C_i \quad (7-53)$$

In Eq. (7-53) the feed and effluent molar rates N_{i0} and N_i are expressed in terms of volumetric flow rates q_0 and q (inlet and outlet, respectively) and concentrations. Thus Eq. (7-52) can be rewritten as

$$\tau_{\text{CSTR}} = \frac{C_{i0} - (q/q_0)C_i}{\sum v_{ij} r_j} \quad (7-54)$$

Equation (7-54) allows calculation of the residence time required to achieve a given conversion or effluent composition. In the case of a network of reactions, knowing the reaction rates as a function of volumetric concentrations allows solution of the set of often nonlinear algebraic material balance equations using an implicit solver such as the multi variable Newton-Raphson method to determine the CSTR effluent concentration as a function of the residence time. As for batch reactors, for a single reaction all compositions can be expressed in terms of a component conversion or volumetric concentration, and Eq. (7-54) then becomes a single nonlinear algebraic equation solved by the Newton-Raphson method (for more details on this method see the relevant section this handbook).

A special case of Eq. (7-54) is a constant-density system (e.g., a liquid-phase reaction), with the true average residence time τ_{CSTR}

$$\tau_{\text{CSTR}} = \frac{C_{i0} - C_i}{\sum v_{ij} r_j} \quad q = q_0 \quad (7-55)$$

When a number of such CSTRs are employed in series, the concentration profile is step-shaped if the abscissa is the total residence time or the stage number as indicated by a typical reactant concentration profile in Fig. 7-2c.

PLUG FLOW REACTOR (PFR)

In a *plug flow reactor* all portions of the feed stream move with the same radially uniform velocity along parallel streamlines and therefore have the same residence time; that is, there is no mixing in the axial direction but complete mixing radially (Fig. 7-1c). As the reaction proceeds, the concentration falls off with distance. A PFR can be operated under either transient conditions or steady-state conditions. In this section we limit the discussion to steady-state conditions. This eliminates the need to consider partial differential equations in time and space. We further limit the discussion to isothermal operation, which together with the defined plug flow also eliminates the need for energy and momentum balance equations. Due to the radially uniform composition, the component material balances are simple ordinary differential equations with axial distance from inlet as the independent variable. An isothermal single-phase steady-state PFR in which a general reaction network takes place has the following general material balance equation:

$$\frac{dN_i}{dV} = \sum v_{ij} r_j \quad N_i = N_{i0} \quad \text{at } V = 0 \quad (7-56)$$

Note the similarity between the ideal batch and the plug flow reactors, Eqs. (7-45) and (7-56), respectively. In terms of conversion, Eq. (7-56) can be written as

$$N_{i0} \frac{dX_i}{dV} = - \sum v_{ij} r_j \quad (7-57)$$

Equation (7-57) can be integrated to calculate the reactor volume required to achieve a given conversion X_i :

$$V = -N_{i0} \int_{X_{i0}}^{X_{if}} \frac{dX_i}{\sum v_{ij} r_j} \quad (7-58)$$

An *apparent residence time* based on feed conditions can be defined for a single-phase PFR as follows:

$$\tau_{\text{PFR}} = \frac{V}{q_0} \quad (7-59)$$

Equation (7-58) becomes

$$\tau_{\text{PFR}} = -C_{i0} \int_{X_{i0}}^{X_{if}} \frac{dX_i}{\sum v_{ij} r_j} \quad (7-60)$$

Equation (7-60) is identical to that of the ideal batch reactor, Eq. (7-47), and the two reactor systems can be modeled in identical fashion.

For a constant-density system with no change in number of moles, with the true residence time τ_{PFR} :

$$\tau_{\text{PFR}} = \int_{C_{i0}}^{C_{if}} \frac{dC_i}{\sum v_{ij} r_j} \quad (7-61)$$

This is identical to the corresponding ideal batch reactor, Eq. (7-49).

Ideal Recycle Reactor All reactor modes can sometimes be advantageously operated with recycling part of the product or intermediate streams. Heated or cooled recycle streams serve to moderate undesirable temperature gradients, and they can be processed for changes in composition such as separating products to remove equilibrium limitations, before being returned. Say the recycle flow rate in

TABLE 7-2 Consecutive and Parallel First-Order Reactions in an Isothermal Constant-Volume Ideal Batch or Plug Flow Reactor.

The independent variable t is either the batch time or the plug flow residence time.

Reaction network	Material balances	Concentration profiles
$A \xrightarrow{1} B \xrightarrow{2} C$	$\frac{dC_a}{dt} = -k_1 C_a$	$C_a = C_{a0} e^{-k_1 t}$
	$\frac{dC_b}{dt} = k_1 C_a - k_2 C_b$	$C_b = C_{b0} e^{-k_2 t} + \frac{k_1 C_{a0}}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$
	$\frac{dC_c}{dt} = k_2 C_b$	$C_c = C_{a0} + C_{b0} + C_{c0} - C_a - C_b$
$A \xrightarrow{1} B$ $A \xrightarrow{2} C$	$\frac{dC_a}{dt} = -(k_1 + k_2) C_a$	$C_a = C_{a0} e^{-(k_1 + k_2)t}$
	$\frac{dC_b}{dt} = k_1 C_a$	$C_b = C_{b0} + \frac{k_1 C_{a0}}{k_2 + k_1} (1 - e^{-(k_1 + k_2)t})$
	$\frac{dC_c}{dt} = k_2 C_a$	$C_c = C_{a0} + C_{b0} + C_{c0} - C_a - C_b$

a PFR is q_R and the fresh feed rate is q_0 . With a fresh feed concentration of C_0 and a product concentration of C_2 , the composite reactor feed concentration C_1 and the recycle ratio R are

$$C_1 = \frac{C_0 + RC_2}{1 + R} \quad R = \frac{q_R}{q_0} \quad (7-62)$$

The change in concentration across the reactor becomes

$$\Delta C = C_1 - C_2 = \frac{C_2 - C_0}{1 + R} \quad (7-63)$$

Accordingly, the change in concentration (or in temperature) across the reactor can be made as small as desired by increasing the recycle ratio. Eventually, the reactor can become a well-mixed unit with essentially constant concentration and temperature, while substantial differences in composition will concurrently arise between the fresh feed inlet and the product withdrawal outlet, similar to a CSTR. Such an operation is useful for obtaining experimental data for analysis of rate

equations. In the simplest case, where the product is recycled without change in composition, the flow reactor equation at constant density is

$$\tau_{PFR} = (1 + R) \int_{C_{i0}}^{C_{if}} \frac{dC_i}{\sum v_j f_j} \quad (7-64)$$

Hence, recycling increases the residence time or reactor size required to achieve a given conversion, since $1 + R > 1$.

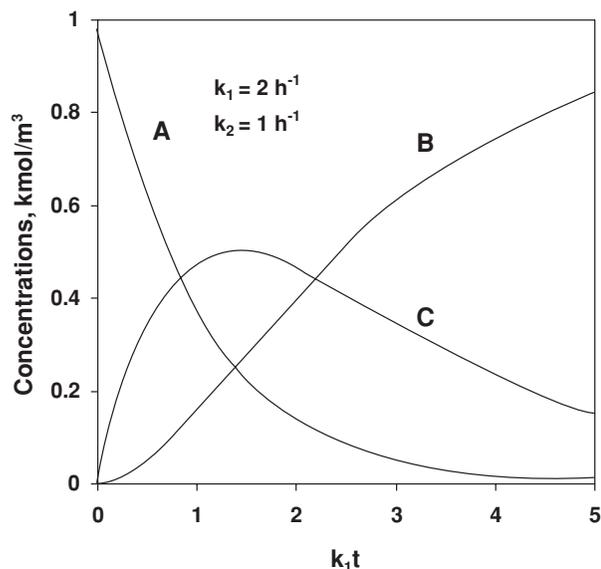
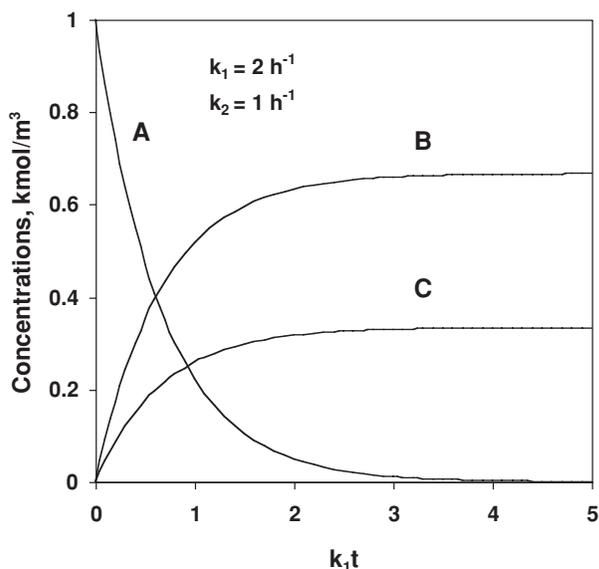
EXAMPLES FOR SOME SIMPLE REACTIONS

Table 7-2 and Figs. 7-3 and 7-4 show the analytical solution of the integrals for two simple first-order reaction systems in an isothermal constant-volume batch reactor or plug flow reactor. Table 7-3 shows the analytical solution for the same reaction systems in an isothermal constant-density CSTR.

Section 19 provides discussion about advantages and disadvantages of CSTRs versus PFR and BR for various reaction systems.

TABLE 7-3 Consecutive and Parallel First-Order Reactions in an Isothermal Constant-Volume Ideal CSTR

Reaction network	Material balances	Concentration profiles
$A \xrightarrow{1} B \xrightarrow{2} C$	$C_{a0} - C_a - \tau k_1 C_a = 0$	$C_a = \frac{C_{a0}}{1 + \tau k_1}$
	$C_{b0} - C_b + \tau(k_1 C_a - k_2 C_b) = 0$	$C_b = \frac{C_{b0}}{1 + \tau k_2} + \frac{\tau k_1 C_{a0}}{(1 + \tau k_1)(1 + \tau k_2)}$
	$C_{c0} - C_c + \tau k_2 C_b = 0$	$C_c = C_{a0} + C_{b0} + C_{c0} - C_a - C_b$
$A \xrightarrow{1} B$ $A \xrightarrow{2} C$	$C_{a0} - C_a - \tau(k_1 + k_2) C_a = 0$	$C_a = \frac{C_{a0}}{1 + \tau(k_1 + k_2)}$
	$C_{b0} - C_b + \tau k_1 C_a = 0$	$C_b = C_{b0} \frac{\tau k_1 C_{a0}}{1 + \tau(k_1 + k_2)}$
	$C_{c0} - C_c + \tau k_2 C_a = 0$	$C_c = C_{a0} + C_{b0} + C_{c0} - C_a - C_b$

FIG. 7-3 Concentration profiles for the reaction $A \rightarrow B \rightarrow C$.FIG. 7-4 Concentration profiles for the reaction $A \rightarrow B$ and $A \rightarrow C$.

KINETICS OF COMPLEX HOMOGENEOUS REACTIONS

Global or complex reactions are not usually well represented by mass action kinetics because the rate results from the combined effect of several simultaneous elementary reactions (each subject to mass action kinetics) that underlie the global reaction. The elementary steps include short-lived and unstable intermediate components such as free radicals, ions, molecules, transition complexes, etc.

The reason many global reactions between stable reactants and products have complex mechanisms is that these unstable intermediates have to be produced in order for the reaction to proceed at reasonable rates. Often simplifying assumptions lead to closed-form kinetic rate expressions even for very complex global reactions, but care must be taken when using these since the simplifying assumptions are valid over limited ranges of compositions, temperature, and pressure. These assumptions can fail completely—in that case the full elementary reaction network has to be considered, and no closed-form kinetics can be derived to represent the complex system as a global reaction.

Typical simplifying assumptions include these:

- *Pseudo-steady-state* approximation for the unstable intermediate; i.e., the concentration of these does not change during reaction
- Equilibrium for certain fast reversible reactions and completion of very fast irreversible steps
- *Rate-determining step(s)*; i.e., the global reaction rate is determined by the rate(s) of the slowest step(s) in the reaction network composing the overall or global reaction

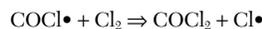
These simplifying assumptions allow elimination of some reaction steps, and representation of free radical and short-lived intermediates concentrations in terms of the concentration of the stable measurable components, resulting in complex non-mass action rate expressions.

Complex reactions can proceed through *chain* or *nonchain* mechanisms. In a *chain reaction*, the active unstable components are produced in an *initiation* step and are repeatedly regenerated through *propagation* steps, and only a small fraction of these are converted to stable components through a *termination* step. Free radicals are examples of such unstable components frequently encountered in chain reactions: free radicals are molecular fragments having one or more unpaired electrons, are usually short-lived (milliseconds), and are highly reactive. They are detectable spectroscopically, and some have been isolated. They occur as initiators and intermediates in such

basic phenomena as oxidation, combustion, photolysis, and polymerization. Several examples of free radical mechanisms possessing non-integral power law or hyperbolic rate equations are cited below. In a *nonchain reaction*, the unstable intermediate, such as an *activated complex* or *transition state complex*, reacts further to produce the products, and it is not regenerated through propagation but is continually made from reactants in stoichiometric quantities.

CHAIN REACTIONS

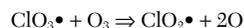
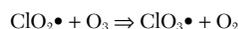
Phosgene Synthesis The global reaction $\text{CO} + \text{Cl}_2 \Rightarrow \text{COCl}_2$ proceeds through the following free radical mechanism:



Assuming the first two reactions are in equilibrium, expressions are found for the concentrations of the free radicals $\text{Cl}\cdot$ and $\text{COCl}\cdot$ in terms of the species CO , Cl_2 , and COCl_2 , and when these are substituted into the mass action rate expression of the third reaction, the rate becomes

$$r_{\text{COCl}_2} = k(\text{CO})(\text{Cl}_2)^{3/2} \quad (7-65)$$

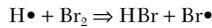
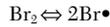
Ozone Conversion to Oxygen in Presence of Chlorine The global reaction $2\text{O}_3 \xrightarrow{\text{Cl}_2} 3\text{O}_2$ in the presence of Cl_2 proceeds through the following sequence:



The chain carriers $\text{ClO}\cdot$, $\text{ClO}_2\cdot$, and $\text{ClO}_3\cdot$ are assumed to attain pseudo-steady state. Then,

$$r_{\text{O}_3} = k(\text{Cl}_2)^{1/2}(\text{O}_3)^{3/2} \quad (7-66)$$

Hydrogen Bromide Synthesis The global reaction $\text{H}_2 + \text{Br}_2 \Rightarrow 2\text{HBr}$ proceeds through the following chain of reactions:

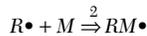


Assuming pseudo-steady state for the concentrations of the free radicals $\text{H}\cdot$ and $\text{Br}\cdot$, the global rate equation becomes

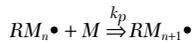
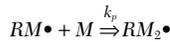
$$r_{\text{HBr}} = \frac{k_1(\text{H}_2)(\text{Br}_2)^{1/2}}{k_2 + \text{HBr}/\text{Br}_2} \quad (7-67)$$

Chain Polymerization For free radical polymerization, the following generic mechanism can be postulated:

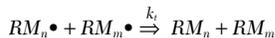
Initiation:



Propagation:



Termination:



The rates of formation of the free radicals $R\cdot$ and $M\cdot$ reach pseudo-steady states, resulting in the following polymerization rate:

$$r_p = k_p(M)(M^*) = k_p\left(\frac{k_i}{k_t}\right)^{1/2}(M)(I)^{1/2} \quad (7-68)$$

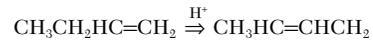
NONCHAIN REACTIONS

Nonchain reactions proceed through an active intermediate to the products. Many homogeneous nonchain reactions are also homogeneously catalyzed reactions, discussed below.

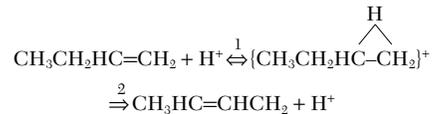
HOMOGENEOUS CATALYSIS

Homogeneous catalysts proceed through an activated or transition state complex between reactant(s) and catalysts, which decomposes into products. Homogeneous catalysts are dissolved in the homogeneous reaction mixture and include among others acids/bases, metal salts, radical initiators, solvents, and enzymes.

Acid-Catalyzed Isomerization of Butene-1 Butene-1 isomerizes to butene-2 in the presence of an acid according to the global reaction



Even though this appears to be a monomolecular reaction, it is not, as it proceeds through the following mechanism:



Assuming reaction 1 is in equilibrium, the reaction rate is

$$r = k_2K_1[\text{H}^+][\text{CH}_3\text{CH}_2\text{HC}=\text{CH}_2] \quad (7-69)$$

Enzyme Kinetics Enzymes are homogeneous catalysts for cellular and enzymatic reactions. The enzyme E and the reactant S are

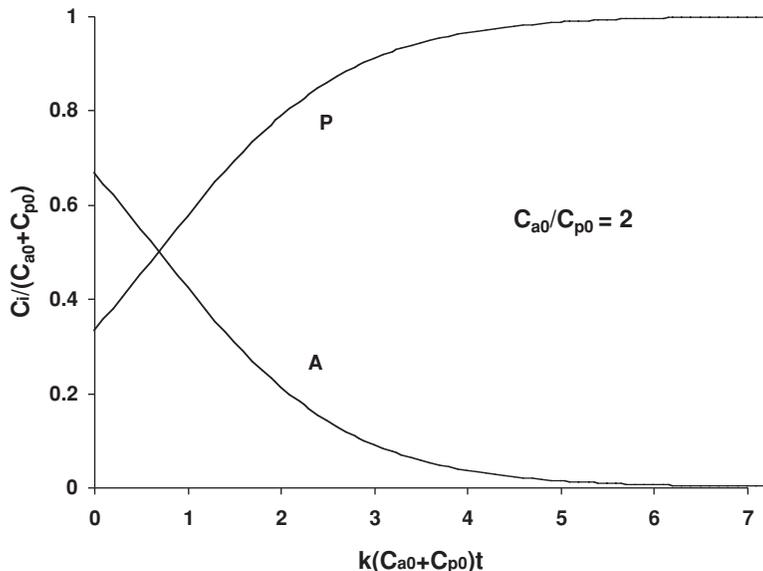
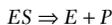
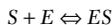


FIG. 7-5 Product concentration profile for the autocatalytic reaction $A + P \Rightarrow 2P$ with rate $r = kC_aC_p$.

7-16 REACTION KINETICS

assumed to form a complex ES that then dissociates into product P and releases the enzyme:



Assuming equilibrium for the first step results in the following rate, developed by Michaelis and Menten [*Biochem. Zeit.*, **49**:333 (1913)] and named Michaelis-Menten kinetics,

$$r_p = -r_s = \frac{k(S)}{K_m + (S)} \quad (7-70)$$

Here K_m is the inverse of the equilibrium constant for the first reaction.

AUTOCATALYSIS

In an autocatalytic reaction, a reactant reacts with a product to make more product. For the reaction to proceed, therefore, product must be present

initially in a batch or in the feed of a continuous reactor. Examples are cell growth in fermentation and combustion of fuels. For instance, the irreversible elementary reaction $A + P \Rightarrow 2P$ has the mass action kinetics

$$r = kC_a C_p \quad (7-71)$$

For an ideal batch reactor (see, e.g., Steinfeld, Francisco, and Hase, *Chemical Kinetics and Dynamics*, Prentice-Hall, 1989):

$$\frac{dC_a}{dt} = -kC_a C_p \quad \frac{dC_p}{dt} = kC_a C_p \quad C_a + C_p = C_{a0} + C_{p0} \quad (7-72)$$

Integration results in the following concentration profile:

$$C_p = \frac{C_{a0} + C_{p0}}{1 + (C_{a0}/C_{p0})e^{-k(C_{a0} + C_{p0})t}} \quad C_a = C_{a0} + C_{p0} - C_p \quad (7-73)$$

Figure 7-5 illustrates the dimensionless concentration profile for the reactant A and product P , $C_i/(C_{a0} + C_{p0})$, for $C_{a0}/C_{p0} = 2$, indicative of a maximum rate at the inflexion point (maximum in slope of the concentration-time curve), typical to autocatalytic reactions.

INTRINSIC KINETICS FOR FLUID-SOLID CATALYTIC REACTIONS

There are a large number of fluid-solid catalytic reactions, mostly gas-solid, including catalytic cracking, oxidation of polluting gases in automotive and power generation catalytic converters, partial oxidation synthesis reactions such as HCN synthesis, chemical vapor deposition, etc. (see, e.g., Sec. 19 for more examples). Examples of solid catalysts include, among others, supported metals, transition metal oxides and sulfides, solid acids and bases, and immobilized homogeneous catalysts and enzymes. Solid catalysts can be a fine powder (suspended in a liquid or fluidized by a flowing gas), cylindrical, spherical, and more-complex-shaped particles (in a packed bed), a thin layer of active components (on the walls of a monolith or a foam) and gauzes. The solid catalyst can be porous with active component distributed throughout the particle volume, or nonporous with active component present on the exposed catalyst external surface alone.

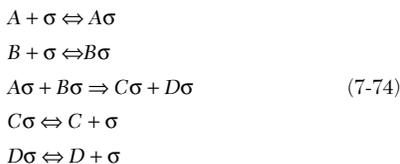
The analysis of Langmuir [*J. Am. Chem. Soc.* **40**:1361 (1918)] and Hinshelwood (*Kinetics of Chemical Change*, Oxford, 1940) form the basis for the simplified treatment of kinetics on heterogeneous catalysts. For a solid catalyzed reaction between gas phase reactants A and B , the postulated mechanism consists of the following steps in series:

1. The reactants from the gas adsorb to bond to active sites on the catalyst surface as molecules or dissociated atoms. The rate of adsorption is proportional to the partial pressure of reactants and to the fraction of uncovered surface sites ϑ_v . More than one type of active site can be present. The adsorption isotherms such as the Langmuir isotherm relate the partial pressure of an adsorbed species to its surface coverage, and the form of this relationship is indicative of the type of adsorption process taking place (see, for more details, Masel, *Chemical Kinetics and Catalysis*, Wiley, 2001).

2. The adsorbed species react on the surface to form adsorbed products. The rate of reaction between adsorbed species is proportional to their adsorbed concentrations on the surface.

3. The adsorbed products desorb into the gas. The rate of desorption of species A is proportional to the fraction of the surface covered by A , ϑ_a .

For instance, for the simple irreversible reaction $A + B \Rightarrow C + D$, the postulated mechanism is



$A\sigma$, $B\sigma$, $C\sigma$, and $D\sigma$ above are adsorbed species on the catalyst surface, and σ is an available active site. We will consider a variety of possible scenarios for this simple solid-catalyzed system. Note that the intrinsic specific reaction rate for such systems is often expressed on a unit mass catalyst basis (r_m) instead of unit reaction volume basis (r_v), and the latter is related to the former through the catalyst loading (mass catalyst/reaction volume) or bed density:

$$r_v = \frac{r_m M_{\text{cat}}}{V} = r_m \rho_B \quad (7-75)$$

ADSORPTION EQUILIBRIUM

Assuming equilibrium for all adsorption steps (e.g., the surface reaction is rate-limiting), the net rates of adsorption of reactants and product are all zero.

$$r_i = k_i p_i \vartheta_v - k_{-i} \vartheta_i \Rightarrow 0 \quad i = a, b, c, d \quad (7-76)$$

A material balance on all sites yields

$$\vartheta_v = 1 - \vartheta_a - \vartheta_b - \vartheta_c - \vartheta_d \quad (7-77)$$

and solving for the surface coverages gives

$$\begin{aligned} \vartheta_a &= \left(\frac{k_a}{k_{-a}} \right) p_a \vartheta_v = K_a p_a \vartheta_v & \vartheta_b &= \left(\frac{k_b}{k_{-b}} \right) p_b \vartheta_v = K_b p_b \vartheta_v \\ \vartheta_c &= \left(\frac{k_c}{k_{-c}} \right) p_c \vartheta_v = K_c p_c \vartheta_v & \vartheta_d &= \left(\frac{k_d}{k_{-d}} \right) p_d \vartheta_v = K_d p_d \vartheta_v \end{aligned} \quad (7-78)$$

The fraction of surface not covered is

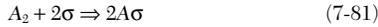
$$\vartheta_v = \frac{1}{1 + K_a p_a + K_b p_b + K_c p_c + K_d p_d} \quad (7-79)$$

In the denominator, terms may be added for adsorbed inerts (e.g., $K_i p_i$) that may be present, and analogous expressions for the other participants. The rate of reaction or the rate-determining step is that between adsorbed reactant species:

$$r = k p_a p_b \vartheta_v^2 = \frac{k p_a p_b}{(1 + K_a p_a + K_b p_b + K_c p_c + K_d p_d)^2} \quad (7-80)$$

DISSOCIATION

A diatomic molecule A_2 may adsorb dissociatively as atoms



with the result

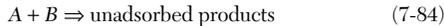
$$\theta_a = \frac{\sqrt{K_a p_a}}{1 + \sqrt{K_a p_a} + K_b p_b + \dots} = \sqrt{K_a p_a} \theta_v \tag{7-82}$$

and the rate-determining step and its rate are



DIFFERENT SITES

When A and B adsorb on chemically different sites σ_1 and σ_2 , the rate of the reaction, with surface reaction controlling,



is

$$r = \frac{k p_a p_b}{(1 + K_a p_a)(1 + K_b p_b)} \tag{7-85}$$

CHANGE IN NUMBER OF MOLES

When the numbers of moles of product is larger than that of the reactants, extra sites are required:

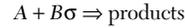


and the rate is

$$r = k \left(\theta_a \theta_v - \frac{\theta_m \theta_n}{K} \right) = \left(p_a - \frac{p_m p_n}{K} \right) \theta_v^2 = \frac{k(p_a - p_m p_n / K)}{(1 + K_a p_a + K_m p_m + K_n p_n)^2} \tag{7-88}$$

REACTANT IN THE GAS PHASE

When A in the gas phase reacts directly with adsorbed B :

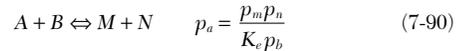


$$r = k p_a \theta_b = k p_a p_b \theta_v = \frac{k p_a p_b}{1 + \sum K_i p_i} \tag{7-89}$$

This mechanism is called the *Ely-Rideal kinetics*.

CHEMICAL EQUILIBRIUM IN GAS PHASE

When A is not in adsorptive equilibrium but it is in chemical equilibrium in the gas phase according to



this expression is substituted for p_a wherever it appears in the rate equation. If the rate-determining step is the surface reaction between adsorbed species, then

$$r = k p_a p_b \theta_v^2 = \frac{k p_m p_n / K_e}{1 + K_a (p_m p_n / K_e p_b) + K_b p_b + K_m p_m + K_n p_n} \tag{7-91}$$

Table 7-4 summarizes some examples of reactions where all substances are in adsorptive equilibrium and the surface reaction controls the rate. In Table 7-5, substance A is not in adsorptive equilibrium, and its adsorption rate is controlling. Details of the derivations of these and some other equations are presented by Yang and Hougen [*Chem. Eng.*

TABLE 7-4 Surface-Reaction Controlling.

Adsorptive equilibrium maintained for all participants.

Reaction	Special condition	Basic rate equation	Driving force	Adsorption term
1. $A \rightarrow M + N$ $A \rightarrow M + N$ $A \rightarrow M + N$	General case Sparsely covered surface Fully covered surface	$r = k \theta_a$ $r = k \theta_a$ $r = k \theta_a$	p_a p_a 1	$1 + K_a p_a + K_m p_m + K_n p_n$ 1 1
2. $A \rightleftharpoons M$		$r = k_1 \theta_a - k_{-1} \theta_m$	$p_a - \frac{p_m}{K}$	$1 + K_a p_a + K_m p_m$
3. $A \rightleftharpoons M + N$	Adsorbed A reacts with vacant site	$r = k_1 \theta_a \theta_v - k_{-1} \theta_m \theta_v$	$p_a - \frac{p_m p_n}{K}$	$(1 + K_a p_a + K_m p_m + K_n p_n)^2$
4. $A_2 \rightleftharpoons M$	Dissociation of A_2 upon adsorption	$r = k_1 \theta_a^2 - k_{-1} \theta_m \theta_v$	$p_a - \frac{p_m}{K}$	$(1 + \sqrt{K_a p_a} + K_m p_m)^2$
5. $A + B \rightarrow M + N$ $A + B \rightarrow M + N$	Adsorbed B reacts with A in gas but not with adsorbed A	$r = k \theta_a \theta_b$ $r = k p_a \theta_b$	$p_a p_b$ $p_a p_b$	$(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n)^2$ $1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n$
6. $A + B \rightleftharpoons M$		$r = k_1 \theta_a \theta_b - k_{-1} \theta_m \theta_v$	$p_a p_b - \frac{p_m}{K}$	$(1 + K_a p_a + K_b p_b + K_m p_m)^2$
7. $A + B \rightleftharpoons M + N$		$r = k_1 \theta_a \theta_b - k_{-1} \theta_m \theta_n$	$p_a p_b - \frac{p_m p_n}{K}$	$(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n)^2$
8. $A_2 + B \rightleftharpoons M + N$	Dissociation of A_2 upon adsorption	$r = k_1 \theta_a^2 \theta_b - k_{-1} \theta_m \theta_n \theta_v$	$p_a p_b - \frac{p_m p_n}{K}$	$(1 + \sqrt{K_a p_a} + K_b p_b + K_m p_m + K_n p_n)^3$

NOTE: The rate equation is:

$$r = \frac{k (\text{driving force})}{\text{adsorption term}}$$

When an inert substance I is adsorbed, the term $K_I p_I$ is to be added to the adsorption term.

SOURCE: From Walas, *Reaction Kinetics for Chemical Engineers*, McGraw-Hill, 1959; Butterworths, 1989.

7-18 REACTION KINETICS

TABLE 7-5 Adsorption-Rate Controlling (Rapid Surface Reaction)

Reaction	Special condition	Basic rate equation	Driving force	Adsorption term
1. $A \rightarrow M + N$		$r = kp_a\theta_c$	p_a	$1 + \frac{K_a p_m p_n}{K} + K_m p_m + K_n p_n$
2. $A \rightleftharpoons M$		$r = k\left(p_a\theta_c - \frac{\theta_a}{K_a}\right)$	$p_a - \frac{p_m}{K}$	$1 + \frac{K_a p_m}{K} + K_m p_m$
3. $A \rightleftharpoons M + N$		$r = k\left(p_a\theta_c - \frac{\theta_a}{K_a}\right)$	$p_a - \frac{p_m p_n}{K}$	$1 + \frac{K_a p_m p_n}{K} + K_m p_m + K_n p_n$
4. $A_2 \rightleftharpoons M$	Dissociation of A_2 upon adsorption	$r = k\left(p_a\theta_c^2 - \frac{\theta_a^2}{K_a}\right)$	$p_a - \frac{p_m}{K}$	$\left(1 + \sqrt{\frac{K_a p_m}{K} + K_m p_m}\right)^2$
5. $A + B \rightarrow M + N$	Unadsorbed A reacts with adsorbed B	$r = kp_a\theta_c$	p_a	$1 + \frac{K_a p_m p_n}{K p_b} + K_b p_b + K_m p_m + K_n p_n$
6. $A + B \rightleftharpoons M$		$r = k\left(p_a\theta_c - \frac{\theta_a}{K_a}\right)$	$p_a - \frac{p_m}{K p_b}$	$1 + \frac{K_a p_m}{K p_b} + K_b p_b + K_m p_m$
7. $A + B \rightleftharpoons M + N$		$r = k\left(p_a\theta_c - \frac{\theta_a}{K_a}\right)$	$p_a - \frac{p_m p_n}{K p_b}$	$1 + \frac{K_a p_m p_n}{K p_b} + K_b p_b + K_m p_m + K_n p_n$
8. $A_2 + B \rightleftharpoons M + N$	Dissociation of A_2 upon adsorption	$r = k\left(p_a\theta_c^2 - \frac{\theta_a^2}{K_a}\right)$	$p_a - \frac{p_m p_n}{K p_b}$	$\left(1 + \sqrt{\frac{K_a p_m p_n}{K p_b} + K_b p_b + K_m p_m + K_n p_n}\right)^2$

NOTES: The rate equation is:

$$r = \frac{k (\text{driving force})}{\text{adsorption term}}$$

Adsorption rate of substance A is controlling in each case. When an inert substance I is adsorbed, the term $K_I p_I$ is to be added to the adsorption term.

SOURCE: From Walas, *Reaction Kinetics for Chemical Engineers*, McGraw-Hill, 1959; Butterworths, 1989.

Prog. **46**:146 (1950)], Walas (*Reaction Kinetics for Chemical Engineers*, McGraw-Hill, 1959; Butterworths, 1989, pp. 153–164), and Rase (*Chemical Reactor Design for Process Plants*, vol. 1, Wiley, 1977, pp. 178–191).

NO RATE-CONTROLLING STEP

All the relations developed above assume that only one step is controlling. In a reaction system, changing the operating conditions may shift the control from one step to another. It is therefore also obvious that at certain conditions there is no single step controlling. In that case all the reactions and their respective rates have to be considered, and the adsorbed species cannot be eliminated from the rate expressions to obtain a single closed-form kinetic rate.

LIQUID-SOLID CATALYTIC REACTIONS

An analogous treatment for liquid-solid catalysis can be derived, with partial pressures replaced by liquid volumetric concentrations. Otherwise all the analyses hold.

BIOCATALYSIS

Biochemical reactions such as *aerobic* and *anaerobic fermentations* occur in the presence of living organisms or *cells*, such as bacteria, algae, and yeast. These reactions can be considered as *biocatalyzed* by the organism. Thus in a typical bioreactor a *substrate* (such as glucose) is fed into the *fermenter* or *bioreactor* in the presence of an initial amount of cells. The desired product can be the cells themselves or a secreted chemical called a *metabolite*. In either case the cells multiply in the presence of the substrate, and the rate of production of cells is proportional to the concentration of the cells—hence this process is autocatalytic. In a batch reactor with ample

supply of substrate, this results in *exponential growth* of the culture. A typical cell or biomass growth rate function, called the *Monod kinetics*, is identical in form to the Michaelis-Menten enzyme kinetics in Eq. (7-70):

$$\mu = \frac{\mu_{\max} C_s}{K_s + C_s} \quad (7-92)$$

In Eq. (7-92) μ is the *specific growth rate* of the culture. It is measured in units of reciprocal time (h^{-1}). Growth rate μ is related to the *volumetric growth rate* r_x of the culture: $r_x = C_A \mu$. This means that the true unit of μ is, e.g., (g biomass formed/h)/(g biomass present), where *g biomass* is the *dry-weight* (DW) of the biomass, obtained after evaporation of the water content of the cell (which constitutes about 80 percent of the *wet biomass weight*). Similarly C_s has the unit, e.g., (g DW)/(L medium volume). The variable C_s in Eq. (7-92) is the concentration of the *limiting substrate* in the medium (g/L). There are many substrates (including micronutrients) in the medium, but there is usually just one that determines the specific growth rate. This substrate is often a sugar (most likely glucose) but it could also be a metal ion (Mg^{2+} etc.), or PO_4^{3-} , NH_4^+ , . . . , or perhaps a hormone. The limiting substrate may easily change during a fermentation, and then the rate expression will change.

The two parameters in Eq. (7-92) are the *maximum specific growth rate* μ_{\max} (h^{-1}) and the *saturation constant* K_s (g substrate/L). The value of K_s is obtained as the substrate concentration at which $\mu = 1/2 \mu_{\max}$ (see Fig. 7-6). The form of Eq. (7-92) is entirely empirical, but it incorporates two important features: (1) At high substrate concentration the whole cell machinery is involved in cell synthesis, and the specific growth rate reaches a maximum μ_{\max} ; (2) at low substrate concentration formation of biomass is a first-order rate process (as in any other chemical reaction) and $\mu \rightarrow (\mu_{\max}/K_s)C_s$. Note that for many commonly used microorganisms K_s is much

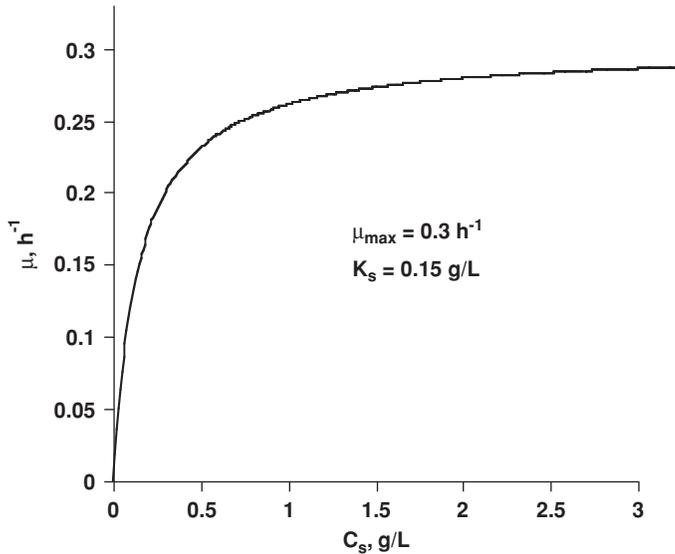


FIG. 7-6 The effect of substrate concentration on specific growth rate.

smaller than the substrate concentration C_s . Thus in batch cultivations K_s is several orders of magnitude smaller than C_s until the very end of the batch, and this is what gives the well-known *exponential growth* [see Eq. (7-93)]. Equation (7-93) applies for batch cultures after an initial *lag phase* when cell machinery is synthesized. Typical values for K_s are 150 mg/L (*Saccharomyces cerevisiae*), 5 to 10 mg/L (lactic bacteria and *E. coli*), and less than 1 mg/L (filamentous fungi).

$$\frac{dC_x}{dt} = \mu C_x \quad C_x = C_{x0} e^{\mu t} \quad (7-93)$$

Equation (7-93) may have to be modified by subtraction of a *death-rate* term $\mu_d C_x$. μ_d may well increase during the batch fermentation in which case the net growth rate of (viable) cells eventually becomes negative, and the concentration of (viable) cells will start to decrease.

FLUID-SOLID REACTIONS WITH MASS AND HEAT TRANSFER

GAS-SOLID CATALYTIC REACTIONS

The Langmuir-Hinshelwood mechanism of adsorption/reaction described above allowed us to relate the gas concentrations and partial pressures in the vicinity of the catalyst surface to the adsorbed species concentration at the active sites, which in turn determined the surface reaction rates. In practice, two additional mass-transfer processes may need to be considered:

1. Diffusion to and from the bulk gas to the external catalyst surface, represented as an external mass-transfer process across a film or boundary layer concentration gradient. For nonporous catalyst this is the only mass-transfer step.

2. Diffusion to and from the catalyst external surface through pores in a porous catalyst particle to active sites inside the catalyst particle where the adsorption and reaction occur, represented as intraparticle diffusion and modeled as a diffusion-reaction process.

External Mass Transfer In a reactor, the solid catalyst is deposited on the surface of narrow tubes (such as monolith or foams), is packed as particles in a tube, or is suspended in slurry or in a fluidized bed as fine particles. For these systems, the bulk concentration of the gas phase approaches that on the catalyst surface if the mass-transfer rate from bulk to surface is substantially larger than the reaction rates on the surface. This, however, is often not the case. The mechanism of mass transfer and reaction on the external catalyst surface includes the following consecutive steps:

1. Mass transfer of gas reactants from the bulk gas to the solid catalyst surface, also called external mass transfer
2. Adsorption, reaction on the surface, and desorption of products, e.g., Langmuir-Hinshelwood kinetics
3. Mass transfer of products from the catalyst surface to the bulk gas

At steady state all these rates are equal.

For example, for a first-order irreversible reaction $A \Rightarrow B$, the rate of mass transfer equals the rate of intrinsic reaction:

$$k_s a_s (C_a - C_{as}) = k C_{as} \quad (7-94)$$

Here a_s is, for instance, the external particle surface area/volume of reactor. Eliminating the surface concentration C_{as} in terms of the observable bulk gas concentration C_a yields the overall specific rate of consumption of A:

$$r_{\text{obs}} = k C_a = \frac{C_a}{1/(k_s a_s) + 1/k} \quad (7-95)$$

$$k_{\text{obs}} = \frac{1}{1/(k_s a_s) + 1/k}$$

Hence the observable overall rate constant k_{obs} is actually a combination of the mass-transfer coefficient and the intrinsic rate

7-20 REACTION KINETICS

coefficient; or in terms of resistances (in units of time) the overall resistance is the sum of the mass transfer and intrinsic kinetic resistance. For this first-order rate case, the overall behavior remains first order in bulk gas concentration. The two limiting cases are mass transfer and reaction control, respectively:

$$\begin{aligned} k_{\text{obs}} &= k_s a_s & \text{and } r_{\text{obs}} &= k_s a_s C_a & \text{for } k_s a_s \ll k & \text{Mass transfer control} \\ k_{\text{obs}} &= k & \text{and } r_{\text{obs}} &= k C_a & \text{for } k_s a_s \gg k & \text{Kinetic control} \end{aligned} \quad (7-96)$$

The mass-transfer coefficient depends on the geometry of the solid surface, on the hydrodynamic conditions in the vicinity of the catalyst (which are a function, e.g., of the reactor type, geometry, operating conditions, flow regime), and it also depends on the diffusivity of the gas species. Correlations for the mass-transfer coefficient are a large topic and outside the scope of this section. For more details see Bird, Stewart, and Lightfoot, *Transport Phenomena*, 2d ed., John Wiley & Sons, New York, 2002, and relevant sections in this handbook. For non-first-order kinetics a closed-form relationship such as the series of resistances cannot always be derived, but the steady-state assumption of the consecutive mass and reaction steps still applies.

Intraparticle Diffusion As indicated above, the larger the catalyst surface area per unit reaction volume a_s , the larger the overall reaction rate. For a fixed mass of catalyst, decreasing the particle size increases the total external surface area available for the reaction. Another way to increase the surface area is by providing a porous catalyst with lots of internal surface area. The internal structure of the catalyst determines how accessible these internal sites are to the gas-phase reactant and how easily can the products escape back to the gas. The analysis is based on the pseudo-homogeneous reaction diffusion equation, with the gas reactant diffusing through the pores and reacting at active sites inside the catalyst particle. For a first-order irreversible reaction of species A in an infinite slab geometry, the diffusion-reaction equations describe the decreasing reactant concentration from the external surface to the center of the slab:

$$\begin{aligned} D_{ea} \frac{d^2 C_{ay}}{dy^2} - k C_{ay} &= 0 & C_{ay}(L) &= C_{as} \\ \frac{dC_{ay}}{dy} &= 0 \end{aligned} \quad (7-97)$$

The concept of effectiveness factor has been developed to calculate the overall reaction rate in terms of the concentration at the external surface C_{as} :

$$r = \eta k C_{as} \quad (7-98)$$

Hence the effectiveness factor is the ratio of the actual rate to that if the reactions were to occur at the external surface concentration, i.e., in absence of intraparticle diffusion resistance:

$$\eta = \frac{(1/L) \int_0^L r(C_{ay}) dy}{r(C_{as})} = \frac{\text{rate with pore diffusion resistance}}{\text{rate at external surface conditions}} \quad (7-99)$$

The effectiveness factor can be written as a function of a dimensionless independent variable called the Thiele modulus, which for a first-order reaction is defined below together with the corresponding effectiveness factor derived by integration of the corresponding diffusion-reaction equation (7-97):

$$\phi_{\text{slab}} = L \sqrt{\frac{k}{D_{ea}}} \quad \eta = \frac{\tanh \phi_{\text{slab}}}{\phi_{\text{slab}}} \quad (7-100)$$

Since the model is pseudo-homogeneous, there is no distinction

between the gas-filled pores and the solid parts of the particle. For most catalysts (except for straight channel monoliths), the diffusion path is not straight and has varying cross section. Hence, the effective diffusivity of A is defined based on the catalyst internal structure and the gas diffusivity of A in the gas mixture as follows:

$$D_{ea} = \frac{\epsilon_s}{\tau} D_a \quad (7-101)$$

The parameters that describe the pore structure are the porosity ϵ_s , accounting for the fact that diffusion only occurs through the gas-filled part of the particle, and the tortuosity τ accounting for the effect of diffusion path length and contraction/expansion of pores along the diffusion path. The diffusion regime depends on the diffusing molecule, pore size, and operating conditions (concentration, temperature, pressure), and this can be visualized in Fig. 7-7. As indicated, the effective diffusion coefficient ranges over many orders of magnitude from very low values in the configurational regime (e.g., in zeolites) to high values in the regular regime.

There is a large body of literature that deals with the proper definition of the diffusivity used in the intraparticle diffusion-reaction model, especially in multicomponent mixtures found in many practical reaction systems. The reader should consult references, e.g., Bird, Stewart, and Lightfoot, *Transport Phenomena*, 2d ed., John Wiley & Sons, New York, 2002; Taylor and Krishna, *Multicomponent Mass Transfer*, Wiley, 1993; and Cussler, *Diffusion Mass Transfer in Fluid Systems*, Cambridge University Press, 1997.

The larger the characteristic length L , the larger the Thiele modulus, the smaller the effectiveness factor, and the steeper the reactant concentration profile in the catalyst particle. A generalized characteristic length definition V_p/S_{px} (particle volume/external particle surface area) brings together the η - ϕ curves for a variety of particle shapes, as illustrated in Table 7-6 and Fig. 7-8 for for slabs, cylinders, and spheres. Here I_0 and I_1 are the corresponding modified Bessel functions of the first kind.

Further generalization of the Thiele modulus and effectiveness factor for a general global reaction and various shapes is

$$\phi = \frac{(V_p/S_{px}) r_a(C_{as})}{\sqrt{\frac{1}{2} \int_{C_{ae}}^{C_{as}} D_{ea}(C_{ay}) r_a(C_{ay}) dC_{ay}}} \quad (7-102)$$

In Eq. (7-102) component A is the limiting reactant. For example, for an n th-order irreversible reaction

$$\phi = \frac{V_p}{S_{px}} \sqrt{\frac{(n+1) k C_{as}^{n-1}}{2 D_{ea}}} \quad (7-103)$$

This generalized Thiele modulus works well with the effectiveness factors for low and high values of the Thiele modulus, but it is not as accurate for intermediate values. However, these differences are not significant, given the uncertainties associated with measuring some of the other key parameters that go into the calculation of the Thiele modulus, e.g., the effective diffusivity and the intrinsic rate constant.

Effect of Intraparticle Diffusion on Observed Order and Activation Energy Taking the n th-order reaction case in the limit of intraparticle diffusion control, i.e., large Thiele modulus, the effectiveness factor is

$$\eta = \frac{1}{\phi} \quad (7-104)$$

the observed rate is

$$r_{\text{obs}} = \eta r = \frac{S_{px}}{V_p} \sqrt{\frac{2 D_{ea} k}{(n+1)}} C_{as}^{(n+1)/2} \quad (7-105)$$

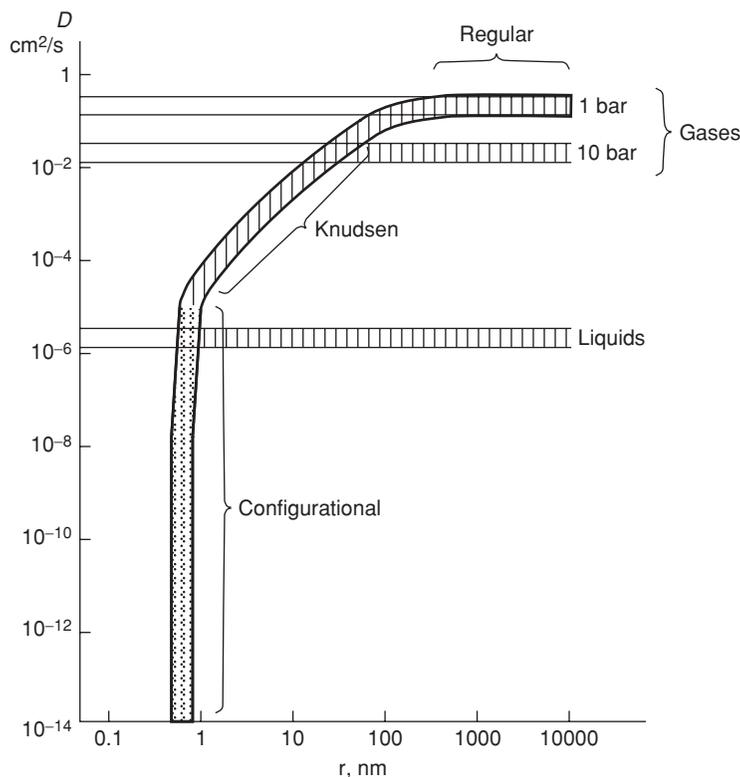


FIG. 7-7 Diffusion regimes in heterogeneous catalysts. [From Weisz, *Trans. Fara. Soc.* **69**: 1696–1705 (1973); Froment and Bischoff, *Chemical Reactor Analysis and Design*, Wiley, 1990, Figure 3.5.1-1.]

and the observed rate constant is

$$k_{\text{obs}} = \eta k = \frac{S_{px}}{V_p} \sqrt{\frac{2}{n+1} D_{\text{eff}} e^{(E_D/RT)} k_0 e^{(E/RT)}} \quad (7-106)$$

Hence, the observed order and activation energy differ from those of the intrinsic n th-order kinetics:

$$n_{\text{obs}} = \frac{n+1}{2} \quad E_{\text{obs}} = \frac{E + E_D}{2} \approx \frac{E}{2} \quad (7-107)$$

Here E_D is the activation energy for diffusion.

TABLE 7-6 Effectiveness Factors for Different Shapes for a First-Order Reaction

Shape	V_p/S_{px}	Effectiveness factor η
Infinite slab	R	$\frac{\tanh \phi}{\phi}$
Infinite cylinder	$R/2$	$\frac{I_1(2\phi)}{\phi I_0(2\phi)}$
Sphere	$R/3$	$\frac{1}{\phi} \left(\frac{3}{\tanh 3\phi} - \frac{1}{\phi} \right)$

The observed and intrinsic reaction order is the same under intraparticle diffusion control only for a first-order reaction. Weisz and Prater [“Interpretation of Measurements in Experimental Catalysis,” *Adv. Catal.* **6**: 144 (1954)] developed general estimates for the observed order and activation energy over the entire range of ϕ :

$$n_{\text{obs}} = n + \frac{n-1}{2} \frac{d \ln \eta}{d \ln \phi} \quad E_{\text{obs}} = E + \frac{E - E_D}{2} \frac{d \ln \eta}{d \ln \phi} \quad (7-108)$$

Weisz and Prater [“Interpretation of Measurements in Experimental Catalysis,” *Adv. Catal.* **6**: 144 (1954)] also developed a general criterion for diffusion limitations, which can guide the lab analysis of rate data:

$$\text{If } \Phi = \left(\frac{3V_p}{S_{px}} \right)^2 \frac{r_{\text{obs}}}{D_{\text{eff}} C_{\text{as}}} \gg 1 \quad \text{then diffusion-limited} \\ \ll 1 \quad \text{then no diffusional resistance} \quad (7-109)$$

Effect of Intraparticle Diffusion for Reaction Networks

For multiple reactions, intraparticle diffusion resistance can also affect the observed selectivity and yield. For example, for consecutive reactions intraparticle diffusion resistance reduces the yield of the intermediate (often desired) product if both reactions have the same order. For parallel reactions diffusion resistance reduces the selectivity to the higher-order reaction. For more details see, e.g., Carberry, *Chemical and Catalytic Reaction Engineering*, McGraw-Hill, 1976; and Levenspiel, *Chemical Reaction Engineering*, 3d ed., Wiley, 1999.

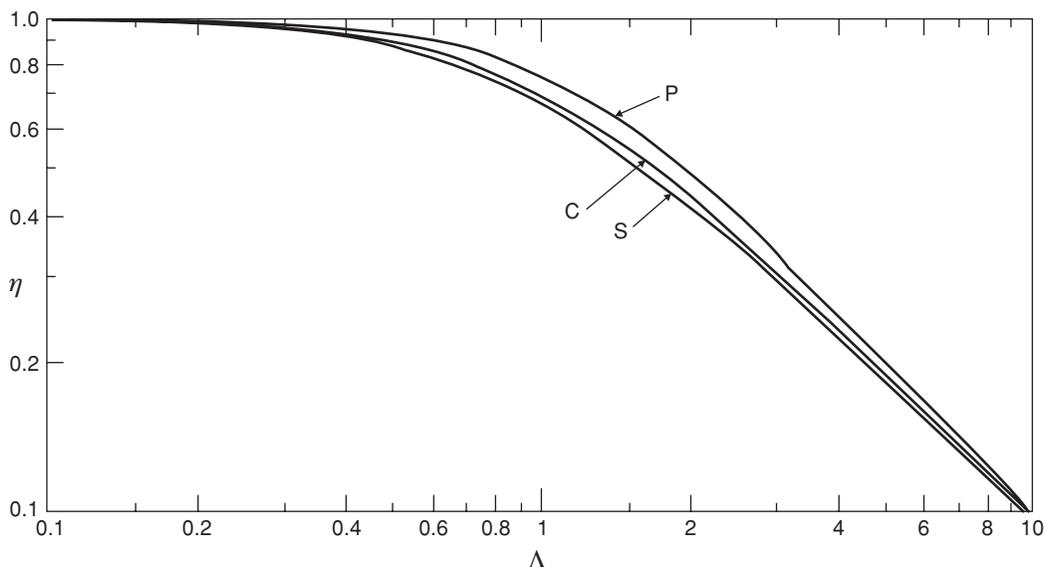


FIG. 7-8 Effectiveness factors for a slab (P), a cylinder (C), and a sphere (S). [Adapted from Fig. 1 in Aris and Rester, "The Effect of Shape on the Effectiveness Factor," Chem. Eng. Sci. **24**: 793 (1969).]

For more complex reactions, the effect of intraparticle diffusion resistance on rate, selectivity, and yield depends on the particulars of the network. Also, the use of the Thiele modulus–effectiveness factor relationships is not as easily applicable, and numerical solution of the diffusion-reaction equations may be required.

Intraparticle Diffusion and External Mass-Transfer Resistance For typical industrial conditions, external mass transfer is important only if there is substantial intraparticle diffusion resistance. This subject has been discussed by Luss, "Diffusion-Reaction Interactions in Catalyst Pellets," in Carberry and Varma (eds.), *Chemical Reaction and Reactor Engineering*, Dekker, 1987. This, however, may not be the case for laboratory conditions, and care must be exerted in including the proper data interpretation. For instance, for a spherical particle with both external and internal mass-transfer limitations and first-order reaction, an overall effectiveness factor η_i can be derived, indicating the series-of-resistances nature of external mass transfer followed by intraparticle diffusion-reaction:

$$\frac{1}{\eta_i} = \frac{1}{\eta} + \frac{\phi^2}{3Sh'} \quad (7-110)$$

$$Sh' = \frac{\epsilon k_p R}{D_{ca}} \quad (7-111)$$

As indicated above, intraparticle diffusion lowers the apparent activation energy. The apparent activation energy is even further lowered under external mass-transfer control. Figure 7-9 illustrates how the rate-controlling step changes with temperature, and as a result the dependence of the apparent first-order rate constant on temperature also changes, from a very strong dependence under kinetic control to virtual independence under external mass-transfer control.

Note that in the limit of external diffusion control, the activation energy $E_{obs} \rightarrow 0$, as can be shown when substituting Eq. (7-110) in Eq. (7-108). For more details on how to represent the combined effect of external and intraparticle diffusion on effectiveness factor for more complex systems, see Luss, "Diffusion-Reaction Interactions in Catalyst Pellets."

Heat-Transfer Resistances A similar analysis regarding external and intraparticle heat-transfer limitations leads to temperature

gradients which add further complexity to the behavior of heterogeneous catalytic systems, including steady-state multiplicity. More details are given in Sec. 19.

Catalyst Deactivation The catalyst life ranges from seconds to minutes to a few days to several years, as the active surface of a catalyst is degraded by chemical, thermal, or mechanical factors. *Chemical deactivation* occurs due to feed or product poisoning or masking. Poisoning may be due to compounds such as P, S, As, Na, and Bi that have free electron pairs and is generally considered irreversible. In some cases a reduced life is simply accepted, as in the case of slow accumulation of trace metals from feed to catalytic cracking; but in other cases the deactivation is too rapid. Sulfur and water are removed from feed to ammonia synthesis, sulfur from feed to platinum reforming, and arsenic from feed to SO_2 oxidation with platinum. Masking may be due to covering of the active sites by contaminants in either the feed or products. Examples of feed masking agents can include Si (from organic silicons) and rust. An example of product masking is coking. Reactivation sometimes is done in place;

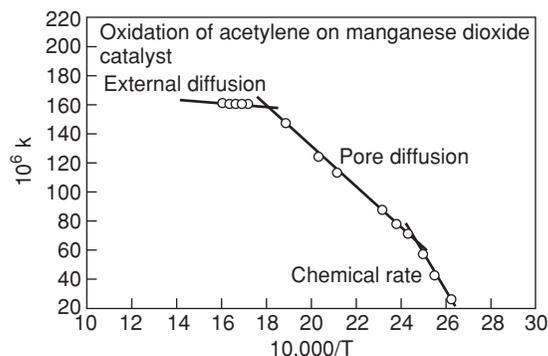


FIG. 7-9 Dependence of the rate-controlling step on temperature.

for instance, coke is burned off cracking catalyst or off nickel and nickel-molybdenum catalysts in a fluidized reactor/regenerator system. *Thermal deactivation* is primarily due to rearrangement of the active sites at high temperature due to *sintering*. Sintering results in agglomeration of active ingredients (lower dispersion). In most cases sintering is irreversible; however Pt/Al₂O₃ catalysts have been regenerated in place by Cl₂ treatment. The catalyst also can be modified by additives, for instance, chromia to nickel to prevent sintering, rhenium to platinum to reduce coking, and so on. *Mechanical deactivation* may be caused by attrition or erosion and subsequent loss of catalyst as fines. The attrition resistance of catalysts is related to the nature of the support and its porosity.

For additional references, see, e.g., Thomas, *Catalytic Processes and Proven Catalysts*, Academic Press, 1970; Butt and Petersen, *Activation, Deactivation and Poisoning of Catalysts*, Academic Press, 1988; and Delmon and Froment, *Catalyst Deactivation*, Elsevier, 1980.

The *activity* α at any time on stream may be simply defined as the ratio of the rate at time t to the rate with fresh catalyst

$$\alpha = \frac{r(t)}{r(t=0)} \quad (7-112)$$

The rate of destruction of active sites and pore structure can be expressed as a kinetic relation that can be generally first- or second-order. For instance, for a second-order dependence,

$$\frac{d\alpha}{dt} = -k_d \alpha^2 \quad (7-113)$$

the corresponding integral is

$$\alpha = \frac{1}{1 + k_d t} \quad (7-114)$$

This type of deactivation mechanism often applies catalyst sintering and coke deactivation. The deactivation rate constant is expected to have an Arrhenius dependence on temperature.

When the feedstock contains constant proportions of reactive impurities, the rate of decline may also depend on the concentration of the main reactant, e.g., for a power law rate

$$\frac{d\alpha}{dt} = -k_d \alpha^p C^q \quad (7-115)$$

Such a differential equation must be solved simultaneously with a rate equation for the main reactant.

The deactivation rate constants are estimated by methods like those for finding constants of any rate equation, given suitable (α, t) data. There are different chemical deactivation mechanisms—two of the most common are described below. For more details see Butt and Petersen, *Activation, Deactivation and Poisoning of Catalysts*, Academic Press, 1988; and Froment and Bischoff, *Chemical Reactor Analysis and Design*, Wiley, 1990. In *uniform deactivation*, the poison is distributed uniformly throughout the pellet and degrades it gradually. In *pore mouth (shell progressive) poisoning*, the poison is so effective that it kills the active site as it enters the pore; hence complete deactivation begins at the mouth and moves gradually inward.

Uniform Deactivation When uniform deactivation occurs, the specific rate declines by a factor $1 - \beta$, where β is the fractional poisoning. β is calculated from the poisoning rate, and it is often assumed to be proportional to the concentration of the poison in the bulk fluid. Then a power law rate equation becomes

$$r = k(1 - \beta)\eta C_s^n \quad (7-116)$$

The effectiveness depends on β through the Thiele modulus

$$\phi = L \sqrt{\frac{k(1 - \beta)C_s^{n-1}}{D_e}} \quad (7-117)$$

To find the effectiveness under poisoned conditions, this form of the Thiele modulus is substituted into the appropriate relation for effectiveness. For example, for a first-order reaction in slab geometry, the effectiveness factor is

$$\eta = \frac{\tanh \phi}{\phi} = \frac{\tanh[L\sqrt{k(1 - \beta)/D_e}]}{L\sqrt{k(1 - \beta)/D_e}} \quad (7-118)$$

Figure 7-10a shows the ratio of the effectiveness factor with uniform poisoning to that without poisoning versus the fraction poisoned for the above case of first-order reaction in a slab.

Pore Mouth (or Shell Progressive) Poisoning This mechanism occurs when the poisoning of a pore surface begins at the mouth of the pore and moves gradually inward. This is a moving boundary problem, and the pseudo-steady-state assumption is made that the boundary moves slowly compared with diffusion of poison and reactants and reaction on the active surface. β is the fraction of the pore that is deactivated. The poison diffuses through the dead zone and deposits at the interface between the dead and active zones. The reactants diffuse across the dead zone without reaction, followed by diffusion-reaction in the active zone.

Figure 7-10b shows simulation results for the ratio of the effectiveness factor with pore mouth poisoning to that without poisoning for a first-order reaction in a slab.

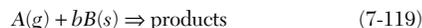
GAS-SOLID NONCATALYTIC REACTIONS

Examples of gas-solid noncatalytic reactions include production of iron from iron ores, roasting of sulfide oxides, combustion of solid fuels, chlorination of Ti ores to make TiCl₄ in the production of TiO₂ pigments, incineration of waste, decomposition of solids to produce gases, e.g., solid propellants and explosives. The kinetic treatment of these reactions has to take into consideration external mass transfer and intraparticle diffusion just as in the case of gas-solid catalytic reactions. However there are major differences, the primary one being consumption of the solid reactant, making the conditions inside the solid particle transient in nature, including change in unreacted particle size, particle density, porosity, etc. For more details see, e.g., Wen ["Noncatalytic Heterogeneous Solid-Fluid Reaction Models," *Ind. Eng. Chem.* **60**(9):34-54 (1968)], Szekeley (in Lapidus and Amundson (eds.), *Chemical Reactor Theory—A Review*, Prentice-Hall, 1977), Doraiswamy and Kulkarni [in Carberry and Varma (eds.), *Chemical Reaction and Reactor Engineering*, Dekker, 1987], and Levenspiel (*Chemical Reaction Engineering*, 3d ed., Wiley, 1999).

The basic steps are identical to those of catalytic gas-solid reactions. However, as indicated above, the process is transient (non-steady-state) due to change in particle size and properties as the reaction progresses.

Several models that describe gas-solid noncatalytic reactions are summarized in Table 7-7. The first two, the sharp interface and volume reaction models, are pseudo-homogeneous, form part of the class of shrinking core models, and can be treated by using the Thiele modulus and effectiveness factor concept. The last three are heterogeneous models.

Sharp Interface Model For a first-order reaction in gas reactant,

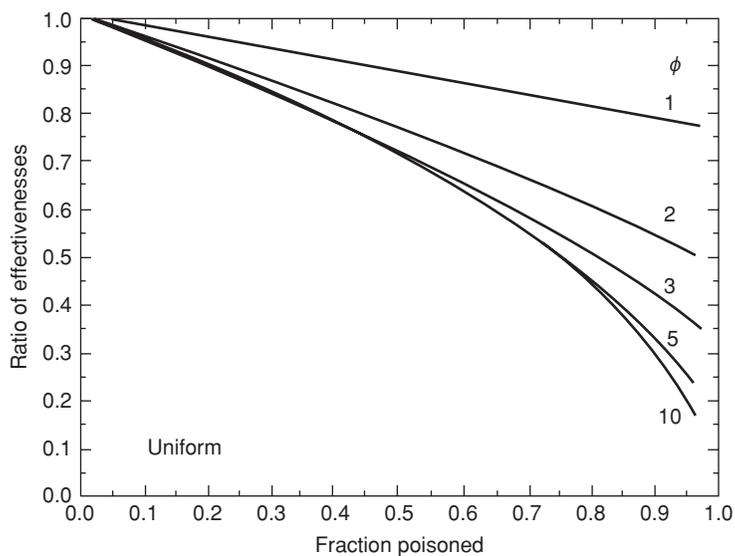


a rate of conversion of the solid B per unit particle volume of

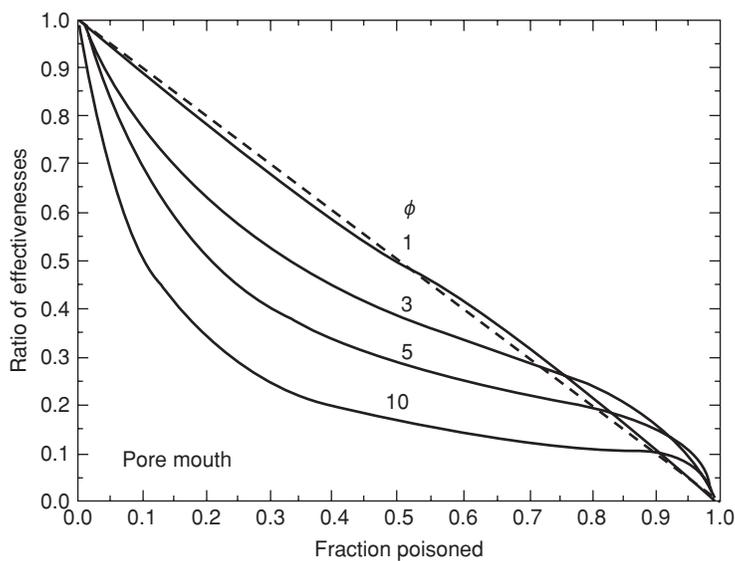
$$r_b = kC_{a0}C_s \quad (7-120)$$

and assuming pseudo-steady state for the gas-phase component, it can be shown that

$$r_{\text{obs}} = \frac{C_{a0}}{\frac{1}{k_p a_p} + \frac{R_p^2}{D_{ca}} \left(\frac{R_p}{R_s} - 1 \right) + \frac{b}{kC_{a0}}} \quad (7-121)$$



(a)



(b)

FIG. 7-10 Poisoning of a first-order reaction. (a) Uniform poisoning. (b) Pore mouth poisoning.

where R_p and R_s are the particle and solid core radii, a_p is the external particle diameter-based interfacial area per particle volume, and k is based on particle volume. Equation (7-121) represents three resistances in series—external mass transfer, diffusion in the reacted (ash) zone, and reaction at the unreacted solid-ash interface.

The conversion of the solid reactant B is obtained from integration of the pseudo-steady-state diffusion model with reaction at the boundary:

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{ea} r^2 \frac{\partial C_{as}}{\partial r} \right) &= 0 \\ D_{ea} \frac{\partial C_{as}}{\partial r} &= \frac{1}{b} k C_{as} C_s \quad \text{at } r = R_s, \\ D_{ea} \frac{\partial C_{as}}{\partial r} &= k_s (C_{a0} - C_{as}) \quad \text{at } r = R_p \end{aligned} \quad (7-122)$$

TABLE 7-7 Noncatalytic Gas-Solid Reaction-Diffusion Models

Model	Main features
Sharp interface model (SIM)	Reacting solid is nonporous. Reacted solid ash is porous. Reaction occurs at the ash-unreacted solid interface.
Volume reaction model	Reacting solid is also porous. Reaction occurs everywhere in the particle.
Grain model	Particle is divided into identical solid spherical grains. Each grain reacts according to the sharp interface model.
Crackling core model	Combination of SIM and grain model.
Nucleation model	Nucleation of metals in metal reduction reactions.

The moving boundary radius R_c is determined from a material balance that relates the unreacted solid volume to the reaction rate. Integration gives the time τ required to achieve a given conversion of the solid B , X_b :

$$\tau = \frac{R_p C_{s0}}{b C_{a0}} \left\{ \frac{1}{3} \left(\frac{1}{k_s} - \frac{R_p}{D_{ea}} \right) X_b + \frac{R_p}{2 D_{ea}} \left[1 - (1 - X_b)^{2/3} \right] + \frac{3b}{C_{s0} R_p k} \left[1 - (1 - X_b)^{1/3} \right] \right\} \quad X_b = 1 - \left(\frac{R_c}{R_p} \right)^3 \quad (7-123)$$

Similar solutions can be obtained for other shapes (Doraiswamy and Kulkarni, in Carberry and Varma (eds.), *Chemical Reaction and Reactor Engineering*, Dekker, 1987). Figure 7-11 shows typical concentration profiles for this case.

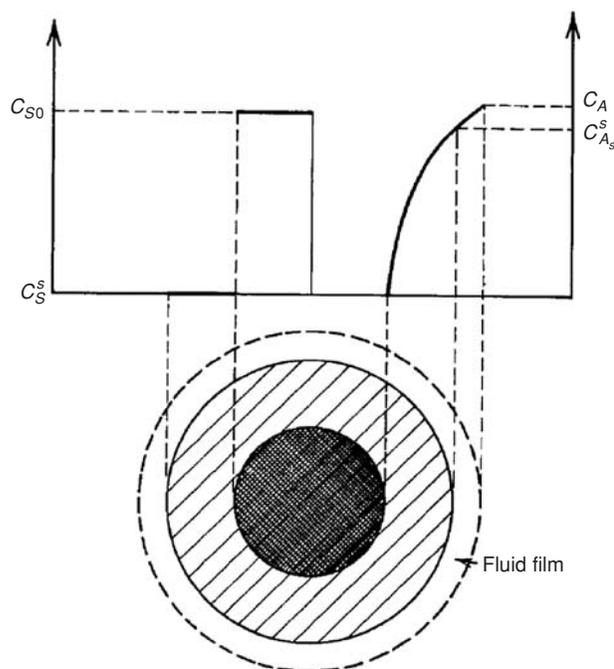


FIG. 7-11 Sharp interface model—concentration profiles. [From Wen, "Noncatalytic Heterogeneous Solid-Fluid Reaction Models," *Ind. Eng. Chem.* **60**(9): 34-54 (1968), Fig. 1.]

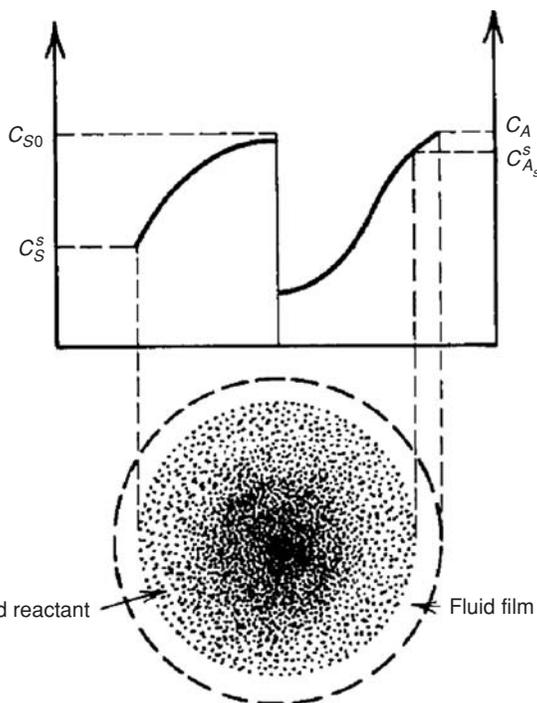


FIG. 7-12 Typical concentration profiles for the volume reaction model. [From Wen, "Noncatalytic Heterogeneous Solid-Fluid Reaction Models," *Ind. Eng. Chem.* **60**(9): 34-54 (1968), Fig. 3.]

Volume Reaction Model A typical concentration profile for the volume reaction model is shown in Fig. 7-12.

A general transient model of diffusion-reaction that uses the effective diffusivity concept described for gas-solid catalytic reactions can be derived here as well, e.g., for a spherical particle:

$$\frac{\partial(\epsilon_s C_{as})}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{ea} r^2 \frac{\partial C_{as}}{\partial r} \right) - r_a \quad \frac{\partial C_s}{\partial t} = -r_s$$

$$C_{as} = C_{as0} \quad C_s = C_{s0} \quad \text{at } t = 0 \quad \frac{\partial C_{as}}{\partial r} = 0 \quad \text{at } r = 0$$

$$D_{ea} \frac{\partial C_{as}}{\partial r} \Big|_{r=R} = k_s (C_a - C_{as}|_{r=R}) \quad (7-124)$$

$$\epsilon_s = \epsilon_{s0} + C_{s0}(v_s - v_p) \left(1 - \frac{C_s}{C_{s0}} \right) \quad \frac{D_{ea}}{D_{ea0}} = \left(\frac{\epsilon_s}{\epsilon_{s0}} \right)^\beta, \quad \beta = 2 - 3 \quad (7-125)$$

Here the porosity and the diffusivity vary with conversion of solid; v_s and v_p are the reactant and product molar volumes. A Thiele modulus ϕ and dimensionless time θ can be defined, e.g., for a rate second-order in A and first-order in S:

$$r = k C_a^2 C_s \quad (7-126)$$

$$\phi = R \sqrt{\frac{k C_{as}(R) C_{s0}}{D_{ea0}}} \quad \theta = b k C_{as0}^2 t \quad (7-127)$$

For the given rate expression, equations (7-124) to (7-127) can be numerically integrated, e.g., in Fig. 7-13 for reaction control and Fig. 7-14 for intraparticle diffusion control, both with negligible external mass-transfer resistance; x is the fractional conversion.

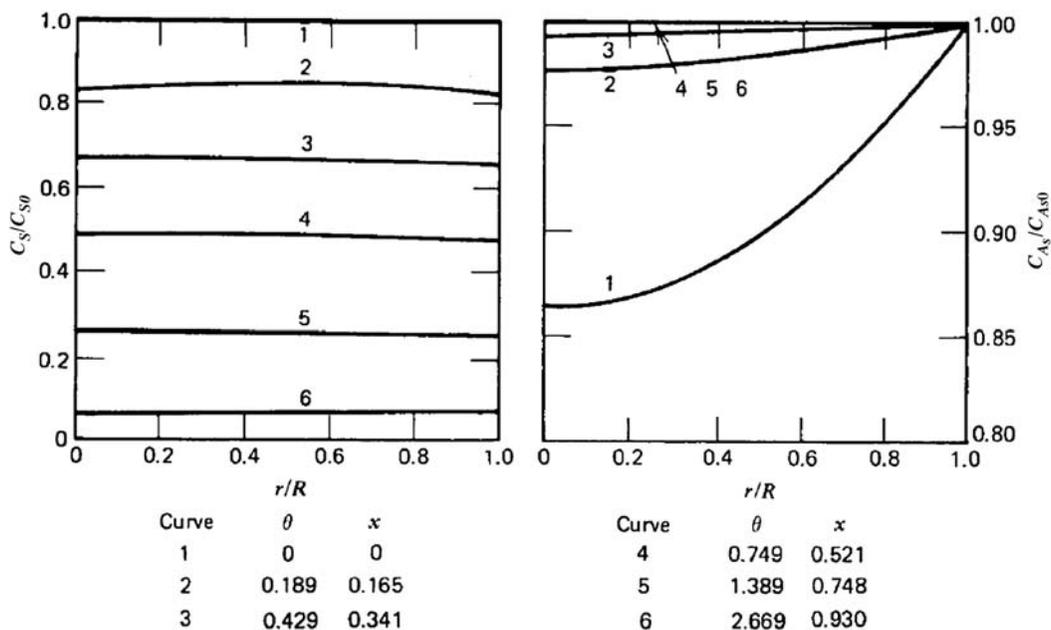


FIG. 7-13 Concentration profiles with reaction control $\phi = 1$, in absence of gas particle mass-transfer resistance. [From Wen, "Noncatalytic Heterogeneous Solid-Fluid Reaction Models," Ind. Eng. Chem. **60**(9): 34-54 (1968), Fig. 11.]

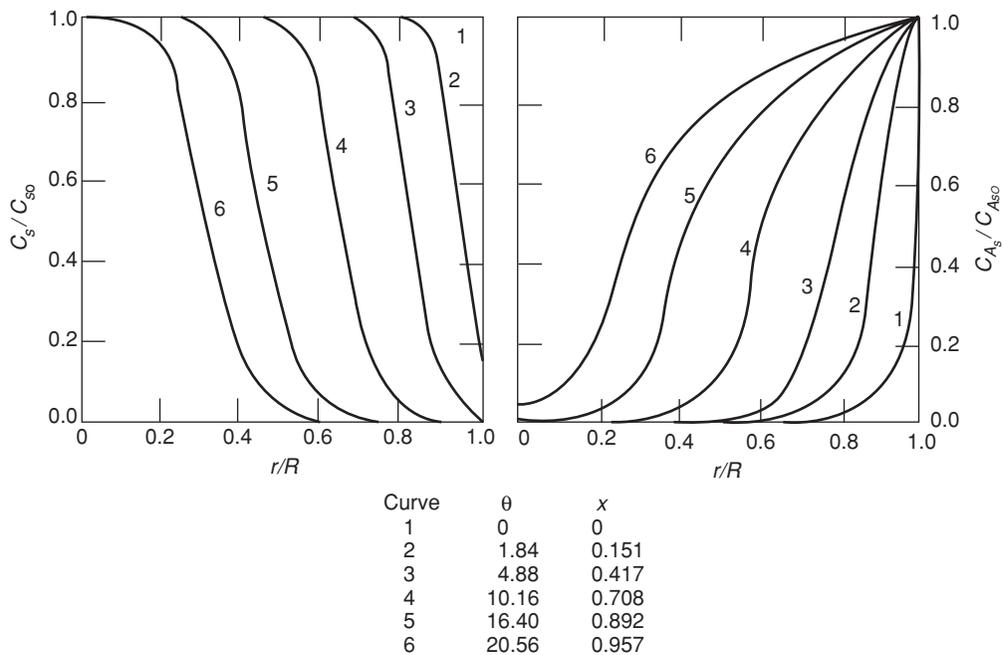


FIG. 7-14 Concentration profiles with intraparticle diffusion control, $\phi = 70$, in absence of gas particle mass-transfer resistance. [From Wen, "Noncatalytic Heterogeneous Solid-Fluid Reaction Models," Ind. Eng. Chem. **60**(9): 34-54 (1968), Fig. 12.]

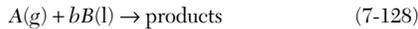
GAS-LIQUID REACTIONS

Many industrial processes employ gas-liquid reactions that can be either noncatalytic or homogeneously catalyzed. These include, for instance, absorption of acid gases (SO₃, NO₂, CO₂), chlorinations (benzene, dodecane, toluene), oxidations (P-Xylene to terephthalic acid, cyclohexane to cyclohexanone and cyclohexanol, acetaldehyde to acetic acid), hydrogenations (olefins, esters to fatty acids), and hydroformylation of olefins to alcohols, to name a few. See also Sec. 19 and Shah (*Gas-Liquid-Solid Reactor Design*, McGraw-Hill, 1979). These reactions include gas reactants dissolving in a liquid and reacting there with a liquid reactant. When determining the kinetics of such reactions from lab data, one needs to understand the mechanism and the controlling steps, just as was the case for heterogeneous gas-solid reactions. The simplest model is the two-film model, and it involves the following consecutive steps for the gaseous reactant:

1. Mass transfer of gas reactant from bulk gas to the gas-liquid interface across the gas film.
2. At the gas-liquid interface, the liquid and gas concentrations of the gaseous reactant are assumed to be at thermodynamic equilibrium.
3. Mass transfer of the dissolved gas reactant to the bulk liquid across the liquid film—if the reaction is fast, the reaction will occur both in the liquid film (in parallel with diffusion) and in the bulk liquid.

For a volatile liquid reactant or a volatile product, these steps are essentially reversed. For a nonvolatile liquid reactant or product, only the reaction and diffusion in the liquid take place. Figure 7-15 describes the absorbing gas concentration profiles in a gas-liquid system.

For a general gas-liquid reaction:



the two-film pseudo-steady-state model is described by the following fluxes across the interface for the gaseous reactant A:

$$N_{aG} = \frac{D_{aG}}{\delta_G} (P_a - P_{ai}) = k_G (P_a - P_{ai}) = N_{aL} = \frac{D_{aL}}{\delta_L} (C_{Lai} - C_{La}) = k_L (C_{Lai} - C_{La}) \quad (7-129)$$

Here the subscript *L* denotes liquid, *G* denotes gas, *i* denotes the gas-liquid interface (where the gas and liquid concentrations are in equilibrium). The thickness of the liquid and gas films is not a directly measurable quantity, and instead mass-transfer coefficients are

defined as indicated above. These depend on the diffusivity of the molecule, geometry, flow, and operating conditions; and typical values can be viewed in Sec. 19. In addition to the two-film steady-state model, other more accurate, non-steady-state models have also been developed such as the surface renewal and penetration models (see, e.g., Astarita, *Mass Transfer with Chemical Reaction*, Elsevier, 1967). In many industrial cases of interest, mass-transfer resistance in the gas-film is negligible, especially considering that gas-phase diffusivities are 2 to 3 orders of magnitude larger for the same species than those in the liquid. Hence we drop the subscripts *L* and *G* from the concentrations since the concentrations considered are in the liquid phase only.

REACTION-DIFFUSION REGIMES

Depending on the relative rates of diffusion and reaction, the following diffusion-reaction regimes occur:

- $t_D \ll t_r$ slow reaction regime with reaction control
- $t_D \gg t_r$ fast reaction regime with diffusion control
- $t_D \approx t_r$ both reaction and diffusion are important

$$t_D = \frac{D_a}{k_L^2} \qquad t_r = \frac{C_{ai} - C_{ae}}{r(C_{ai})} \quad (7-130)$$

Here t_D and t_r are the diffusion and reaction times, respectively, and k_L is the mass-transfer coefficient in the absence of reaction. For the *fast reaction regime*, diffusion and reaction occur in parallel in the liquid film, while for the *slow reaction regime*, there is no reaction in the liquid film and the mass transfer can be considered to occur independently of reaction in a consecutive manner. For the slow reaction regime, the following subregimes can be defined:

- $t_m \ll t_r$ slow reaction kinetic control
- $t_m \gg t_r$ slow reaction mass-transfer control
- $t_m \approx t_r$ both reaction and mass transfer are important

$$t_m = \frac{1}{k_L a} \quad (7-131)$$

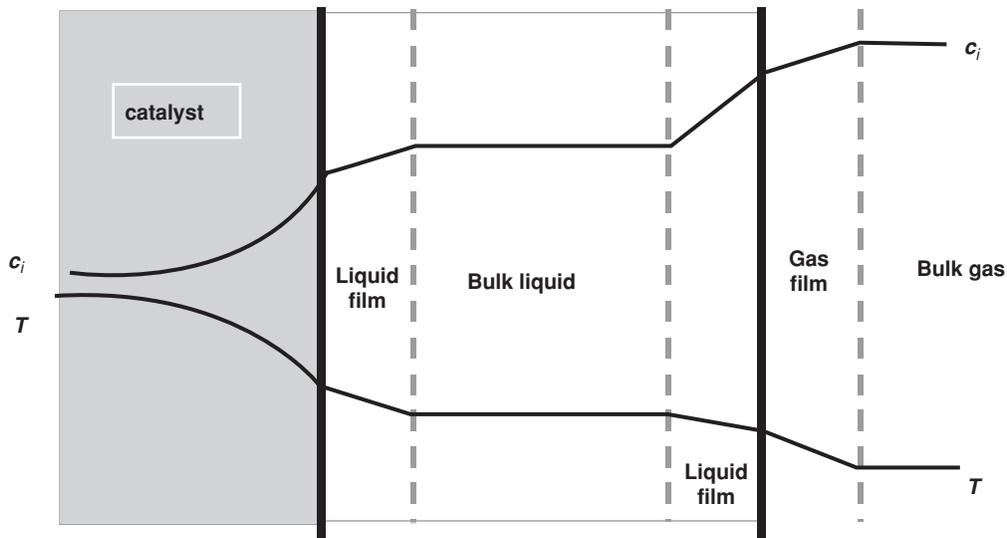


FIG. 7-15 Absorbing gas concentration and temperature profiles (exothermic reaction) in gas-liquid and gas-liquid-solid reactions.

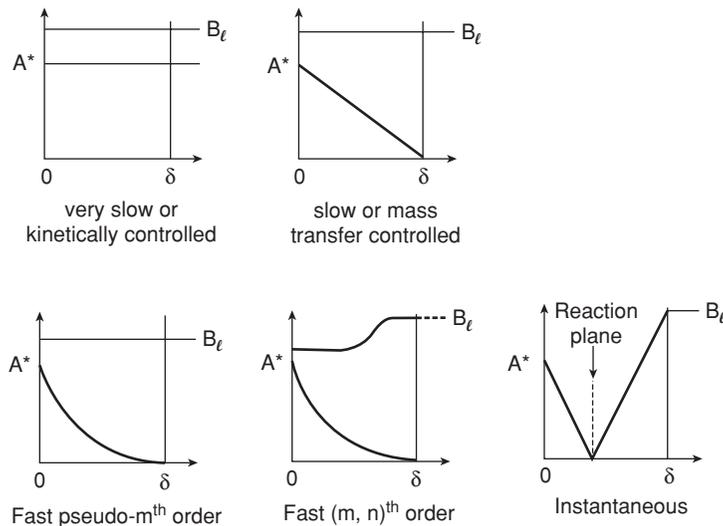


FIG. 7-16 Concentration profiles for the general reaction $A(g) + bB(l) \rightarrow \text{products}$ with the rate $r = kC_a^m C_b^n$. [Adapted from Mills, Ramachandran, and Chaudhari, "Multiphase Reaction Engineering for Fine Chemicals and Pharmaceuticals," *Rev. Chem. Eng.* 8(1-2):1 (1992), Figs. 19 and 20.]

Here t_m is the mass-transfer time. Only under *slow reaction kinetic control regime* can intrinsic kinetics be derived directly from lab data. Otherwise the intrinsic kinetics have to be extracted from the observed rate by using the mass-transfer and diffusion-reaction equations, in a manner similar to those defined for catalytic gas-solid reactions. For instance, in the *slow reaction regime*,

$$r_{a,\text{obs}} = \frac{C_{ai}}{He_a/k_G a + 1/k_1 a + 1/k} \quad (7-132)$$

$$k_{\text{obs}} = \frac{1}{He_a/k_G a + 1/k_1 a + 1/k} \quad (7-133)$$

Here He_a is the Henry constant for the solute a . For the fast reaction regime, instead of the effectiveness factor adjustment for the intrinsic reaction rate, it is customary to define an *enhancement factor* for mass-transfer enhancement by the reaction, defined as the ratio of mass transfer in presence of reaction in the liquid, to mass transfer in absence of reaction:

$$E = k_1/k_{L0} \quad (7-134)$$

Solving the diffusion-reaction equation in the liquid, the enhancement factor can be related to the *Hatta number* Ha , which is similar to the Thiele modulus defined for heterogeneous gas-solid catalysts. Thus, the Hatta number and its relation to the controlling regime are

$$Ha = \frac{t_D}{t_R} = \sqrt{\frac{\text{maximum reaction rate in the film}}{\text{maximum mass transfer rate through film}}}$$

$$Ha \ll 1 \quad \text{slow reaction regime} \quad (7-135)$$

$$Ha \gg 1 \quad \text{fast reaction regime}$$

For instance, for a first-order reaction in the gaseous reactant A (e.g., with large excess of liquid reactant B), the following relates the enhancement factor to the Hatta number:

$$Ha = \delta_L \sqrt{\frac{k}{D_a}} = \frac{\sqrt{kD_a}}{k_{L0}} \quad \text{for } C_b \gg C_{ai} \quad (7-136)$$

$$E = \frac{Ha}{\tanh Ha} \left(1 - \frac{C_a}{C_{ai}} \frac{1}{\cosh Ha} \right) > 1 \quad (7-137)$$

When both A and B have comparable concentrations, then the enhancement factor is an increasing function of an additional parameter:

$$\lambda = \frac{D_b C_b}{b D_a C_{ai}} \quad (7-138)$$

In the limit of an instantaneous reaction, the reaction occurs at a plane where the concentration of both reactants A and B is zero and the flux of A equals the flux of B . The criterion for an instantaneous reaction is

$$Ha^{1/2} \gg \frac{C_b}{b C_{ai}} \quad E_{\infty} = 1 + \lambda \gg 1 \quad (7-139)$$

Figure 7-16 illustrates typical concentration profiles of A and B for the various diffusion-reaction regimes.

GAS-LIQUID-SOLID REACTIONS

GAS-LIQUID-SOLID CATALYTIC REACTIONS

Many solid catalyzed reactions take place with one of the reactants absorbing from the gas phase into the liquid and reacting with a liquid reactant on the surface or inside the pores of a solid catalyst (see Fig. 7-15). Examples include the Fischer-Tropsch synthesis of hydrocarbons from synthesis gas (CO and H_2) in the presence of Fe or Co -

based heterogeneous catalysts, methanol synthesis from synthesis gas ($\text{H}_2 + \text{CO}$) in the presence of heterogeneous CuO/ZnO catalyst, and a large number of noble metal catalyzed hydrogenations among others. For a slow first-order reaction of a gaseous reactant, the concept of resistances in series can be expanded as follows, e.g., for a slurry reactor with fine catalyst powder:

$$r_{a, \text{obs}} = \frac{C_{ai}}{\frac{H_e}{k_c a} + \frac{1}{k_{1a}} + \frac{1}{k_{2a_s}} + \frac{1}{k}} \quad k_{\text{obs}} = \frac{1}{\frac{H_e}{k_c a} + \frac{1}{k_{1a}} + \frac{1}{k_{2a_s}} + \frac{1}{k}} \quad (7-140)$$

Intraparticle diffusion resistance may become important when the particles are larger than the powders used in slurry reactors, such as for catalytic packed beds operating in trickle flow mode (gas and liquid downflow), in upflow gas-liquid mode, or countercurrent gas-liquid mode. For these the effectiveness factor concept for intraparticle diffusion resistance has to be considered in addition to the other resistances present. See more details in Sec. 19.

POLYMERIZATION REACTIONS

Polymers are high-molecular-weight compounds assembled by the linking of small molecules called monomers. Most polymerization reactions involve two or three phases, as indicated below. There are several excellent references dealing with *polymerization kinetics* and reactors, including Ray in Lapidus and Amundson, (eds.), *Chemical Reactor Theory—A Review*, Prentice-Hall, 1977; Tirrel et al. in Carberry and Varma (eds.), *Chemical Reaction and Reactor Engineering*, Dekker, 1987; and Meyer and Keurentjes (eds.), *Handbook of Polymer Reaction Engineering*, Wiley, 2005.

Polymerization can be classified according to the main phase in which the reaction occurs as liquid (most polymerizations), vapor (e.g., Ziegler Natta polymerization of olefins), and solid phase (e.g., finishing of melt step polymerization). Polymerization reactions occur in liquid phase and can be further subclassified into

1. Bulk mass polymerization:
 - a. Polymer soluble in monomer
 - b. Polymer insoluble in monomer
 - c. Polymer swollen by monomer
2. Solution polymerization
 - a. Polymer soluble in solvent
 - b. Polymer insoluble in solvent
3. Suspension polymerization with initiator dissolved in monomer
4. Emulsion polymerization with initiator dissolved in dispersing medium

Polymerization can be catalytic or noncatalytic, and can be homogeneously or heterogeneously catalyzed. Polymers that form from the liquid phase may remain dissolved in the remaining monomer or solvent, or they may precipitate. Sometimes beads are formed and remain in suspension; sometimes emulsions form. In some processes solid polymers precipitate from a fluidized gas phase. Polymerization processes are also characterized by extremes in temperature, viscosity, and reaction times. For instance, many industrial polymers are mixtures with molecular weights of 10^4 to 10^7 . In polymerization of styrene the viscosity increased by a factor of 10^6 as conversion increased from 0 to 60 percent. The adiabatic reaction temperature for complete polymerization of ethylene is 1800 K (3240°R). Initiators of the chain reactions have concentration as low as 10^{-8} g·mol/L, so they are highly sensitive to small concentrations of poisons and impurities.

Polymerization mechanism and kinetics require special treatment and special mathematical tools due to the very large number of similar reaction steps. Some polymerization types are briefly described next.

Bulk Polymerization The monomer and initiators are reacted with or without mixing, e.g., without mixing to make useful shapes directly. Because of viscosity limitations, stirred bulk polymerization is not carried to completion. For instance, for addition polymerization conversions as low as 30 to 60 percent are achieved, with the remaining monomer stripped out and recycled (e.g., in the case of polystyrene).

Bead Polymerization Bulk reaction proceeds in droplets of 10- to 1000- μm diameter suspended in water or other medium and insulated from each other by some colloid. A typical suspending agent is polyvinyl alcohol dissolved in water. The polymerization can be done to high conversion. Temperature control is easy because of the moderating thermal effect of the water and its low viscosity. The suspensions sometimes are unstable and agitation may be critical. Examples

are polyvinyl acetate in methanol, copolymers of acrylates and methacrylates, and polyacrylonitrile in aqueous ZnCl_2 solution.

Emulsion Polymerization Emulsions have particles of 0.05- to 5.0- μm diameter. The product is a stable latex, rather than a filterable suspension. Some latexes are usable directly, as in paints, or they may be coagulated by various means to produce very high-molecular-weight polymers. Examples are polyvinyl chloride and butadiene-styrene rubber.

Solution Polymerization These processes may retain the polymer in solution or precipitate it. Examples include polyethylene, the copolymerization of styrene and acrylonitrile in methanol, the aqueous solution of acrylonitrile to precipitate polyacrylonitrile.

Polymer Characterization The physical properties of polymers depend largely on the *molecular weight distribution (MWD)*, which can cover a wide range. Since it is impractical to fractionate the products and reformulate them into desirable ranges of molecular weights, immediate attainment of desired properties must be achieved through the correct choice of reactor type and operating conditions, notably of distributions of residence time and temperature. High viscosities influence those factors. For instance, high viscosities prevalent in bulk and melt polymerizations can be avoided with solution, bead, or emulsion operations. The interaction between the flow pattern in the reactor and the type of reaction affects the MWD. If the period during which the molecule is growing is short compared with the residence time in the reactor, the MWD in a batch reactor is broader than in a CSTR. This situation holds for many free radical and ionic polymerization processes where the reaction intermediates are very short lived. In cases where the growth period is the same as the residence time in the reactor, the MWD is narrower in batch than in CSTR. Polymerizations that have no termination step—for instance, polycondensations—are of this type. This topic is treated by Denbigh [*J. Applied Chem.*, 1:227(1951)].

Four types of MWD can be defined: (1) The *number chain length distribution (NCLD)*, relating the chain length distribution to the number of molecules per unit volume; (2) the *weight chain length distribution (WCLD)* relating the chain length distribution to the weight of molecules per unit volume; (3) the *number molecular weight distribution (NMWD)* relating the chain length distribution to molecular weight; and (4) the *weight molecular weight distribution (WMWD)* relating the weight distribution to molecular weight. Two average molecular weights and corresponding average chain lengths are typically defined: the *number average molecular weight* M_n and the corresponding *number average chain length* μ_n ; and the *weight average molecular weight* M_w and the corresponding *weight average chain length* μ_w . Their ratio is called *polydispersity* and describes the width of the molecular weight distribution.

$$M_n = \frac{w \sum_{j=1}^{\infty} j P_j}{\sum_{j=1}^{\infty} P_j} \quad \mu_n = \frac{\sum_{j=1}^{\infty} j P_j}{\sum_{j=1}^{\infty} P_j} \quad M_w = \frac{w \sum_{j=1}^{\infty} j^2 P_j}{\sum_{j=1}^{\infty} j P_j} \quad \mu_w = \frac{\sum_{j=1}^{\infty} j^2 P_j}{\sum_{j=1}^{\infty} j P_j}$$

$$\text{polydispersity} = \frac{M_w}{M_n} = \frac{\mu_w}{\mu_n} \quad (7-141)$$

The average chain lengths can be related to the *moments* λ_k of the distribution as follows:

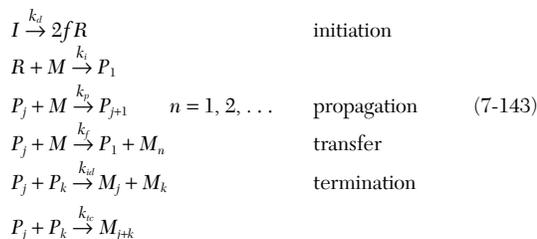
$$\mu_n = \frac{\lambda_1}{\lambda_0} \quad \mu_w = \frac{\lambda_2}{\lambda_1} \quad \text{polydispersity} = \frac{\lambda_0 \lambda_2}{\lambda_1^2} \quad \lambda_k = \sum_{j=1}^{\infty} j^k P_j \quad (7-142)$$

Here P_j is the concentration of the polymer with chain length j —the same symbol is also used for representing the polymer species P_j ; w is the molecular weight of the repeating unit in the chain.

A factor in addition to the residence time distribution and temperature distribution that affects the molecular weight distribution is the type of the chemical reaction (e.g., step or addition polymerization).

Two major polymerization mechanisms are considered: *chain growth* and *step growth*. In addition, polymerization can be *homopolymerization*—a single monomer is used—and *copolymerization* usually with two monomers with complementary functional groups.

Chain Homopolymerization Mechanism and Kinetics Free radical and ionic polymerizations proceed through this type of mechanism, such as styrene polymerization. Here one monomer molecule is added to the chain in each step. The general reaction steps and corresponding rates can be written as follows:



Here P_j is the *growing* or *live polymer*, and M_j is the *dead* or *product polymer*. Assuming reaction steps independent of chain length and assuming pseudo-steady-state approximation for the radicals lead to the following rates for monomer and initiator conversion and live polymer distribution. The growing chains distribution is the most probable distribution [see, e.g., Ray in Lapidus and Amundson (eds.), *Chemical Reactor Theory—A Review*, Prentice-Hall, 1977; Tirrel et al. in Carberry and Varma (eds.), *Chemical Reaction and Reactor Engineering*, Dekker, 1987]:

$$\begin{aligned}
 P_n &= (1 - \alpha)P\alpha^{n-1} \quad \alpha = \frac{k_p M}{(k_p + k_t)M + (k_{tc} + k_{td})P} \\
 P &= \left(\frac{2fk_d I}{k_{tc} + k_{td}} \right)^{1/2} \quad \frac{dI}{dt} = -k_d I \quad (7-144) \\
 r = \frac{dM}{dt} &= -k_p \left(\frac{2fk_d}{k_{tc} + k_{td}} \right)^{1/2} I^{1/2} M \quad DP_n^{\text{inst}} = \frac{k_p M}{(0.5k_{tc} + k_{td})P}
 \end{aligned}$$

Here r is the rate of polymerization, α is the *probability of propagation*, DP_n^{inst} is the *instantaneous degree of polymerization*, i.e., the number of monomer units on the dead polymer, and f is the *initiation efficiency*. Compare r in Eq. (7-144) with the simpler Eq. (7-68). When chain transfer is the primary termination mechanism, such as in anionic polymerization, then the polydispersity is 2.

Mathematically, the infinite set of equations describing the rate of each chain length can be solved by using the z transform method (a discrete method), *continuous variable approximation method*, or the *method of moments* [see, e.g., Ray in Lapidus and Amundson (eds.), *Chemical Reactor Theory—A Review*, Prentice-Hall, 1977].

Typical ranges of the kinetic parameters for low conversion homopolymerization are given in Table 7-8. For more details see Hutchenson in Meyer and Keurentjes (eds.), *Handbook of Polymer Reaction Engineering*, Wiley, 2005.

Step Growth Homopolymerization Mechanism and Kinetics

Here any two growing chains can react with each other. The propagation mechanism is an infinite set of reactions:



TABLE 7-8 Typical Ranges of Kinetic Parameters

Coefficient/concentration	Typical range
k_{ds} , 1/s	10^{-6} – 10^{-4}
f	0.4–0.9
k_p , L/(mol/s)	10^2 – 10^4
k_t , L/(mol/s)	10^6 – 10^8
k_{tr}/k_p	10^{-6} – 10^{-4}
I , mol/L	10^{-4} – 10^{-2}
M , mol/L	1–10

SOURCE: Hutchenson, "Typical Ranges of Kinetic Parameters," in *Handbook of Reaction Engineering*, Wiley, 2005, Table 4.1.

For instance, some nylons are produced through this mechanism. This is usually modeled under the simplifying assumption that the rate constants are independent of chain length. This assumption was proved pretty accurate, and by using the z transform it results in the *Flory distribution*:

$$\begin{aligned}
 P_n &= \frac{P_{10}(P_{10}\tau)^{n-1}}{(P_{10}\tau + 1)^{n+1}} \quad n \geq 1 \quad k_{pnm} = k_p \quad \text{for all } n, m \quad \tau = \int_0^t k_p M dt \\
 \mu_n &= \frac{2 - \alpha}{1 - \alpha} \quad \mu_w = \frac{2}{(1 - \alpha)(2 - \alpha)} \quad \text{polydispersity} = \frac{\mu_w}{\mu_n} = \frac{2}{(2 - \alpha)^2} \\
 \alpha &= \frac{P_{10}\tau}{P_{10}\tau + 1} \quad (7-146)
 \end{aligned}$$

Copolymerization Copolymerization involves more than one monomer, usually two comonomers, as opposed to the single monomer involved in the chain growth and step homopolymerization schemes above. Examples are some nylons, polyesters, and aramids. Here as well there are step growth and chain growth mechanisms, and these are much more complex [see, e.g., Ray in Lapidus and Amundson (eds.), *Chemical Reactor Theory—A Review*, Prentice-Hall, 1977].

BIOCHEMICAL REACTIONS

Mechanism and kinetics in biochemical systems describe the cellular reactions that occur in living cells. Biochemical reactions involve two or three phases. For example, aerobic fermentation involves gas (air), liquid (water and dissolved nutrients), and solid (cells), as described in the "Biocatalysis" subsection above. Bioreactors convert feeds called *substrates* into more *cells* or *biomass* (cell growth), proteins, and *metabolic products*. Any of these can be the desired product in a commercial *fermentation*. For instance, methane is converted to biomass in a commercial process to supply fish meal to the fish farming industry. Ethanol, a metabolic product used in transportation fuels, is obtained by fermentation of corn-based or sugar-cane-based sugars. There is a substantial effort to develop genetically modified biocatalysts that produce a desired metabolite at high yield.

Bioreactions follow the same general laws that govern conventional chemical reactions, but the complexity of the mechanism is higher due to the close coupling of bioreactions and *enzymes* that are turned on (*expressed*) or off (*repressed*) by the cell depending on the conditions in the fermenter and in the cell. Thus the rate expression (7-92) can mainly be used to design bioreaction processes when the culture is in *balanced growth*, i.e., for steady-state cultivations or batch growth for as long as the substrate concentration is much higher than C_s . After a sudden process upset (e.g., a sudden change in substrate concentration or pH), the *control network* of the cell that lies under the *mass flow network* is activated, and dramatic changes in the kinetics of product formation can occur. Table 7-9 summarizes key differences between biochemical and conventional chemical systems [see, e.g., Leib, Pereira, and Villadsen, "Bioreactors, A Chemical Engineering Perspective," *Chem. Eng. Sci.* **56**: 5485–5497 (2001)].

TABLE 7-9 Biological versus Chemical Systems

- There is tighter control on conditions (e.g., pH, temperature, substrate and product concentrations, dissolved O₂ concentration, avoidance of contamination by foreign organisms).
- Pathways can be turned on/off by the microorganism through expression of certain enzymes depending on the substrate type and concentration and operating conditions, leading to a richness of behavior unparalleled in chemical systems.
- The global stoichiometry changes with operating conditions and feed composition; kinetics and stoichiometry obtained from steady-state (chemostat) data cannot be used reliably over a wide range of conditions, unless fundamental models are employed.
- Long-term adaptations (mutations) may occur in response to environment changes that can alter completely the product distribution.
- Only the substrates that maximize biomass growth are utilized even in the presence of multiple substrates.
- Cell energy balance requirements pose additional constraints on the stoichiometry that can make it very difficult to predict flux limitations.

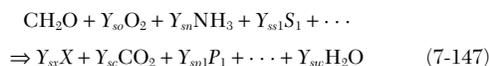
TABLE 7-10 Hierarchy of Kinetic Models in Biological Systems

- Stoichiometric black box models (similar to a single global chemical reaction) represent the biochemistry by a single global reaction with fixed stoichiometric or *yield coefficients* (limited to a narrow range of conditions). Black box models can be used over a wider range of conditions by establishing different sets of yield coefficient for different conditions. These are also needed to establish the quantitative amounts of various nutrients needed for the completion of the bioreaction.
- Unstructured models view the cell as a single component interacting with the fermentation medium, and each bioreaction is considered to be a global reaction, with a corresponding empirical rate expression.
- Structured models include information on individual reactions or groups of reactions occurring in the cell, and cell components such as DNA, RNA, and proteins are included in addition to the primary metabolites and substrates (see, e.g., the active cell model of Nielsen and Villadsen, *Bioreaction Engineering Principles*, 2d ed., Kluwer Academic/Plenum Press, 2003).
- Fundamental models include cell dimensions, transport of substrates and metabolites across the cell membrane, and the elementary cell bioreaction steps and their corresponding enzyme induction mechanism. In recent years further kinetic steps have been added to the above models which are based on the conversion of substrates to metabolites. Thus the kinetics of protein synthesis by *transcription* and *translation* from the *genome* add much further complexity to cell kinetics.

The network of bioreactions is called the *metabolic network*, the series of consecutive steps between key intermediates in the network are called *metabolic pathways*, and the determination of the mechanism and kinetics is called *metabolic flux analysis*. As for chemical systems, there are several levels of mechanistic and kinetic representation and analysis, listed in order of increasing complexity in Table 7-10.

Additional complexity can be included through cell population balances that account for the distribution of cell generation present in the fermenter through use of stochastic models. In this section we limit the discussion to simple black box and unstructured models. For more details on bioreaction systems, see, e.g., Nielsen, Villadsen, and Liden, *Bioreaction Engineering Principles*, 2d ed., Kluwer, Academic/Plenum Press, 2003; Bailey and Ollis, *Biochemical Engineering Fundamentals*, 2d ed., McGraw-Hill, 1986; Blanch and Clark, *Biochemical Engineering*, Marcel Dekker, 1997; and Sec. 19.

Mechanism Stoichiometric balances are done on a C atom basis called *C-moles*, e.g., relative to the substrate (denoted by subscript *s*), and the corresponding stoichiometric coefficients Y_{si} (based on C-mole of the primary substrate) are called *yield coefficients*. For instance,



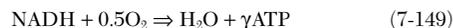
Here the reactants (substrates) are glucose (CH_2O), O_2 , NH_3 , and a sulfur-providing nutrient S_1 , and the products are biomass X, CO_2 , metabolic product P_1 , and H_2O .

The products of bioreactions can be reduced or oxidized, and all feasible pathways have to be *redox neutral*. There are several cofactors that transfer redox power in a pathway or between pathways, each equivalent to the reducing power of a molecule of H_2 , e.g., nicotinamide adenine dinucleotide (NADH), and these have to be included in the stoichiometric balances as H equivalents through redox balancing. For instance, for the reaction of glucose to glycerol (CH_3O), $\frac{1}{3}$ NADH equivalent is consumed:



The stoichiometry in the biochemical literature often does not show H_2O produced by the reaction; however, for complete elemental balance, water has to be included, and this is easily done once an O_2 requirement has been determined based on a redox balance. Likewise for simplicity, the other form of the cofactor [e.g., the oxidized form of the cofactor NADH in Eq. (7-148)] is usually left out. In

addition to C balances, for aerobic systems cell respiration has to be accounted for as well through a stoichiometric equation:



The associated free energy produced or consumed in each reaction is captured in units of adenosine triphosphate (ATP). The ATP stoichiometry is usually obtained from biochemical tables since the energy has to be also balanced for the cell. Thus for Eq. (7-148) the stoichiometric ATP requirement to convert one C-mole of glucose to one C-mole of glycerol is $\frac{1}{3}$. In calculations of the carbon flux distribution in different pathways this ATP requirement has to be added on the left-hand side of the equation. Again the other form of the cofactor ATP is usually left out to simplify the reaction equation.

There are several metabolic pathways that are repeated for many living cells, and these are split into two: *catabolic* or energy-producing and *anabolic* or energy-consuming, the later producing building blocks such as amino acids and the resulting macromolecules such as proteins. Of course the energy produced in catabolic steps has to be balanced by the energy consumed in anabolic steps. Catabolic pathways include the well-studied *glycolysis*, *TCA cycle*, *oxidative phosphorylation*, and *fermentative pathways*. For more details see Stephanopoulos, Aristidou, and Nielsen, *Metabolic Engineering: Principles and Methodologies*, Academic Press, 1998; and Nielsen, Villadsen, and Liden, *Bioreaction Engineering Principles*, 2d ed., Kluwer, Academic/Plenum Press, 2003; Bailey and Ollis, *Biochemical Engineering Fundamentals*, 2d ed., McGraw-Hill, 1986.

Monod-Type Empirical Kinetics Many bioreactions show increased biomass growth rate with increasing substrate concentration at low substrate concentration for the limiting substrate, but no effect of substrate concentration at high concentrations. This behavior can be represented by the Monod equation (7-92). Additional variations on the Monod equation are briefly illustrated below. For two essential substrates the Monod equation can be modified as

$$\mu = \frac{\mu_{\max}C_{s1}C_{s2}}{(K_{s1} + C_{s2})(K_{s2} + C_{s2})} \quad (7-150)$$

This type of rate expression is often used in models for water treatment, and many environmental factors can be included (the effect of, e.g., phosphate, ammonia, volatile fatty acids, etc.). The correlation between parameters in such complicated models is, however, severe, and very often a simple Monod model (7-92) with only one limiting substrate is sufficient.

When *substrate inhibition* occurs,

$$\mu = \frac{\mu_{\max}C_s}{K_s + C_s + K_i/C_s^2} \quad (7-151)$$

O_2 is typically a substrate that in high concentrations leads to substrate inhibition, but a high concentration of the carbon source can also be inhibiting (e.g., in bioremediation of toxic waste a high concentration of the organic substrate can well lead to severe inhibition or death of the microorganism).

When *product inhibition* is present,

$$\mu = \frac{\mu_{\max}C_s}{K_s + C_s} \left(1 - \frac{C_p}{C_{p\max}} \right) \quad (7-152)$$

Here the typical example is the inhibitor effect of ethanol on yeast growth. Considerable efforts are made by the biocompanies to develop yeast strains that are tolerant to high ethanol concentrations since this will give considerable savings in, e.g., production of biofuel by fermentation.

The various component reaction rates for a single reaction can be related to the growth rate by using the stoichiometric (yield) coefficients, e.g., from Eq. (7-147):

$$r_i = Y_{si}\mu C_x = \frac{Y_{si}}{Y_{sx}}\mu C_x \quad (7-153)$$

7-32 REACTION KINETICS

Chemostat with Empirical Kinetics Using the CSTR equation (7-54) for a constant-volume single reaction [Eq. (7-147)], the substrate, biomass, and product material balances are

$$\begin{aligned} \frac{1}{Y_{sx}} \mu C_x + D(C_{s0} - C_s) &= 0 \\ \mu C_x - DC_x &= 0 \rightarrow D = \mu \\ \frac{Y_{sp}}{Y_{sx}} \mu C_x - DC_p &= 0 \end{aligned} \quad (7-154)$$

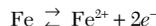
Here C_{s0} is the feed substrate concentration, and D is the *dilution rate*, which at steady-state constant volume is equal to both the feed and effluent volumetric flow rates and to the specific growth rate. The effluent concentrations of substrate, biomass, and products can be calculated by using a suitable expression for the specific growth rate μ such as one of the relevant variants of the Monod kinetics described above.

ELECTROCHEMICAL REACTIONS

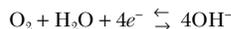
Electrochemical reactions involve coupling between chemical reactions and electric charge transfer and may have two or three phases, for instance, a gas (e.g., H_2 or O_2 evolved at the electrodes or fed as reactants), a liquid (the electrolyte solution), and solids (electrodes). Electrocatalysts may be employed to enhance the reaction for a particular desired product. Hence, electrochemical reactions are heterogeneous reactions that occur at the surface of electrodes and involve the transfer of charge in the form of electrons as part of a chemical reaction. The electrochemical reaction can produce a chemical change by passing an electric current through the system (e.g., electrolysis), or reversely a chemical change can produce electric energy (e.g., using a battery or fuel cell to power an appliance). There are a variety of practical electrochemical reactions, some occurring naturally, such as corrosion, and others used in production of chemicals (e.g., the decomposition of HCl to produce Cl_2 and H_2 , the production of caustic soda and chlorine, the smelting of aluminum), electroplating, and energy generation (e.g., fuel cells and photovoltaics). Electrochemical reactions are reversible and can be generally written as a *reduction-oxidation (redox)* couple:



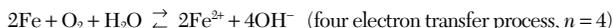
where O is an oxidized and R is a reduced species. For instance, the corrosion process includes oxidation at the *anode*:



and reduction at the *cathode*:



The overall electrochemical reaction is the stoichiometric sum of the anode and cathode reactions:



The anode and cathode reactions are close coupled in that the electric charge is conserved; therefore, the overall production rate is a direct function of the electric charge passed per unit time, the electric current I .

For references on electrochemical reaction kinetics and mechanism, see, e.g., Newman and Thomas-Alvea, *Electrochemical Systems*, 3d ed., Wiley Interscience, 2004; Bard and Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2d ed., Wiley, 2001; Bethune and Swendeman, "Table of Electrode Potentials and Temperature Coefficients," *Encyclopedia of Electrochemistry*, Van Nostrand Reinhold, New York 1964, pp. 414–424; and Bethune and Swendeman, *Standard Aqueous Electrode Potentials and Temperature Coefficients*, C. A. Hampel Publisher, 1964.

Faraday's law relates the charge transferred by ions in the electrolyte and electrons in the external circuit, to the moles of chemical species reacted (Newman and Thomas-Alvea, *Electrochemical Systems*, 3d ed., Wiley Interscience, 2004):

$$\begin{aligned} Q &= nmF & F &= 96,485 \text{ C/equiv} \\ I &= \frac{Q}{t} = \frac{\text{charge}}{\text{time}} & A \end{aligned} \quad (7-155)$$

where n is the number of equivalents per mole, m is the number of moles, F is the Faraday constant, Q is the charge, and t is time. The total current passed may represent several parallel electrochemical reactions; therefore, we designate a current efficiency for each chemical species. The chemical species production rate (mass/time) is related to the total current passed I , the species *current efficiency* $\epsilon_{\text{current},i}$, and the molecular weight of the chemical species MW_i :

$$\begin{aligned} \dot{m} &= \frac{I \times \epsilon_{\text{current},i} \times MW_i}{nF} = \frac{\text{mass}}{\text{time}} \\ j &= \frac{\text{current}}{\text{area}} = \frac{I}{A_{\text{projected}}} \end{aligned} \quad (7-156)$$

Since electrochemical reactions are heterogeneous at electrode surfaces, the current I is generally normalized by dividing it by the geometric or projected area of the electrode, resulting in the quantity known as the *current density* j , in units of kA/m^2 .

The overall electrochemical cell *equilibrium potential* E°_{cell} , as measured between the cathode and the anode, is related to the Gibbs free energy change for the overall electrochemical reaction:

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ = -nFE^\circ_{\text{cell}} \\ E^\circ_{\text{cell}} &= -\frac{\Delta G^\circ}{nF} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \end{aligned} \quad (7-157)$$

Each electrode reaction, anode and cathode, or half-cell reaction has an associated energy level or electrical potential (volts) associated with it. Values of the standard equilibrium electrode reduction potentials E° at unit activity and 25°C may be obtained from the literature (de Bethune and Swendeman Loud, *Encyclopedia of Electrochemistry*, Van Nostrand Reinhold, 1964). The overall electrochemical cell *equilibrium potential* either can be obtained from ΔG values or is equal to the cathode half-cell potential minus the anode half-cell potential, as shown above.

The *Nernst equation* allows one to calculate the *equilibrium potential* E^{eq} when the activity of the reactants or products is not at unity:

$$\begin{aligned} \sum_i \nu_i M_i^{\nu_i} &\rightarrow ne^- \\ E^{\text{eq}} &= E^\circ - \frac{RT}{nF} \ln(\Pi a_i^{\nu_i}) \\ \left(\frac{\partial E}{\partial T} \right)_p &= \frac{\Delta S}{nF} \end{aligned} \quad (7-158)$$

where ν_i is the stoichiometric coefficient of chemical species i (positive for products; negative for reactants), M_i is the symbol for species i , n_i is the charge number of the species, a_i is the activity of the chemical species, E is the *formal potential*, and Π represents the product of all respective activities raised to their stoichiometric powers as required by the reaction. Please note that if the value of the equilibrium potential is desired at another temperature, E° must also be evaluated at the new temperature as indicated.

Kinetic Control In 1905, Julius Tafel experimentally observed that when mass transport was not limiting, the *current density* j of electrochemical reactions exhibited the following behavior:

$$j = a' e^{\eta_{\text{act}}/b'} \quad \text{or} \quad \eta_{\text{act}} = a + b \log j$$

where the quantity η_{act} is known as the *activation overpotential* $E - E^{\text{eq}}$, and is the difference between the actual electrode potential

E and the reversible equilibrium potential of the electrochemical reaction E^{eq} . Thus the driving force for the electrochemical reaction is not the absolute potential; it is the activation overpotential η_{act} .

This relationship between the current density and activation overpotential has been further developed and resulted in the Butler-Volmer equation:

$$r = \frac{j}{nF} = k_f C_o - k_r C_r \quad j = j_0 (e^{-(\alpha_a F/RT)\eta_{act}} - e^{[(1-\alpha_c)F/RT]\eta_{act}})$$

$$\eta_{act} = E - E^{eq} \quad (7-159)$$

Here the reaction rate r is defined per unit electrode area, moles per area per time, j_0 is the *equilibrium exchange current* when $E = E^{eq}$, η_{act} is the *activation overpotential*, and α is the *transfer coefficient*. For large activation overpotentials, the *Tafel empirical equation* applies:

$$\eta_{act} = a + b \log j \quad \text{for } \eta_{act} > 100 \text{ mV, } b = \text{Tafel slope} \quad (7-160)$$

For small activation overpotentials, linearization gives

$$j = j_0 \frac{nF}{RT} \eta_{act} \quad (7-161)$$

Mass-Transfer Control The surface concentration at the electrodes differs significantly from the bulk electrolyte concentration. The Nernst equation applies to the surface concentrations (or activities in case of nonideal solutions):

$$E^{eq} = E^o - \frac{RT}{nF} \ln(\Pi a_{i,surf}^{\nu_i}) \quad (7-162)$$

DETERMINATION OF MECHANISM AND KINETICS

Laboratory data are the predominant source for reaction mechanism and kinetics in industrial practice. However, often laboratory data intended for scoping and demonstration studies rather than for kinetic evaluation have to be used, thus reducing the effectiveness and accuracy of the resulting kinetic model. The following are the steps required to obtain kinetics from laboratory data:

1. Develop initial guesses on mechanism, reaction time scale, and potential kinetic models from the literature, scoping experiments, similar chemistries, and computational chemistry calculations, when possible.

2. Select a suitable laboratory reactor type and scale, and analytical tools for kinetic measurements.

3. Develop a priori factorial experimental design or sequential experimental design.

4. When possible, provide ideal reactor conditions, e.g., good mechanical agitation in batch and CSTR, high velocity flow in PFR.

5. Estimate the limiting diffusion-reaction regimes under the prevailing lab reactor conditions for heterogeneous reactions, and use the appropriate lab reactor model. When possible, operate the reactor under kinetic control.

6. Discriminate between competing mechanisms and kinetic rates by forcing maximum differentiation between competing hypotheses through the experimental design, and by obtaining the best fit of the kinetic data to the proposed kinetic forms.

LABORATORY REACTORS

Selection of the laboratory reactor type and size, and associated feed and product handling, control, and analytical schemes depends on the type of reaction, reaction time scales, and type of analytical methods required. The criteria for selection include equipment cost, ease of operation, ease of data analysis, accuracy, versatility, temperature uniformity, and controllability, suitability for mixed phases, and scale-up

If mass transfer is limiting, then a *limiting current* is obtained for each chemical species i :

$$j_{i,lim} = \frac{nFD_i C_i}{\delta} = nFk_{L,i} C_i \quad (7-163)$$

where D_i is the diffusion coefficient, δ is the boundary layer thickness, and $k_{L,i}$ is the mass-transfer coefficient of species i . The effect of mass transfer is included as follows:

$$j = j_0 \left[\left(1 - \frac{j}{j_{a,lim}} \right) e^{-(\alpha_a F/RT)\eta_{act}} - \left(1 - \frac{j}{j_{c,lim}} \right) e^{[(1-\alpha_c)F/RT]\eta_{act}} \right]$$

$$\frac{C_{i,surf}}{C_i} = \left(1 - \frac{j}{j_{i,lim}} \right) \quad i = o, r \quad (7-164)$$

Ohmic Control The overall electrochemical reactor cell voltage may be dependent on the kinetic and mass-transfer aspects of the electrochemical reactions; however, a third factor is the potential lost within the electrolyte as current is passing through this phase. The potential drops may become dominant and limit the electrochemical reactions requiring an external potential to be applied to drive the reactions or significantly lower the delivered electrical potential in power generation applications such as batteries and fuel cells.

Multiple Reactions With multiple reactions, the total current is the sum of the currents from the individual reactions with anodic currents positive and cathodic currents negative. This is called the *mixed potential principle*. For more details see Bard and Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2d ed., Wiley, 2001.

feasibility. Many configurations of laboratory reactors have been employed. Rase (*Chemical Reactor Design for Process Plants*, Wiley, 1977) and Shah (*Gas-Liquid-Solid Reactor Design*, McGraw-Hill, 1979) each have about 25 sketches, and Shah's bibliography has 145 items classified into 22 categories of reactor types. Jankowski et al. [*Chemische Technik* 30: 441-446 (1978)] illustrate 25 different kinds of gradientless laboratory reactors for use with solid catalysts.

Laboratory reactors are of two main types:

1. Reactors used to obtain fundamental data on intrinsic chemical rates free of mass-transfer resistances or other complications. Some of the gas-liquid lab reactors, for instance, employ known interfacial areas, thus avoiding the uncertainty regarding the area for gas to liquid mass transfer. When ideal behavior cannot be achieved, intrinsic kinetic estimates need to account for mass- and heat-transfer effects.

2. Reactors used to obtain scale-up data due to their similarity to the reactor intended for the pilot or commercial plant scale. How to scale down from the conceptual commercial or pilot scale to lab scale is a difficult problem in itself, and it is not possible to maintain all key features while scaling down.

The first type is often the preferred one—once the intrinsic kinetics are obtained at “ideal” lab conditions, scale-up is done by using models or correlations that describe large-scale reactor hydrodynamics coupled with the intrinsic kinetics. However, in some cases ideal conditions cannot be achieved, and the laboratory reactor has to be adequately modeled to account for mass and heat transfer and non-ideal mixing effects to enable extraction of intrinsic kinetics. In addition, with homogeneous reactions, attention must be given to prevent wall-catalyzed reactions, which can result in observed kinetics that are fundamentally different from intrinsic homogeneous kinetics. This is a problem for scale-up, due to the high surface/volume ratio in small reactors versus the low surface/volume ratio in large-scale systems, resulting in widely different contributions of wall effects at different scales. Similar issues arise in bioreactors with the potential of

undesirable wall growth of the biocatalyst cells masking the homogeneous growth kinetics. In catalytic reactions certain reactor configurations may enhance undesirable homogeneous reactions, and the importance of these reactions may be different at larger scale, causing potential scale-up pitfalls.

The reaction rate is expressed in terms of chemical compositions of the reacting species, so ultimately the variation of composition with time or space must be found. The composition is determined in terms of a property that is measured by some instrument and calibrated. Among the measures that have been used are titration, pressure, refractive index, density, chromatography, spectrometry, polarimetry, conductimetry, absorbance, and magnetic resonance. Therefore, batch or semibatch data are converted to composition as a function of time (C, t), or to composition and temperature as functions of time (C, T, t), to prepare for kinetic analysis. In a steady CSTR and PFR, the rate and compositions in the effluent are observed as a function of residence time.

When a reaction has many reactive species (which may be the case even for apparently simple processes such as pyrolysis of ethane or synthesis of methanol), a factorial or sequential experimental design should be developed and the data can be subjected to a *response surface analysis* (Box, Hunter, and Hunter, *Statistics for Experimenters*, 2d ed., Wiley Interscience, 2005; Davies, *Design and Analysis of Industrial Experiments*, Oliver & Boyd, 1954). This can result in a black box correlation or statistical model, such as a quadratic (limited to first- and second-order effects) for the variables x_1, x_2 , and x_3 :

$$r = k_1x_1 + k_2x_2 + k_3x_3 + k_{12}x_1x_2 + k_{13}x_1x_3 + k_{23}x_2x_3$$

Analysis of such statistical correlations may reveal the significant variables and interactions and may suggest potential mechanisms and kinetic models, say, of the Langmuir-Hinshelwood type, that could be analyzed in greater detail by a regression process. The variables x_i could be various parameters of heterogeneous processes as well as concentrations. An application of this method to isomerization of *n*-pentane is given by Kittrel and Erjavec [*Ind. Eng. Chem. Proc. Des. Dev.* 7: 321 (1968)].

Table 7-11 summarizes laboratory reactor types that approach the three ideal concepts BR, CSTR and PFR, classified according to reaction types.

TABLE 7-11 Laboratory Reactors

Reaction	Reactor
Homogeneous gas	Isothermal U-tube in temperature-controlled batch
Homogeneous liquid	Mechanically agitated batch or CSTR with jacketed cooling/heating
Catalytic gas-solid	Packed tube in furnace Isothermal U-tube in temperature-controlled bath Rotating basket with jacketed cooling/heating Internal recirculation (Berty) reactor with jacketed cooling/heating
Noncatalytic gas-solid	Packed tube in furnace
Liquid-solid	Packed tube in furnace
Gas-liquid	CSTR with jacketed cooling/heating Fixed interface CSTR Wetted wall Laminar jet
Gas-liquid-solid	Slurry CSTR with jacketed cooling/heating Packed bed with downflow, upflow, or countercurrent
Solid-solid	Packed tube in furnace

For instance, Fig. 7-17 summarizes laboratory reactor types and hydrodynamics for gas-liquid reactions.

Batch Reactors In the simplest kind of investigation, reactants can be loaded into a number of sealed tubes, kept in a thermostatic bath for various periods, shaken mechanically to maintain uniform composition, and analyzed. In terms of cost and versatility, the stirred batch reactor is the unit of choice for homogeneous or heterogeneous slurry reactions including gas-liquid and gas-liquid-solid systems. For multiphase systems the reactants can be semibatch or continuous. The BR is especially suited to reactions with half-lives in excess of 10 min. Samples are taken at time intervals, and the reaction is stopped by cooling, by dilution, or by destroying a residual reactant such as an acid or base; analysis can then be made at a later time. Analytic methods that do not necessitate termination of reaction include nonintrusive measurements of (1) the amount of gas produced, (2) the gas pressure in a constant-volume vessel, (3) absorption of light, (4) electrical or thermal conductivity, (5) polarography, (6) viscosity of polymerization, (7) pH and DO probes, and so on. Operation may be isothermal, with the important effect of temperature determined from several isothermal runs, or the composition and temperature may be recorded simultaneously and the

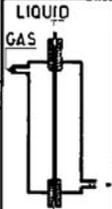
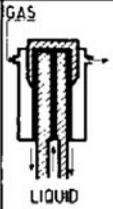
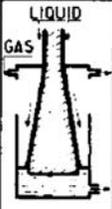
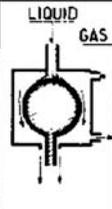
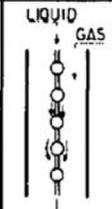
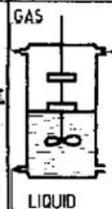
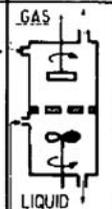
TYPE	LAMINAR JET	CYLINDRICAL WETTED WALL	CONIC WETTED WALL	SPHERICAL WETTED WALL	STRING OF DISKS	ROTATING DRUM	STIRRED VESSEL	STIRRED VESSEL
SCHEME								
k_L cm/sec	0.016 -0.16	$3.6 \cdot 10^{-3}$ -0.016	$5 \cdot 10^{-3}$ -0.011	$5 \cdot 10^{-3}$ -0.016	$3.6 \cdot 10^{-3}$ -0.016	0.016 -0.36	$1.6 \cdot 10^{-3}$ -0.02	$2 \cdot 10^{-3}$ -0.02
CONTACT TIMES	10^{-3} - 10^{-1} sec	10^{-1} -2 sec	0.2-1 sec	0.1-1 sec	10^{-1} -2 sec	$2 \cdot 10^{-4}$ -10 sec	0.06-10 sec	0.08-10 sec
INTERFACIAL AREA	0.3-10 cm ² high precision	10-100 cm ² high precision	80 cm ² high precision	10-40 cm ² high precision	30-360 cm ² moderate precision	diameter 10 cm length 12 cm high precision	80 cm ² good precision	diameter 10 cm length 15 cm 2-30% open

FIG. 7-17 Principal types of laboratory reactors for gas-liquid reactions. [From Fig. 8 in J. C. Charpentier, "Mass Transfer Rates in Gas-Liquid Absorbers and Reactors," in Drew et al. (eds.), *Advances in Chemical Engineering*, vol. 11, Academic Press, 1981.]

data regressed. On the laboratory scale, it is essential to ensure that a BR is stirred to uniform composition, and for critical cases such as high viscosities this should be checked with tracer tests.

Flow Reactors CSTRs and other devices that require flow control are more expensive and difficult to operate. However, CSTRs and PFRs are the preferred laboratory reactors for steady operation. One of the benefits of CSTRs is their isothermicity and the fact that their mathematical representation is algebraic, involving no differential equations, thus making data analysis simpler. For laboratory research purposes, CSTRs are considered feasible for holding times of 1 to 4000 s, reactor volumes of 2 to 1000 cm³ (0.122 to 61 in³), and flow rates of 0.1 to 2.0 cm³/s. Fast reactions and those in the gas phase are generally done in tubular flow reactors, just as they are often done on the commercial scale. Usually it is not possible to measure compositions along a PFR, although temperatures can be measured using a thermowell with fixed or mobile thermocouple bundle. PFRs can be kept at nearly constant temperatures; small-diameter tubes immersed in a fluidized sand bed or molten salt can hold quite constant temperatures of a few hundred degrees. Other PFRs are operated at near adiabatic conditions by providing dual radial temperature control to minimize the radial heat flux, with multiple axial zones. A recycle unit can be operated as a differential reactor with arbitrarily small conversion and temperature change. Test work in a tubular flow unit may be desirable if the intended commercial unit is of that type.

Multiphase Reactors Reactions between gas-liquid, liquid-liquid, and gas-liquid-solid phases are often tested in CSTRs. Other laboratory types are suggested by the commercial units depicted in appropriate sketches in Sec. 19 and in Fig. 7-17 [Charpentier, *Mass Transfer Rates in Gas-Liquid Absorbers and Reactors*, in Drew et al. (eds.), *Advances in Chemical Engineering*, vol. 11, Academic Press, 1981]. Liquids can be reacted with gases of low solubilities in stirred vessels, with the liquid charged first and the gas fed continuously at the rate of reaction or dissolution. Some of these reactors are designed to have known interfacial areas. Most equipment for gas absorption without reaction is adaptable to absorption with reaction. The many types of equipment for liquid-liquid extraction also are adaptable to reactions of immiscible liquid phases.

Solid Catalysts Processes with solid catalysts are affected by diffusion of heat and mass (1) within the pores of the pellet, (2) between the fluid and the particle, and (3) axially and radially within the packed bed. Criteria in terms of various dimensionless groups have been developed to tell when these effects are appreciable, and some of these were discussed above. For more details see Mears [*Ind. Eng. Chem. Proc. Des. Devel.* **10**: 541–547 (1971); *Ind. Eng. Chem. Fund.* **15**: 20–23 (1976)] and Satterfield (*Heterogeneous Catalysis in Practice*, McGraw-Hill, 1991, p. 491). For catalytic investigations, the rotating basket or fixed basket with internal recirculation is the standard device, usually more convenient and less expensive than equipment with external recirculation. In the fixed-basket type, an internal recirculation rate of 10 to 15 or so times the feed rate effectively eliminates external diffusional resistance, and temperature gradients (see, e.g., Berty, *Experiments in Catalytic Reaction Engineering*, Elsevier, 1999). A unit holding 50 cm³ (3.05 in³) of catalyst can operate up to 800 K (1440°R) and 50 bar (725 psi). When deactivation occurs rapidly (in a few seconds during catalytic cracking, for instance), the fresh activity can be maintained with a transport reactor through which both reactants and fresh catalyst flow without slip and with short contact time. Since catalysts often are sensitive to traces of impurities, the time deactivation of the catalyst usually can be evaluated only with commercial feedstock. Physical properties of catalysts also may need to be checked periodically, including pellet size, specific surface, porosity, pore size and size distribution, effective diffusivity, and active metals content and dispersion. The effectiveness of a porous catalyst is found by measuring conversions with successively smaller pellets until no further change occurs. These topics are touched on by Satterfield (*Heterogeneous Catalysis in Industrial Practice*, McGraw-Hill, 1991).

To determine the deactivation kinetics, long-term deactivation studies at constant conditions and at different temperatures are required. In some cases, accelerated aging can be induced to reduce the time required for the experimental work, by either increasing the feed flow

rate (if the deactivation is a result of feed or product poisoning) or increasing the temperature above the standard reaction temperature. These require a good understanding of how the higher-temperature or rate-accelerated deactivation correlates with deactivation at the operating reaction temperature and rate.

Bioreactors There are several types of laboratory bioreactors used with live organisms as biocatalysts:

1. Mechanically agitated batch/semibatch with pH control and nutrients or other species either fed at the start or added continuously based on a recipe or protocol.

2. CSTR to maintain a constant *dilution rate* (the feed rate). These require some means to separate the biocatalyst from the product and recycle to the reactor, such as centrifuge or microfiltration:

a. *Chemostat* controls the flow to maintain a constant fermentation volume.

b. *Turbidostat* controls the biomass or cells concentration.

c. *pH-auxostat* controls pH in the effluent (same as pH in reactor).

d. *Productostat* controls the effluent concentration of one of the metabolic products.

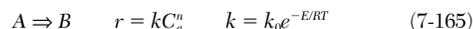
The preferred reactor for kinetics is the chemostat, but semibatch reactors are more often used owing to their simpler operation.

Calorimetry Another category of laboratory systems that can be used for kinetics includes *calorimeters*. These are primarily used to establish temperature effects and thermal runaway conditions, but can also be employed to determine reaction kinetics. Types of calorimeters are summarized in Table 7-12; for more details see Reid, "Differential Microcalorimeters," *J. Physics E: Scientific Instruments*, **9** (1976).

Additional methods of laboratory data acquisition are described in Masel, *Chemical Kinetics and Catalysis*, Wiley, 2001.

KINETIC PARAMETERS

The kinetic parameters are constants that appear in the intrinsic kinetic rate expressions and are required to describe the rate of a reaction or reaction network. For instance, for the simple global *n*th-order reaction with Arrhenius temperature dependence:



The kinetic parameters are k_0 , E , and n , and knowledge of these parameters and the prevailing concentration and temperature fully determines the reaction rate.

For a more complex expression such as the Langmuir-Hinshelwood rate for gas reaction on heterogeneous catalyst surface with equilibrium adsorption of reactants *A* and *B* on two different sites and non-adsorbing products, Eq. (7-85) can be rewritten as

$$r = \frac{k_0 e^{-E/RT} P_a P_b}{(1 + K_{a0} e^{-E_a/RT})(1 + K_{b0} e^{-E_b/RT})} \quad (7-166)$$

and the kinetic parameters are k_0 , E , K_{a0} , E_{a0} , K_{b0} , and E_{b0} .

A number of factors limit the accuracy with which parameters needed for the design of commercial equipment can be determined. The kinetic parameters may be affected by inaccurate accounting for laboratory reactor heat and mass transport, and hydrodynamics; correlations for these are typically determined under nonreacting conditions at ambient temperature and pressure and with nonreactive model fluids and may not be applicable or accurate at reaction conditions. Experimental uncertainty including errors in analysis, measurement,

TABLE 7-12 Calorimetric Methods

Adiabatic	Nonadiabatic
Accelerating rate calorimeter (ARC)	Reaction calorimeter (RC1) + IR
Vent sizing package (VSP) calorimeter	Differential scanning calorimeter (DSC)
PHI-TEC	Thermal gravimetry (TG)
Dewar	Isothermal calorimetry
Automatic pressure tracking adiabatic calorimeter (APTAC)	Differential thermal analysis (DTA)
	Differential microcalorimeters
	Advanced reaction system screening tool (ARSSST)

and control is also a contributing factor (see, e.g., Hoffman, "Kinetic Data Analysis and Parameter Estimation," in de Lasa (ed.), *Chemical Reactor Design and Technology*, Martinus Nijhoff, 1986.

DATA ANALYSIS METHODS

In this section we focus on the three main types of ideal reactors: BR, CSTR, and PFR. Laboratory data are usually in the form of concentrations or partial pressures versus batch time (batch reactors), concentrations or partial pressures versus distance from reactor inlet or residence time (PFR), or rates versus residence time (CSTR). Rates can also be calculated from batch and PFR data by differentiating the concentration versus time or distance data, usually by numerical curve fitting first. It follows that a general classification of experimental methods is based on whether the data measure rates directly (differential or direct method) or indirectly (integral of indirect method). Table 7-13 shows the pros and cons of these methods.

Some simple reaction kinetics are amenable to analytical solutions and graphical linearized analysis to calculate the kinetic parameters from rate data. More complex systems require numerical solution of nonlinear systems of differential and algebraic equations coupled with nonlinear parameter estimation or regression methods.

Differential Data Analysis As indicated above, the rates can be obtained either directly from differential CSTR data or by differentiation of integral data. A common way of evaluating the kinetic parameters is by rearrangement of the rate equation, to make it linear in parameters (or some transformation of parameters) where possible. For instance, using the simple n th-order reaction in Eq. (7-165) as an example, taking the natural logarithm of both sides of the equation results in a linear relationship between the variables $\ln r$, $1/T$, and $\ln C_a$:

$$\ln r = \ln k_0 - \frac{E}{RT} + n \ln C_a \quad (7-167)$$

Multilinear regression can be used to find the constants k_0 , E , and n . For constant-temperature (isothermal) data, Eq. (7-167) can be simplified by using the Arrhenius form as

$$\ln r = \ln k + n \ln C_a \quad (7-168)$$

and the kinetic parameters n and k can be determined as the intercept and slope of the best straight-line fit to the data, respectively, as shown in Fig. 7-18.

The preexponential k_0 and activation energy E can be obtained from multiple isothermal data sets at different temperatures by using the linearized form of the Arrhenius equation

$$\ln k = \ln k_0 - \frac{E}{RT} \quad (7-169)$$

as shown in Fig. 7-19.

Integral Data Analysis Integral data such as from batch and PFR relate concentration to time or distance. Integration of the BR equation for an n th-order homogeneous constant-volume reaction yields

TABLE 7-13 Comparison of Direct and Indirect Methods

Direct method	Indirect method
Advantages	Disadvantages
Get rate equation directly	Must infer rate equation
Easy to fit data to a rate law	Hard to analyze rate data
High confidence on final rate equation	Low confidence on final rate equation
Disadvantages	Advantages
Difficult experiment	Easier experiment
Need many runs	Can do a few runs and get important information
Not suitable for very fast or very slow reactions	Suitable for all reactions including very fast or very slow ones

SOURCE: Masel, *Chemical Kinetics and Catalysis*, Wiley, 2001, Table 3.2.

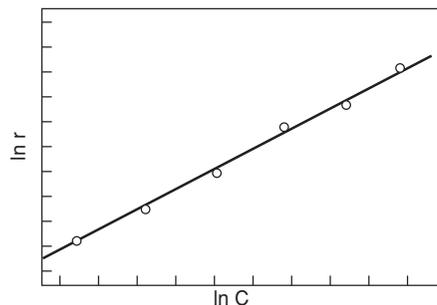


FIG. 7-18 Determination of the rate constant and reaction order.

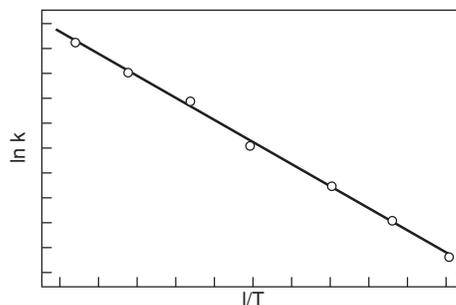


FIG. 7-19 Determination of the activation energy.

$$\ln \frac{C_{a0}}{C_a} = k\tau \quad \text{for } n = 1 \quad (7-170)$$

$$\left(\frac{C_{a0}}{C_a} \right)^{n-1} = 1 + k\tau(n-1)C_{a0}^{n-1} \quad \text{for } n \neq 1$$

For the first-order case, the rate constant k can be obtained directly from the slope of the graph of the left-hand side of Eq. (7-170) versus batch time, as shown in Fig. 7-20.

For orders other than first, plotting the natural log of Eq. (7-170) can at least indicate if the order is larger or smaller than 1, as shown in Fig. 7-21.

The Half-Life Method The half-life is the batch time required to get 50 percent conversion. For an n th-order reaction,

$$\tau_{1/2} = \frac{\ln 2}{k} \quad \text{for } n = 1 \quad (7-171)$$

$$\tau_{1/2} = \frac{2^{n-1} - 1}{(n-1)kC_{a0}^{n-1}} \quad \text{for } n \neq 1$$

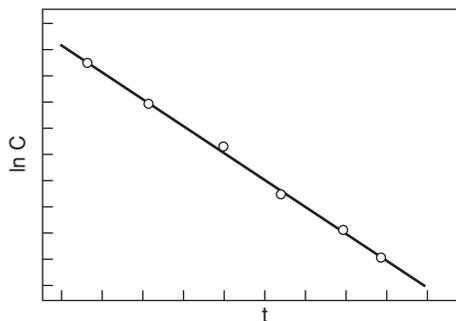


FIG. 7-20 Determination of first-order rate constant from integral data.

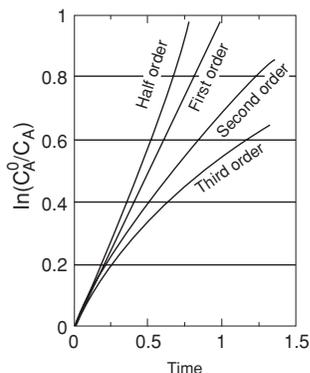


FIG. 7-21 Reaction behavior for n th-order reaction. (Masek, *Chemical Kinetics and Catalysis*, Wiley, 2001, Fig. 3.15.)

Thus for first-order reactions, the *half-life* is constant and independent of the initial reactant concentration and can be used directly to calculate the rate constant k . For non-first-order reactions, Eq. (7-171) can be linearized as follows:

$$\ln \tau_{1/2} = \ln \frac{2^{n-1} - 1}{(n-1)k} - (n-1) \ln C_{a0} \quad \text{for } n \neq 1 \quad (7-172)$$

The reaction order n can be obtained from the slope and the rate constant k from the intercept of the plot of Eq. (7-172), shown in Fig. 7-22.

Complex Rate Equations The examples above are for special cases amenable to simple treatment. Complex rate equations and reaction networks with complex kinetics require individual treatment, which often includes both numerical solvers for the differential and algebraic equations describing the laboratory reactor used to obtain the data and linear or nonlinear parameter estimation.

PARAMETER ESTIMATION

The straightforward method to obtain kinetic parameters from data is the numerical fitting of the concentration data (e.g., from BR or PFR) to integral equations, or the rate data (e.g., from a CSTR or from differentiation of BR or PFR) to rate equations. This is done by parameter estimation methods described here. An excellent reference for experimental design and parameter estimation (illustrated for heterogeneous gas-solid reactions) is the review paper of Froment and Hosten, "Catalytic Kinetics—Modeling," in *Catalysis—Science and Technology*, Springer-Verlag, New York, 1981. Two previous papers devoted to this topic by Hofmann [in *Chemical Reaction Engineering*, ACS *Advances in Chemistry*, **109**: 519–534 (1972); in de Lasa (ed.),

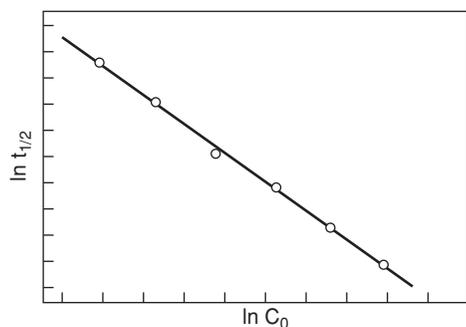


FIG. 7-22 Determination of reaction order and rate constant from half-life data.

Chemical Reactor Design and Technology, Martinus Nijhoff, 1985, pp. 69–105] are also very useful. As indicated above, the acquisition of kinetic data and parameter estimation can be a complex endeavor. It includes statistical design of experiments, laboratory equipment, computer-based data acquisition, complex analytical methods, and statistical evaluation of the data.

Regression is the procedure used to estimate the kinetic parameters by fitting kinetic model predictions to experimental data. When the parameters can be made to appear linear in the kinetic model (through transformations, grouping of parameters, and rearrangement), the regression is linear, and an accurate fit to data can be obtained, provided the form of the kinetic model represents well the reaction kinetics and the data provide enough width in temperature, pressure, and composition for statistically significant estimates. Often such linearization is not possible.

Linear Models in Parameters, Single Reaction We adopt the terminology from Froment and Hosten, "Catalytic Kinetics—Modeling," in *Catalysis—Science and Technology*, Springer-Verlag, New York, 1981. For n observations (experiments) of the concentration vector y for a model linear in the parameter vector β of length $p < n$, the *residual error* ϵ is the difference between the kinetic model-predicted values and the measured data values:

$$\epsilon = y - X\beta = y - \hat{y} \quad (7-173)$$

The linear model is represented as a linear transformation of the parameter vector β through the model matrix X . Estimates b of the true parameters β are obtained by minimizing the *objective function* $S(\beta)$, the *sum of squares of the residual errors*, while varying the values of the parameters:

$$S(\beta) = \epsilon^T \epsilon = \sum_{i=1}^n (y_i - \hat{y}_i)^2 \xrightarrow{\beta} \text{Min} \quad (7-174)$$

This linear optimization problem, subject to constraints on the possible values of the parameters (e.g., requiring positive preexponentials, activation energies, etc.) can be solved to give the estimated parameters:

$$b = (X^T X)^{-1} X^T y \quad (7-175)$$

When the error is *normally distributed* and has zero mean and variance σ^2 , then the *variance-covariance matrix* $V(b)$ is defined as

$$V(b) = (X^T X)^{-1} \sigma^2 \quad (7-176)$$

An estimate for σ^2 , denoted s^2 , is

$$s^2 = \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n - p} \quad (7-177)$$

When $V(b)$ is known from experimental observations, a *weighted objective function* should be used for optimization of the objective function:

$$S(\beta) = \epsilon^T V^{-1} \epsilon \xrightarrow{\beta} \text{Min} \quad (7-178)$$

and the estimates b are obtained as

$$b = (X^T V^{-1} X)^{-1} X^T V^{-1} y \quad (7-179)$$

The parameter fit is adequate if the *F test* is satisfied, that is, F_c , the calculated F , is larger than the tabulated statistical one at the *confidence level* of $1 - \alpha$:

$$F_c = \frac{\frac{\text{LFSS}}{n - p - n_e + 1}}{\frac{\text{PESS}}{n_e - 1}} \geq F(n - p - n_e + 1, n_e - 1; 1 - \alpha) \quad (7-180)$$

7-38 REACTION KINETICS

$$\text{LFSS} = \sum_{i=1}^n (y_i - \hat{y}_i)^2 - \sum_{i=1}^{ne} (y_i - \bar{y}_i)^2 \quad \text{PESS} = \sum_{i=1}^{ne} (y_i - \bar{y}_i)^2$$

Here \bar{y}_i are the averaged values of the data for replicates. Equation (7-180) is valid if there are n replicate experiments and the pure error sum of squares (PESS) is known. Without replicates,

$$F_c = \frac{\frac{\text{RgSS}}{p}}{\frac{\text{RSS}}{n-p}} \geq F(p, n-p; 1-\alpha) \quad \text{RgSS} = \sum_{i=1}^n \hat{y}_i^2$$

$$\text{RSS} = \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (7-181)$$

The bounds on the parameter estimates are given by the t statistics:

$$b_i - t\left(n-p; 1 - \frac{\alpha}{2}\right) \leq \beta_i \leq b_i + t\left(n-p; 1 - \frac{\alpha}{2}\right) \quad (7-182)$$

An example of a linear model in parameters is Eq. (7-167), where the parameters are $\ln k_0$, E , and n , and the linear regression can be used directly to estimate these.

Nonlinear Models in Parameters, Single Reaction In practice, the parameters appear often in nonlinear form in the rate expressions, requiring nonlinear regression. Nonlinear regression does not guarantee optimal parameter estimates even if the kinetic model adequately represents the true kinetics and the data width is adequate. Further, the statistical tests of model adequacy apply rigorously only to models linear in parameters, and can only be considered approximate for nonlinear models.

For a general nonlinear model $f(x, \beta)$, where x is the vector of the independent model variables and β is the vector of parameters,

$$\varepsilon = y - f(x, \beta) \quad (7-183)$$

An example of a model nonlinear in parameters is Eq. (7-166). Here it is not possible through any number of transformations to obtain a linear form in all the parameters k_0 , E , K_{ab} , E_{aa} , K_{bb} , E_{ab} . Note that for some Langmuir-Hinshelwood rate expressions it is possible to linearize the model in parameters at isothermal conditions and obtain the kinetic constants for each temperature, followed by Arrhenius-type plots to obtain activation energies (see, e.g., Churchill, *The Interpretation and Use of Rate Data: The Rate Concept*, McGraw-Hill, 1974).

Minimization of the sum of squares of residuals does not result in a closed form for nonlinear parameter estimates as for the linear case; rather it requires an iterative numerical solution, and having a reasonable initial estimate for the parameter values and their feasible ranges is critical for success. Also, the minima in the residual sum of squares are local and not global. To obtain global minima that better represent the kinetics over a wide range of conditions, parameter estimation has to be repeated with a wide range of initial parameter guesses to increase the chance of reaching the global minimum. The nonlinear regression procedure typically involves a *steepest descent* optimization search combined with *Newton's linearization* method when a minimum is approached, enhancing the convergence speed [e.g., the *Marquardt-Levenberg* or *Newton-Gauss* method; Marquardt, *J. Soc. Ind. Appl. Math.* **2**: 431 (1963)].

An integral part of the parameter estimation methodology is *mechanism discrimination*, i.e., selection of the best mechanism that would result in the best kinetic model. Nonlinear parameter estimation is an extensive topic and will not be further discussed here. For more details see Froment and Hosten, "Catalytic Kinetics—Modeling," in *Catalysis—Science and Technology*, Springer-Verlag, New York, 1981.

Network of Reactions The statistical parameter estimation for multiple reactions is more complex than for a single reaction. As indicated before, a single reaction can be represented by a single con-

centration [e.g., Eq. 7-39]. With a network of reactions, there are a number of dependent variables equal to the number of stoichiometrically independent reactions, also called *responses*. In this case the objective function has to be modified. For details see Froment and Hosten, "Catalytic Kinetics—Modeling," in *Catalysis—Science and Technology*, Springer-Verlag, New York, 1981.

THEORETICAL METHODS

Prediction of Mechanism and Kinetics Reaction mechanisms for a variety of reaction systems can be predicted to some extent by following a set of heuristic rules derived from experience with a wide range of chemistries. For instance, Masel, *Chemical Kinetics and Catalysis*, Wiley, 2001, chapter 5, enumerates the rules for gas-phase chain and nonchain reactions including limits on activation energies for various elementary steps. Other reaction systems such as ionic reactions, and reactions on metal and acid surfaces, are also discussed by Masel, although these mechanisms are not as well understood. Nevertheless, the rules can lead to computer-generated mechanisms for complex systems such as homogeneous gas-phase combustion and partial oxidation of methane and higher hydrocarbons. Developments in computational chemistry methods allow, in addition to the derivation of most probable elementary mechanisms, prediction of thermodynamic and kinetic reaction parameters for relatively small molecules in homogeneous gas-phase and liquid-phase reactions, and even for some heterogeneous catalytic systems. This is especially useful for complex kinetics where there is no easily discernible rate-determining step, and therefore no simple closed-form global reaction rate can be determined. In particular, estimating a large number of kinetic parameters from laboratory data requires a large number of experiments and use of intermediate reaction components that are not stable or not readily available. The nonlinear parameter estimation with many parameters is difficult, with no assurance that global minima are actually obtained. For such complex systems, computational chemistry estimates are an attractive starting point, requiring experimental validation.

Computational chemistry includes a wide range of methods of varying accuracy and complexity, summarized in Table 7-14. Many of these methods have been implemented as software packages that require high-speed supercomputers or parallel computers to solve realistic reactions. For more details on computational chemistry, see, e.g., Cramer, *Essentials of Computational Chemistry: Theories and Models*, 2d ed., Wiley, 2004.

Lumping and Mechanism Reduction It is often useful to reduce complex reaction networks to a smaller reaction set which still maintains the key features of the detailed reaction network but with a much smaller number of representative species, reactions, and kinetic parameters. Simple examples were already given above for reducing simple networks into global reactions through assumptions such as pseudo-steady state, rate-limiting step, and equilibrium reactions.

In general, *mechanism reduction* can only be used over a limited range of conditions for which the simplified system simulates the original complete reaction network. This reduces the number of kinetic parameters that have to be either estimated from data or calculated by

TABLE 7-14 Computational Chemistry Methods

Abinitio methods (no empirical parameters)	
Electronic structure determination (time-independent Schrodinger equation)	
Hartree-Fock (HF) with corrections	
Quantum Monte Carlo (QMT)	
Density functional theory (DFT)	
Chemical dynamics determination (time-dependent Schrodinger equation)	
Split operator technique	
Multiconfigurational time-dependent Hartree-Fock method	
Semiclassical method	
Semiempirical methods (approximate parts of HF calculations such as two-electron integrals)	
Huckel	
Extended Huckel	
Molecular mechanics (avoids quantum mechanical calculations)	
Empirical methods (group contributions)	
Polanyi linear approximation of activation energy	

using computational chemistry. The simplified system also reduces the computation load for reactor scale-up, design, and optimization.

A type of mechanism reduction called *lumping* is typically performed on a reaction network that consists of a large number of similar reactions occurring between similar species, such as homologous series or molecules having similar functional groups. Such situations occur, for instance, in the oil refining industry, examples including catalytic reforming, catalytic cracking, hydrocracking, and hydrotreating. Lumping is done by grouping similar species, or molecules with similar functional groups, into pseudo components called lumped species. The behavior of the lumped system depends on the initial composition, the distribution of the rate constants in the detailed system, and the form of the rate equation. The two main issues in lumping are

1. Determination of the lump structure that simulates the detailed system over the required range of conditions

2. Determination of the kinetics of the lumped system from general knowledge about the type of kinetics and the overall range of parameters of the detailed system

Lumping has been applied extensively to first-order reaction networks [e.g., Wei and Kuo, "A Lumping Analysis in Monomolecular Reaction Systems," *I&EC Fundamentals* **8**(1): 114–123 (1969); Golikeri and Luss, "Aggregation of Many Coupled Consecutive First Order Reactions," *Chem. Eng. Sci.* **29**: 845–855 (1974)]. For instance, it has been shown that a lumped reaction network of first-order reactions can behave under certain conditions as a global second-order reaction. Where analytical solutions were not available, others, such as Golikeri and Luss, "Aggregation of Many Coupled Consecutive First Order Reactions," *Chem. Eng. Sci.* **29**: 845–855 (1974), developed bounds that bracketed the behavior of the lump for first-order reactions as a function of the initial composition and the rate constant distribution. Lumping has not been applied as successfully to nonlinear or higher-order kinetics. More recent applications of lumping were published, including structure-oriented lumping that lumps similar structural groups, by Quann and Jaffe, "Building Useful Models of Complex Reaction Systems in Petroleum Refining," *Chem. Eng. Sci.* **51**(10): 1615–1635 (1996).

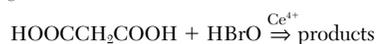
For other types of systems such as highly branched reaction networks for homogeneous gas-phase combustion and combined homogeneous and catalytic partial oxidation, mechanism reduction involves pruning branches and pathways of the reaction network that do not contribute significantly to the overall reaction. This pruning is done by using *sensitivity analysis*. See, e.g., Bui et al., "Hierarchical Reduced Models for Catalytic Combustion: H₂/Air Mixtures near Platinum Surfaces," *Combustion Sci. Technol.* **129**(1–6):243–275 (1997).

Multiple Steady States, Oscillations, and Chaotic Behavior
There are reaction systems whose steady-state behavior depends on

the initial or starting conditions; i.e., for different starting conditions, different steady states can be reached at the same final operating conditions. This behavior is called steady-state multiplicity and is often the result of the interaction of kinetic and transport phenomena having distinct time scales. For some cases, the cause of the multiplicity is entirely reaction-related, as shown below. Associated with steady-state multiplicity is hysteresis, and higher-order instabilities such as self-sustained oscillations and chaotic behavior. The existence of multiple steady states may be relevant to analysis of laboratory data, since faster of slower rates may be observed at the same conditions depending on how the lab reactor is started up.

For example, CO oxidation on heterogeneous Rh catalyst exhibits hysteresis and multiple steady states, and one of the explained causes is the existence of two crystal structures for Rh, each with a different reactivity (Masel, *Chemical Kinetics and Catalysis*, Wiley, 2001, p. 38).

Another well-known example of chemistry-related instability includes the oscillatory behavior of the Bheulousov-Zhabotinsky reaction of malonic acid and bromate in the presence of homogeneous Ce catalyst having the overall reaction



Ce can be in two oxidation states, Ce³⁺ and Ce⁴⁺, and there are competing reaction pathways. Complex kinetic models are required to predict the oscillatory behavior, the most well known being that of Noyes [e.g., Showalter, Noyes, and Bar-Eli, *J. Chem. Phys.* **69**(6): 2514–2524 (1978)].

A large body of work has been done to develop criteria that determine the onset of chemistry and transport chemistry-based instabilities. More details and transport-reaction coupling-related examples are discussed in Sec. 19.

SOFTWARE TOOLS

There are a number of useful software packages that enable efficient analysis of laboratory data for developing the mechanism and kinetics of reactions and for testing the kinetics by using simple reactor models. The reader is referred to search the Internet as some of these software packages change ownership or name. Worth mentioning are the Aspen Engineering Suite (Aspen), the Thermal Safety Software suite (Cheminform St. Petersburg), the Matlab suite (Mathworks), the Chemkin software suite (Reaction Design), the NIST Chemical Kinetics database (NIST), and Gepasi for biochemical kinetics (freeware). The user is advised to experiment and validate any software package with known data and kinetics to ensure robustness and reliability.

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