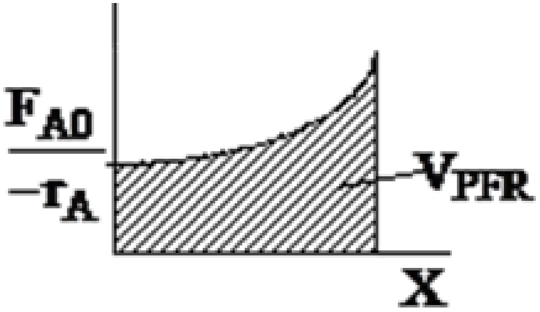
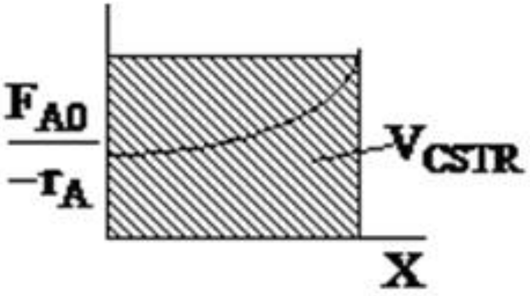
3. Rate Law and Stoichiometry

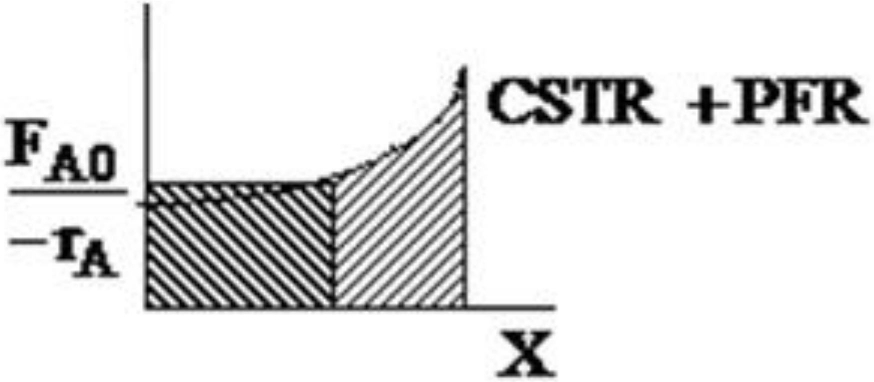
- Objectives
  - Write the relationship between the relative rates of reaction.
  - Write a rate law and define reaction order and activation energy.
  - Set up a stoichiometric table for both batch and flow systems and express concentration as a function or conversion.
  - Write $-r_A$ solely as a function of conversion given the rate law and then entering concentration.
  - Calculate the equilibrium conversion for both gas and liquid phase reactions.

0. Rationale for Chapter 3 I

- **Review of Chap 2_1**
  - **if we had $-r_A$ as a function of X, $[-r_A = f(X)]$, we could size many reactors and reactor sequences and systems.**







0. Rationale for Chapter 3 II

○ **Review of Chap 2_2**

- How do we obtain $-r_A = f(X)$?

« We do this in two steps »

1. **Part 1 Rate Law – Find the rate as a function of concentration,**

   $$-r_A = k\ \text{fn}\ (C_A, C_B \ldots)$$

2. **Part 2 Stoichiometry – Find the concentration as a function of conversion**

   $$C_A = g(X)$$

⇒ Combine Part 1 and Part 2 to get $-r_A = f(X)$

1. Basic Definitions I

- **Homogeneous rxn**

  - Involves only one phase

- **Heterogeneous rxn**

  - Involves more than one phase and rxn occurs at the interface btn the phases

- **Irreversible rxn**

  - Proceeds in only one direction to exhaust

- **Reversible rxn**

  - Proceeds in either direction depending on the conc. of reactants and products relative to the corresponding equilibrium conc.

1. Basic Definitions II

- ○ **Molecularity of a rxn**
  - **- Number of atoms, ions, or molecules colliding in a rxn step**
    - **unimolecular, bimolecular, termolecular**
- ○ **Common examples**
  - **- Unimolecular**

$$ {}_{92}\mathrm{U}^{238} \rightarrow {}_{90}\mathrm{Th}^{234} + {}_{2}\mathrm{He}^{4} \quad -r_{\mathrm{U}} = kC_{\mathrm{U}} $$

  - **- Bimolecular**

$$ \mathrm{Br}\bullet + \mathrm{C_2H_6} \rightarrow \mathrm{HBr} + \mathrm{C_2H_5}\bullet \quad -r_{\mathrm{Br}\bullet} = kC_{\mathrm{Br}\bullet}C_{\mathrm{C_2H_6}} $$

  - **- Termolecular**

$$ 2\mathrm{NO} + \mathrm{O_2} \rightarrow 2\mathrm{NO} \quad \Rightarrow Chap7 $$

1. Basic Definitions III

- Relative Rates of Reaction (p. 81)

$$\mathrm{A} + \frac{b}{a}\mathrm{B} \rightarrow \frac{c}{a}\mathrm{C} + \frac{d}{a}\mathrm{D}$$

- For every mole of A consumed, *c/a* moles of C appears

- rate of formation of C = (c/a)(rate of disappearance of A)

$$r_{\mathrm{C}} = \frac{c}{a}(\text{-}r_{\mathrm{A}}) = -\frac{c}{a}(r_{\mathrm{A}})$$

- likewise $r_{\mathrm{C}} = \frac{c}{d}(r_{\mathrm{D}})$

- In general

$$\boxed{\frac{-r_{\mathrm{A}}}{a} = \frac{-r_{\mathrm{B}}}{b} = \frac{r_{\mathrm{C}}}{c} = \frac{r_{\mathrm{D}}}{d}}$$

$$\boxed{\frac{r_{\mathrm{A}}}{-a} = \frac{r_{\mathrm{B}}}{-b} = \frac{r_{\mathrm{C}}}{c} = \frac{r_{\mathrm{D}}}{d}}$$

1. Basic Definitions IV

○ **Example 1**

$$2\mathrm{NO} + \mathrm{O}_2 \leftrightarrow 2\mathrm{NO}$$

- Then

$$\frac{r_{\mathrm{NO}}}{-2} = \frac{r_{\mathrm{O}_2}}{-1} = \frac{r_{\mathrm{NO}_2}}{2}$$

- If NO_2 is being formed at a rate of 4 mol/m^3/s

- **rate of formation of NO**

$$r_{\mathrm{NO}} = \frac{-2}{2} r_{\mathrm{NO}_2} = -4\ \mathrm{mol/m^3/s}$$

- **rate of disappearance of NO**

$$-r_{\mathrm{NO}} = 4\ \mathrm{mol/m^3/s}$$

- **rate of disappearance of O_2**

$$r_{\mathrm{O}_2} = \frac{-1}{-2} r_{\mathrm{NO}_2} = 2\ \mathrm{mol/m^3/s}$$

1. Basic Definitions V

- **Example 2**

- The Reaction:

$2A + 3B \rightarrow 3C$

is carried out in a reactor. If at a particular point, the rate of disappearance of A is 10 mol/dm^3/s, what are the rates of B and C?

- **$-r_A = 10$ mol/dm^3/s**

$$\frac{r_A}{-2} = \frac{r_B}{-3} = \frac{r_C}{5}$$

$\Rightarrow -r_B = (10 \text{ mol/dm}^3\text{/s})(3/2) = 15 \text{ mol/dm}^3\text{/s}$

$r_C = (10 \text{ mol/dm}^3\text{/s})(5/2) = 25 \text{ mol/dm}^3\text{/s}$

2. The Rxn Order and the Rate Law I

○ **Rxn rate**

- **Depends on temperature and composition**

$$\boxed{-r_A = [k_A(T)][\mathrm{fn}(C_A, C_B, \ldots)]}$$

- **rate constant, *k*$_A$**
  - **specific rate of rxn**
  - **always refers to a particular species in the rxn**

○ **Power law model**

$$\boxed{-r_A = k_A C_A^{\alpha} C_B^{\beta}}$$

β order w.r.t reactant A

α order w.r.t reactant A

overall order of rxn $n = \alpha + \beta$

2. The Rxn Order and the Rate Law II

- Unit of the specific rxn rate
  - With rxn order n

$$k = \frac{(\text{Concentration})^{1\text{-}n}}{\text{Time}}$$

  - Zero-order (n = 0), {k} = $\text{mol/dm}^3\cdot\text{s}$
  - First-order (n = 1), {k} = s^{-1}
  - Second-order (n = 2), {k} = $\text{dm}^3\text{/mol}\cdot\text{s}$
  - Third-order (n = 2), {k} = $(\text{dm}^3\text{/mol})^{2\cdot}\text{s}^{-1}$
- Elementary rxn
  - Single step
  - Power in the rate law = stoichiometry coefficient

☞ Some non-elementary rxns follow elementary law

2. The Rxn Order and the Rate Law III

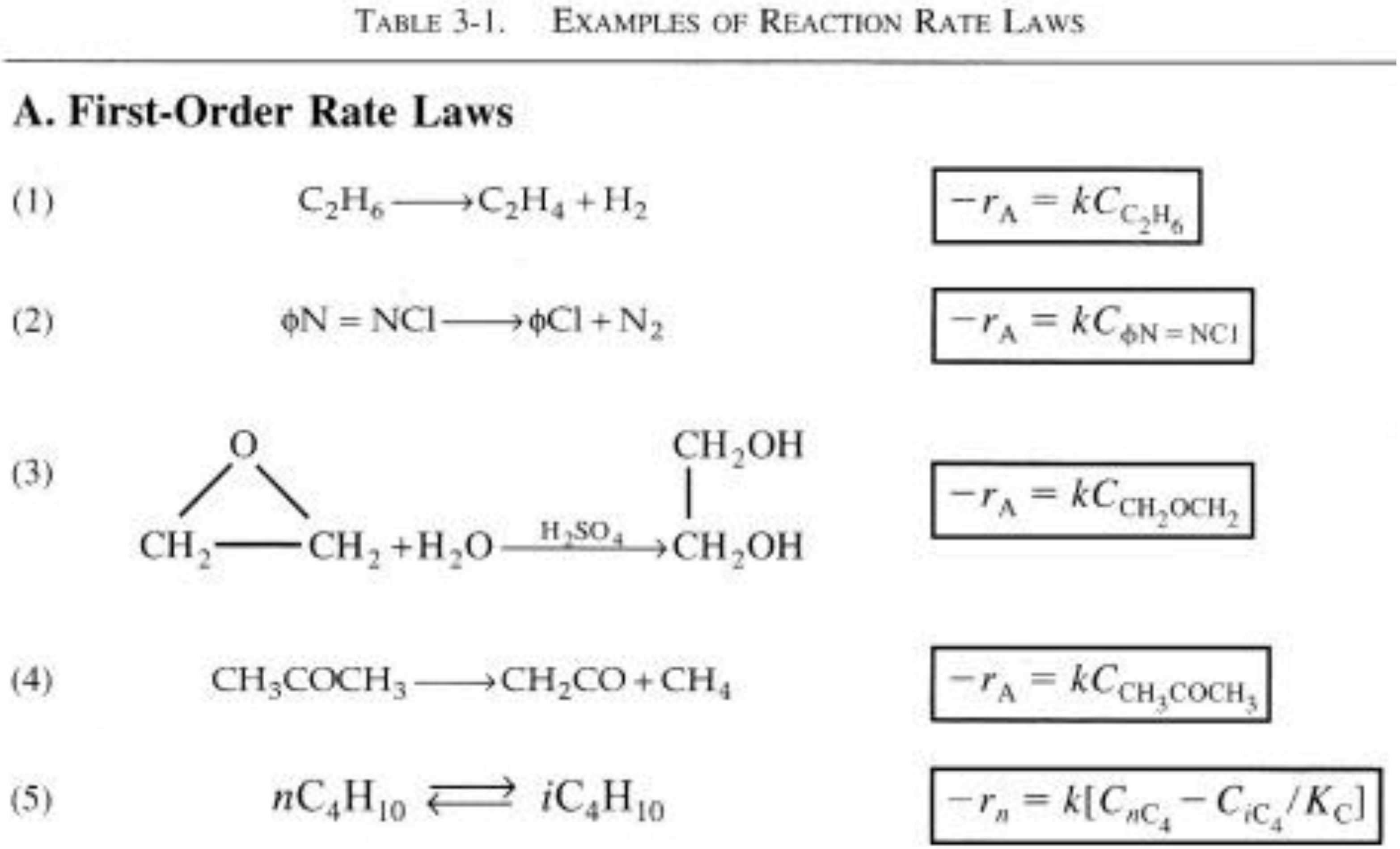
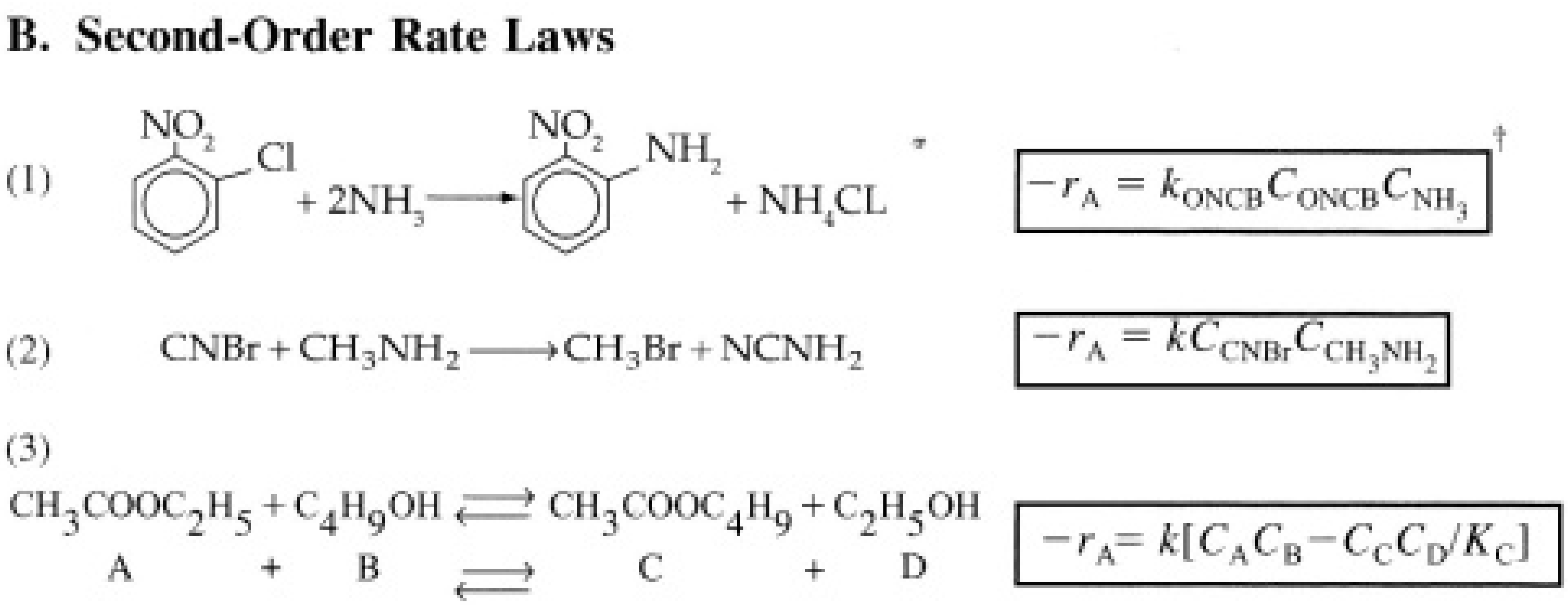


TABLE 3-1. EXAMPLES OF REACTION RATE LAWS

A. First-Order Rate Laws

(1)	$C_2H_6 \longrightarrow C_2H_4 + H_2$	$\boxed{-r_A = kC_{C_2H_6}}$
(2)	$\phi N = NCl \longrightarrow \phi Cl + N_2$	$\boxed{-r_A = kC_{\phi N = NCl}}$
(3)	$\overset{O}{CH_2 - CH_2} + H_2O \xrightarrow{H_2SO_4} \underset{CH_2OH}{\overset{CH_2OH}{\vert}}$	$\boxed{-r_A = kC_{CH_2OCH_2}}$
(4)	$CH_3COCH_3 \longrightarrow CH_2CO + CH_4$	$\boxed{-r_A = kC_{CH_3COCH_3}}$
(5)	$nC_4H_{10} \rightleftarrows iC_4H_{10}$	$\boxed{-r_n = k[C_{nC_4} - C_{iC_4}/K_C]}$

2. The Rxn Order and the Rate Law IV



B. Second-Order Rate Laws

(1) $$\boxed{-r_A = k_{ONCB} C_{ONCB} C_{NH_3}}^{\dagger}$$

(2) $CNBr + CH_3NH_2 \longrightarrow CH_3Br + NCNH_2$ $$\boxed{-r_A = kC_{CNBr} C_{CH_3NH_2}}$$

(3)

$$\begin{array}{ccccccc} CH_3COOC_2H_5 & + & C_4H_9OH & \rightleftarrows & CH_3COOC_4H_9 & + & C_2H_5OH \\ A & + & B & \rightleftarrows & C & + & D \end{array}$$

$$\boxed{-r_A = k[C_A C_B - C_C C_D / K_C]}$$

2. The Rxn Order and the Rate Law V

○ **Nonelementary rate laws**

- Most of both homogeneous & heterogeneous rxns

- **homogeneous rxn** $CO + Cl_2 \rightarrow COCl_2$

$$-r_{CO} = kC_{CO}C_{Cl_2}^{3/2}$$

- Complex rate expressions, $2N_2O \rightarrow 2N_2 + O_2$

$$-r_{N_2O} = \frac{k_{N_2O}C_{N_2O}}{1 + k'C_{O_2}}$$

- **apparent rxn orders**

both k values are strongly T-dependent

☞ **at low O_2 conc.,** $1 >> k'C_{O_2}$ ⇒ **apparent 1st order**

at high O_2 conc., $1 << k'C_{O_2}$

⇒ **apparent -1 order wrt O_2, 1st order wrt N_2O**

2. The Rxn Order and the Rate Law VI

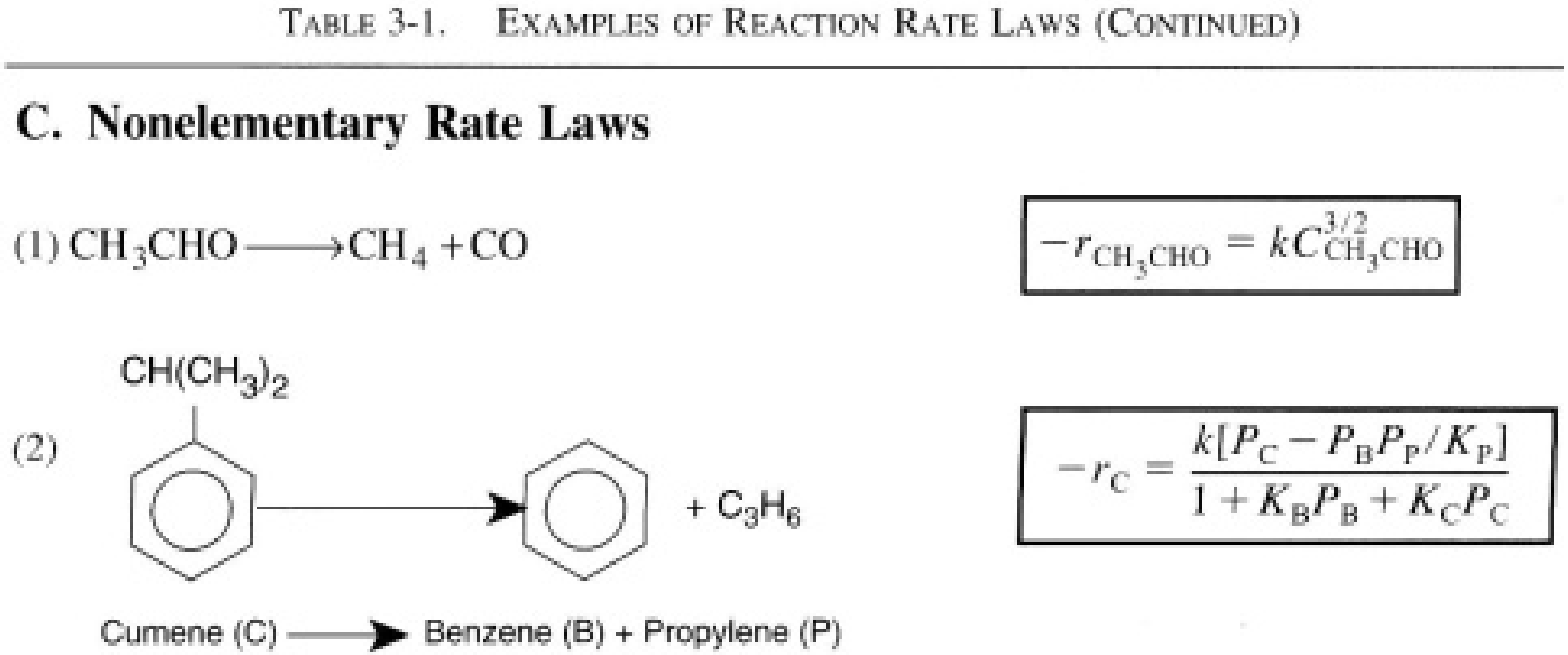


TABLE 3-1. EXAMPLES OF REACTION RATE LAWS (CONTINUED)

C. Nonelementary Rate Laws

(1) $CH_3CHO \longrightarrow CH_4 + CO$

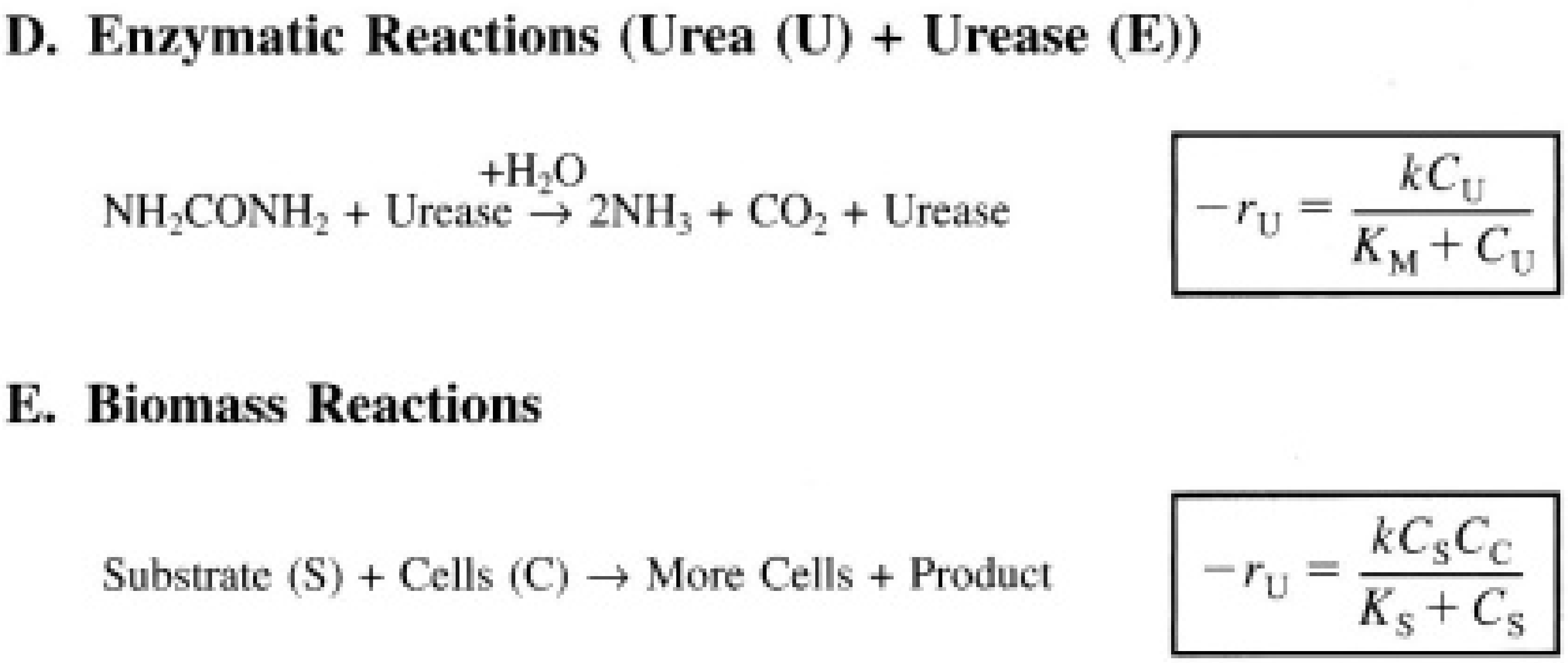
$$\boxed{-r_{CH_3CHO} = kC_{CH_3CHO}^{3/2}}$$

(2)

Cumene (C) → Benzene (B) + Propylene (P)

$$\boxed{-r_C = \frac{k[P_C - P_BP_P/K_P]}{1 + K_BP_B + K_CP_C}}$$

2. The Rxn Order and the Rate Law VII



D. Enzymatic Reactions (Urea (U) + Urease (E))

$$NH_2CONH_2 + \text{Urease} \xrightarrow{+H_2O} 2NH_3 + CO_2 + \text{Urease}$$

$$\boxed{-r_U = \frac{kC_U}{K_M + C_U}}$$

E. Biomass Reactions

Substrate (S) + Cells (C) → More Cells + Product

$$\boxed{-r_U = \frac{kC_SC_C}{K_S + C_S}}$$

2. The Rxn Order and the Rate Law VIII

- Reversible rxns 1

  - Gas-phase rxn, elementary & reversible 1

$$2C_6H_6 \xleftrightarrow[k_B, k_{-B}]{} C_{12}H_{10} + H_2$$

or in symbolic $2B \xleftrightarrow[k_B, k_{-B}]{} D + H_2$

- benzene (B) is depleted by the forward rxn

$$2C_6H_6 \xrightarrow{k_B} C_{12}H_{10} + H_2$$

- the rate of disappearance $-r_{B,\text{forward}} = k_B C_B^2$

- benzene (B) is produced by the reverse rxn

$$C_{12}H_{10} + H_2 \xrightarrow{k_{-B}} 2C_6H_6$$

- the rate of production $r_{B,\text{reverse}} = k_{-B} C_D C_{H_2}$

2. The Rxn Order and the Rate Law IX

- Reversible rxns 2
  - Gas-phase rxn, elementary & reversible 2
    - net rate of formation = (forward + reverse) rate

$$r_{\mathrm{B}} \equiv r_{\mathrm{B,\,net}} = -r_{\mathrm{B,\,forward}} + r_{\mathrm{B,\,reverse}}$$

$$r_{\mathrm{B}} = -k_{\mathrm{B}} C_{\mathrm{B}}^2 + k_{\mathrm{-B}} C_{\mathrm{D}} C_{\mathrm{H_2}}$$

    - or the rate of disappearance of benzene

$$-r_{\mathrm{B}} = k_{\mathrm{B}} C_{\mathrm{B}}^2 - k_{\mathrm{-B}} C_{\mathrm{D}} C_{\mathrm{H_2}} = k_{\mathrm{B}} \left(C_{\mathrm{B}}^2 - \frac{k_{\mathrm{-B}}}{k_{\mathrm{B}}} C_{\mathrm{D}} C_{\mathrm{H_2}} \right)$$

    - or with in equilibrium constant

$$-r_{\mathrm{B}} = k_{\mathrm{B}} \left(C_{\mathrm{B}}^2 - \frac{C_{\mathrm{D}} C_{\mathrm{H_2}}}{K_C} \right), \quad \text{where} \frac{k_{\mathrm{B}}}{k_{\mathrm{-B}}} = K_C \ \text{Conc eqlm const}$$

3. Rate Constant, k (p 91)

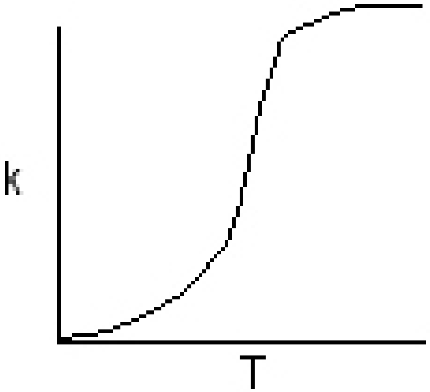
- **Specific reaction rate**
  - **k is the specific reaction rate (constant) and is given by the Arrhenius Equation:**

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

$$\mathrm{T} \rightarrow \infty \quad \mathrm{k} \rightarrow \mathrm{A}$$

$$\mathrm{T} \rightarrow 0 \quad \mathrm{k} \rightarrow 0$$

$$A \approx 10^{13}$$



Where: E = activation energy (cal/mol)
R = gas constant (cal/mol*K)
T = temperature (K)
A = frequency factor (units of A, and k, depend on overall reaction order)