Reaction Kinetics

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Nomenclature and Units

Following is a listing of typical nomenclature expressed in SI and U.S. customary units. Specific definitions and units are stated at the place of application in this section.

Symbol	Definition	SI units	U.S. customary units
A, B, C, ...	Names of substances, or their concentrations		
A⁺	Free radical, as $CH_3^{\bullet}$		
C_a	Concentration of substance A	kg mol/m³	lb mol/ft³
C^0	Initial mean concentration in vessel	kg mol/m³	lb mol/ft³
C_p	Heat capacity	kJ/(kg·K)	Btu/(lbm·°F)
CSTR	Continuous stirred tank reactor		
D, D_e, D_x	Dispersion coefficient	m²/s	ft²/s
D_{eff}	Effective diffusivity	m²/s	ft²/s
D_K	Knudsen diffusivity	m²/s	ft²/s
$E(t)$	Residence time distribution		
$E(t_r)$	Normalized residence time distribution		
f_a	C_a/C_{a0} or n_a/n_{a0}, fraction of A remaining unconverted		
$F(t)$	Age function of tracer		
ΔG	Gibbs energy change	kJ	Btu
Ha	Hatta number		
ΔH_r	Heat of reaction	kJ/kg mol	Btu/lb mol
K, K_e, K_y, K_ϕ	Chemical equilibrium constant		
k, k_c, k_p	Specific rate of reaction	Variable	Variable
L	Length of path in reactor	m	ft
n	Parameter of Erlang or Gamma distribution, or number of stages in a CSTR battery		
n_a	Number of mols of A present		
n_a'	Number of mols flowing per unit time; the prime (') may be omitted when context is clear		
n_t	Total number of mols		
p_a	Partial pressure of substance A	kP$_a$	psi
Pe	Peclet number for dispersion		
PFR	Plug flow reactor		
Q	Heat transfer	kJ	Btu
r	Radial position	m	ft
r_a	Rate of reaction of A per unit volume	Variable	Variable
R	Radius of cylindrical vessel	m	ft
Re	Reynolds number		
Sc	Schmidt number		

Symbol	Definition	SI units	U.S. customary units
t	Time	s	s
$\bar{t}$	Mean residence time	s	s
t_r	$t/\bar{t}$, reduced time		
TFR	Tubular flow reactor		
u	Linear velocity	m/s	ft/s
$u(t)$	Unit step input		
V	Volume of reactor contents	m³	ft³
V'	Volumetric flow rate	m³/s	ft³/s
V_r	Volume of reactor	m³	ft³
x	Axial position in a reactor	m	ft
x_a	$1 - f_a = 1 - C_a/C_{a0}$ or $1 - n_a/n_{a0}$, fraction of A converted		
z	x/L, normalized axial position		

Greek letters			
β	r/R, normalized radial position		
$\gamma^3(t)$	Skewness of distribution		
$\delta(t)$	Unit impulse input, Dirac function		
ε	Fraction void space in a packed bed		
θ	$t/\bar{t}$, reduced time, fraction of surface covered by adsorbed species		
η	Effectiveness of porous catalyst		
$\Lambda(t)$	Intensity function		
μ	Viscosity	Pa·s	lbm/(ft·s)
ν	υ/ρ, kinematic viscosity	m²/s	ft²/s
π	Total pressure	Pa	psi
ρ	Density	kg/m³	lbm/ft³
ρ	r/R, normalized radial position in a pore		
$\sigma^2(t)$	Variance		
$\sigma^2(t_r)$	Normalized variance		
τ	$t/\bar{t}$, reduced time		
τ	Tortuosity		
ϕ	Thiele modulus		
ϕ_m	Modified Thiele modulus		

Subscripts			
0	Subscript designating initial or inlet conditions, as in C_{a0}, n_{a0}, V_0, ...		

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REACTION KINETICS

INTRODUCTION

From an engineering viewpoint, reaction kinetics has these principal functions:

Establishing the chemical mechanism of a reaction
Obtaining experimental rate data
Correlating rate data by equations or other means
Designing suitable reactors

Specifying operating conditions, control methods, and auxiliary equipment to meet the technological and economic needs of the reaction process

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

1. Irreversible
2. Reversible
3. Simultaneous
4. Consecutive

A further classification from the point of view of mechanism is with respect to the number of molecules participating in the reaction, the *molecularity:*

1. Unimolecular
2. Bimolecular and higher

Related to the preceding is the classification with respect to *order.* In the power law rate equation $r = kC_a^p C_b^q$, the exponent to which any particular reactant concentration is raised is called the order p or q with respect to that substance, and the sum of the exponents $p + q$ is the order of the reaction. At times the order is identical with the molecularity, but there are many reactions with experimental orders of zero or fractions or negative numbers. Complex reactions may not conform to any power law. Thus, there are reactions of:

1. Integral order
2. Nonintegral order
3. Non–power law; for instance, hyperbolic

With respect to *thermal conditions,* the principal types are:

1. Isothermal at constant volume
2. Isothermal at constant pressure
3. Adiabatic
4. Temperature regulated by heat transfer

According to the *phases* involved, reactions are:

1. Homogeneous, gaseous, liquid or solid
2. Heterogeneous:
   Controlled by diffusive mass transfer
   Controlled by chemical factors

A major distinction is between reactions that are:

1. Uncatalyzed
2. Catalyzed with homogeneous or solid catalysts

Equipment is also a basis for differentiation, namely:

1. Stirred tanks, single or in series
2. Tubular reactors, single or in parallel
3. Reactors filled with solid particles, inert or catalytic:
   Fixed bed
   Moving bed
   Fluidized bed, stable or entrained

Finally, there are the *operating modes:*

1. Batch
2. Continuous flow
3. Semibatch or semiflow

Clearly, these groupings are not mutually exclusive. The chief distinctions are between homogeneous and heterogeneous reactions and between batch and flow reactions. These distinctions most influence the choice of equipment, operating conditions, and methods of design.

PRIMARY NOMENCLATURE

The participant A is identified by the subscript *a.* Thus, the concentration is C_a; the number of mols is n_a; the fractional conversion is x_a; the partial pressure is p_a; and the rate of decomposition is r_a. Capital letters are also used to represent concentration on occasion; thus, A instead of C_a. The flow rate in mol is n_a' but the prime ($'$) is left off when the meaning is clear from the context. The volumetric flow rate is V'; reactor volume is V_r or simply V of batch reactors; the total pressure is π; and the temperature is T. The concentration is $C_a = n_a/V$ or n_a'/V'.
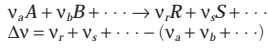
Throughout this section, equations are presented without specification of units. Use of any consistent unit set is appropriate.

SUMMARY

Basic kinetic relations of this section are summarized in Table 7-1.

TABLE 7-1　Basic Rate Equations

1. The *reference reaction* is

$$\nu_a A + \nu_b B + \cdots \rightarrow \nu_r R + \nu_s S + \cdots$$
$$\Delta\nu = \nu_r + \nu_s + \cdots - (\nu_a + \nu_b + \cdots)$$

2. *Stoichiometric balance* for any component *i*:

$$n_i = n_{i0} \pm \left(\frac{\nu_i}{\nu_a}\right)(n_{a0} - n_a)$$

$\begin{cases} + \text{ for product (right-hand side, RHS)} \\ - \text{ for reactant (left-hand side, LHS)} \end{cases}$

$$C_i = C_{i0} \pm \left(\frac{\nu_i}{\nu_a}\right)(C_{a0} - C_a), \qquad \text{at constant } T \text{ and } V \text{ only}$$

$$n_t = n_{t0} + \left(\frac{\Delta\nu}{\nu_a}\right)(n_{a0} - n_a)$$

3. *Law of mass action:*

$$r_a = -\frac{1}{V_r}\frac{dn_a}{dt} = kC_a^{\nu_a}C_b^{\nu_b}\cdots$$

$$= kC_a^{\nu_a}[C_{b0} - \left(\frac{\nu_b}{\nu_a}\right)(C_{a0} - C_a)]^{\nu_b}\cdots$$

$$r_a = kC_a^{\alpha}[C_{b0} - \left(\frac{\nu_b}{\nu_a}\right)(C_{a0} - C_a)]^{\beta}\cdots$$

where it is not necessarily true that $\alpha = \nu_a$, $\beta = \nu_b$, ...

4. At *constant volume,* $C_a = n_a/V_r$

$$kt = \int_{C_a}^{C_{a0}} \frac{1}{C_a^{\alpha}[C_{b0} - (\nu_b/\nu_a)(C_{a0} - C_a)]^{\beta}\cdots}\, dC_a$$

$$kt = \int_{n_a}^{n_{a0}} \frac{V_r^{-1+\alpha+\beta}}{n_a^{\alpha}[n_{b0} + (\nu_b/\nu_a)(n_{a0} - n_a)]^{\beta}\cdots}\, dn_a$$

Completed integrals for some values of α and β are in Table 7-4.

5. *Ideal gases at constant pressure:*

$$V_r = \frac{n_t RT}{P} = \frac{RT}{P}\left[n_{t0} + \frac{\Delta\nu}{\nu_a}(n_{a0} - n_a)\right]$$

$$r_a = kC_a^{\alpha}$$

$$kt = \left(\frac{RT}{P}\right)^{\alpha-1}\int_{n_a}^{n_{a0}} \frac{[n_{t0} + (\Delta\nu/\nu_a)(n_{a0} - n_a)]^{\alpha-1}}{n_a^{\alpha}}\, dn_a$$

6. *Temperature effect* on the specific rate:

$$k = k_{\infty}\exp\left(\frac{-E}{RT}\right) = \exp\left(a' - \frac{b'}{T}\right)$$

E = energy of activation

7. *Simultaneous reactions.* The overall rate is the algebraic sum of the rates of the individual reactions. For example, take the three reactions:

$$A + B \xrightarrow{k_1} C + D \tag{1}$$
$$C + D \xrightarrow{k_2} A + B \tag{2}$$
$$A + C \xrightarrow{k_3} E \tag{3}$$

The rates are related by:

$r_a = r_{a1} + r_{a2} + r_{a3} = k_1 C_a C_b - k_2 C_c C_d + k_3 C_a C_c$
$r_b = -r_b = k_1 C_a C_b - k_2 C_c C_d$
$r_c = k_1 C_a C_b + k_2 C_c C_d + k_3 C_a C_c$
$r_e = -k_3 C_a C_c$

The number of independent rate equations is the same as the number of independent stoichiometric relations. In the present example, Reactions (1) and (2) are reversible reactions and are not independent. Accordingly, C_c and C_d, for example, can be eliminated from the equations for r_a and r_b which then become an integrable system. Usually only systems of linear differential equations with constant coefficients are solvable analytically.

8. *Mass transfer resistance:*

C_{ai} = interfacial concentration of reactant A

$$r_a = -\frac{dC_a}{dt} = k_d(C_a - C_{ai}) = kC_{ai}^{\alpha} = k\left(C_a - \frac{r_a}{k_d}\right)^{\alpha}$$

$$kt = \int_{C_a}^{C_{a0}} \frac{1}{(C_a - r_a/k_d)^{\alpha}}\, dC_a$$

The relation between r_a and C_a must be established (numerically if need be) from the second line before the integration can be completed.

9. *Solid-catalyzed reactions.* Some Langmuir-Hinshelwood mechanisms for the reference reaction A + B → R + S (see also Tables 7.2, 7.3):

- Adsorption rate of A controlling:

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = kP_a\theta_v$$

$$\theta_v = 1\bigg/\left[1 + \frac{K_a}{K_e}\frac{P_r P_s}{P_b} + K_b P_b + K_r P_r + K_s P_s + K_l P_l\right] \tag{1}$$

$K_e = P_r P_s/P_a P_b$ (equilibrium constant)

l is an adsorbed substance that is chemically inert.

- Surface reaction rate controlling:

$$r = kP_a P_b \theta_v^2$$

$$\theta_v = \frac{1}{1 + \sum K_j P_j}, \qquad \text{summation over all substances absorbed} \tag{2}$$

- Reaction A_2 + B → R + S, with A_2 dissociated upon adsorption and with surface reaction rate controlling:

$$r_a = kP_a P_b \theta_v^3$$

$$\theta_v = \frac{1}{(1 + \sqrt{K_a P_a} + K_b P_b + \cdots)} \tag{3}$$

- At constant P and T the P_i are eliminated in favor of n_i and the total pressure by:

$$P_a = \frac{n_a}{n_t} P$$

$$P_i = \frac{n_i}{n_t} P = \frac{n_{i0} \pm (\nu_i/\nu_a)(n_{a0} - n_a)}{n_{t0} + (\Delta\nu/\nu_a)(n_{a0} - n_a)} P$$

$\begin{cases} + \text{ for products, RHS} \\ - \text{ for reactants, LHS} \end{cases}$

$$V = \frac{n_t RT}{P}$$

$$kt = \int_{n_a}^{n_{a0}} \frac{dn_a}{V P_a P_b \theta_v^2}, \qquad \text{for a Case (2) batch reaction} \tag{4}$$

10. A *continuously stirred tank reactor* (CSTR) battery

Material balances:

$$n'_{a0} = n'_a + r_{a1}V_{r1}$$

$$n'_{a,j-1} = n'_{aj} + r_{aj}V_{rj}, \qquad \text{for the } j\text{th stage}$$

For a first-order reaction, with $r_a = kC_a$:

$$\frac{C_{aj}}{C_{a0}} = \frac{1}{(1 + k_1\bar{t}_1)(1 + k_2\bar{t}_2)\cdots(1 + k_j\bar{t}_j)}$$

$$= \frac{1}{(1 + k\bar{t}_i)^j}$$

for j tanks in series with the same temperatures and residence times $\bar{t}_i = V_{ri}/V_i$, where V' is the volumetric flow rate.
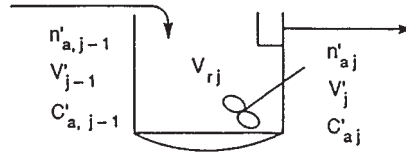
11. *Plug flow reactor* (PFR):

$$r_s = -\frac{dn'_a}{dV_r} = kC_a^{\alpha}C_b^{\beta}\cdots$$

$$= k\left(\frac{n'_a}{V'}\right)^{\alpha}\left(\frac{n'_b}{V'}\right)^{\beta}\cdots$$

TABLE 7-1 Basic Rate Equations (*Concluded*)
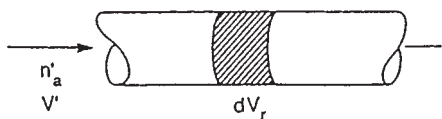
12. *Material and energy balances* for batch, CSTR, and PFR in Tables 7-5, 7-6, and 7-7.

13. *Notation.* A, B, R, S are participants in the reaction; the letters also are used to represent concentrations.

$C_i = n_i/V_r$ or n_i'/V', concentration
n_i = mol of component i in the reactor
n_i' = molal flow rate of component i
V_r = volume of reactor
V' = volumetric flow rate
ν_i = stoichiometric coefficient
r_i = rate of reaction of substance i [mol/(unit time)(unit volume)]
α, β = empirical exponents in a rate equation

SOURCE: Adapted from Walas, *Chemical Process Equipment Selection and Design,* Butterworth-Heinemann, 1990.

RATE EQUATIONS

RATE OF REACTION

The term *rate of reaction* means the rate of decomposition per unit volume,

$$r_a = -\frac{1}{V}\frac{dn_a}{dt}, \qquad \text{mol/(unit time) (unit volume)} \qquad (7\text{-}1)$$

$$= \frac{n_{a0}}{V}\frac{dx_a}{dt}, \qquad n_0 = n_{a0}(1 - x_a) \qquad (7\text{-}2)$$

where x_a is the fractional conversion of substance A. A rate of formation will have the opposite sign. The negative sign is required for the rate of decomposition to be a positive number. When the volume is constant,

$$r_a = -\frac{dC_a}{dt} \qquad \text{only at constant volume} \qquad (7\text{-}3)$$

Law of Mass Action The effect of concentration on the rate is isolated as

$$r_a = kf(C_a, C_b, \ldots) \qquad (7\text{-}4)$$

where the specific rate k is independent of concentration but does depend on temperature, catalysts, and other factors. The law of mass action states that the rate is proportional to the concentrations of the reactants. For the reaction

$$\nu_a A + \nu_b B + \nu_c C + \cdots \Rightarrow \nu_r R + \nu_s S + \cdots \qquad (7\text{-}5)$$

the rate equation is

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = kC_a^p C_b^q C_c^r \ldots \qquad (7\text{-}6)$$

$$\Rightarrow -\frac{dC_a}{dt} \qquad \text{at constant volume} \qquad (7\text{-}7)$$

The exponents ($p, q, r, \ldots$) are empirical, but they are identical with the stoichiometric coefficients ($\nu_a, \nu_b, \nu_c, \ldots$) when the stoichiometric equation truly represents the mechanism of reaction. The first group of exponents identifies the *order* of the reaction, the stoichiometric coefficients the *molecularity*.

Effect of Temperature The *Arrhenius equation* relates the specific rate to the absolute temperature,

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

$$= \exp\left(A - \frac{B}{T}\right) \qquad (7\text{-}9)$$

$$\ln k = A - \frac{B}{T} \qquad (7\text{-}10)$$

E is called the *activation energy* and k_0 the *preexponential factor.* When presumably accurate data deviate from linearity as stated by the last equation, the reaction is believed to have a complex mechanism (Fig. 7-1*g*).

CONCENTRATION, MOLES, PARTIAL PRESSURE, AND MOLE FRACTION

Any property of a reacting system that changes regularly as the reaction proceeds can be formulated as a rate equation which should be convertible to the fundamental form in terms of concentration, Eq. (7-4). Examples are the rates of change of electrical conductivity, of pH, or of optical rotation. The most common other variables are partial pressure p_i and mole fraction N_i. The relations between these units are

$$n_i = VC_i = n_t N_i = \frac{n_t p_i}{\pi} \qquad (7\text{-}11)$$

where the subscript t denotes the total mol and π the total pressure. For ideal gases,

$$V = \frac{n_t RT}{\pi}$$

$$n_i = \frac{n_t RT}{\pi} \; C_i = \frac{n_i}{\pi} \; p_i = \frac{V}{RT} \; p_i = \frac{\pi V}{RT} \; N_i \qquad (7\text{-}12)$$

Other volume-explicit equations of state are sometimes required, such as the compressibility equation $V = zRT/P$ or the truncated virial equation $V = (1 + B'P)RT/P$. The quantities z and B' are not constants, so some kind of averaging will be required. More accurate equations of state are even more difficult to use but are not often justified for kinetic work.

Designate δ_a as the increase in the total mol per mol decrease of substance A according to the stoichiometric equation Eq. (7-5):

$$\delta_a = \frac{(\nu_r + \nu_s + \cdots) - (\nu_a + \nu_b + \nu_c + \cdots)}{\nu_a} \qquad (7\text{-}13)$$

The total number of mols present is

$$n_t = n_{t0} + \delta_a(n_{a0} - n_a) = n_{t0} + \delta_a x_a = n_{t0} + \delta_b x_b = \cdots \qquad (7\text{-}14)$$

Accordingly,

$$-\frac{dn_t}{dt} = \delta_a \frac{dn_a}{dt} = \delta_b \frac{dn_b}{dt} = \delta_c \frac{dn_c}{dt} = \cdots \qquad (7\text{-}15)$$

The various differentials are

$$dn_i = d(VC_i) = \frac{1}{RT} d(Vp_i) = d(n_t N_i) = \frac{n_t}{1 + \delta_i N_i} dN_i \qquad (7\text{-}16)$$

The rate equation

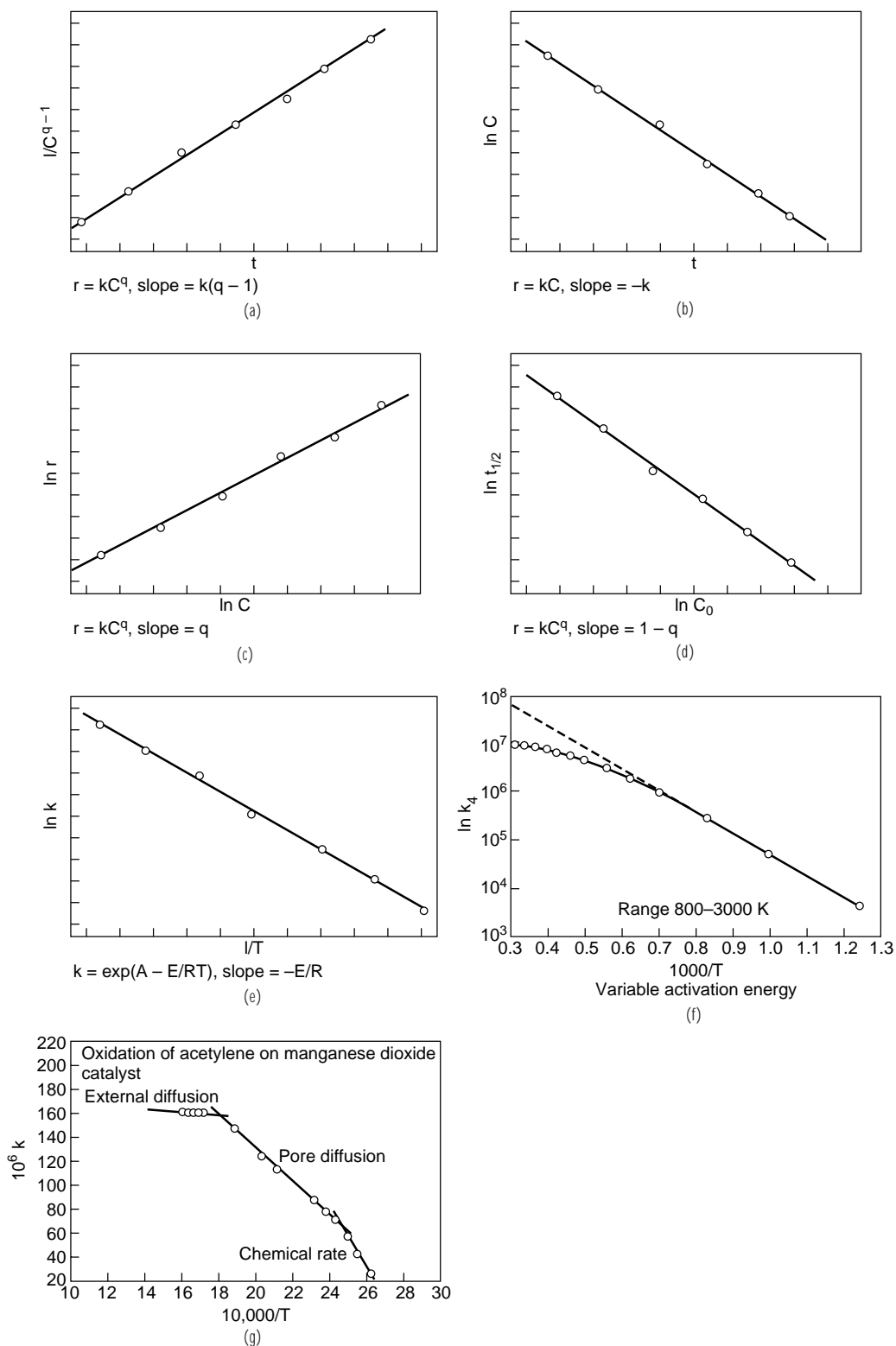$$r_a = -\frac{1}{V}\frac{dC_a}{dt} = k_c C_a^\alpha \qquad (7\text{-}17)$$

FIG. 7-1   Constants of the power law and Arrhenius equations by linearization: (*a*) integrated equation, (*b*) integrated first order, (*c*) differential equation, (*d*) half-time method, (*e*) Arrhenius equation, (*f*) variable activation energy, and (*g*) change of mechanism with temperature (*T* in K).

can be expressed in terms of pressure and mole fraction,

$$-\frac{1}{RTV}\frac{d(Vp_a)}{dt} = k_c\left(\frac{1}{RT}\right)^\alpha p_a^\alpha \qquad (7\text{-}18)$$

or at constant volume,

$$-\frac{dp_a}{dt} = k_c\left(\frac{1}{RT}\right)^{\alpha-1} p_a^\alpha = k_p p_a^\alpha \qquad (7\text{-}19)$$

where the specific rate in terms of partial pressure is

$$k_p = k_c\left(\frac{1}{RT}\right)^{\alpha-1} \qquad (7\text{-}20)$$

Typical Units of Specific Rates For order α, typical units are:
k_c (L/g mol)$^{\alpha-1}\cdot$s^{-1}, and s^{-1} when first order
k_p (g mol)/L$\cdot$s$\cdot$atm$^\alpha$
Furthermore,

$$-\frac{n_t}{V(1+\delta_a N_a)}\frac{dN_a}{dt} = k_c\left(\frac{n_t}{V}\right)^\alpha N_a^\alpha$$

or

$$-\frac{dN_a}{dt} = k_c\left(\frac{n_t}{V}\right)^{\alpha-1}\left(\frac{1}{1+\delta_a N_a}\right)N_a^\alpha$$

$$= k_c\left(\frac{\pi}{RT}\right)^{\alpha-1}\left(\frac{1}{1+\delta_a N_a}\right)N_a^\alpha \qquad (7\text{-}21)$$

Various derivatives are evaluated in numerical Example 1.

Example 1: Rates of Change at Constant V or Constant P
Consider the ideal gas reaction $2A \Rightarrow B + 2C$ occurring at 800°R, starting with 5 lb mol of pure A at 10 atm. The rate equation is

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = 700\,C_a^2 \text{ lb mol/(ft}^3\cdot\text{h)}$$

Evaluate the various rates of change at the time when the rate of reaction is $r_a = 0.1$ lb mol/(ft$^3\cdot$h) and the reaction proceeds at (1) constant volume, and (2) constant pressure.

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = 700\,C_a^2 = 0.1 \text{ lb mol/(ft}^3\cdot\text{h)}$$

$$C_a = \sqrt{\frac{0.1}{700}} = 0.01195 \text{ lb mol/ft}^3$$

$$V_0 = \frac{n_{a0}RT}{\pi_0} = \frac{5(0.729)(800)}{10} = 291.6 \text{ ft}^3$$

$$C_{a0} = \frac{n_{a0}}{V_0} = \frac{5}{291.6} = 0.01715 \text{ lb mol/ft}^3$$

$$n_t = 0.5(3n_{a0} - n_a) \text{ lb mol}$$

$$V = \frac{(3n_{a0} - n_a)\,RT}{2\pi_0} = 29.16(15 - n_a) \text{ ft}^3$$

$$\pi = \frac{n_t}{n_{t0}}\pi_0 = 3n_{a0} - n_a \text{ atm}$$

At constant volume, $n_a = V_0 C_a = 291.6(0.01195) = 3.4853$ lb mol

$$\frac{dn_a}{dt} = V_0\frac{dC_a}{dt} = -291.6(0.1) = -29.16 \text{ lb mol/h}$$

$$N_a = \frac{n_a}{n_t} = \frac{2n_a}{3n_{a0} - n_a}$$

$$\frac{dN_a}{dt} = \frac{6}{n_{a0}(3 - n_a/n_{a0})^2}\left(\frac{dn_a}{dt}\right) = \frac{6}{5(3 - 3.4853/5)^2}(-29.16)$$

$$= -6.598 \text{ h}^{-1}$$

$$p_a = \frac{n_a RT}{V_0} \text{ atm}$$

$$\frac{dp_a}{dt} = \frac{RT}{V_0}\left(\frac{dn_a}{dt}\right) = \frac{0.729(800)}{291.6}(-29.16) = -58.32 \text{ atm/h}$$

$$\pi = \frac{n_t}{n_{t0}}\pi_0 = \frac{3n_{a0} - n_a}{2n_{a0}}\pi_0 = 5\left(3 - \frac{n_a}{n_{a0}}\right) \text{atm}$$

$$\frac{d\pi}{dt} = -\frac{5}{n_{a0}}\frac{dn_a}{dt} = 29.16 \text{ atm/h}$$

At constant pressure, $n_a = VC_a = 29.16(15 - n_a)\,(0.01195) = 3.8768$ lb mol

$$\frac{dn_a}{dt} = -Vr_a = -324.4(0.1) = -32.44 \text{ lb mol/h}$$

since $V = 29.16\,(15 - 3.8768) = 324.4 \text{ ft}^3$

$$C_a = \frac{n_a}{V} = \frac{n_a}{29.16(15 - n_a)} \text{ lb mol/ft}^3$$

$$\frac{dC_a}{dt} = \frac{1}{29.16}\left[\frac{15}{(15 - n_a)^2}\right]\frac{dn_a}{dt} = \frac{1}{29.16}\left[\frac{15}{(15 - 3.8768)^2}\right](-32.44)$$

$$= 0.1349 \text{ lb mol/(ft}^3\cdot\text{h)}$$

$$\frac{dN_a}{dt} = \frac{6n_{a0}}{(3n_{a0} - n_a)^2}\frac{dn_a}{dt} = \frac{30}{(15 - 3.8768)^2}(-32.44) = -7.8658 \text{ h}^{-1}$$

$$p_a = N_a\pi_0 = \frac{2\pi_0 n_a}{3n_{a0} - n_a} \text{ atm}$$

$$\frac{dp_a}{dt} = \frac{6\pi_0}{(3n_{a0} - n_a)^2}\frac{dn_a}{dt} = \frac{(6)(10)(5)}{(15 - 3.8768)^2}(-32.44) = -78.66 \text{ atm/h}$$

$$V = \frac{(3n_{a0} - n_a)RT}{2\pi_0} \text{ ft}^3$$

$$\frac{dV}{dt} = \frac{RT}{2\pi_0}\left(-\frac{dn_a}{dt}\right) = \frac{0.729(800)}{20}(32.44) = 945.95 \text{ ft}^3/\text{h}$$

$$\frac{dx_a}{dt} = \frac{d}{dt}\left(\frac{n_{a0} - n_a}{n_{a0}}\right) = -\frac{1}{n_{a0}}\frac{dn_a}{dt} = -\frac{1}{5}(-32.44) = 6.488 \text{ h}^{-1}$$

SUMMARY

Rate	At constant V	At constant P
dn_a/dt, lb mol/h	−29.16	−32.44
dN_a/dt, h^{-1}	−6.598	−7.866
dp_a/dt, atm/h	−58.32	−78.66
$d\pi/dt$, atm/h	29.16	0
dV/dt, ft^3/h	0	946.0
dx_a/dt, h^{-1}	5.832	6.488

REACTION TIME IN FLOW REACTORS

Flow reactors usually operate at nearly constant pressure, and thus at variable density when there is a change of moles of gas or of temperature. An *apparent residence time* is the ratio of reactor volume and the inlet volumetric flow rate,

$$\bar{t}_{\text{app}} = \frac{V_r}{V_0'} \qquad (7\text{-}22)$$

The *true residence time* is obtained by integration of the rate equation,

$$\bar{t} = \int \frac{dV_r}{V'} = \int \frac{dn}{V'r} = \int \frac{dn}{kV'(n/V')^q} \qquad (7\text{-}23)$$

The apparent time is readily evaluated and is popularly used to indicate the loading of a flow reactor.

A related concept is that of *space velocity,* which is a ratio of a flow rate at STP (usually 60°F, 1 atm) to the size of the reactor. The most common versions in typical units are:

GHSV (gas hourly space velocity) = (volumes of feed as gas at STP/h)/(volume of reactor or its content of catalyst) = SCFH gas feed/ft^3.

LHSV (liquid hourly space velocity) = (volume of liquid feed at 60°F/h)/(ft^3 of reactor) = SCFH liquid feed/ft^3.

WHSV (weight hourly space velocity) = (lb feed/h)/(lb catalyst).

It is usually advisable to spell out the units when the acronym is used, since the units are arbitrary.

CONSTANTS OF THE RATE EQUATION

The problem is to apply experimental data to find the constants of assumed rate equations, of which some of the simpler examples are:

$$r = -\frac{dC}{dt} = kC^q \tag{7-24}$$

or

$$r = -\frac{dC}{dt} = \exp\left(a - \frac{b}{t}\right) C^q \tag{7-25}$$

or

$$r_a = -\frac{dC_a}{dt} = kC_a^p C_b^q \tag{7-26}$$

Experimental data that are most easily obtained are of (C, t), (p, t), (r, t), or (C, T, t). Values of the rate are obtainable directly from measurements on a continuous stirred tank reactor (CSTR), or they may be obtained from (C, t) data by numerical means, usually by first curve fitting and then differentiating. When other properties are measured to follow the course of reaction—say, conductivity—those measurements are best converted to concentrations before kinetic analysis is started.

The most common ways of evaluating the constants are from linear rearrangements of the rate equations or their integrals. Figure 7-1 examines power law and Arrhenius equations, and Fig. 7-2 has some more complex cases.

From the Differential Equation Linear regression can be applied with the differential equation to obtain constants. Taking logarithms of Eq. (7-25),

$$\ln r = a - \frac{b}{T} + q \ln C \tag{7-27}$$

The variables that are combined linearly are $\ln r$, $1/T$, and $\ln C$. Multilinear regression software can be used to find the constants, or only three sets of the data suitably spaced can be used and the constants found by simultaneous solution of three linear equations. For a linearized Eq. (7-26) the variables are logarithms of r, C_a, and C_b. The logarithmic form of Eq. (7-24) has only two constants, so the data can be plotted and the constants read off the slope and intercept of the best straight line.

From the Integrated Equation The integral of Eq. (7-24) is

$$k = \frac{1}{t - t_0} \ln \frac{C_0}{C}, \quad \text{when } q = 1 \tag{7-28}$$

$$\frac{C_0^{q-1}}{(t - t_0)(q - 1)}\left[\left(\frac{C_0}{C}\right)^{q-1} - 1\right], \quad \text{when } q \neq 1 \tag{7-29}$$

A value of q is assumed and values of k are calculated for each data point. The correct value of q has been chosen when the values of k are nearly constant or show no drift. This procedure is applicable for a rate equation of any complexity if it can be integrated. Eqs. (7-28) and (7-29) can also be put into linear form:

$$\ln\left(\frac{C_0}{C}\right) = k(t - t_0), \quad \text{when } q = 1 \tag{7-30}$$

$$\left(\frac{1}{C}\right)^{q-1} = \left(\frac{1}{C_0}\right)^{q-1} + k(q - 1)(t - t_0), \quad \text{when } q \neq 1 \tag{7-31}$$

When the plots are collinear, the correct value of k is found from the slope of the best straight line.

From Half-Times The time by which one-half of the reactant has been converted is called the *half-time.* From Eq. (7-24),

$$kt_{1/2} = \ln 2, \qquad q = 1$$

$$\frac{2^{q-1} - 1}{(q - 1)C_0^{q-1}} \qquad q \neq 1 \tag{7-32}$$

When several sets of $(C_0, t_{1/2})$ are known, values of q are tried until one is found that makes all k values substantially the same. Alternatively, the constants may be found from a linearized plot,

$$\ln t_{1/2} = \ln \frac{2^{q-1} - 1}{(q - 1)k} + (1 - q) \ln C_0 \tag{7-33}$$

Complex Rate Equations Complex rate equations may require individual treatment, although the examples in Fig. 7-2 are all linearizable. A perfectly general procedure is nonlinear regression. For instance, when $r = f(C, a, b, \ldots)$ where $(a, b, \ldots)$ are the constants to be found, the condition is

$$\sum [r_i - f(C_i, a, b, \ldots)]^2 \Rightarrow \text{Minimum} \tag{7-34}$$

and

$$\frac{\partial \Sigma}{\partial a} = \frac{\partial \Sigma}{\partial b} = \cdots = 0 \tag{7-35}$$

Much professional software is devoted to this problem. A diskette for sets of differential and algebraic equations with parameters to be found by this method is by Constantinides (*Applied Numerical Methods with Personal Computers,* McGraw-Hill, 1987).

The acquisition of kinetic data and parameter estimation can be at quite a sophisticated level, particularly for solid catalytic reactions: statistical design of experiments, refined equipment, computer monitoring of data acquisition, and statistical evaluation of the data. Two papers are devoted to this topic by Hofmann (in *Chemical Reaction Engineering, ACS Advances in Chemistry,* **109,** 519–534 [1972]; in de Lasa, ed., *Chemical Reactor Design and Technology,* Martinus Nijhoff, 1985, pp. 69–105).

MULTIPLE REACTIONS AND STOICHIOMETRIC BALANCES

Single Reaction For the stoichiometric equation, Eq. (7-5), the relations between the conversions of the several participants are

$$\frac{x}{\nu_a} = \frac{n_{a0} - n_a}{\nu_a} = \frac{n_{b0} - n_b}{\nu_b} = \cdots = -\frac{n_{r0} - n_r}{\nu_r} = -\frac{n_{s0} - n_s}{\nu_s} = \cdots \tag{7-36}$$

$$C_a = \frac{n_a}{V} = \frac{n_{a0} - x}{V}, \quad C_b = \frac{n_{b0} - \nu_b x/\nu_a}{V}, \quad C_c = \frac{C_{c0} - \nu_c x/\nu_a}{V}, \text{ and so on} \tag{7-37}$$

Also,

$$C_b = C_{b0} - \frac{\nu_b}{\nu_a}(C_{a0} - C_a)$$

$$C_c = C_{c0} - \frac{\nu_c}{\nu_a}(C_{a0} - C_a), \text{ and so on} \tag{7-38}$$

Accordingly, the rate equation can be written in terms of the single dependent variable x; thus,

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = \frac{1}{V}\frac{dx}{dt}$$

$$= k\left(\frac{n_{a0} - x}{V}\right)^p \left(\frac{n_{b0} - \nu_b x/\nu_a}{V}\right)^q \left(\frac{n_{c0} - \nu_c x/\nu_a}{V}\right)^r \cdots \tag{7-39}$$

and in terms of concentrations,

$$r_a = -\frac{dC_a}{dt} = kC_a^p C_b^q C_c^r \cdots$$

$$= kC_a^p\left[C_{b0} - \frac{\nu_b}{\nu_a}(C_{a0} - C_a)\right]^q \left[C_{c0} - \frac{\nu_c}{\nu_a}(C_{a0} - C_a)\right]^r \cdots \tag{7-40}$$

Eq. (7-39) becomes integrable when V is properly expressed in terms of the composition of the system, and Eq. (7-40) can be integrated as it stands.

Multiple Reactions When a substance participates in several reactions at the same time, its net rate of decomposition is the algebraic sum of its rates in the individual reactions. Identify the rates of the individual steps with subscripts, $(dC/dt)_1$, $(dC/dt)_2$, ... Take this case of three reactions,

$$A + B \overset{1}{\Rightarrow} C$$

$$A + C \overset{2}{\Rightarrow} D + E$$

$$D + E \overset{3}{\Rightarrow} A + C$$
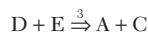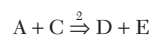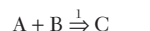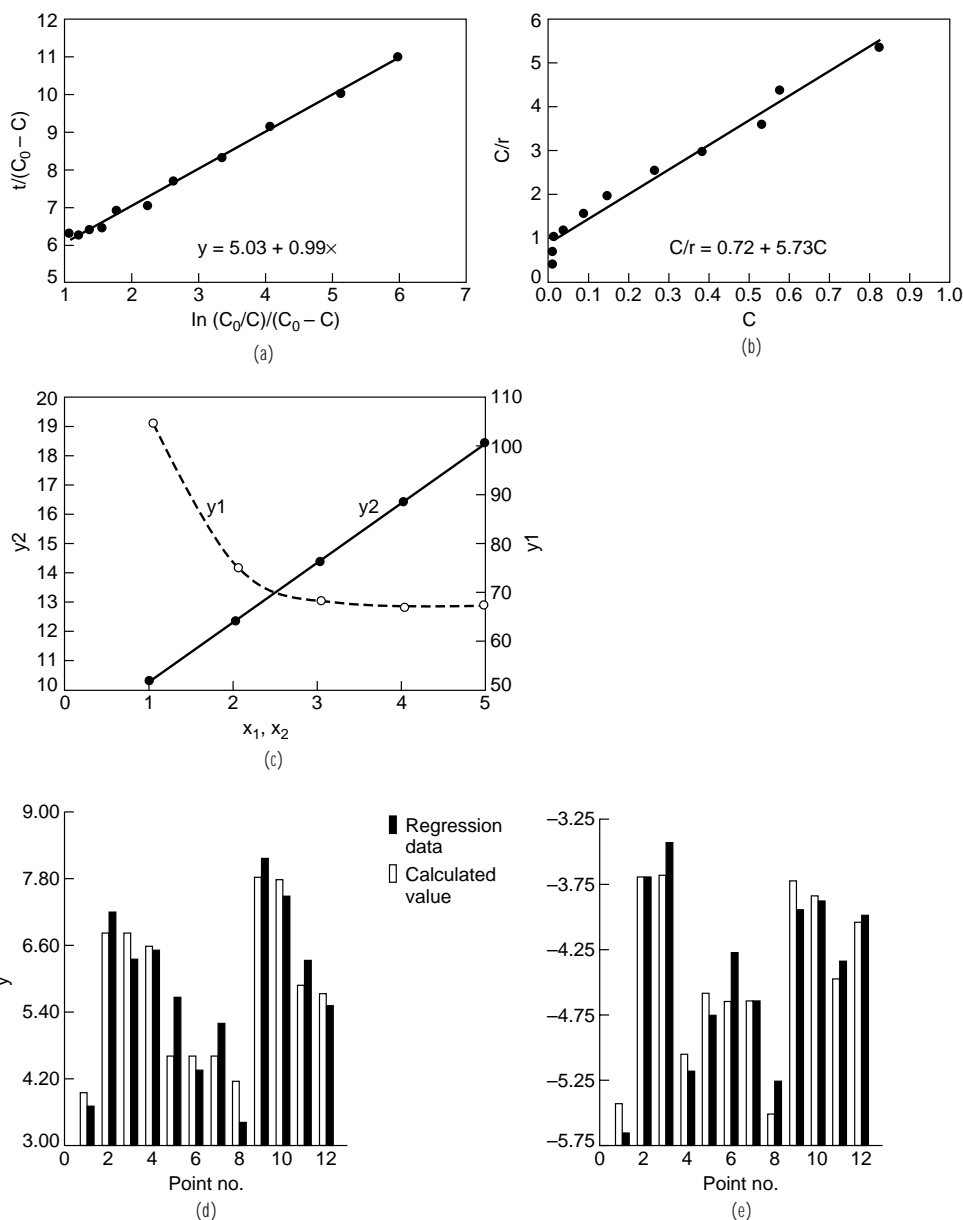
FIG. 7-2   Linear analysis of catalytic rate equations. (*a*), (*b*) Sucrose hydrolysis with an enzyme, $r = kM/(M + C)$. Data are (C, t) curve-fitted with a fourth-degree polynomial and differentiated for $r - (-dC/dt)$. Integrated equation,

$$\frac{t}{C_0 - C} = \frac{1}{k} + \frac{M}{k}\frac{\ln (C_0/C)}{C_0 - C}, \qquad k = 0.199, \; M = 4.98$$

Linearized rate equation,

$$\frac{C}{r} = \frac{M}{k} + \frac{C}{k}, \qquad M = 4.13$$

poor agreement. (*c*) For a solid catalyzed reaction, two possible equations in linear form are $y_1 = P_a/r = a + bp_a$ and $y_2 = P_a/\sqrt{r} = a + bp_a$, of which the second appears to fit. (*d*), (*e*) Hydrogenation of octenes, Hougen and Watson (*Chemical Process Principles,* Wiley, 1947, p. 943). The hyperbolic and power law fits are of about equal quality. Pressure in atm; r in lb mol/(ft^3·h).

$$y = \sqrt{\frac{P_u P_h}{r}} = a + bp_u + cp_s + dp_h$$

$$= 2.7655 + 1.5247p_u + 1.0092p_s + 1.1291p_h$$

$$\ln r = \ln k + a \ln P_u + b \ln p_s + c \ln p_h$$

$$= -4.059 + 0.469 \ln p_u - 0.2356 \ln p_s + 0.5997 \ln p_h$$

$$r = 0.0173 \, P_u^{0.469} \, p_s^{-0.2356} \, P_h^{0.5997}$$

The overall rates of the several participants are

$$r_a = r_{a1} + r_{a2} + r_{a3} = -k_1 C_a C_b - k_2 C_a C_c + k_3 C_d C_e$$

$$r_b = -k_1 C_a C_b$$

$$r_c = k_1 C_a C_b - k_2 C_a C_c + k_3 C_d C_e$$

$$r_d = r_e = k_2 C_a C_e - k_3 C_d C_e \qquad (7\text{-}41)$$

The number of independent rate equations is the same as the number of independent stoichiometric relations. In this example, reactions 2 and 3 are reversible and are not independent, so there are only two independent rate equations.

Some reactions apparently represented by single stoichiometric equations are in reality the result of several reactions, often involving short-lived intermediates. After a set of such elementary reactions is postulated by experience, intuition, and exercise of judgment, a rate equation is deduced and checked against experimental rate data. Several examples are given under "Mechanisms of Some Complex Reactions," following.

Stoichiometric Balances   The amounts of all participants in a group of reactions can be expressed in terms of a number of key components equal to the number of independent stoichiometric relations. The independent rate equations will then involve only those key components and will be, in principle, integrable.

For a single equation, Eqs. (7-36) and (7-37) relate the amounts of the several participants. For multiple reactions, the procedure for finding the concentrations of all participants starts by assuming that the reactions proceed consecutively. Key components are identified. Intermediate concentrations are identified by subscripts. The resulting concentration from a particular reaction is the starting concentration for the next reaction in the series. The final value carries no subscript. After the intermediate concentrations are eliminated algebraically, the compositions of the excess components will be expressible in terms of the key components.

Example 2: Analysis of Three Simultaneous Reactions   Consider the three reactions

$$A + 2B \overset{1}{\Rightarrow} 3C$$
$$A + C \overset{2}{\Rightarrow} 2D$$
$$C + D \overset{3}{\Rightarrow} 2E$$
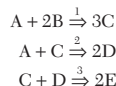
with A, B, and C the key components. Apply Eq. (7-37),

$$A_0 - A_1 = \frac{B_0 - B}{2} = \frac{C_1 - C_0}{3}$$

$$A_1 - A = C_1 - C_2 = \frac{D_2 - D_0}{2}$$

$$C_2 - C = D_2 - D = \frac{E - E_0}{2} \qquad (7\text{-}42)$$

Elimination of the concentrations with subscripts 1 and 2 will find D and E in terms of A, B, and C, with the same results that are achieved by the following method.

This alternative procedure is called the ***xyz*** method. The amount of change by the first reaction is x, by the second y, and by the third z. For the same example,

$$A = A_0 - x - y$$
$$B = B_0 - 2x$$
$$C = C_0 + 3x - y - z$$
$$D = D_0 + 2y - z$$
$$E = E_0 + 2z \qquad (7\text{-}43)$$

Elimination of x, y, and z gives for the excess components:

$$D_0 - D = -3(A_0 - A) + 3(B_0 - B)$$
$$E_0 - E = 2(A_0 - A) - 4(B_0 - B) - 2(C_0 - C) \qquad (7\text{-}44)$$

The differential equations for the three key components become:

$$\frac{dA}{dt} = -k_1 AB^2 - k_2 AC$$

$$\frac{dB}{dt} = -2k_1 AB^2$$

$$\frac{dC}{dt} = 3k_1 AB^2 - k_2 AC - k_3 CD$$

$$= 3k_1 AB^2 - C\{k_2 A + k_3[D_0 + 3(A_0 - A) - 3(B_0 - B)]\} \qquad (7\text{-}45)$$
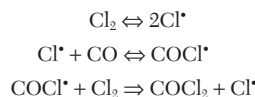
These equations will have to be solved numerically for *A, B,* and *C* as functions of time; then *D* and *E* can be found by algebra. Alternatively, five differential equations can be written and solved directly for the five participants as functions of time, thus avoiding the use of stoichiometric balances, although these are really involved in the formulation of the differential equations.

MECHANISMS OF SOME COMPLEX REACTIONS

The rates of many reactions are not represented by application of the law of mass action on the basis of their overall stoichiometric relations. They appear, rather, to proceed by a sequence of first- and second-order processes involving short-lived intermediates which may be new species or even unstable combinations of the reactants; for $2A + B \Rightarrow C$, the sequence could be $A + B \Rightarrow AB$ followed by $A + AB \Rightarrow C$.

Free radicals are molecular fragments having one or more unpaired electrons, usually short-lived (milliseconds) and 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. The rate equation of a process in which they are involved is developed on the postulate that each free radical is at equilibrium or its net rate of formation is zero. Several examples of free radical and catalytic mechanisms will be cited, all possessing nonintegral power law or hyperbolic rate equations.

Phosgene Synthesis $CO + Cl_2 \Rightarrow COCl_2$, but with the sequence:

$$Cl_2 \Leftrightarrow 2Cl^\bullet$$
$$Cl^\bullet + CO \Leftrightarrow COCl^\bullet$$
$$COCl^\bullet + Cl_2 \Rightarrow COCl_2 + Cl^\bullet$$

Assuming the first two reactions to be in equilibrium, an expression is found for the concentration of $COCl^\bullet$ and when this is substituted into the third equation the rate becomes

$$r_{COCl_2} = k(CO)(Cl_2)^{3/2} \qquad (7\text{-}46)$$

Ozone and Chlorine   The assumed sequence is:

$$Cl_2 + O_3 \Rightarrow ClO^\bullet + ClO_2^\bullet$$
$$ClO_2^\bullet + O_3 \Rightarrow ClO_3^\bullet + O_2$$
$$ClO_3^\bullet + O_3 \Rightarrow ClO_2^\bullet + 2O_2$$
$$ClO_3^\bullet + ClO_3^\bullet \Rightarrow Cl_2 + 3O_2$$
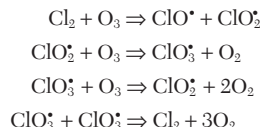
The chain carriers $ClO_2^\bullet$ and $ClO_3^\bullet$ are assumed to attain steady state. Then,

$$r_{O_3} = k(Cl_2)^{1/2}(O_3)^{3/2} \qquad (7\text{-}47)$$

Hydrogen Bromide $H_2 + Br_2 \Rightarrow 2HBr$ (Bodenstein, 1906). The chain of reactions is:

$$Br_2 \overset{1}{\Rightarrow} 2Br^\bullet$$
$$Br^\bullet + H_2 \overset{2}{\Rightarrow} HBr$$
$$H^\bullet + Br_2 \overset{3}{\Rightarrow} HBR + Br^\bullet$$
$$H^\bullet + HBr \Rightarrow H_2 + Br^\bullet$$
$$Br^\bullet + Br^\bullet \Rightarrow Br_2$$
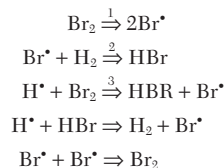
Assuming equilibrium for the concentrations of the free radicals, the rate equation becomes

$$\frac{d(HBr)}{dt} = k_1(Br^\bullet)(H_2) + k_2(H^\bullet)(Br_2) - k_3(H^\bullet)(HBr)$$

$$= \frac{k_1(H_2)(Br_2)^{3/2}}{k_2(Br_2) + k_3(HBr)} \qquad (7\text{-}48)$$

Enzyme Kinetics   The enzyme E and the reactant S are assumed to form a complex ES that then dissociates into product P and uncombined enzyme.

$$S + E \overset{1}{\underset{2}{\Leftrightarrow}} ES$$

$$ES \overset{3}{\Rightarrow} E + P$$
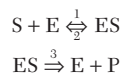
If equilibrium holds,

$$\frac{(S)(E)}{(ES)} = \frac{(S)[(E_0) - (ES)]}{(ES)} = K_m$$

where (E_0) is the total of the free and combined enzyme and K_m is a dissociation constant. Solve for (ES) and substitute into the rate equation,

$$r_p = \frac{d(P)}{dt} = k(ES) = \frac{k(E_0)(S)}{K_m + (S)} \tag{7-49}$$

This hyperbolic equation is named after Michaelis and Menten (*Biochem. Zeit.,* **49,** 333 [1913]).

Chain Polymerization   The growth process of a polymer postulates a three-step mechanism:
1.   An initiator I generates a free radical R$^\bullet$
2.   The free radical reacts repeatedly with monomer by a process called *propagation.*
3.   The free radical eventually disappears by some reaction, called *termination.* The stoichiometric equations are

$$I \overset{1}{\Rightarrow} 2R^\bullet$$

$$R^\bullet + M \overset{2}{\Rightarrow} RM^\bullet, \qquad \text{initiation}$$

$$RM^\bullet + M \overset{k_p}{\Rightarrow} RM_2^\bullet$$

or $\qquad RM_n^\bullet + M \overset{k_p}{\Rightarrow} RM_{n+1}^\bullet, \qquad$ propagation

$$RM_n^\bullet + RM_m^\bullet \overset{k_t}{\Rightarrow} R_2M_{n+m}$$

or $\qquad RM_n + RM_m, \qquad\qquad$ termination
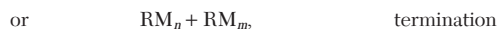
The rates of formation of the free radicals R$^\bullet$ and M$^\bullet$ reach steady states,

$$\frac{dR_n^\bullet}{dt} = 2k_1(I) - k_2(R^\bullet)(M) = 0$$

$$\frac{dM^\bullet}{dt} = k_2(R^\bullet)(M) - 2k_t(M^\bullet)^2 = 0$$

These equations are solved for (R$^\bullet$) and (M$^\bullet$) and substituted into the propagation equation. The rate of polymerization becomes

$$r_p = -\frac{dM}{dt} = k_p(M^\bullet)(M) = k_p\left(\frac{k_1}{k_t}\right)^{1/2}(M)(I)^{1/2} \tag{7-50}$$

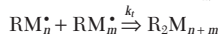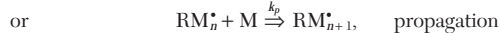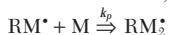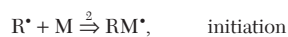Thus, the process of chain polymerization is first-order with respect to monomer and half-order with respect to initiator.

Solid Catalyzed Reaction   The pioneers were Langmuir (*J. Am. Chem. Soc.,* **40,** 1361 [1918]) and Hinshelwood (*Kinetics of Chemical Change,* Oxford, 1940). For a gas phase reaction A + B $\Rightarrow$ Products, catalyzed by a solid, the postulated mechanism consists of the following:
1.   The reactants are first adsorbed on the surface, where they subsequently react and the product is desorbed.
2.   The rate of adsorption is proportional to the partial pressure and to the fraction of uncovered surface ϑ_v.
3.   The rate of desorption of A is proportional to the fraction ϑ_a of the surface covered by A.
4.   Adsorptive equilibrium is maintained.
5.   The rate of reaction between adsorbed species is proportional to their amounts on the surface.

The net rates of adsorption are:

$$r_a = k_a p_a \vartheta_v - k_{-a}\vartheta_a \Rightarrow 0$$

$$r_b = k_b p_b \vartheta_v - k_{-b}\vartheta_b \Rightarrow 0$$

Substitute $\vartheta_v = 1 - \vartheta_a - \vartheta_b$ and solve for the coverages:

$$\vartheta_a = \left(\frac{k_a}{k_{-a}}\right) p_a\vartheta_v = K_a p_a\vartheta_v$$

$$\vartheta_b = \left(\frac{k_b}{k_{-b}}\right) p_b\vartheta_v = K_b p_b\vartheta_v$$

$$\vartheta_v = \frac{1}{1 + K_a p_a + K_b p_b}$$

The rate of surface reaction is:

$$r = k\vartheta_a\vartheta_b = \frac{kK_aK_b p_a p_b}{(1 + K_a p_a + K_b p_b)^2} \tag{7-51}$$

The linearized form can be used to find the constants,

$$y = \sqrt{\frac{p_a p_b}{r}} = \frac{1 + K_a P_a + K_b p_b}{\sqrt{kK_aK_b}}$$

More about this topic is presented later.

WITH DIFFUSION BETWEEN PHASES

When reactants are distributed between several phases, migration between phases ordinarily will occur: with gas/liquid, from the gas to the liquid; with fluid/solid, from the fluid to the solid; between liquids, possibly both ways because reactions can occur in either or both phases. The case of interest is at steady state, where the rate of mass transfer equals the rate of reaction in the destined phase. Take a hyperbolic rate equation for the reaction on a surface. Then,

$$r = r_d = r_s$$

$$= k_1(C - C_s) = \frac{k_2 C_s}{1 + k_3 C_s} = \frac{k_2(C - r/k_1)}{1 + k_3(C - r/k_1)} \tag{7-52}$$

The unknown intermediate concentration C_s has been mathematically eliminated from the last term. In this case, r can be solved for explicitly, but that is not always possible with surface rate equations of greater complexity. The mass transfer coefficient k_1 is usually obtainable from correlations. When the experimental data are of (C, r) the other constants can be found by linear plotting.

CATALYSIS BY SOLIDS: LANGMUIR-HINSHELWOOD MECHANISM

A plausible mechanism of solid catalytic reactions is that the participants chemisorb on the surface and react while in the adsorbed state. The process of adsorption of A on an active site of the surface σ is represented by

$$A + \sigma \Rightarrow A\sigma$$
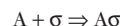
and the reaction between adsorbed molecules, for instance, by

$$A\sigma + B\sigma \Rightarrow C\sigma + D\sigma$$
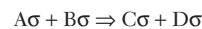
Adsorptive Equilibrium   The fraction of the surface covered by A at equilibrium is

$$\vartheta_a = K_a p_a\vartheta_v \tag{7-53}$$

$$\vartheta_v = \frac{1}{1 + K_a p_a + K_b p_b + K_c P_c + K_d p_d + \cdots} \tag{7-54}$$

where terms may be added for adsorbed inerts that may be present, and analogous expressions for the other participants. The rate of reaction between species in adsorptive equilibrium is then

$$r = kp_a p_b\vartheta_v^2 \tag{7-55}$$

Dissociation   A diatomic molecule A_2 may adsorb as atoms,

$$A_2 + 2\sigma \Rightarrow 2A\sigma$$
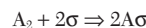
with the result,

$$\vartheta_a = \frac{\sqrt{K_a p_a}}{1 + \sqrt{K_a p_a} + K_b p_b + \cdots} = \sqrt{K_a p_a}\,\vartheta_v$$

and the rate of the reaction is

$$2A\sigma + B\sigma \Rightarrow \text{Products}$$

$$r = k'\vartheta_a^2\vartheta_b = kp_a p_b\vartheta_v^3 \tag{7-56}$$

Different Sites   When A and B adsorb on chemically different sites σ_1 and σ_2, the rate of the reaction A + B $\Rightarrow$ Unadsorbed products

is

$$r = \frac{k p_a p_b}{(1 + K_a p_a)(1 + K_b p_b)} \tag{7-57}$$

Dual Sites When the numbers of moles of reactants and products are unequal, $A \Leftrightarrow M + N$, the mechanism is assumed to be

$$A\sigma + \sigma \Leftrightarrow M\sigma + N\sigma$$
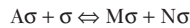
and the rate

$$r = k\left(\vartheta_a\vartheta_v - \frac{\vartheta_m\vartheta_n}{K}\right) = k\left(p_a - \frac{p_m p_n}{K}\right)\vartheta_v^2$$

$$= \frac{k(p_a - p_m p_n/K)}{(1 + K_a p_a + K_m p_m + K_n p_n)^2} \tag{7-58}$$

Reactant in the Gas Phase When A in the gas phase reacts with adsorbed B,

$$A + B\sigma \Rightarrow \text{Products}$$

$$r = k p_a \vartheta_b = k p_a p_b \vartheta_v = \frac{k p_a p_b}{(1 + \Sigma K_i p_i)} \tag{7-59}$$

Chemical Equilibrium When A is not in adsorptive equilibrium, it is assumed to be in chemical equilibrium, with $p_a^e = p_m p_n/K_e p_b$. This expression is substituted for p_a wherever it appears in the rate equation. Then

$$r = k p_a^e p_b \vartheta_v^2 = \frac{k p_m p_n/K_e}{(1 + K_a p_m p_n/K_e p_b + K_b p_b + K_m p_m + K_n p_n)^2} \tag{7-60}$$

All of these relations are brought together in the fundamental form

$$r = \frac{(\text{kinetic term})(\text{driving force})}{\text{adsorption term}} \tag{7-61}$$

Table 7-2 summarizes the cases when all substances are in adsorptive equilibrium and the surface reaction controls. In Table 7-3, substance A is not in adsorptive equilibrium, so its adsorption rate is controlling.

Details of the derivations of these and some other equations are presented by Yang and Hougen (*Chem. Eng. 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).

All of the relations developed here assume that only one step is controlling. A more general case is that of the reaction $A \Rightarrow B$ with five steps controlling, namely

$$r = k_1(p_{ag} - p_{ai}) \qquad \text{Diffusion of A to the surface}$$

$$r = k_2\left(p_{ai}\theta_v - \frac{\theta_a}{k_3}\right) \qquad \text{Adsorption of A}$$

$$r = k_4\theta_a \qquad \text{Surface reaction}$$

$$r = k_5\left(p_{bi}\theta_v - \frac{\theta_b}{k_6}\right) \qquad \text{Desorption of B}$$

$$r = k_7(p_{bi} - p_{bg}) \qquad \text{Diffusion of B from the surface} \tag{7-62}$$

where $\theta_v = 1 - \theta_a - \theta_b$.

At steady state these rates are all the same. Upon elimination of the unmeasurable quantities p_{ai}, p_{bi}, ϑ_a, ϑ_b, and ϑ_v, the relation becomes

$$r = \frac{k_5(k_7 p_{bg} + r)}{k_7}\left(1 - \frac{r}{k_4}\right)$$

$$- k_5\left(p_{bg} + \frac{r}{k_7} + \frac{1}{k_6}\right)\left[1 - \frac{r}{k_4} - \frac{k_1 r}{k_1 p_{ag} - r}\left(\frac{1}{k_2} + \frac{1}{k_3 k_4}\right)\right] \tag{7-63}$$

Combinations of several adsorption and surface reaction steps are usually not felt to be necessary, since so many alternatives are available individually. Single steps in combination with diffusion to the surface are usually adequate, as in the case leading to Eq. (7-52).

Over the usual limited range of conditions, a power law rate equation often appears to be as satisfactory a fit of the data as a more complex Langmuir-Hinshelwood equation. The example of the hydrogenation of octenes is shown in Fig. 7-2*d* and 7-2*e*, and another case follows.

Example 3: Phosgene Synthesis Rate data were obtained by Potter and Baron (*Chem. Eng. Prog.,* **47,** 478 [1951]) for the reaction CO (A) + Cl$_2$ (B$_2$) $\Rightarrow$ COCl$_2$ (C) at 30.6. Three correlations of approximately equal statis-

TABLE 7-2 Surface-reaction Controlling (Adsorptive Equilibrium Maintained of 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. $A \rightleftharpoons M$		$r = k_1\theta_a - k_{-1}\theta_m$	$p_a - \dfrac{p_m}{K}$	$1 + K_a p_a + K_m p_m$
3. $A \rightleftharpoons M + N$	Adsorbed A reacts with vacant site	$r = k_1\theta_a\theta_v - k_{-1}\theta_m\theta_n$	$p_a - \dfrac{p_m p_n}{K}$	$(1 + K_a p_a + K_m p_m + K_n p_n)^2$
4. $A_2 \rightleftharpoons M$	Dissociation of A_2 upon adsorption	$r = k_1\theta_a^2 - k_{-1}\theta_m\theta_v$	$p_a - \dfrac{p_m}{K}$	$(1 + \sqrt{K_a p_a} + K_m p_m)^2$
5. $A + B \rightarrow M + N$ $A + B \rightarrow M + N$	Adsorbed B reacts with A in gas but not with adsorbed A	$r = k\theta_a\theta_b$ $r = kp_a\theta_b$	$p_a p_b$ $p_a p_b$	$(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n)^2$ $1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n$
6. $A + B \rightleftharpoons M$		$r = k_1\theta_a\theta_b - k_{-1}\theta_m\theta_v$	$p_a p_b - \dfrac{p_m}{K}$	$(1 + K_a p_a + K_b p_b + K_m p_m)^2$
7. $A + B \rightleftharpoons M + N$		$r = k_1\theta_a\theta_b - k_{-1}\theta_m\theta_n$	$p_a p_b - \dfrac{p_m p_n}{K}$	$(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n)^2$
8. $A_2 + B \rightleftharpoons M + N$	Dissociation of A_2 upon adsorption	$r = k_1\theta_a^2\theta_b - k_{-1}\theta_m\theta_n\theta_v$	$p_a p_b - \dfrac{p_m p_n}{K}$	$(1 + \sqrt{K_a p_a} + K_b p_b + K_m p_m + K_n p_n)^3$

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.

TABLE 7-3   Adsorption-rate Controlling (Rapid Surface Reaction)

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

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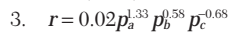SOURCE: From Walas, *Reaction Kinetics for Chemical Engineers,* McGraw Hill, 1959; Butterworths, 1989.

tical validity are:

1. $A\sigma + 2B\sigma \Rightarrow C + 3\sigma$

$$y = \left(\frac{p_a p_b}{r}\right)^{1/3} = 0.34(1 - 0.061p_a + 0.0032\sqrt{p_b} - 0.00046p_c)$$

2. $A\sigma + B_2\sigma \Rightarrow C + 2\sigma$

$$y = \left(\frac{p_a p_b}{r}\right)^{1/2} = 2.38(1 + 1.98p_b + 0.59p_c)$$

3. $r = 0.02 p_a^{1.33}\, p_b^{0.58}\, p_c^{-0.68}$

The data are partial pressures, atm and the rate *r*, g mol phosgene made/(h·g catalyst).

The first is ruled out because the constants physically cannot be negative. Although the other correlations are equally valid statistically, the Langmuir-Hinshelwood may be preferred to the power law form because it is more likely to be amenable to extrapolation.

CHEMICAL EQUILIBRIUM

The rate of a reversible reaction

$$aA + bB \underset{k_2}{\overset{k_1}{\Longleftrightarrow}} cC + dD$$
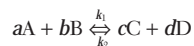
may be written

$$r = k_1\left(C_a^a C_b^b - \frac{C_c^c C_d^d}{K_e}\right) \tag{7-64}$$

In terms of the compositions at equilibrium, the equilibrium constant is

$$K_e = \frac{C_{ce}^c C_{de}^d}{C_{ae}^a C_{be}^b}$$

With the aid of the stoichiometric "degree of advancement,"

$$\varepsilon = \frac{C_{a0} - C_a}{a} = \frac{C_{b0} - C_b}{b} = -\frac{C_{C0} - C_c}{c} = -\frac{C_{d0} - C_d}{d}$$

the equilibrium constant can be written in terms of a single variable. When several reactions occur simultaneously, each reaction is characterized by its own ε_i. When the K_es are known, the composition can be found by simultaneous solution of the several equations. The equilibrium composition of a mixture of known chemical species also can be found by a process of Gibbs energy minimization without the formulation of stoichiometric equations. Examples of the calculation of equilibria are in books on thermodynamics and in Walas (*Phase Equilibria in Chemical Engineering,* Butterworths, 1985).

The equilibrium constant depends on temperature according to

$$\frac{d\ln K}{dT} = \frac{\Delta H_r}{RT^2}$$

This is integrable to

$$\ln K = \ln K_{298} + \frac{1}{R}\int_{298}^{T}\frac{\Delta H_{r298} + \int_{298}^{T}\Delta Cp\,dT}{T^2}\,dT \tag{7-65}$$

where ΔH_r is the enthalpy change of reaction. Over a moderate temperature range, an adequate form of relation is

$$K = \exp\left(a + \frac{b}{t}\right) \tag{7-66}$$

Gaseous equilibria are expressed in terms of **fugacities** or fugacity coefficients. In terms of partial pressures, $p_i = y_i\pi$,

$$K_p = \frac{p_c^c p_d^d}{p_a^a p_b^b} = K_y\pi^{c + d - a - b} \tag{7-67}$$

Pressure affects the composition of an equilibrium mixture, but not the equilibrium constant itself.

Although the equilibrium constant can be evaluated in terms of kinetic data, it is usually found independently so as to simplify finding the other constants of the rate equation. With K_e known, the correct exponents of Eq. (7-64) can be found by choosing trial sets until k_1 comes out approximately constant. When the exponents are small integers or simple fractions, this process is not overly laborious.

Example 4: Reaction between Methane and Steam   At 600°C the principal reactions between methane and steam are

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \qquad CO + H_2O \Leftrightarrow CO_2 + H_2$$

$$1 - x \quad 5 - x \quad x \quad 3x \qquad x - y \quad 5 - x - y \quad y \quad 3x + y \quad \Sigma = 6 + 2x$$
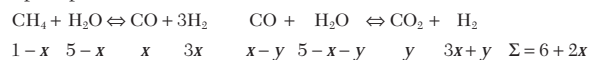
where $K_1 = 0.574$, $K_2 = 2.21$. Starting with 1 mol methane and 5 mol steam,

$$\frac{(x-y)(3x+y)^3}{(1-x)(5-x-y)(6+2x)^2} = 0.574, \qquad \frac{y(3x+y)}{(x-y)(5-x-y)} = 2.21$$

Simultaneous solution by the Newton-Raphson method yields $x = 0.9121$, $y = 0.6328$. Accordingly, the fractional compositions are:

$$CH_4 = \frac{(1-x)}{(6+2x)} = 0.0112$$

$$CO = \frac{(x-y)}{(6+2x)} = 0.0357$$

$$CO_2 = \frac{y}{(6+2x)} = 0.0809$$

$$H_2O = \frac{(5-x-y)}{(6+2x)} = 0.4416$$

$$H_2 = \frac{(3x+y)}{(6+2x)} = 0.4306$$

Approach to Equilibrium As equilibrium is approached the rate of reaction falls off, and the reactor size required to achieve a specified conversion goes up. At some point, the cost of increased reactor size will outweigh the cost of discarded or recycled unconverted material. No simple rule for an economic appraisal is really possible, but sometimes a basis of 95 percent of equilibrium conversion is taken. For adiabatic operation, a certain approach to equilibrium temperature is common practice, say within 10 to 20°C (18 to 36°F), a number possibly based on experience with a particular process.

Example 5: Percent Approach to Equilibrium For a reversible reaction with rate equation $r = k[A^2 - (1-A)^2/16]$, the size function kV_r/V of a plug flow reactor will be found in terms of percent approach to equilibrium:

$$\frac{kV_r}{V} = \int_A^1 \frac{dA}{A^2 - (1-A)^2/16}, \qquad A_{\text{equilib}} = 0.2000$$

Percent approach	70	90	95	98	99	99.5	100
A	0.440	0.280	0.240	0.216	0.208	0.204	0.2
kV_r/V	1.319	3.053	4.309	6.090	7.600	9.315	∞

The volume escalates rapidly at high percent approaches.

INTEGRATION OF RATE EQUATIONS

In either batch or flow systems, many single-rate equations lead to integrands that are ratios of low-degree polynomials that can be integrated by inspection or with the briefest of integral tables. Some of the cases of frequent occurrence are summarized in Table 7-4. When the problem is to relate C and t, the constants are known, and the polynomials are of second degree or higher, numerical integration may save

TABLE 7-4 Some Isothermal Rate Equations and Their Integrals

1. $A \rightarrow$ Products:

$$-\frac{dA}{dt} kA^q$$

$$\frac{A}{A_0} = \begin{vmatrix} \exp[-k(t-t_0)], & q = 1 \\ \left[\dfrac{1}{1+(q-1)kA_0^{q-1}(t-t_0)}\right]^{1/(q-1)}, & q \neq 1 \end{vmatrix}$$

2. $A + B \rightarrow$ Products:

$$-\frac{dA}{dt} = kAB = kA(A + B_0 - A_0)$$

$$k(t-t_0) = \frac{1}{B_0 - A_0} \ln \frac{A_0(A + B_0 - A_0)}{AB_0}$$

3. Reversible reaction $A \overset{k_1}{\underset{k_2}{\rightleftharpoons}} B$:

$$-\frac{dA}{dt} = k_1 A - k_2(A_0 + B_0 - A) = (k_1 + k_2)A - k_2(A_0 + B_0)$$

$$(k_1 + k_2)(t - t_0) = \ln \frac{k_1 A_0 - k_2 B_0}{(k_1 + k_2)A - k_2(A_0 + B_0)}$$

4. Reversible reaction, second order, $A + B \overset{k_1}{\underset{k_2}{\rightleftharpoons}} R + S$:

$$-\frac{dA}{dt} = k_1 AB - k_2 RS = k_1 A(A + B_0 - A_0)$$
$$- k_2(A_0 + R_0 - A)(A_0 + S_0 - A)$$
$$= \alpha A^2 + \beta A - \gamma$$
$$\alpha = k_1 - k_2$$
$$\beta = k_1(B_0 - A_0) + k_2(2A_0 + R_0 + S_0)$$
$$\gamma = k_2(A_0 + R_0)(A_0 + S_0)$$
$$q = \sqrt{\beta^2 + 4\alpha\gamma}$$

$$k(t-t_0) = \begin{cases} \dfrac{2\alpha A_0 + \beta}{2\alpha A + \beta}, & q = 0 \\ \dfrac{1}{q} \ln\left[\left(\dfrac{2\alpha A_0 + \beta - q}{2\alpha A_0 + \beta + q}\right)\left(\dfrac{2\alpha A + \beta + q}{2\alpha A + \beta - q}\right)\right], & q \neq 0 \end{cases}$$

5. The reaction $\nu_a A \rightarrow \nu_r R + \nu_s S$ between ideal gases at constant T and P:

$$-\frac{dn_a}{dt} = \frac{kn_a^\alpha}{V^{\alpha-1}}$$

$$V = n_t \frac{RT}{P} = \left[n_{t0} + \frac{\Delta\nu}{\nu_a}(n_{a0} - n_a)\right]\frac{RT}{P}$$

$$k(t-t_0) = \begin{cases} \displaystyle\int_{n_a}^{n_{a0}} \frac{V^{\alpha-1}}{n_a^\alpha} dn_a, & \text{in general} \\ \dfrac{RT}{P}\left[n_{b0} + \dfrac{\Delta\nu}{\nu_a}\left(\dfrac{1}{n_a} - \dfrac{1}{n_{a0}}\right)\right. \\ \left. - \dfrac{\Delta\nu}{\nu_a}\ln\left(\dfrac{n_{a0}}{n_a}\right)\right], & \text{when } \alpha = 2 \end{cases}$$

6. Equations readily solvable by Laplace transforms. For example:

$$A \overset{k_1}{\underset{k_3}{\rightleftharpoons}} B \overset{k_2}{\rightarrow} C$$

Rate equations are

$$-\frac{dA}{dt} = k_1 A - k_3 B$$

$$-\frac{dB}{dt} = -k_1 A + (k_2 + k_3)B$$

$$-\frac{dC}{dt} = -k_2 B$$

Laplace transformations are made and rearranged to

$$(s + k_1)\bar{A} + k_3\bar{B} = A_0$$
$$-k_1\bar{A} + (s + k_2 + k_3)\bar{B} = B_0$$
$$-k_2\bar{B} + s\bar{C} = C_0$$

These linear equations are solved for the transforms as

$$D = s^2 + (k_1 + k_2 + k_3)s + k_1 k_2$$
$$\bar{A} = \frac{A_0 s + (k_2 + k_3)A_0 + K_3 B_0}{D}$$
$$\bar{B} = \frac{B_0 s + k_1(A_0 + B_0)}{D}$$
$$\bar{C} = \frac{k_2\bar{B} + C_0}{s}$$

Inversion of the transforms can be made to find the concentrations A, B, and C as functions of the time t.

SOURCE: Adapted from Walas, *Chemical Process Equipment Selection and Design,* Butterworth-Heinemann, 1990.

time and preserve reliability. Some 40 cases of integrations at constant volume are developed by Capellos and Bielski (*Kinetic Systems Mathematical Descriptions of Chemical Kinetics,* Wiley, 1972).

Sets of first-order rate equations are solvable by Laplace transform (Rodiguin and Rodiguina, *Consecutive Chemical Reactions,* Van Nostrand, 1964). The methods of linear algebra are applied to large sets of coupled first-order reactions by Wei and Prater (*Adv. Catal.,* **13,** 203 [1962]). Reactions of petroleum fractions are examples of this type.

Example 6: Laplace Transform Application   For the reaction

$$A \xrightarrow{1} B \underset{3}{\overset{2}{\rightleftharpoons}} C$$
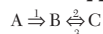
with

$$B_0 = C_0 = 0$$

the rate equations are

$$\frac{dA}{dt} = k_1 A$$

$$\frac{dB}{dt} = k_1 A - k_2 B + k_3 (A_0 - A - B)$$

The transforms are

$$s\overline{A} - A_0 = -k_1\overline{A}$$

$$s\overline{B} = \frac{k_3 A_0}{s} + (k_1 - k_3)\,\overline{A} - (k_2 + k_3)\,\overline{B}$$

Explicitly,

$$\overline{A} = \frac{A_0}{s + k_1} \qquad \overline{B} = \frac{A_0}{s + k_2 + k_3}\left(\frac{k_3}{s} + \frac{k_1 - k_3}{s + k_1}\right)$$

A and B as functions of t are found by inversion with a table of L-T pairs.

When even second-order reactions are included in a group to be analyzed, individual integration methods may be needed. Three cases of coupled first- and second-order reactions will be touched on. All of them are amenable only with difficulty to the evaluation of specific rates from kinetic data. Numerical integrations are often necessary.

1.   The reactions are $2A \xrightarrow{1} B \xrightarrow{2} C$. The partial solutions are

$$A = \frac{A_0}{(1 + 2k_1 A_0\, t)}$$

$$\frac{dB}{dt} + k_2 B = \frac{k_1 A_0^2}{(1 + 2k_1 A_0 t)^2}$$

Although the differential equation is first-order linear, its integration requires evaluation of an infinite series of integrals of increasing difficulty.

2.   The reactions are $A \xrightarrow{1} B$ and $A + B \xrightarrow{2} C$. After A is expressed in terms of B by elimination of *t,*

$$\frac{dB}{dt} = (k_1 - k_2 B)\left[A_0 - B_0 + B - 2k \ln\frac{B - k}{B + k}\right], \qquad k = \frac{k_1}{k_2}$$

but this cannot be integrated analytically.

3.   For the reactions $A \xrightarrow{1} B$, $2B \xrightarrow{2} C$; $2A \xrightarrow{1} B \xrightarrow{2} C$; $2A \xrightarrow{1} B$, $2B \xrightarrow{2} C$; the rate equations are solved in terms of higher transcendental functions by Chien (*J. Am. Chem. Soc.,* **76,** 2256 [1948]). For the first case, with $B_0 = 0$:

$$A = \exp(-k_1 t)$$

$$B = A_0\sqrt{\frac{\tau}{K}}\,\frac{iJ_1(\gamma) - \beta H_1^{(i)}(\gamma)}{J_0(\gamma) + \beta\, i H_0^{(i)}}$$

where $\tau = \exp(-k_1 t)$
$K = k_1 k_2 A_0$
$\gamma = 2i\sqrt{K\tau}$
$\beta = iJ_1(\gamma)/H_1^{(i)}(\gamma)$

The notation of the Bessel functions is that of Jahnke and Emde (*Tables of Functions with Formulas and Curves,* Dover, 1945; Teubner, 1960).

IDEAL REACTORS

INTRODUCTION

A useful classification of kinds of reactors is in terms of their concentration distributions. The concentration profiles of certain limiting cases are illustrated in Fig. 7-3; namely, of batch reactors, continuously stirred tanks, and tubular flow reactors. Basic types of flow reactors are illustrated in Fig. 7-4. Many others, employing granular catalysts and for multiphase reactions, are illustrated throughout Sec. 23. The present material deals with the sizes, performances and heat effects of these ideal types. They afford standards of comparison.

In a batch reactor, all the reactants are loaded at once; the concentration then varies with time, but at any one time it is uniform throughout. Agitation serves to mix separate feeds initially and to enhance heat transfer. In a semibatch operation, some of the reactants are charged at once and the others are then charged gradually.

In an ideal continuously stirred tank reactor (CSTR), the conditions are uniform throughout and the condition of the effluent is the same as the condition in the tank. When a battery of such vessels is employed in series, the concentration profile is step-shaped if the abscissa is the total residence time or the stage number. The residence time of individual molecules varies exponentially from zero to infinity, as illustrated in Fig. 7-3*e.*

In another kind of ideal flow reactor, all portions of the feed stream have the same residence time; that is, there is no mixing in the axial direction but complete mixing radially. It is called a *plug flow reactor* (PFR), or a *tubular flow reactor* (TFR), because this flow pattern is characteristic of tubes and pipes. As the reaction proceeds, the concentration falls off with distance.

Often, complete mixing cannot be approached for economic reasons. Inactive or dead zones, bypassing, and limitations of energy input are common causes. Packed beds are usually predominantly used in plug flow reactors, but they may also have small mixing zones superimposed in series or in parallel. In tubular reactors for viscous fluids, laminar or non-Newtonian behavior gives rise to variations of residence time. Deviations from ideal behavior are analyzed at length in Sec. 23.

MATERIAL AND ENERGY BALANCES

These balances are based on the general conservation law,

Input + Sources = Outputs + Sinks + Accumulation   (7-68)

The terms may be quantities or rates of flow of material or enthalpy. *Inputs* and *outputs* are streams that cross the vessel boundaries. A heat of reaction within the vessel is a *source.* A depletion of reactant in the vessel is a *sink. Accumulation* is the time derivative of the content of the reference quantity in the vessel; of the volume times the concentration, $\partial V_r C_a/\partial t$; or of the total enthalpy of the vessel contents, $\partial[WC_p(T - T_{ref})]/\partial t$.

BATCH REACTORS

Batch reactors are tanks, usually provided with agitation and some mode of heat transfer to maintain temperature within a desirable range. They are primarily employed for relatively slow reactions of several hours duration, since the downtime for filling and emptying large equipment may be an hour or so. Agitation maintains uniformity and improves heat transfer. Modes of heat transfer are illustrated in Figs. 23-1 and 23-2.

Except in the laboratory, batch reactors are mostly liquid phase. In semibatch operation, a gas of limited solubility may be fed in gradually as it is used up. Batch reactors are popular in practice because of their flexibility with respect to reaction time and to the kinds and quantities of reactions that they can process.
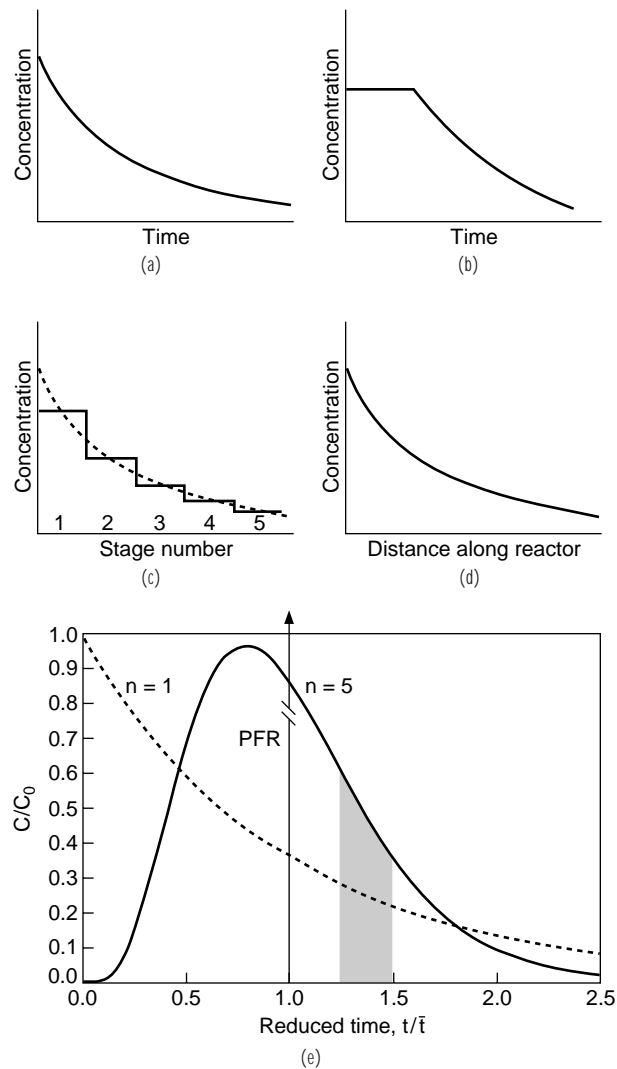
FIG. 7-3 Concentration profiles in batch and continuous flow: (*a*) batch time profile, (*b*) semibatch time profile, (*c*) five-stage distance profile, (*d*) tubular flow distance profile, (*e*) residence time distributions in single, five-stage, and PFR; the shaded area represents the fraction of the feed that has a residence time between the indicated abscissas.

Material and energy balances of a nonflow reactor are summarized in Table 7-5. Several batch operations are summarized in Fig. 7-5.

Daily Yield   Say the downtime for filling and emptying a reactor is t_d and no reaction occurs during these periods. The reaction time t_r of a first-order reaction, for instance, is given by $kt_r = -\ln(1-x)$. The daily yield with n batches per day will be

$$y = nV_r(C_0 - C) = \frac{24V_rC_0x}{t_r + t_d} = \frac{24V_rkC_0x}{-\ln(1-x) + kt_d}$$ (7-69)

Some conditions at which the daily yield is a maximum are

kt_d	0.01	0.1	0.5	5.0
x	0.13	0.45	0.68	0.88

Thus, the required conversion goes up as the downtime increases. Details are in Problem P2 of the "Solved Problems" subsection.

Filling and Emptying Periods   Say the pumping rate is V', the full tank volume is V_{rl}, and the rate of reaction is $r = kC_a^q$. For $t \le V_{rl}/V'$, the material balances with Eq. (7-68) are as follows.
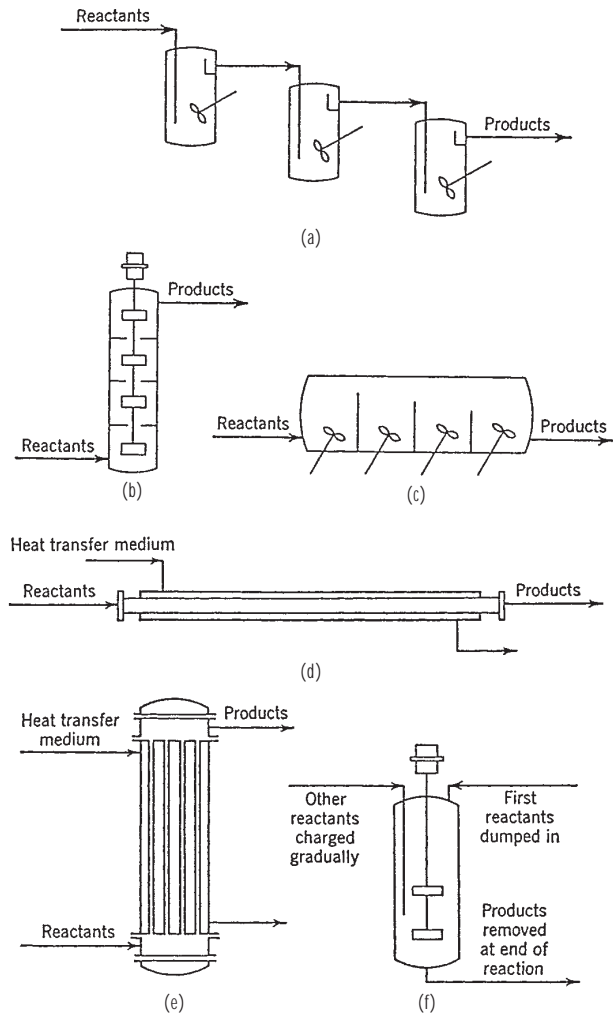
FIG. 7-4 Types of flow reactors: (*a*) stirred tank battery, (*b*) vertically staged, (*c*) compartmentalized, (*d*) single-jacketed tube, (*e*) shell and tube, (*f*) semiflow stirred tank.

Filling: $V_r = V't$, $C_a = C_{a0}$,   when $t = 0$,

$$V'C_{a0} = 0 + rV_r + \frac{d(V_rC_a)}{dt} = kV_rC_a^q + V'C_a + V't\frac{dC_a}{dt}$$

or $$C_{a0} = C_a + k\left(\frac{V_r}{V'}\right)C_a^q + t\frac{dC_a}{dt}$$ (7-70)

where the variables are separable.

Emptying: $V_r = V_{rl} - V't$, $C_a = C_{a1}$,   when $t = 0$,

$$0 = V'C_a + kV_rC_a^q + \frac{d(V_rC_a)}{dt} = V'C_a + kV_rC_a^q - V'C_a + V_r\frac{dC_a}{dt}$$

$$\frac{dC_a}{dt} = -kC_a^q$$ (7-71)

This is the same equation as for the full tank, but applies only for $t \le V_{rl}/V'$. Figure 7-5*e* shows a complete batch cycle.

Optimum Operation of Reversible Reactions   Often, equilibrium composition becomes less favorable and the rate of reaction becomes more favorable as the temperature increases, so a best condition may exist. If the temperature is adjusted at each composition to

TABLE 7-5   Material and Energy Balances of a Nonflow Reactor

Rate equations:

$$r_a = -\frac{1}{V_r}\frac{dn_a}{d\theta} = kC_a^\alpha = k\left(\frac{n_a}{V_r}\right)^\alpha \tag{1}$$

$$k = \exp\left(a' - \frac{b'}{T'}\right) \tag{2}$$

Heat of reaction:

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T}\Delta C_p\,dT \tag{3}$$

Rate of heat transfer:

$$Q' = UA(T_s - T) \tag{4}$$

(the simplest case is when UA and T_s are constant)

Enthalpy balance:

$$\frac{dT}{dn_a} = \frac{1}{\rho V_r \overline{C}_p}\left[\Delta H_r + \frac{UA(T_s-T)}{V_r k(n_a/V_r)^\alpha}\right] \tag{5}$$

$$\frac{dT}{dC_a} = \frac{1}{\rho \overline{C}_p}\left[\Delta H_r + \frac{UA(T_s-T)}{V_r kC_a^\alpha}\right] \tag{6}$$

$$T = T_0 \quad \text{when} \quad C_a = C_{a0} \tag{7}$$

$$\overline{C}_p = \frac{1}{\rho V_r}\sum n_i C_{pi} \tag{8}$$

Solve Eq. (6) to find $T = f(C_a)$; combine Eqs. (1) and (2) and integrate as

$$\theta = \int_{C_a}^{C_{a0}}\frac{1}{C_a^\alpha \exp\,[a' - b'/f(C_a)]}\,dC_a \tag{9}$$

SOURCE: Adapted from Walas, *Chemical Process Equipment Selection and Design,* Butterworth-Heinemann, 1990.

make the rate a maximum, then a minimum reactor size or maximum conversion will result. Take the first-order reversible process,

$$r = k_1(1-x) - k_2 x$$

$k_1 = A_1 \exp(-B_1/T)$ and $k_2 = A_2 \exp(-B_2/T)$. The condition

$$(\partial r/\partial T)_x = 0$$

leads to

$$T = \frac{B_1 - B_2}{\ln\dfrac{A_1 B_1(1-x)}{A_2 B_2 x}} \tag{7-72}$$

which tells what the temperature must be at each fractional conversion for the minimum reactor size. Practically, it may be difficult to vary the temperature of a batch reactor in this way, but the operation may be more nearly feasible with a CSTR battery or a PFR. Figure 7-5*f* shows an example of such a temperature profile for a batch reactor.

CONTINUOUS STIRRED TANK REACTORS (CSTR)

Flow reactors are used for greater production rates when the reaction time is comparatively short, when uniform temperature is desired, when labor costs are high. CSTRs are used singly or in multiple units in series, in either separate vessels or single, compartmented shells.

Material and energy balances are based on the conservation law, Eq. (7-69). In the operation of liquid phase reactions at steady state, the input and output flow rates are constant so the holdup is fixed. The usual control of the discharge is on the liquid level in the tank. When the mixing is adequate, concentration and temperature are uniform, and the effluent has these same properties. The steady state material balance on a reactant A is

$$V_0' C_{a0} = V' C_a + V_r r_a \tag{7-73}$$

Changes in density because of reaction or temperature changes are often small enough to be ignored. Then the volumetric flow rate is uniform and the balance becomes

$$C_{a0} = C_a + \bar{t}r_a \tag{7-74}$$

where the residence time is

$$\bar{t} = \frac{V_r}{V'} \tag{7-75}$$

A useful rearrangement,

$$r_a = \frac{C_{a0} - C_a}{\bar{t}} \tag{7-76}$$

emphasizes how CSTR measurements can provide data for the development of rate equations without integrating them.

During startup or discharge the material balance becomes

$$V_0' C_{a0} = V' C_a + V_r r_a + \frac{d(V_r C_a)}{dt} \tag{7-77}$$

where the reactor volume V_r is a known function of time.

For a power law rate equation at steady state,

$$C_{a0} = C_a + k\bar{t}C_a^q \tag{7-78}$$

A summary of material and energy balances is in Table 7-6.

For each vessel of a series,

$$C_{a,\,n-1} = C_{an} + \bar{t}_n r_{an} \tag{7-79}$$

The set of equations for all stages can be solved in succession, starting with the inlet to the first stage as C_{a0}.

Example 7: A Four-Stage Unit When the material balances are $C_{n-1} = C_n + 1.5[C_n/(0.2 + C_n)]^2$ and $C_0 = 2$, the successive outlet concentrations are found by *RootSolver* to be 0.985, 0.580, 0.389, and 0.281.

The simplest problem is when all of the stages have the same $k\bar{t}$; then one of the three variables ($k\bar{t}$, n, or C_{an}) can be found when the others are specified. For first-order reactions,

$$\frac{C_{an}}{C_{a0}} = \frac{1}{(1 + k_1\bar{t}_1)(1 + k_2\bar{t}_2)\cdots(1 + k_n\bar{t}_n)} \tag{7-80}$$

$$\Rightarrow \frac{1}{(1 + k\bar{t}_{total}/n)^n} \tag{7-81}$$

for identical stages.

For multiple reactions, material balances are required for each stoichiometry.

Example 8: Consecutive Reactions Take the reaction $A \xrightarrow{1} B \xrightarrow{2} C$, with $B_0 = C_0 = 0$. Define $\vartheta = k_1\bar{t}A_0$, $\alpha = 1/(1 + k_1\bar{t})$, $\beta = 1/(1 + k_2\bar{t})$. Then by setting up successive material balances, equations for the effluent from the nth stage are derived as

$$A_n = A_0\alpha^n \qquad B_n = \frac{\alpha\beta\vartheta}{\alpha - \beta}(\alpha^n - \beta^n) \qquad C_n = A_0 - A_n - B_n \tag{7-82}$$

When $n \Rightarrow \infty$, this equation reduces to

$$\frac{B}{A_0} = \frac{k_1}{k_2 - k_1}[\exp(-k_1\bar{t}) - \exp(-k_2\bar{t})] \tag{7-83}$$

This is the equation for a plug flow reactor. It can be derived directly from the rate equations with the aid of Laplace transforms. The sequences of second-order reactions of Figs. 7-5*a* and 7-5*c* required numerical integrations.

When CSTRs are operated in series, the sum of the reactor volumes drops off sharply with the number of stages. An economical number often is only 3 to 6, since the benefit of reduced volume may be outweighed by the increased cost of multiple agitators, pumps, and controls. When all stages are in a single shell, the economics are more favorable to large numbers of stages, but the single-shell arrangements lose some of the flexibility of the multiple-tank designs.

Example 9: Comparison of Batch and CSTR Volumes For a first-order reaction, the ratio of n-stage CSTR and batch volumes is

$$\text{Ratio} = \frac{n[(C_0/C)^{1/n} - 1]}{\ln(C_0/C)}$$
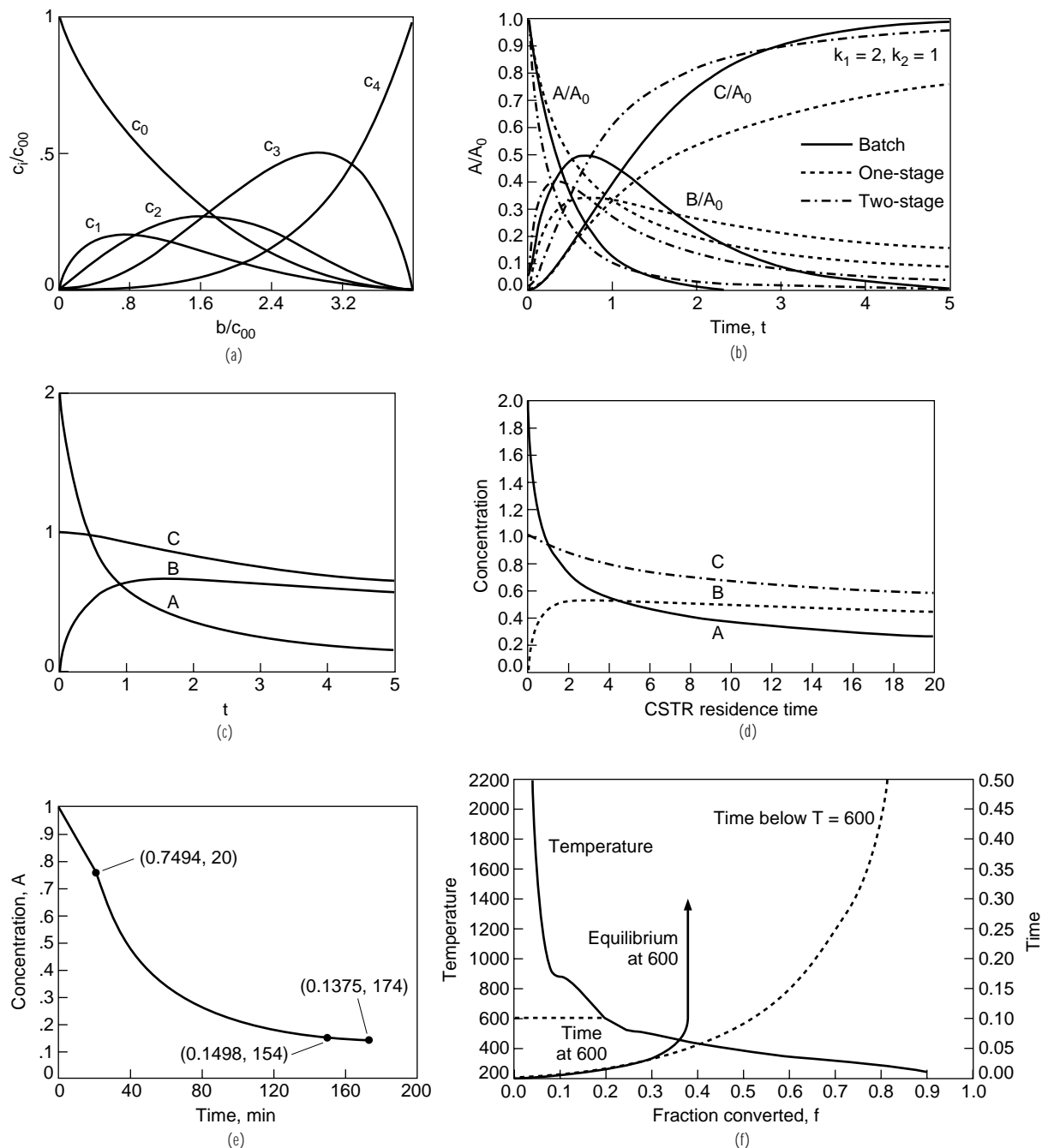
FIG. 7-5 Some batch operations, the P-code refers to detailed solutions in Walas (*Chemical Reaction Engineering Handbook of Solved Problems,* Gordon & Breach, 1995). (*a*) Methane chlorination in batch reactor or PFR; abscissa is ratio of chlorine to methane; P4.03.20. (*b*) Product yields of $A \Rightarrow B \Rightarrow C$ with $k_1 = 2$ and $k_2 = 1$ in batch reactor and CSTR; P4.04.60. (*c*) The reactions $2A \Rightarrow B$ and $2B + 2C \Rightarrow D$ with $k_1 = 1.0$ in batch reactor; P4.04.46. (*d*) Same as *c* but in CSTR. (*e*) Fill for 20 min, react, and discharge for 20 min with $r_a = 0.03[C_a(0.2 + C_a) - 0.04(1 - C_a)^2]$; P4.09.18. (*f*) Best temperature profile for a reversible reaction, $r = k_1(1 - x) - k_2x$; when $t = 0.1$, $x = 0.37$ at 600 R, and $x = 0.51$ with optimum temperature profile; $x = 0.81$ when $t = 0.5$ and final temperature is 250 R; the full range is impractical; P4.11.02.

TABLE 7-6   Material and Energy Balance of a CSTR

The sketch identifies the nomenclature.

Mean residence time:

$$\bar{t} = \frac{V_r}{V'} \tag{1}$$

Temperature dependence:

$$k = \exp\left(a' - \frac{b'}{T}\right) \tag{2}$$

Rate equation:

$$r_a = kC_a^\alpha = kC_{a0}^\alpha(1-x)^\alpha, \qquad x = \frac{(C_{a0} - C_a)}{C_{a0}} \tag{3}$$

Material balance:

$$C_{a0} = C_a + k\bar{t}C_a \tag{4}$$

$$x = ktC_{a0}^{\alpha-1}(1-x)^\alpha \tag{5}$$
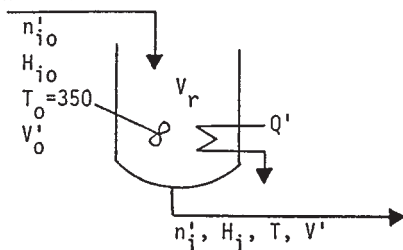
Enthalpy balance:

$$\sum n_i'H_i - \sum n_{i0}'H_{i0} = Q' - \Delta H_r(n_{a0}' - n_a') \tag{6}$$

$$H_i = \int_{298}^{T} C_{pi}\, dT \tag{7}$$

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T} \Delta C_p\, dT \tag{8}$$

For the reaction $aA + bB \rightarrow rR + sS$:

$$\Delta C_p = rC_{pr} + sC_{ps} - aC_{pa} - bC_{pb} \tag{9}$$

When the heat capacities are equal and constant, the heat balance is:

$$\overline{C}_p \rho V'(T - T_0) = Q' - \Delta H_{r298}V'(C_{a0} - C_a) \tag{10}$$

SOURCE: Adapted from Walas, *Chemical Process Equipment Selection and Design,* Butterworth-Heinemann, 1990.

Some values are

n	C_0/C		
	2	10	20
1	2.89	3.91	6.34
5	1.07	1.27	1.37

The ratio goes up sharply as the conversion increases and down sharply as the number of stages increases. For higher-order reactions the numbers are of comparable magnitudes.

Different Sizes   Ordinarily, it is most economical to make all stages of a CSTR battery the same size. For a first-order reaction the resulting total volume is a minimum for a specified performance, but not so for other orders. Take a two-stage battery:

$$\bar{t}_1 + \bar{t}_2 = \frac{C_0 - C_1}{kC_1^q} + \frac{C_1 - C_2}{kC_2^q}$$

With C_0 and C_2 specified, the condition for a minimum is

$$\frac{\partial(\bar{t}_1 + \bar{t}_2)}{\partial C_1} = 0$$

and

$$C_1^{q+1} + C_2^q[(q-1)C_1 - qC_0] = 0$$

when $q = 1$, $C_1 = \sqrt{C_0 C_2}$,   and $\bar{t}_1 = \bar{t}_2$

For higher orders $\bar{t}_1 \neq \bar{t}_2$ and the sum is less than twice the sum of equal stages, although usually not much different from that sum. As an example, when the second-order reaction between benzoquinone and cyclopentadiene is done in a three-stage unit, the reactor sizes are 3.25, 4.68, and 6.27, totaling 14.20, as compared to 14.56 with three equal stages (where consistent units are used). Details are in Walas (*Chemical Reaction Engineering Handbook of Solved Problems,* p. 4.11.15, Gordon & Breach, 1995).

Selectivity   A significant respect in which CSTRs may differ from batch (or PFR) reactors is in the product distribution of complex reactions. However, each particular set of reactions must be treated individually to find the superiority. For the consecutive reactions $A \Rightarrow B \Rightarrow C$, Fig. 7-5b shows that a higher peak value of B is reached in batch reactors than in CSTRs; as the number of stages increases the batch performance is approached.

TUBULAR AND PACKED BED FLOW REACTORS

Tubular reactors are made up of one or more tubes in parallel, each of less than approximately 100-mm (3.94-in) diameter. With fluids of normal viscosity, plug flow exists in tubes of this size, with all molecules having essentially the same residence time. In packed beds of larger diameters, large-scale convection may be inhibited to such an extent that plug flow is also approached. Continuous gas phase reactions are predominantly done in such units, as are many liquid phase processes. Immiscible liquids are best handled in stirred tanks, although in-line mixers can facilitate such reactions in pipes. Reaction times are mostly short, made feasible by elevated temperatures. In such large-scale operations as oil cracking, the tubes may be several hundred meters long in a trombonelike arrangement. Temperature control is by heat transfer through the walls or by cold-shot injection. Shell-and-tube arrangements can provide large amounts of heat transfer. Product distribution of complex reactions is like that of batch reactors, but different from that of CSTRs.

Material and energy balances of a plug flow reactor are summarized in Table 7-7.

For convenience, the loading on a flow reactor is expressed as a size of reactor per unit of flow rate, say V_r/V', and is labeled the **space velocity.** Some of the units in practical use are stated in the Introduction. How the actual residence time is calculated when the density of flow varies is illustrated in Table 7-8.

Tubular flow reactors operate at nearly constant pressure. How the differential material balance is integrated for a number of second-order reactions will be explained. When n_a is the molal flow rate of reactant A the **flow reactor equation** is

$$-dn_a = n_{a0}\, dx = -V'dC_a = r_a dV_r \tag{7-84}$$

or

$$V_r = \int_{n_a}^{n_{a0}} \frac{dn_a}{r_a} \tag{7-85}$$

The equation is rendered integrable by application of the stoichiometry of the reaction, the ideal gas law, and, for instance, the power law for rate of reaction. Some details are shown in Table 7-9.

Frictional Pressure Drop   Usually this does not have a significant effect on the reactor size, except perhaps when the flow is two-phase. Some approximate relations will be cited that are adequate for pressure-drop calculations of homogeneous flow reactions in pipelines. The pressure drop is given by

$$-dP = \frac{f\rho u^2}{2gD}\, dL \tag{7-86}$$

A good approximation to the friction factor in the turbulent flow range is

$$f = 0.046(\text{Re})^{-0.2} = 0.044\left(\frac{\mu D}{W}\right)^{0.2} \tag{7-87}$$

The mass flow rate is

$$W = 0.7854D^2\rho u$$

TABLE 7-7   Material and Energy Balances of a Plug Flow Reactor (PFR)

The balances are made over a differential volume dV_r of the reactor. Rate equation:

$$dV_r = \frac{-dn'_a}{r_a} \tag{1}$$

$$= -\frac{1}{k}\left(\frac{V'}{n'_a}\right)^\alpha dn'_a \tag{2}$$

$$= -\exp\left(-a' + \frac{b'}{T}\right)\left(\frac{n'_t RT}{Pn'_a}\right)^\alpha dn'_a \tag{3}$$
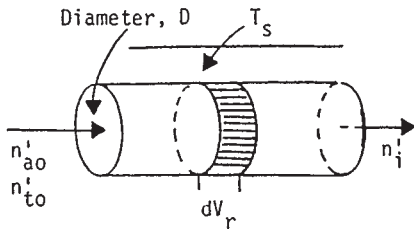
Enthalpy balance:

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T} \Delta C_p\, dT \tag{4}$$

$$dQ = U(T_s - T)\, dA_p = \frac{4U}{D}(T_s - T)\, dV_r$$

$$= -\frac{4U(T_s - T)}{Dr_a}\, dn'_a \tag{5}$$

$$dQ + \Delta H_r\, dn'_a = \sum n_i dH_i = \sum n_i C_{pi} dT \tag{6}$$

$$\frac{dT}{dn'_a} = \frac{\Delta H_r - 4U(T_s - T)/Dr_a}{\sum n_i c_{pi}} = f(T, T_s, n'_a) \tag{7}$$

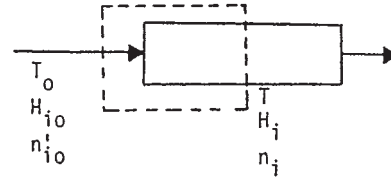At constant T_s, Eq. (7) may be integrated numerically to yield the temperature as a function of the number of moles

$$T = \phi(n'_a) \tag{8}$$

Then the reactor volume is found by integration

$$V_r = \int_{n'_a}^{n'_{a0}} \frac{1}{\exp\left[a' - b'/\phi(n'_a)\right]\left[Pn'_a/n'_t R\phi(n'_a)\right]^\alpha}\, dn'_a \tag{9}$$

Adiabatic process:

$$dQ = 0 \tag{10}$$

The balance around one end of the reactor is

$$\sum n_{i0} H_{i0} - \sum H_{r0}(n'_{a0} - n'_a) = \sum n_i H_i = \sum n_i \int C_{pi}\, dT \tag{11}$$

With reference temperature at T_0, enthalpies $H_{i0} = 0$

$$\Delta H_{r0} = \Delta H_{r298} + \int_{298}^{T_0} \Delta C_p\, dT \tag{12}$$

Substituting Eq. (12) into Eq. (10)

$$\left[-\Delta H_{r298} + \int_{298}^{T_0} \Delta C_p\, dT\right](n'_{a0} - n'_a) = \sum n_i \int_{T_0}^{T} C_{pi}\, dT \tag{13}$$

Adiabatic process with $\Delta C_p = 0$ and with constant heat capacities

$$T = T_0 - \frac{\Delta H_{r298}(n'_{a0} - n'_a)}{\sum n_i C_{pi}} \tag{14}$$

This expression is substituted instead of Eq. (8) to find the volume with Eq. (9).

The density in terms of the molecular weight M is

$$\rho = \frac{M}{V} = \frac{PM_0 n_{f0}}{RTn_t}$$

Also, in terms of the tube length dL,

$$dV_r = 0.7854 D^2 dL$$

Combining, $$-dP = \frac{0.046 W^{1.8}\mu^{0.2}RT[n_{f0} + \delta_a(n_{a0} - n_a)]}{gD^{6.8}M_0 n_{f0}P}\, dV_r \tag{7-88}$$

This is to be solved simultaneously with the flow reactor equation, Eq. (7-84). Alternatively, dV_r can be eliminated from Eq. (7-88) for a direct relation between P and n_a.

More accurate relations than Eqs. (7-86) and (7-87) are described in Sec. 11 of this Handbook.

RECYCLE AND SEPARATION MODES

All reactor modes can sometimes be advantageously operated with recycling of part of the product or intermediate streams. Heated or cooled recycle streams serve to moderate undesirable temperature travels, and they can be processed for changes in composition before being returned.

Say the recycle flow rate in a PFR is V'_r and the fresh feed rate is V'_0, with the ratio $R = V'_r/V'_0$. With a fresh feed concentration of C_0 and a product of C_2 the composite feed concentration is

$$C_1 = \frac{C_0 + RC_2}{1 + R} \tag{7-89}$$

The change in concentration across the reactor becomes

$$\Delta C = C_1 - C_2 = \frac{C_2 - C_0}{1 + R} \tag{7-90}$$

Accordingly, the change in concentration (or in temperature) across the reactor can be made as small as desired by upping the recycle ratio. Eventually, the reactor can become a differential unit with substantially constant temperature, while substantial differences will concurrently arise between the fresh feed inlet and the product withdrawal outlet. 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, the flow reactor equation at constant density with a power law is

$$-V'_0(1 + R)dC = kC^q dV_r$$

and $$V_r = V'_0(1 + R)\int_{C_2}^{C_1} \frac{dC}{kC^q} \tag{7-91}$$

Recycling increases the size of the reactor and degrades the plug flow characteristics, so there must be practical compensation by adjustment of the temperature or composition.

Example 10: Reactor Size with Recycle   For first-order reaction with $C_0/C_2 = 10$ and $R = 5$, $C_1/C_2 = 2.5$. The relative reactor sizes with recycle and without are

$$\text{Ratio} = \frac{(1 + 5)\ln(C_1/C_2)}{\ln(C_0/C_2)} = \frac{5.497}{4.605} = 1.193$$

With reversible reactions, recycling is warranted when improvement in conversion can be realized by removing some of the product in a separator and returning only unconverted material. In some CSTR operations, the product is removed continuously by extraction or azeotropic distillation. The gasoline addi-

TABLE 7-8   True Contact Time in A PFR

The ratio V_r/V_0' is of the volume of the reactor to the incoming volumetric rate and has the dimensions of time. It will be compared with the true residence time when the number of mols changes as reaction goes on, or P and T also change.

$$r_\alpha = k\left(\frac{n_\alpha}{V'}\right)^q = k\left(\frac{\pi}{RT}\right)^q\left(\frac{n_\alpha}{n_t}\right)^q$$

$$V' = \frac{n_t RT}{\pi}$$

The differential balance on the reactant is:

$$-dn_\alpha = r_\alpha dV_r$$

$$dV_r = -\frac{1}{k}\left(\frac{RT}{\pi}\right)^q\left(\frac{n_t}{n_\alpha}\right)^q dn_\alpha$$

$$\frac{dV_r}{V_0'} = -\frac{1}{kn_{t0}}\left(\frac{RT}{\pi}\right)^{q-1}\left(\frac{n_t}{n_\alpha}\right)^q dn_\alpha \tag{1}$$

The definition of the rate of reaction and the law of mass action is:

$$r_\alpha = -\frac{1}{V'}\frac{dn_\alpha}{dt} = k\left(\frac{n_\alpha}{V'}\right)^q$$

Rearrange to

$$dt = -\frac{1}{V'}\frac{dn_\alpha}{r_\alpha} = -\frac{1}{kV'}\left(\frac{V'}{n_\alpha}\right)^q dn_\alpha = -\frac{1}{k}\left(\frac{RT}{\pi}\right)^{q-1}\left(\frac{n_t^{q-1}}{n_\alpha^q}\right) dn_\alpha \tag{2}$$

Eqs. (1) and (2) are the desired comparison. Before integrating, substitute

$$n_t = n_{t0} + \delta_\alpha(n_{\alpha0} - n_\alpha)$$

Example: Take $q = 1$, $n_{t0} = n_{\alpha0}$.

$$\frac{V_r}{V_0'} = \int_{n_\alpha}^{n_{\alpha0}} \frac{(\delta_\alpha + 1)n_{\alpha0} - \delta_\alpha n_\alpha}{n_\alpha}\, dn_\alpha = \frac{1}{k}\left[(\delta_\alpha + 1)\ln\frac{1}{1-x} - \delta_\alpha x\right]$$

$$t = \frac{1}{k}\int_{n_\alpha}^{n_{\alpha0}} \frac{dn_\alpha}{n_\alpha} = \frac{1}{k}\ln\frac{1}{1-x}$$

The ratio

$$y = \frac{t}{V_r/V_0'} = \delta_\alpha + 1 - \frac{\delta_\alpha x}{\ln[1/(1-x)]}$$

$$\begin{array}{lll} > 1 & \text{when} & \delta_\alpha < 0 \\ < 1 & \text{when} & \delta_\alpha > 0 \end{array}$$

tive methyl-*tert*-butyl ether is made in a distillation column where reaction and simultaneous separation occur.

HEAT EFFECTS

The heat balance of a reactor is made up of three terms: Heat of reaction + Heat transfer = Gain of sensible and latent heats by the mixture. This establishes the temperature as a function of the composition

$$T = f(n_a)$$

which may be substituted into the equations of the specific rate and the equilibrium constant

$$k = \exp\left[A + \frac{B}{f(n_a)}\right]$$

$$K_e = \exp\left[C + \frac{D}{f(n_a)}\right]$$

With these substitutions the rate equation remains a function of the composition alone.

Heat balances of several kinds of reactors are summarized in Tables 7-5, 7-6, 7-7 and 7-10.

Enthalpy changes of processes depend only on the end states. Normally the enthalpy change of reaction is known at some standard tem-

TABLE 7-9   Integration of Rate Equations of a PFR at Constant Pressure

Tubular flow reactors usually operate at nearly constant pressure. For a reactant A, the differential material balance is:

$$-dn_\alpha = n_{\alpha0}dx = -V'dC_\alpha = V'C_{\alpha0}dx = r_\alpha dV_r$$

One form of the integration is:

$$\frac{V_r}{n_{\alpha0}} = \int_{x_0}^x \frac{dx}{r_\alpha}, \qquad \frac{\text{reactor volume}}{\text{molal input rate}}$$

$$n_t = n_{t0} + \delta_\alpha(n_{\alpha0} - n_\alpha) = n_{t0} + \delta_\alpha x$$

$$V' = n_t RT/\pi$$

$$C_\alpha = \frac{n_\alpha}{V'} = \left(\frac{\pi}{RT}\right)\left(\frac{n_\alpha}{n_t}\right) = \left(\frac{\pi}{RT}\right)\left(\frac{n_{\alpha0} - x}{n_{t0} + \delta_\alpha x}\right)$$

The rate equations will be stated in these terms for a number of reactions. In all these cases, the integrands are ratios of second-degree equations. The moderately complex integrations are accomplished with the aid of a table of integrals, or by MATHEMATICA, or numerically when the constants are known.

$$\begin{array}{ll} 2\,A \Rightarrow M & (1) \\ A + B \Rightarrow M & (2) \\ 2A \Leftrightarrow M & (3) \\ A + B \Leftrightarrow M & (4) \end{array}$$

Part (1):

$$\delta_\alpha = \frac{(1-2)}{2} = -0.5$$

$$V' = \left(\frac{RT}{\pi}\right)(n_{t0} - 0.5x)$$

$$\frac{V_r}{n_{\alpha0}} = \int \frac{dx}{r_\alpha} = \frac{1}{k}(\overline{RT})^2 \int_{x_0}^x \left(\frac{n_{t0} - 0.5x}{n_{\alpha0} - x}\right)^2 dx$$

Part (2):

$$\delta_\alpha = \frac{(1-2)}{1} = -1$$

$$V' = \left(\frac{RT}{\pi}\right)(n_{t0} - x)$$

$$\frac{V_r}{n_{\alpha0}} = \frac{1}{k}\left(\frac{\pi}{RT}\right)^2 \int_{x_0}^x \frac{(n_{\alpha0} - x)(n_{b0} - x)}{(n_{t0} - x)^2} dx$$

Part (3):

$$\delta_a = -0.5$$

$$V' = \left(\frac{RT}{\pi}\right)(n_{t0} - 0.5x)$$

$$r_\alpha = k_1\left(\frac{RT}{\pi}\right)^2\left(\frac{n_{\alpha0} - x}{n_{t0} - 0.5x}\right)^2 - k_2\left(\frac{RT}{\pi}\right)\left(\frac{n_{m0} + 0.5n_{\alpha0}x}{n_{t0} - 0.5x}\right)$$

Part (4):

$$\delta_\alpha = -0.5$$

$$r_\alpha = k_1\left(\frac{RT}{\pi}\right)^2\frac{(n_{\alpha0} - x)(n_{b0} - x)}{(n_{t0} - 0.5x)^2} - k_2\left(\frac{RT}{\pi}\right)\left(\frac{n_{m0} + 0.5n_{\alpha0}x}{n_{t0} - 0.5x}\right)$$

perature, $T_b = 298$ K (536 R), for instance. The simplest formulation of the heat balance, accordingly, is to consider the reaction to occur at this temperature, transfer whatever heat is required, and raise the enthalpy of the reaction products to their final values.

Batch Reactions   For a batch reaction, the heat balance is

$$-(\Delta H_r)_{T_b}(n_{a0} - n_a) + Q = \sum n_i(H_{iT} - H_{iT_b}) \tag{7-92}$$

TABLE 7-10 Material and Energy Balances of a Packed Bed Reactor

Diffusivity and thermal conductivity are taken appreciable only in the radial direction.

Material balance equation:

$$\frac{\partial x}{\partial z} - \frac{D}{u}\left(\frac{\partial^2 x}{\partial r^2} + \frac{1}{r}\frac{\partial x}{\partial r}\right) - \frac{\rho}{u_0 C_0} r_c = 0 \qquad (1)$$

Energy balance equation:

$$\frac{\partial T}{\partial z} - \frac{k}{G C_p}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \frac{\Delta H_r \rho}{G C_p} r_c = 0 \qquad (2)$$

At the inlet:

$$x(0, r) = x_0 \qquad (3)$$
$$T(0, r) = T_0 \qquad (4)$$

At the center:

$$r = 0, \qquad \frac{\partial x}{\partial r} = \frac{\partial T}{\partial r} = 0 \qquad (5)$$

At the wall:

$$r = R, \qquad \frac{\partial x}{\partial r} = 0 \qquad (6)$$

$$\frac{\partial T}{\partial r} = \frac{U}{k}(T' - T) \qquad (7)$$

When the temperature T' of the heat-transfer medium is not constant, another enthalpy balance must be formulated to relate T' with the process temperature T.

A numerical solution of these equations may be obtained in terms of finite difference equivalents, taking m radial increments and n axial ones. With the following equivalents for the derivatives, the solution may be carried out by direct iteration:

$$r = m(\Delta r)$$

$$z = n(\Delta z) \qquad (8)$$

$$\frac{\partial T}{\partial z} = \frac{T_{m,n+1} - T_{m,n}}{\Delta z} \qquad (9)$$

$$\frac{\partial T}{\partial r} = \frac{T_{m+1,n} - T_{m,n}}{\Delta r} \qquad (10)$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{T_{m+1,n} - 2T_{m,n} + T_{m-1,n}}{(\Delta r)^2} \qquad (11)$$

Expressions for the x derivatives are of the same form:

r_c = rate of reaction, a function of s and T
G = mass flow rate, mass/(time)(superficial cross section)
u = linear velocity
D = diffusivity
k = thermal conductivity

SOURCE: Adapted from Walas, *Chemical Process Equipment Selection and Design,* Butterworth-Heinemann, 1990.

The solvent, as well as any other inerts, and the mass of the vessel are included in this summation. The heat exchange through a jacket or coils at temperature T_m is

$$Q = UA(T_m - T) \qquad (7-93)$$

When phase changes are absent,

$$-(\Delta H_r)_{T_b}(n_{a0} - n_a) + UA(T_m - T) = \sum n_i \int_{T_b}^{T} C_{pi}\, dT \qquad (7-94)$$

When the mixture can be characterized by an overall heat capacity,

$$-(\Delta H_r)_{T_b}(n_{a0} - n_a) + UA(T_m - T) = V_r \rho C_p(T - T_b) \qquad (7-95)$$

or

$$-(\Delta H_r)_{T_b}(C_{a0} - C_a) + \left(\frac{UA}{V_r}\right)(T_m - T) = \rho C_p(T - T_b) \qquad (7-96)$$

CSTR Reactions For a CSTR reaction, the quantities n_i are molal flow rates. Per unit of time,

$$-(\Delta H_r)_{T_b} V_r r_a + Q = \sum n_i(H_{iT} - H_{iT_b}) \qquad (7-97)$$

$$\Rightarrow \sum n_i \int_{T_b}^{T} C_{pi}\, dT \qquad (7-98)$$

The last equation applies in the absence of phase change.

Plug Flow Reactions The differential relations in a cylindrical vessel are

$$dA = \left(\frac{4}{D}\right) dV_r \qquad -\Delta H_{rT}\, dn_a + \frac{4UA}{D}\, dV_r = \sum n_i C_{pi}\, dT \qquad (7-99)$$

$$\Rightarrow n_t C_{pt}\, dT \qquad (7-100)$$

Note that the enthalpy change of reaction is a function of temperature, but a mean value often is adequate.

The various heat balances are to be solved simultaneously with the appropriate material balances, but when the temperatures can be solved for explicitly their equivalents are simply substituted into the equations for k and K_e and the material balance is solved alone.

Packed Bed Reactors The commonest vessels are cylindrical. They will have gradients of composition and temperature in the radial and axial directions. The partial differential equations of the material and energy balances are summarized in Table 7-10. Example 4 of "Modeling of Chemical Reactions" in Sec. 23 is an application of such equations.

A variety of provisions for heat transfer are illustrated in Figs. 23-1 to 23-3 and elsewhere in Sec. 23.

UNSTEADY CONDITIONS WITH ACCUMULATION TERMS

Unsteady material and energy balances are formulated with the conservation law, Eq. (7-68). The sink term of a material balance is $V_r c_a$ and the accumulation term is the time derivative of the content of reactant in the vessel, or $\partial(V_r C_a)/\partial t$, where both V_r and C_a depend on the time. An unsteady condition in the sense used in this section always has an accumulation term. This sense of unsteadiness excludes the batch reactor where conditions do change with time but are taken account of in the sink term. Startup and shutdown periods of batch reactors, however, are classified as unsteady; their equations are developed in the "Batch Reactors" subsection. For a semibatch operation in which some of the reactants are preloaded and the others are fed in gradually, equations are developed in Example 11, following.

For a CSTR the unsteady material balance is

$$V'C_{a0} = V'C_a + V_r r_a + \frac{d(V_r C_a)}{dt} \qquad (7-101)$$

Enthalpy balances also will have accumulation terms.

Conditions that give rise to unsteadiness are changes in feed rate, composition, or temperature. In the case of Fig. 7-6, a sinusoidal input of feed rate is introduced. The output concentration also appears to vary sinusoidally. The amplitude of the response is lower as the specific rate is increased.

If a sinusoidal variation of the temperature of the heat transfer medium in the jacket or coil occurs, say

$$T_m = T_{m0}(1 + \alpha \sin \beta t) \qquad (7-102)$$

the balances will be

$$-\Delta H_r V_r r_a + UA(T_m - T) = V'\rho C_p(T - T_0) + \rho V_r C_p \frac{dT}{dt} \qquad (7-103)$$

$$V'C_{a0} = V'C_a + V_r r_a + V_r \frac{dC_a}{dt} \qquad (7-104)$$

Since each input of mass to a perfect plug flow unit is independent of what has been input previously, its condition as it moves along the
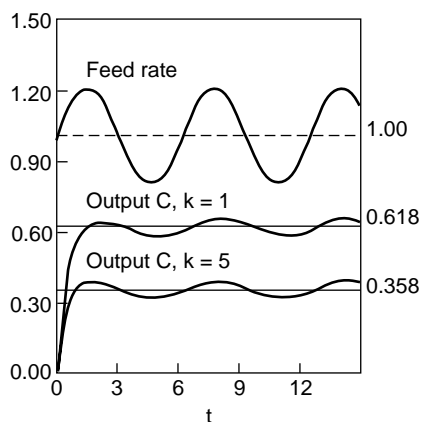
FIG. 7-6   Sinusoidal input of feed rate to a CSTR. Input: $F = 1 + 0.2 \sin(t)$; output: $dC/dt = (1 - C)[1 + 0.2 \sin(t)] - kc^2$. Straight lines are for constant feed rate.

reactor will be determined solely by its initial condition and its residence time, independently of what comes before and after. Practically, of course, some interaction will occur at the boundaries of successive inputs of different compositions or temperatures. This is governed by diffusional behaviors that are beyond the scope of the present work.

Example 11: Balances of a Semibatch Process   The reaction A + B ⇒ Products is carried out by first charging B into the vessel to a concentration C_{b0} and a volume V_{r0}, then feeding a solution of concentration C_{a0} at volumetric rate V' for a time **t**.

Volume of solution in the tank:

$$V_r = V_{r0} + V't \qquad (7\text{-}105)$$

Stoichiometric balance:

$$V'tC_{a0} - V_rC_a = V_{r0}C_{b0} - V_rC_b$$

$$C_b = C_a + \frac{V_{r0}C_{b0} - V'tC_{a0}}{V_{r0} + V't} \qquad (7\text{-}106)$$

Material balance on A:

$$\text{Input} = \text{Output} + \text{Sink} + \text{Accumulation}$$

$$V'C_{a0} = 0 + kV_rC_aC_b + \frac{d(C_aV_r)}{dt}$$

$$= kV_rC_aC_b + V_r\frac{dC_a}{dt} + C_aV'$$

$$\frac{dC_a}{dt} + kC_aC_b + \frac{V'C_a}{V_r} = \frac{V'C_{a0}}{V_r} \qquad (7\text{-}107)$$

Eqs. (7-105), (7-106), and (7-107) are combined into

$$\frac{dC_a}{dt} = \frac{V'}{V_{r0} + V't}(C_{a0} - C_a) - kC_a\left(C_a + \frac{V_{r0}C_{b0} - V'tC_{a0}}{V_{r0} + V't}\right) \qquad (7\text{-}108)$$

A numerical integration is required.

LARGE SCALE OPERATIONS

INTRODUCTION

In this category are included a number of topics that become especially significant on the industrial scale. Some of this material is covered at length in Sec. 23, so only an outline is provided here.

MULTIPLE STEADY STATES

Phenomena of multiple steady states and instabilities occur particularly with nonisothermal CSTRs. Some isothermal processes with hyperbolic rate equations and processes with porous catalysts also can have such behavior.

Mathematically, multiplicities become evident when heat and material balances are combined. Both are functions of temperature, the latter through the rate equation which depends on temperature by way of the Arrhenius law. The curves representing these balances may intersect in several points. For first order in a CSTR, the material balance in terms of the fraction converted can be written

$$x = \frac{k\bar{t}}{1 + k\bar{t}}, \qquad k = \exp\left(a - \frac{b}{T}\right) \qquad (7\text{-}109)$$

and the energy balance

Heat generation = Sensible heat gain

$$\frac{-\Delta H_r V_r C_f(1 - x)}{\bar{t}} + UA(T_m - T) = \rho C_p V_r(T - T_f) \qquad (7\text{-}110)$$

These balances can be plotted two ways, as shown in Fig. 7-7:

1. x from both equations can be plotted against T, with the intersections at the steady state values of T and corresponding values of x.

2.   The LHS (heat generation) and RHS (heat removal) of Eq. (7-110) are plotted against T after x has been eliminated between the two balances; the intersections identify the same steady state temperatures as the plot in Fig. 7-7a.

Conditions at which the slope of the heat generation line is greater than that of the heat removal line are unstable, and where it is less the condition is stable (see Fig. 7-7b). At an unstable point, any fluctua-

tion in conditions will move the temperature to a neighboring point. Control systems always produce small fluctuations of the process variables, as in the sinusoidal case of Fig. 7-6. If the fluctuations occur while the system is at an unstable point, the steadiness will disappear. In the case of Fig. 7-7c, as the unstable position is approached ($T = 280$, $C = 2.4$) the profiles of T and C become erratic and eventually degenerate to the condition at the stable point on the right (Figs. 7-7d and 7-7e).

Either of the two stable operating conditions can be selected by adjusting the positions of the curves so that only one intersection is obtained. In a plant, long-time unstable operation is unlikely because of imprecise temperature control.

Plug flow reactors with recycle exhibit some of the characteristics of CSTRs, including the possibility of multiple steady states. This topic is explored by Perlmutter (***Stability of Chemical Reactors,*** Prentice-Hall, 1972).

Endothermic reactions possess only one steady state.

For complex reactions and with multistage CSTRs, more than three steady states can exist (as in Fig. 23-17c). Most of the work on multiplicities and instabilities has been done only on paper. No plant studies and a very few laboratory studies are mentioned in the comprehensive reviews of Razon and Schmitz (***Chem. Eng. Sci., 42,*** 1,005–1,047 [1987]) and Morbidelli et al. (in Carberry and Varma, ***Chemical Reaction and Reactor Engineering,*** Dekker, 1987, pp. 973–1,054).

NONIDEAL BEHAVIOR

Reactors that are nominally CSTRs or PFRs may in practice deviate substantially from ideal mixing or nonmixing. This topic is developed at length in Sec. 23, so only a few summary statements are made here. More information about this topic also may be found in Nauman and Buffham (***Mixing in Continuous Flow Systems,*** Wiley, 1983).

Laminar Flow   With highly viscous fluids the linear velocity along a streamline varies with the radial position. Laminar flow is characteristic of some polymeric systems. Figure 23-21 shows how the conversion is poorer in laminar flow than with uniform flow over the
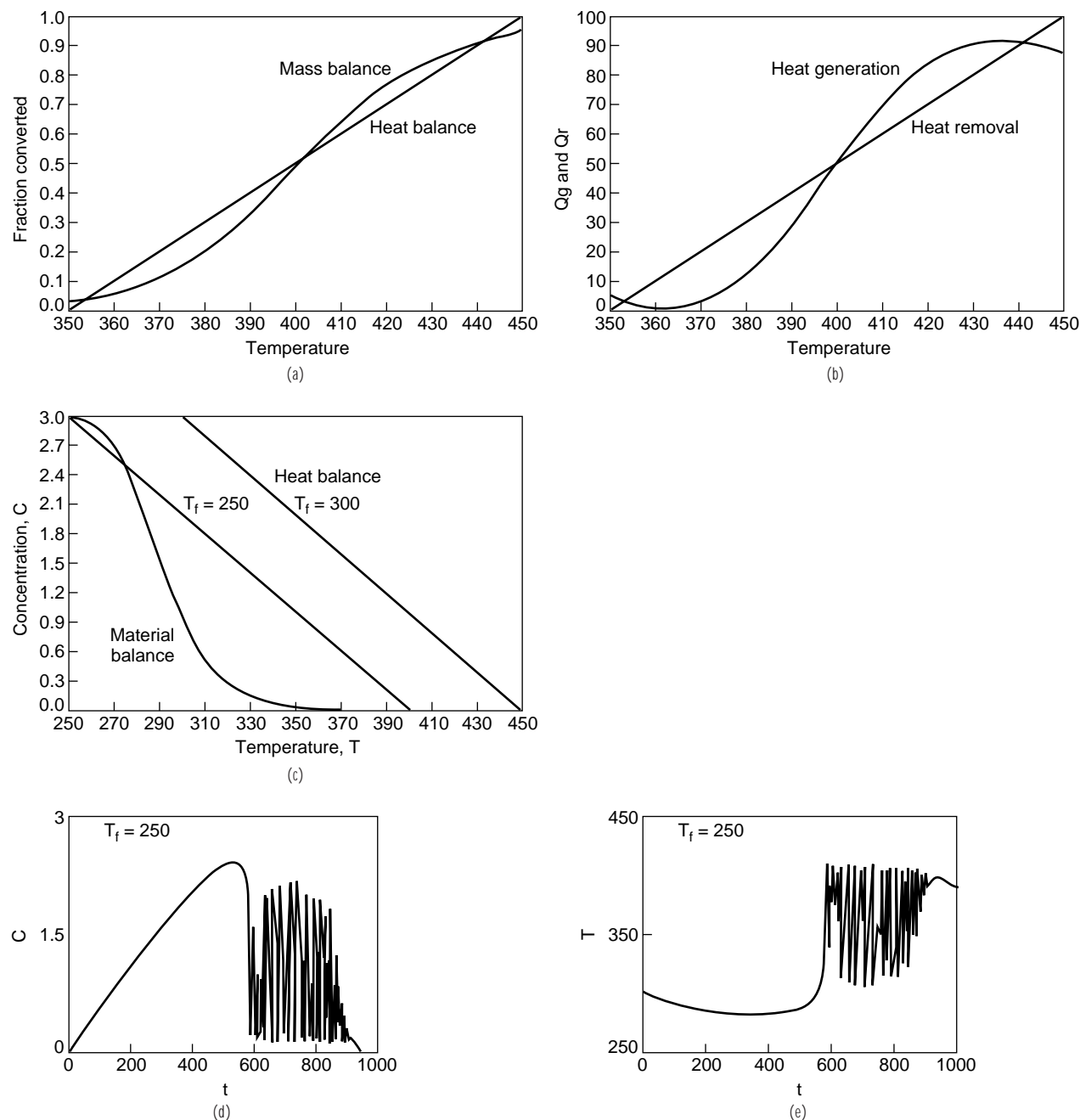
FIG. 7-7 Multiplicity and instability of first-order reactions in CSTRs. For (*a*) and (*b*), $k = \exp(25 - 10{,}000/T)$, $x = k/(1 + k)$, $200x + (350 - T) = T - 350$. For curves (*c*) to (*e*), $k = \exp(25 - 7{,}550/T)$, $C = 3/(1 + 300k)$, $C = 3 - 0.2(T - T_f)$. Unsteady state, $300\,dC/dt = 3 - (1 + 300k)C$, $C_0 = 0$; $300\,dT/dt = T_f - T + 15{,}000kC$, $T_0 = 300$. Temperature in °C.

cross section for first- and second-order reactions. Another adverse effect with viscous solutions is poor heat transfer. Accordingly, stirred tanks are often preferred to tubular units for such applications. The equations for radial and axial distributions of composition and temperature in laminar flow are studied by Nauman (*Chemical Reactor Design,* Wiley, 1987, pp. 165–203).

Residence Time Distribution (RTD)   This is established by injecting a known amount of tracer into the feed stream and monitor-

ing its concentration in the effluent. At present there are no correlations of this kind of behavior that could be used for design of a new process, but such information about existing units is of value for diagnostic purposes.

The RTD is a distinctive characteristic of mixing behavior. In Fig. 7-3*e*, the CSTR has an RTD that varies as the negative exponential of the time and the PFR is represented by a vertical line at $t_r = 1$. Multistage units and many packed beds have bell-shaped RTDs, like that of

the five-stage unit of Fig. 7-3*e* and the large-scale units of Figs. 23-10 and 23-11. An equation that represents such shapes is called the Erlang,

$$\text{RTD} = \frac{n^n}{\Gamma(n)}\, t_r^{n-1} \exp(-nt_r) \qquad (7\text{-}111)$$

where n is interpreted as a number of CSTRs in series. When n is integral, $\Gamma(n)$ is replaced by $(n-1)!$. Plots of these curves are shown in Fig. 23-9.

When the RTD of a vessel is known, its performance as a reactor for a first-order reaction, and the range within which its performance will fall for other orders, can be predicted.

Segregated Flow   A real example is *bead polymerization* of styrene and some other materials. The reactant is in the form of individual small beads suspended in a fluid and retarded from agglomeration by colloids on their surfaces. Accordingly, they go through the reactor as independent bodies and attain conversions under batch conditions with their individual residence times. This is called *segregated flow*. With a particular RTD, conversion is a maximum with this flow pattern. The mean conversion of all the segregated elements then is given by

$$\frac{\overline{C}}{C_0} = \int_0^\infty (\text{RTD}) \left(\frac{C}{C_0} \right)_{\text{batch}} dt_r \qquad (7\text{-}112)$$

For first order $\left(\dfrac{C}{C_0} \right)_{\text{batch}} = \exp(-\bar{k}tt_r) \qquad (7\text{-}113)$

For second order $\left(\dfrac{C}{C_0} \right)_{\text{batch}} = \dfrac{1}{(1 + kC_0\bar{t}t_r)} \qquad (7\text{-}114)$

Example 12: Segregated Flow   The pilot unit of Fig. 23-11 with $n = 9.3$ has

$$\text{RTD} = 13188 t_r^{8.3} \exp(-9.3 t_r)$$

Some values of mean concentration ratio $\overline{C}/C_0$ of first- and second-order reactions obtained with Eq. (7-112) are:

$\bar{k}t$ or $kC_0\bar{t}$	1	2	5	10
First order $\overline{C}/C_0$	0.386	0.163	0.018	
Second order $\overline{C}/C_0$	0.513	0.349	0.180	0.100
Second order PFR	0.500	0.333	0.167	0.091

Maximum Mixedness   With a particular RTD, this pattern provides a lower limit to the attainable conversion. It is explained in Sec. 23. Some comparisons of conversions with different flow patterns are made in Fig. 23-14. Segregated conversion is easier to calculate and is often regarded as a somewhat plausible mechanism, so it is often the only one taken into account.

Dispersion   In tubes, and particularly in packed beds, the flow pattern is disturbed by eddies whose effect is taken into account by a dispersion coefficient in Fick's diffusion law. A PFR has a dispersion coefficient of 0 and a CSTR of ∞. Some rough correlations of the Peclet number *uL/D* in terms of Reynolds and Schmidt numbers are Eqs. (23-47) to (23-49). There is also a relation between the Peclet number and the value of *n* of the RTD equation, Eq. (7-111). The dispersion model is sometimes said to be an adequate representation of a reactor with a "small" deviation from plug flow, without specifying the magnitude of *small*. As a point of superiority to the RTD model, the dispersion model does have the empirical correlations that have been cited and can therefore be used for design purposes within the limits of those correlations.

OPTIMUM CONDITIONS

Optimization of a process is an activity whereby the *best* conditions are found for attainment of a maximum or minimum of some desired objective. In the broadest sense, an industrial process has maximum profit as its goal, but there are also problems with less-ambitious goals that do not involve money or the whole plant.

The best quality to be found may be a temperature, a temperature program, a concentration, a conversion, a yield of preferred product, a cycle period for a batch reaction, a daily production level, a kind of reactor, a size for a reactor, an arrangement of reactor elements, provisions for heat transfer, profit or cost, and so on—a maximum or minimum of some of these factors. Among the constraints that may be imposed on the process are temperature range, pressure range, corrosiveness, waste disposal, and others.

Once the objective and the constraints have been set, a mathematical model of the process can be subjected to a search strategy to find the optimum. Simple calculus is adequate for some problems, or Lagrange multipliers can be used for constrained extrema. When a full plant simulation can be made, various alternatives can be put through the computer. Such an operation is called *flowsheeting*. A chapter is devoted to this topic by Edgar and Himmelblau (*Optimization of Chemical Processes,* McGraw-Hill, 1988) where they list a number of commercially available software packages for this purpose, one of the first of which was Flowtran.

With many variables and constraints, linear and nonlinear programming may be applicable, as well as various numerical gradient search methods. Maximum principle and dynamic programming are laborious and have had only limited applications in this area. The various mathematical techniques are explained and illustrated, for instance, by Edgar and Himmelblau (*Optimization of Chemical Processes,* McGraw-Hill, 1988).

A few specific conclusions about optimum performance can be stated:

1.   The minimum total volume of a CSTR battery for first-order reaction, and near-minimum for second-order, is obtained when all vessels are the same size.

2.   An economical optimum number of CSTRs and their auxiliaries in series is 4 to 5.

3.   In a sequence of PFR and CSTR, better performance is obtained with the PFR last. Performance of reversible reactions is improved with the CSTR at a higher temperature.

4.   For the consecutive reactions A $\Rightarrow$ B $\Rightarrow$ C, a higher yield of intermediate B is obtained in batch reactors or PFRs than in CSTRs.

5.   When the desirable product of a complex reaction is favored by a high concentration of some reactant, batch or semibatch reactors can be made superior to CSTRs.

6.   Conversion by a reversible reaction is enhanced by starting out at high temperature and ending at low temperature if equilibrium conversion drops off at high temperature.

7.   For a reversible reaction, the minimum size or maximum conversion is obtained when the rate of reaction is kept at a maximum at each conversion by adjustment of the temperature.

Variables   It is possible to identify a large number of variables that influence the design and performance of a chemical reactor with heat transfer, from the vessel size and type; catalyst distribution among the beds; catalyst type, size, and porosity; to the geometry of the heat-transfer surface, such as tube diameter, length, pitch, and so on. Experience has shown, however, that the reactor temperature, and often also the pressure, are the primary variables; feed compositions and velocities are of secondary importance; and the geometric characteristics of the catalyst and heat-exchange provisions are tertiary factors. Tertiary factors are usually set by standard plant practice. Many of the major optimization studies cited by Westerterp et al. (1984), for instance, are devoted to reactor temperature as a means of optimization.

The complexity of temperature regulation of three major commercial reversible processes are represented in Figs. 23-3*a*, 23-3*e*, and 23-3*f*. Presumably, these profiles have been established by fine-tuning the operations over a period of time.

Objective Function   This is the quantity for which a minimax is sought. For a complete manufacturing plant, it is related closely to the economy of the plant. Subsidiary problems may be to optimize conversion, production, selectivity, energy consumption, and so on in terms of temperature, pressure, catalyst, or other pertinent variables.

Case Studies   Several collections of more or less detailed solutions of optimization problems are cited, as follows:

1.   Of the 23 studies listed under "Modeling of Chemical Reactors" in Sec. 23, a number are optimization oriented. Added to them

may be a detailed study of an existing sulfuric acid plant by Crowe et al. (*Chemical Plant Simulation,* Prentice-Hall, 1971).

2. Chen (*Process Reactor Design,* Allyn & Bacon, 1983) does the following examples mostly with simple calculus:

Batch reactors—optimum residence time for series and complex reactions, minimum cost, optimal operating temperature, and maximum rate of reaction

CSTRs—minimum volume of battery, maximum yield, optimal temperature for reversible reaction, minimum total cost, reactor volume with recycle, maximum profit for reversible reaction with recycle, and heat loss

Tubular flow reactors—minimum volume for second-order reversible reactions, maximum yield of consecutive reactions, minimum cost with and without recycle, and maximum profit with recycle

Packed bed reactor optimization

Size comparison for first- and second-order and reversible reactions

Selectivity of parallel and consecutive reactions and of reactions in a porous catalyst

3. Edgar and Himmelblau (*Optimization of Chemical Processes,* McGraw-Hill, 524–550, 1988) supply many references to other problems in the literature:

Optimal residence time for the reactions $A \Leftrightarrow B$ followed by $B \Rightarrow P$ or X

Optimal time for a biochemical CSTR

Selection of feedstock for thermal cracking to ethylene by linear programming

Maximum yield from a four-stage CSTR by nonlinear programming

Optimal design of ammonia synthesis by differential equation solution and a numerical gradient search

A C_4 alkylation process by sequential quadratic programming

4. Westerterp, van Swaaij, and Beenackers (*Chemical Reactor Design and Operation,* Wiley, 1984, pp. 674–746) also supply many references to other problems in the literature:

Optimized costs for several gas phase reactions: (1) $A + B \Rightarrow P$; (2) $A + B \Leftrightarrow P$; and (3) $A + B \Rightarrow P$, $A + 2B \Rightarrow X$, $P + B \Rightarrow X$

Ammonia cold-shot converter

Maximum yield of first-order consecutive reactions in CSTR by application of Lagrange multipliers

Autothermal reactor for methanol synthesis using a numerical search technique

Minimum reactor volumes of isothermal and nonisothermal cascades by dynamic programming

Optimum temperature profiles of $2A \Rightarrow B \Rightarrow P$ by the maximum principle

Optimizing the temperature for $A \Rightarrow P$ and $A \Rightarrow X$ by the maximum principle

Westerterp et al. (1984; see Case Study 4, preceding) conclude, "Thanks to mathematical techniques and computing aids now available, any optimization problem can be solved, provided it is realistic and properly stated. The difficulties of optimization lie mainly in providing the pertinent data and in an adequate construction of the objective function."

HETEROGENEOUS REACTIONS

Heterogeneous reactions of industrial significance occur between all combinations of gas, liquid, and solid phases. The solids may be inert or reactive or catalysts in granular form. Some noncatalytic examples are listed in Table 7-11, and processes with solid catalysts are listed under "Catalysis" in Sec. 23. Equipment and operating conditions of heterogeneous processes are covered at some length in Sec. 23; only some highlights will be pointed out here.

Reactants migrate between phases in order to react: from gas phase to liquid, from fluid to solid, and between liquids when the reaction occurs in both phases. One of the liquids usually is aqueous. Resistance to mass transfer may have a strong effect on the overall rate of reaction. A principal factor is the *interfacial area.* Its magnitude is enhanced by agitation, spraying, sparging, use of trays or packing, and by size reduction or increase of the porosity of solids. These are the same operations that are used to effect physical mass transfer between

TABLE 7-11   Industrial Noncatalytic Heterogeneous Reaction

Gas/solid
  Action of chlorine on uranium oxide to recover volatile uranium chloride
  Removal of iron oxide impurity from titanium oxide by volatilization by action of chlorine
  Combustion and gasification of coal
  Manufacture of hydrogen by action of steam on iron
  Manufacture of blue gas by action of steam on carbon
  Calcium cyanamide by action of atmospheric nitrogen on calcium carbide
  Burning of iron sulfide ores with air
  Nitriding of steel

Liquid/solid
  Ion exchange
  Acetylene by action of water on calcium carbide
  Cyaniding of steel
  Hydration of lime
  Action of liquid sulfuric acid on solid sodium chloride or on phosphate rock or on sodium nitrate
  Leaching of uranium ores with sulfuric acid

Gas/liquid
  Sodium thiosulfate by action of sulfur dioxide on aqueous sodium carbonate and sodium sulfide
  Sodium nitrite by action of nitric oxide and oxygen on aqueous sodium carbonate
  Sodium hypochlorite by action of chlorine on aqueous sodium hydroxide
  Ammonium nitrate by action of ammonia on aqueous nitric acid
  Nitric acid by absorption of nitric oxide in water
  Recovery of iodine by action of sulfur dioxide on aqueous sodium iodate
  Hydrogenation of vegetable oils with gaseous hydrogen
  Desulfurization of gases by scrubbing with aqueous ethanolamines

Liquid/liquid
  Caustic soda by reaction of sodium amalgam and water
  Nitration of organic compounds with aqueous nitric acid
  Formation of soaps by action of aqueous alkalies on fats or fatty acids
  Sulfur removal from petroleum fractions by aqueous ethanolamines
  Treating of petroleum products with sulfuric acid

Solid/solid
  Manufacture of cement
  Boron carbide from boron oxide and carbon
  Calcium silicate from lime and silica
  Calcium carbide by reaction of lime and carbon
  Leblanc soda ash

Gas/liquid/solid
  Hydrogenation or liquefaction of coal in oil slurry

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

phases and the equipment can be similar, except that more heat transfer may be needed because of substantial heats of reaction.

Chemical reaction always enhances the rate of mass transfer between phases. The possible magnitudes of such enhancements are indicated in Tables 23-6 and 23-7. They are no more predictable than are specific rates of chemical reactions and must be found experimentally for each case, or in the relatively sparse literature on the subject.

Mechanisms   The most widely investigated heterogeneous reactions have been gas/liquid and fluid/solid catalyst. The Hatta theory or Langmuir-Hinshelwood mechanisms can suggest the forms of rate equations but they always involve parameters to be found empirically. Because liquid diffusivities are low, most liquid/liquid reactions are believed to be mass-transfer controlled. In some cases the phase in which reaction occurs has been identified, but there are cases where both phases are active. Phase-transfer catalysts enhance the transfer of reactant from an aqueous to an organic phase and thus speed up reactions. Mass transfer responds less strongly to change of temperature than does chemical rate, so this feature can be used to discriminate between possible controlling mechanisms. A sensitivity to stirring rate or to a change in linear velocity also will indicate the presence of major resistance to mass transfer. No single pattern appears to hold for reactions of solids, but much is known about the behavior of important operations like cement manufacturing, ore roasting, and lime burning.

Reaction and Separation   Some multiphase operations combine simultaneous reaction and separation. A few examples follow.

1.   The yield of furfural from xylose is improved by countercurrent extraction with tetralin (Schoenemann, *Proc. 2d Europ. Symp. Chem. React. Eng.,* Pergamon, 1961, p. 30).

2.   The reaction of vinyl acetate and stearic acid makes vinyl stearate and acetic acid but also some unwanted ethylidene acetate. A high selectivity is obtained by reaction in a distillation column with acetic acid overhead and vinyl stearate to the bottom (Geelen and Wiffels, *Proc. 3d Europ. Symp. Chem. React. Eng.,* Pergamon, 1964, p. 125).

3.   The hydrolysis of fats is improved by running in a counter-current extraction column (Donders et al., *Proc. 4th Europ. Symp. Chem. React. Eng.,* Pergamon, 1968, pp. 159–168).

4.   In the production of KNO_3 from KCl and HNO_3, the product HCl is removed continuously from the aqueous phase by contact with amyl alcohol, thus forcing the reaction to completion (Baniel and Blumberg, *Chim. Ind.,* **4,** 27 [1957]).

5.   Methyl-*tert*-butyl ether, a gasoline additive, is made from isobutene and methanol with distillation in a bed of acidic ion-exchange resin catalyst. The MTBE goes to the bottom with purity above 99 percent and unreacted materials overhead.

ACQUISITION OF DATA

INTRODUCTION

Kinetic data are acquired in the laboratory as a basis for design of large-scale equipment or for an understanding of its performance, or for the interpretation of possible reaction mechanisms. All levels of sophistication of equipment, statistical design of experiments, execution, and statistical analysis of the data are reported in the literature. Before serious work is undertaken, the appropriate literature should be consulted. The bibliography of Shah (*Gas-Liquid-Solid Reactor Design,* McGraw-Hill, 1979), for instance, has 145 items classified into 22 categories of reactor types.

The criteria for selection of laboratory reactors include equipment cost, ease of operation, ease of data analysis, accuracy, versatility, temperature uniformity, and controllability, suitability for mixed phases, and scale-up feasibility.

A number of factors limit the accuracy with which parameters for the design of commercial equipment can be determined. The parameters may depend on transport properties for heat and mass transfer that have been determined under nonreacting conditions. Inevitably, subtle differences exist between large and small scale. Experimental uncertainty is also a factor, so that under good conditions with modern equipment kinetic parameters can never be determined more precisely than ±5 to 10 percent (Hofmann, in de Lasa, *Chemical Reactor Design and Technology,* Martinus Nijhoff, 1986, p. 72).

Composition   The law of mass action is expressed as a rate in terms of chemical compositions of the participants, so ultimately the variation of composition with time must be found. The composition is determined in terms of a property that is measured by some instrument and calibrated in terms of composition. Among the measures that have been used are titration, pressure, refractive index, density, chromatography, spectrometry, polarimetry, conductimetry, absorbance, and magnetic resonance. In some cases the composition may vary linearly with the observed property, but in every case a calibration is needed. Before kinetic analysis is undertaken, the data are converted to composition as a function of time (C, t), or to composition and temperature as functions of time (C, T, t). In a steady CSTR the rate is observed as a function of residence time.

When a reaction has many participants, which may be the case even of apparently simple processes like pyrolysis of ethane or synthesis of methanol, a factorial or other experimental design can be made and the data subjected to a *response surface analysis* (Davies, *Design and Analysis of Industrial Experiments,* Oliver & Boyd, 1954). A quadratic of this type for the variables x_1, x_2, and x_3 is

$$r = k_1 x_1 + k_2 x_2 + k_3 x_3 + k_{11} x_1^2 + k_{22} x_2^2 + k_{33} x_3^2 + k_{12} x_1 x_2 + k_{13} x_1 x_3 + k_{23} x_2 x_3$$

(7-115)

Analysis of such a correlation may reveal the significant variables and interactions, and may suggest some model, say of the L-H type, that could be analyzed in more 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]).

The constants of rate equations of single reactions often can be found by one of the linearization schemes of Fig. 7-1. Nonlinear regression methods can treat any kind of rate equation, even models made up of differential and algebraic equations together, for instance

$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dB}{dt} = k_1 A - k_2 B^2 + k_3 C$$

$$C = A_0 + B_0 + C_0 - A - B$$

Software for these procedures is supplied, for example, by Constantinides (*Applied Numerical Methods with Personal Computers,* McGraw-Hill, 1987, pp. 577–614, with diskette) and by the commercial product *SimuSolv* (Mitchell and Gauthier Associates, 200 Baker Street, Concord, MA 01742). These do the integration, find the constants and their statistical criteria, and make the plots. *SimuSolv* is claimed "to provide maximum efficiency in problem solving with minimum involvement in computational procedures." Since the computer does the work, many possibilities may be considered. For the reaction cyclohexanol to cyclohexanone, 36 experiments at 6 temperature levels were made and more than 50 rate equations were tested (Hofmann, in de Lasa, *Chemical Reactor Design and Technology,* Martinus Nijhoff, 1986, p. 72). A rate equation for methanol from CO_2 and H_2 was selected from 44 possibilities by Beenackers and Graaf (in Cheremisinoff, *Handbook of Heat and Mass Transfer,* vol. 3, Gulf Publishing, 1989, pp. 671–699). They used a spinning basket reactor like the item shown in Fig. 23-29*c.*

EQUIPMENT

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.   Designed to obtain such fundamental data as chemical rates free of mass transfer resistances or other complications. Some of the heterogeneous reactors of Fig. 23-29, for instance, employ known interfacial areas, thus avoiding one uncertainty.

2.   Simulations of the kinds of reactor intended for the pilot or plant scale. How to do the scale-up to the plant size, however, is a sizable problem in itself.

Batch Reactors   In the simplest kind of investigation, reactants can be loaded into a number of ampules, kept in a thermostatic bath for various periods, and analyzed.

In terms of cost and versatility, the stirred batch reactor is the unit of choice for homogeneous or slurry reactions and even gas/liquid reactions when provision is made for recirculation of the gas. They are especially suited to reactions with half-lives in excess of 10 min. Sam-

ples are taken at intervals and the reaction is stopped by cooling, usually by at least 50°C (122°F), by dilution, or by destroying a residual reactant such as an acid or base; analysis can then be made at leisure. Analytic methods that do not necessitate termination of reaction include 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, and so on. The readings of any instrument should be calibrated to chemical composition or concentration. 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 data regressed simultaneously. Finding the parameters of the nonisothermal equation $r = \exp{(a + b/T)}\ C^q$ is only a little more difficult than for $r = kC^q$. Rates, dC/dt, are found by numerical differentiation of (C, t) data.

On the laboratory scale, it is usually safe to assume that a batch reactor is stirred to uniform composition, but for critical cases such as high viscosities this could be checked with tracer tests.

CSTRs and other devices that require flow control are more expensive and difficult to operate. Particularly in steady operation, however, the great merit 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 4,000 s, reactor volumes of 2 to 400 cm³ (0.122 to 24.4 in³) and flow rates of 0.1 to 2.0 cm³/s.

Flow Reactors   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. Some heterogeneous reactors are shown in Fig. 23-29; the item in Fig. 23-29*g* is suited to liquid/liquid as well as gas/liquid. Stirred tanks, bubble and packed towers, and other commercial types are also used. The operation of such units can sometimes be predicted from independent data of chemical and mass transfer rates, correlations of interfacial areas, droplet sizes, and other data.

Usually it is not possible to measure compositions along a TFR, although temperatures can sometimes be measured. Mostly TFRs are kept at nearly constant temperatures. Small-diameter tubes immersed in a fluidized sand bed or molten lead or salt can hold quite constant temperatures of a few hundred degrees. A recycle unit like that shown in Fig. 23-29*a* can be operated as a differential reactor with arbitrarily small conversion and temperature change. This and the CSTR are the preferred laboratory devices nowadays, unless the budget allows for only a batch stirred flask. Test work in a tubular flow unit may be desirable if the commercial unit is to be of that type, although rate data from any kind of laboratory equipment are adaptable to the design of most kinds of large-scale equipment. Larger TFRs may be used in pilot plants to test predictions by data from gradientless reactors.

Multiple Phases   Reactions between gas/liquid, liquid/liquid, and fluid/solid phases are often tested in CSTRs. Other laboratory types are suggested by the commercial units depicted in appropriate sketches in Sec. 23. Liquids can be reacted with gases of low solubili-

ties in stirred vessels, with the liquid charged first and the gas fed continuously at the rate of reaction or dissolution, sometimes with recirculation in larger units. The reactors of Fig. 23-29 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 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. They are discussed by 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 are the standard devices nowadays, 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. 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 found 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, preferably in a pilot plant.

Physical properties of catalysts also may need to be checked periodically, including pellet size, specific surface, porosity, pore size and size distribution, and effective diffusivity. 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).

REFERENCES FOR LABORATORY REACTORS

Berty, "Laboratory reactors for catalytic studies", in Leach, ed., *Applied Industrial Catalysis,* vol. 1, Academic, 1983, pp. 41–57.

Danckwerts, *Gas-Liquid Reactions,* McGraw-Hill, 1970.

Hofmann, "Industrial process kinetics and parameter estimation", in *ACS Advances in Chemistry,* **109,** 519–534 (1972); "Kinetic data analysis and parameter estimation", in de Lasa, ed., *Chemical Reactor Design and Technology,* Martinus Nijhoff, 1986, pp. 69–105.

Horak and Pasek, *Design of Industrial Chemical Reactors from Laboratory Data,* Heyden, 1978.

Rase, *Chemical Reactor Design for Process Plants,* Wiley, 1977, pp. 195–259. 124 references.

Shah, *Gas-Liquid-Solid Reactor Design,* McGraw-Hill, 1979, pp. 149–179. 145 references.

SOLVED PROBLEMS

These numerical problems deal with ideal types of batch, continuously stirred, and plug flow reactors, for which the formulas are summarized in Tables 7-5 to 7-7. They find parameters of rate equations, conversions, vessel sizes, or operating conditions. Numerical methods are adopted for most integrations and differential equations. Several ODE softwares are readily available, including POLYMATH, which is obtainable through the AIChE. A larger and broader collection of solutions is provided by Walas (*Chemical Reaction Engineering Handbook of Solved Problems,* Gordon & Breach, 1995).

P1.   EQUILIBRIUM OF FORMATION OF ETHYLBENZENE

Ethylbenzene is made from benzene and ethylene in the gas phase at 260°C and 40 atm.

$$C_6H_6 + C_2H_4 \Leftrightarrow C_6H_5C_2H_5$$
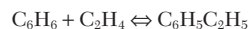
Equimolal proportions of the reactants are used. Thermodynamic data at 298 K are tabulated. The specific heats are averages. Find: (1) the enthalpy change of reaction at 298 and 573 K; (2) equilibrium constant at 298 and 573 K; (3) fractional conversion at 573 K.

	C_p	ΔH_f	ΔG_f
C_6H_6	28	19,820	30,989
C_2H_4	5	12,496	16,282
$C_6H_5C_2H_5$	38	7,120	31,208
Δ	−5	−25,196	−16,063

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p \, dT = -25{,}196 - 5(T - 298)$$

$$= -26{,}576 \text{ at } 573 \text{ K} \tag{1}$$

$$\ln K_{298} = \frac{-\Delta G_{298}}{298R} = \frac{16{,}063}{(1.987)(298)} = 26.90$$

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} = -\frac{23{,}706}{RT^2} - \frac{5}{RT}$$

$$\ln K_{298} = 26.9 - \int_{298}^{573} \left(\frac{11{,}854}{T^2} + \frac{2.50}{T} \right) dT = 6.17 \tag{2}$$

$$K = 485$$

$$= \frac{x(2 - x)}{40(1 - x)^2}$$

$$x = 0.9929, \text{ fraction converted} \tag{3}$$

P2.   OPTIMUM CYCLE PERIOD WITH DOWNTIME

Find the optimum cycle period for a first-order batch reaction with a downtime of ϑ_d h per batch.

$$-\frac{dC}{d\vartheta} = kC$$

$$\vartheta = \frac{1}{k} \ln \left(\frac{C_0}{C} \right)$$

Number of daily batches:

$$n = \frac{24}{\vartheta + \vartheta_d}$$

Daily yield:

$$y = V_r(C_0 - C)_n = \frac{24 V_r(C_0 - C)}{1/k \ln (C_0/C) + \vartheta_d} = \frac{24 k V_r C_0 (1 - C/C_0)}{\ln (C_0/C) + k\vartheta_d}$$

The ordinate of the plot is $y/24 k V_r C_0$ which is proportional to the daily yield. The peaks in this curve are at these values of the parameters:

$k\vartheta_d$	0.01	0.10	1	5
C/C_0	0.87	0.65	0.32	0.12
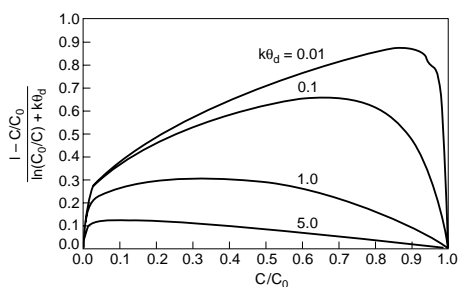
P3.   PARALLEL REACTIONS OF BUTADIENE

Butadiene (B) reacts with acrolein (A) and also forms a dimer according to the reactions

$$C_4H_6 + C_3H_4O \overset{1}{\Rightarrow} C_7H_{10}O, \; 2\,C_4H_6 \overset{2}{\Rightarrow} C_8H_{12}$$

The reaction is carried out in a closed vessel at 330°C, starting at 1 atm with equal concentrations of A and B, 0.010 g mol/L each. Specific rates are $k_1 = 5.900$ and $k_2 = 1.443$ L/(g mol·min). Find (1) B as a function of A; (2) A and B as functions of t.

$$-\frac{dA}{dt} = k_1 AB = 5.9 AB \tag{1}$$

$$-\frac{dB}{dt} = k_1 AB + k_2 B^2 = 5.9 AB + 1.443 B^2 \tag{2}$$

Dividing these equations,

$$\frac{dB}{dA} - \frac{k_2 B}{k_1 A} = 1 \tag{3}$$

This is a linear equation whose solution is

$$B = \frac{k_1}{k_1 - k_2} A + IA^{k_2/k_1} = 1.32A - 0.010 A^{0.245} \tag{4}$$

The integration constant was evaluated with $A_0 = B_0 = 0.010$.
   Substituting (4) into (1),

$$-\frac{dA}{dt} = 5.9 A(1.32A - 0.010 A^{0.245}) \tag{5}$$

The variables are separable, but an integration in closed form is not possible because of the odd exponent. Numerical integration followed by substitution into (4) will provide both A and B as functions of t. The plots, however, are of solutions of the original differential equations with ODE.
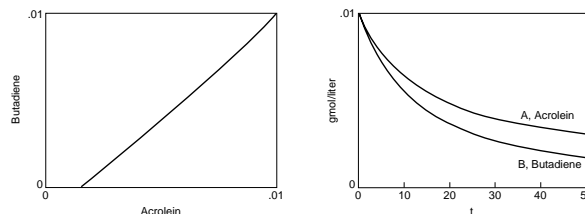
P4.   BATCH REACTION WITH HEAT TRANSFER

A second-order reaction proceeds in a batch reactor provided with heat transfer. Initial conditions are $T_0 = 350$ and $C_0 = 1$. Other data are:

$$k = \exp \left(16 - \frac{5{,}000}{T} \right) \qquad \text{ft}^3/(\text{lb mol·h}) \tag{1}$$

$$\Delta H_r = -(5000 + 5T) \qquad \text{Btu/lb mol} \tag{2}$$

$$\rho C_p = 50$$

The rate of heat transfer is

$$Q = UA(300 - T) \qquad \text{Btu/h} \tag{3}$$

The temperature T and the time t will be found in terms of fractional conversion x when $UA/V_r = 0$ or 150.
   The rate equation may be written:

$$\frac{dt}{dx} = \frac{1}{kC_0(1 - x)^2} \tag{4}$$

The differential heat balance is

$$\rho C_p V_r \, dT = Q \, dt - \Delta H_r V_r C_0 \, dx$$
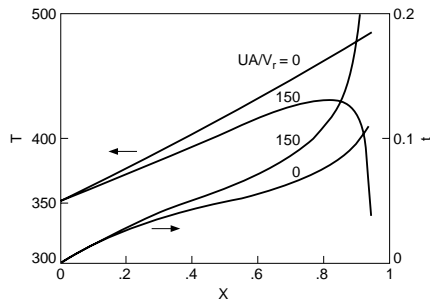
Substituting for dt from Eq. (4) and rearranging,

$$\frac{dT}{dx} = \frac{1}{\rho C_p} \left[\frac{Q}{V_r k C_0 (1 - x)^2} - \Delta H_r C_0 \right]$$

$$= 0.02 \left[\frac{UA(300 - T)}{V_r k (1 - x)^2} + 5000 + 5T \right] \tag{5}$$

Equations (1), (4), and (5) are solved simultaneously with $UA/V_r = 0$ or 150. In the adiabatic case, the temperature tends to run away.

P5. A SEMIBATCH PROCESS

A tank is charged initially with $v_{r0} = 100$ L of a solution of concentration $C_{b0} = 2$ g mol/L. Another solution is then pumped in at $V = 5$ L/min with concentration $C_{a0} = 0.8$ until a stoichiometric amount has been added. The rate equation is

$$r = 0.015 C_a C_b \text{ g mol/(L·min)}$$

Find the concentration during the filling period and for 50 min afterward.

$$V_r = 100 + 5t \tag{1}$$

$$C_b = C_a + \frac{100(2) - 5(0.8)t}{100 + 5t} = C_a + \frac{40 - 0.8t}{20 + t} \tag{2}$$

$$\frac{dC_a}{dt} = \frac{0.8 - C_a}{20 + t} - 0.015 C_a \left(C_a + \frac{40 - 0.8t}{20 + t} \right) \tag{3}$$

The input is continued until 200 lb mol of A have been added, which is for 50 min. Eq. (3) is integrated for this time interval. After input is discontinued the rate equation is

$$-\frac{dC_a}{dt} = k C_a^2 \tag{4}$$

At $t = 50$, $C_a = C_{a1} = 0.4467$.

$$C_a = \frac{1}{1/C_{a1} + k(t - 50)} = \frac{1}{2.2386 + 0.015(t - 50)} \tag{5}$$

Plots are shown for several specific rates, including $k = 0$ when no reaction takes place.
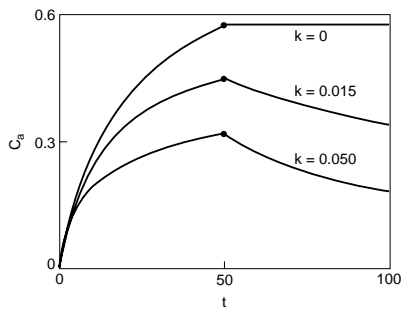
P6. OPTIMUM REACTION TEMPERATURE WITH DOWNTIME

A liquid phase reaction $2A \underset{\Leftarrow}{\overset{1}{\Rightarrow}} B + C$ has the rate equation

$$r_a = k\left(C_a^2 - \frac{C_b C_c}{K_e} \right) = k C_{a0}^2 \left[(1 - f)^2 - \frac{f^2}{K_e} \right], \qquad \text{kg mol/(m}^3\text{·h)}$$

where $f =$ fractional conversion
         $C_{a0} = 1$

$$k = \exp\left(4.5 - \frac{2,500}{T} \right)$$

$$K_e = \exp\left(28.8 - 0.037T - \frac{5,178}{T} \right)$$

The downtime is 1 h per batch. Find the temperature at which the daily production is a maximum.

The reaction time of one batch is

$$t_b = \frac{1}{k} \int_0^f \frac{df}{(1 - f)^2 - f^2/K_e} \tag{1}$$

$$\text{Batches/day} = \frac{24}{t_b + 1}$$

$$\text{Daily production} = \frac{24}{t_b + 1} V_r C_{a0} f$$

Maximize $P = f/(t_b + 1)$ as a function of temperature. Eq. (1) is integrated with POLYMATH for several temperatures and the results are plotted. The tabulation gives the integration at 550 K. The peak value of $P = f/(t_b + 1) = 0.1941$ at 550 K, $t_b = 0.6$, and $f = 0.3105$.

$$\text{Maximum daily production} = 0.1941(24) V_r C_{a0}$$

$$= 4.66 V_r \text{ kg mol/d}$$
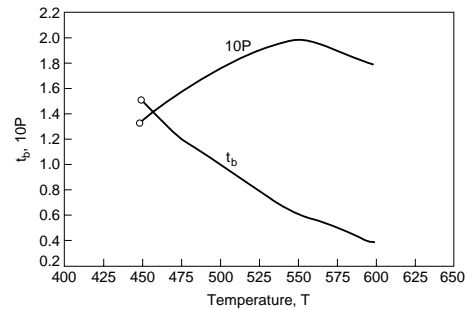
The equations:

$$\frac{d(f)}{d(t)} = k*\left((1 - f)**2 - f** \frac{2}{ke} \right)$$

$$x = 550$$

$$k = \exp\left(4.5 - \frac{2,500}{x} \right)$$

$$ke = \exp\left(28.8 - \frac{5,178}{x - .037*x} \right)$$

$$p = f/(t + 1)$$

Initial values: $t_0 = 0.0$ $f_0 = 0.0$

Final value: $t_f = 2.0000$

t	f	p
0.0	0.0	0.0
0.2000	0.1562	0.1302
0.4000	0.2535	0.1811
0.6000	0.3105	0.1941
0.8000	0.3427	0.1904
1.0000	0.3605	0.1802
1.2000	0.3702	0.1683
1.4000	0.3755	0.1565
1.6000	0.3784	0.1455
1.8000	0.3799	0.1357
2.0000	0.3807	0.1269

P7. RATE EQUATIONS FROM CSTR DATA

For the consecutive reactions $2A \Rightarrow B$ and $2B \Rightarrow C$, concentrations were measured as functions of residence time in a CSTR. In all experiments, $C_{a0} = 1$ lb mol/ft^3. Volumetric flow rate was constant. The data are tabulated in the first three columns. Check the proposed rate equations,

$$r_a = k_1 C_a^\alpha$$

$$r_b = -0.5 k_1 C_a^\alpha + k_2 C_b^\beta$$

Write and rearrange the material balances on the CSTR.

$$C_{a0} = C_a + \bar{t} r_a$$

$$r_a = \frac{C_{a0} - C_a}{\bar{t}} = k_1 C_a^\alpha \qquad (1)$$

$$r_b = \frac{C_{b0} - C_b}{\bar{t}} = -0.5 k_1 C_a^\alpha + k_2 C_b^\beta = -0.5 r_a + k_2 C_b^\beta \qquad (2)$$

Numerical values of r_a, r_b, and $r_b + 0.5 r_a$ are tabulated. The constants of the rate equations are evaluated from the plots of the linearized equations,
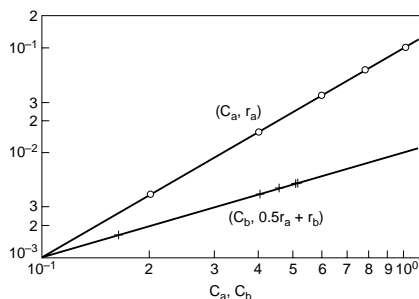
$$\ln r_a = \ln k_1 + \alpha \ln C_a = -2.30 + 2.001 \ln C_a$$

$$\ln (r_b + 0.5 r_a) = \ln k_2 + \beta \ln C_b = -4.606 + 0.9979 \ln C_b$$

which make the rate equations

$$r_a = 0.1003 C_a^{2.00} \qquad (3)$$

$$r_b = -0.0502 C_a^2 + 0.01 C_b^{0.998} \qquad (4)$$

$\bar{t}$	C_a	C_b	r_a	$-r_b$	$r_b + 0.5 r_a$
10	1.000	0.4545	0.100	0.04545	0.00455
20	0.780	0.5083	0.061	0.02542	0.00508
40	0.592	0.5028	0.0352	0.01257	0.00503
100	0.400	0.400	0.0160	0.0040	0.0040
450	0.200	0.1636	0.0040	0.000364	0.00164

P8. COMPARISON OF BATCH AND CSTR OPERATIONS

A solution containing 0.5 lb mol/ft³ of reactive component is to be treated at 25 ft³/h. The rate equation is

$$r = \frac{-dC}{dt} = 2.33 C^{1.7} \text{ lb mol/(ft}^3 \cdot \text{h)}$$

1. If the downtime is 45 min per batch, what size reactor is needed for 90% conversion?

2. What percentage conversion is attained with a two-stage CSTR, each vessel being 50 ft³?

Part 1: The integral of the rate equation is solved for the time,

$$t = \frac{1}{0.7 k} (C^{-0.7} - C_0^{-0.7}) = \frac{1}{0.7(2.33)} \left(\frac{1}{0.05^{0.7}} - \frac{1}{0.5^{0.7}} \right)$$

$$= 4.00 \text{ h}$$

$$\text{Number of batches} = \frac{24}{(4 + 0.75)} = 5.053/\text{d}$$

$$\text{Reactor volume } V_r = \frac{24(25)}{5.053} = 118.7 \text{ ft}^3$$

Part 2:

$$\tau = \frac{50}{25} = 2$$

$$0.5 = C_1 + \tau r = C_1 + 2(2.33) C_1^{1.7}$$

$$C_1 = C_2 + 2(2.33) C_2^{1.7}$$

The solution is,

$$C_1 = 0.1994, \qquad = 60.1\% \text{ conversion}$$

$$C_2 = 0.1025, \qquad = 79.5\% \text{ conversion}$$

P9. INSTANTANEOUS AND GRADUAL FEED RATES

Initially a reactor contains 2 m³ of a solvent. A solution containing 2 kg mol/m³ of reactant A is pumped in at the rate of 0.06 m³/min until the volume becomes 4 m³. The rate equation is $r_a = 0.25 C_a$, 1/min. Compare the time-composition profile of this operation with charging all of the feed instantaneously.

During the filling period,

$$V_r = 2 + 0.06 t$$

$$V' C_{a0} = k V_r C_a + \frac{d(V_r C_a)}{dt} = k V_r C_a + V_r \frac{dC_a}{dt} + C_a \frac{dV_r}{dt}$$
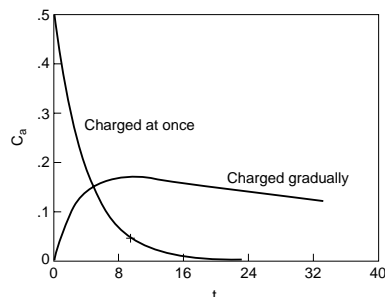
$$0.06(2) = 0.25(2 + 0.06t) C_a + (2 + 0.06t) \frac{dC_a}{dt} + 0.06 C_a$$

$$\frac{dC_a}{dt} = \frac{0.12 - (0.56 + 0.015t) C_a}{2 + 0.06t}, \qquad C_{a0} = 0 \qquad (1)$$

When all of A is charged at the beginning,

$$\frac{dC_a}{dt} = -0.25 C_a, \qquad C_{a0} = 0.5 \qquad (2)$$

The integrals of these two equations are plotted. A peak value, $C_a = 0.1695$, is reached in the first operation at $t = 10$.

P10. FILLING AND UNSTEADY OPERATING PERIOD OF A CSTR

A stirred reactor is being charged at 5 ft³/min with a concentration of 2 mol/ft³. The reactor has a capacity of 150 ft³ but is initially empty. The rate of reaction is

$$r = 0.02 C^2 \text{ lb mol/(ft}^3 \cdot \text{min)}.$$

After the tank is filled, pumping is continued and overflow is permitted at the same flow rate. Find the concentration in the tank when it first becomes full, and find how long it takes for the effluent concentration to get within 95% of the steady state value.

Filling period:

$$V_r = V' t$$

$$V' C_0 = k V_r C^2 + \frac{dV_r C}{dt} = k V_r C^2 + \left(C + t \frac{dC}{dt} \right) V'$$

$$\frac{dC}{dt} = \frac{C_0 - kt C^2 - C}{t} = \frac{2 - 0.02 t C^2 - C}{t}, \qquad C = 2 \quad \text{when} \quad t = 0$$

The numerical solution is $C = 1.3269$ when $t = 30$.

Unsteady period:

$$V' C_0 = V' C + k V_r C^2 + V_r \frac{dC}{dt}$$

$$\frac{dC}{dt} = \frac{C_0 - C - k\tau C^2}{\tau} = \frac{2 - C - 0.02(30) C^2}{30},$$
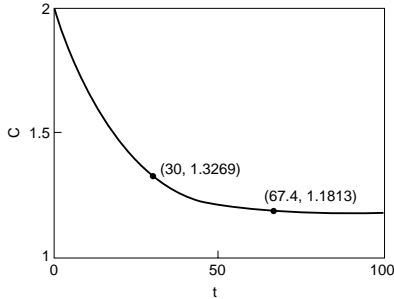
$$C = 1.3269 \quad \text{when} \quad t = 30.$$

The variables are separable, but the plot is of a numerical solution. The steady state concentration is 1.1736.

At 95% approach to steady state from the condition at $t = 30$,

$$C = 0.05(1.3269) + 0.95(1.1736) = 1.1813$$

From a printout of the solution, $t = 67.4$ min at this value.

P11.   SECOND-ORDER REACTION IN TWO STAGES

A second order reaction is conducted in two equal CSTR stages. The residence time per stage is $\tau = 1$ and the specific rate is $kC_0 = 0.5$. Feed concentration is C_0. Two cases are to be examined: (1) with pure solvent initially in the tanks; and (2) with concentrations C_0 initially in both tanks, that is, with $C_{10} = C_{20} = C_0$.

The unsteady balances on the two reactors are

$$f_i = \frac{C_i}{C_0}$$

$$FC_0 = FC_1 + V_r kC_1^2 + V_r \frac{dC_1}{dt}$$

$$1 = f_1 + 0.5f_1^2 + \frac{df_1}{dt} \qquad (1)$$

$$FC_1 = FC_2 + V_r kC_2^2 + V_r \frac{dC_2}{dt}$$

$$f_1 = f_2 + 0.5f_2^2 + \frac{df_2}{dt} \qquad (2)$$

The steady state values are the same for both starting conditions, obtained by zeroing the derivatives in Eqs. (1) and (2). Then

$$f_1 = 0.5702, \qquad f_2 = 0.7321$$

The plots are of numerical solutions.
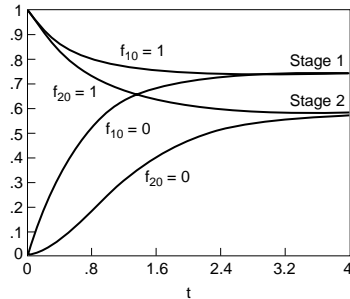
P12.   BUTADIENE DIMERIZATION IN A TFR

A mixture of 0.5 mol of steam per mol of butadiene is dimerized in a tubular reactor at 640°C and 1 atm. The forward specific rate is $k = 118$ g mol/(L·h·atm²) and the equilibrium constant is 1.27. Find the length of 10-cm ID tube for 40% conversion when the total feed rate is 9 kg mol/h.

$$2A \Leftrightarrow B$$

$$n_{a0} = 6 \text{ kg mol/h}$$

$$n_t = n_s + n_a + n_b = 0.5n_{a0} + n_a + 0.5(n_{a0} - n_a) = n_{a0} + 0.5n_a$$

$$P_a = \frac{n_a}{n_{a0} + 0.5n_a} \qquad (1)$$

$$P_b = \frac{0.5(n_{a0} - n_a)}{n_{a0} + 0.5n_a}$$

$$r_a = k\left(P_a^2 - \frac{P_b}{K_e}\right) = \frac{118}{n_{a0} + 0.5n_a}\left(\frac{n_a^2}{n_{a0} + 0.5n_a} - \frac{n_{a0} - n_a}{2(1.27)}\right) \qquad (1)$$

Put $n_{a0} = 6$, substitute Eq. (1) into the flow reactor equation, and integrate numerically.

$$V_r = \int_{3.6}^{6} \frac{dn_a}{r_a} = 0.0905 \text{ m}^3$$

$$L = \frac{0.0905(10^6)}{78.5} = 1{,}153 \text{ cm}$$

P13.   AUTOCATALYTIC REACTION WITH RECYCLE

Part of the effluent from a PFR is returned to the inlet. The recycle ratio is R, fresh feed rate is F_0

$$R = \frac{F_r}{F_0}$$

$$F_t = F_r + F_0 = F_0(R + 1)$$

The concentration of the mixed feed is

$$C_{at} = \frac{C_{a0} + RC_{af}}{1 + R}$$

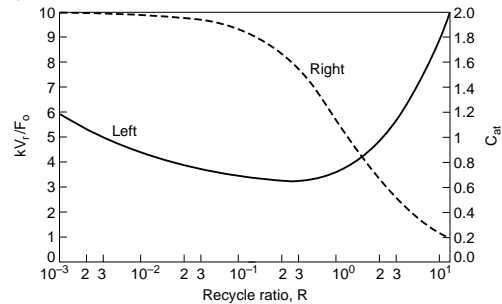where C_{af} is the outlet concentration. For the autocatalytic reaction $A \Rightarrow B$, the rate equation is

$$r_a = kC_a C_b = kC_a(C_{a0} - C_a)$$

The flow reactor equation is

$$-F_t dC_a = -F_0(R + 1)dC_a = r_a dV_r = kC_a(C_{a0} - C_a)dV_r$$

$$\frac{kV_r}{F_0} = (R + 1)\int_{c_{af}}^{c_{at}} \frac{dC_a}{C_a(C_{a0} - C_a)}$$

The plot is for $C_{a0} = 2$ and $C_{af} = 0.04$. The minimum reactor size is at a recycle ratio $R = 0.23$ and mixed feed $C_{at} = 1.57$.

P14.   MINIMUM RESIDENCE TIME IN A PFR

A reversible reaction $A \Leftrightarrow B$ is conducted in a plug flow reactor. The rate equation is

$$r = kC_{a0}\left(1 - x - \frac{x}{K_e}\right)$$

where $C_{a0} = 4$

$$k = \exp\left(17.2 - \frac{5{,}800}{T}\right)$$
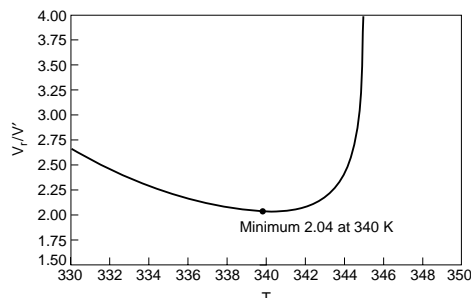
$$K_e = \exp\left(-24.7 + \frac{9{,}000}{T}\right)$$

Find the conditions for minimum V_r/V' when conversion is 80%.
The flow reactor equation is

$$-dn_a = V'C_{a0}dx = kC_{a0}\left(\frac{1-x-x}{K_e}\right)dV_r$$

$$\frac{V_r}{V'} = \frac{1}{k}\int_0^{0.8}\frac{dx}{1-x-x/K_e} = \frac{1}{k(1+1/K_e)}\ln\frac{1}{0.2-0.8/K_e} \quad (1)$$

The plot of this equation shows the minimum to be $V_r/V' = 2.04$ at $T = 340$ K.

P15. HEAT TRANSFER IN A CYLINDRICAL REACTOR

A reaction $A \Rightarrow 2B$ runs in a tube provided with a cooling jacket that keeps the wall at 630 R. Inlet is pure A at 650 R and 50 atm. Other data are stated in the following. Find the profiles of temperature and conversion along the reactor, both with heat transfer and adiabatically.

Tube diameter $D = \dfrac{1}{6}$ ft

$C_{pa} = 20$, $C_{pb} = 15$ Btu/(lb mol R)

$\Delta H_r = -8{,}000$ Btu/(lb mol A)

$k = \exp\left(7.82 - \dfrac{3{,}000}{T}\right) \quad (1)$

Heat transfer coefficient $U = 5$ Btu/(ft³·h R)

Heat transfer area $dA = (4/D)dV_r = 24dV_r$

Rate equation:

$$r_a = k\left(\frac{n_a}{V}\right) = k\left(\frac{\pi}{RT}\right)\left(\frac{n_a}{n_t}\right) = \frac{50k}{0.729T}\left(\frac{n_a}{2n_{a0}-n_a}\right)$$

$$= \frac{68.6k}{T}\left(\frac{1-x}{1+x}\right) \quad (2)$$

$$x = 1 - \frac{n_a}{n_{a0}}$$

Flow reactor:

$$-dn_a = n_{a0}dx = r_a dV_r$$

$$\frac{dx}{d(V_r/n_{a0})} = r_a \quad (3)$$
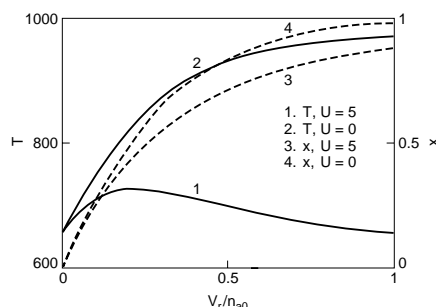
Heat balance over a differential volume dV_r:

$$\Delta H_r dn_a = -\Delta H_r r_a\, dV_r$$

$$= \sum n_i C_{pi}dT + U(T-T_w)dA$$

$$= n_{a0}[20(1-x)+15(2x)dT + 24U(T-T_w)dV_r$$

$$\frac{dT}{d(V_r/n_{a0})} = \frac{-\Delta H_r r_a - 24U(T-T_w)}{20-10x} = \frac{8{,}000r_a - 120(T-630)}{20-10x} \quad (4)$$

Differential Eqs. (3) and (4) are solved simultaneously with auxiliary Eqs. (1) and (2) by ODE. The solutions with $U = 5$ and $U = 0$ are shown.

P16. PRESSURE DROP AND CONVERSION IN A PFR

A reaction $A \Rightarrow 3B$ takes place in a tubular flow reactor at constant temperature and an inlet pressure of 5 atm. The rate equation is

$$r_a = k\left(\frac{n_a}{V'}\right) = \frac{kP}{RT}\left(\frac{n_a}{3n_{a0}-n_a}\right) = \frac{kP}{RT}\left(\frac{1-x}{1+2x}\right)$$

When put into the plug flow equation,

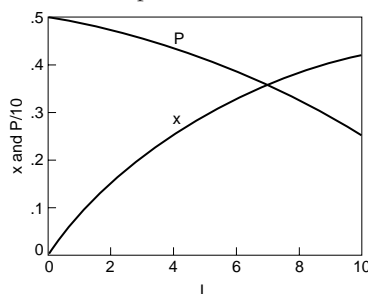$$n_{a0}\,dx = \frac{kP}{RT}\left(\frac{1-x}{1+2x}\right)AdL$$

or

$$\frac{dx}{dL} = 0.02\frac{P(1-x)}{1+2x} \quad (1)$$

where several factors have been combined into the numerical coefficient.

The pressure gradient due to friction is proportional to the flowing mole rate, $1+2x$, and inversely to the density or the pressure. Here again, several factors are incorporated into a numerical coefficient, making

$$-\frac{dP}{dL} = 0.6\frac{1+2x}{P} \quad (2)$$

The numbered equations are integrated and plotted. They show the typical fall in pressure as conversion with an increase in the number of moles proceeds at constant pressure, $x = 0.48$ when $L = 10$.

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