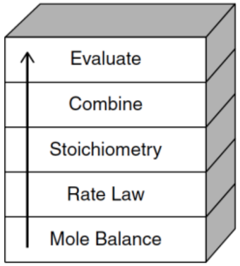
Lecture 3

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 3

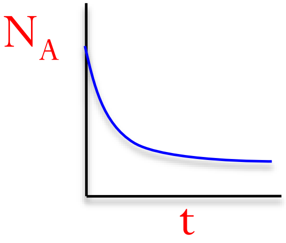
- Review of Lectures 1 and 2
- Building Block 1
  - **Mole Balances** (Review)
  - Size CSTRs and PFRs given $-r_A = f(X)$
  - Conversion for Reactors in Series
- Building Block 2
  - Rate Laws
  - Reaction Orders
  - Arrhenius Equation
  - Activation Energy
  - Effect of Temperature

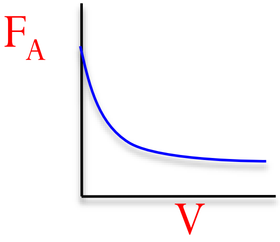


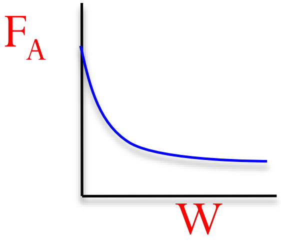
Building Block 1: Mole Balance

The GMBE applied to the four major reactor types (and the general reaction A→B)

Reactor	Differential	Algebraic	Integral
Batch	$\frac{dN_A}{dt}=r_AV$		$t=\int_{N_{A0}}^{N_A}\frac{dN_A}{r_AV}$
CSTR		$V=\frac{F_{A0}-F_A}{-r_A}$	
PFR	$\frac{dF_A}{dV}=r_A$		$V=\int_{F_{A0}}^{F_A}\frac{dF_A}{dr_A}$
PBR	$\frac{dF_A}{dW}=r'_A$		$W=\int_{F_{A0}}^{F_A}\frac{dF_A}{r'_A}$







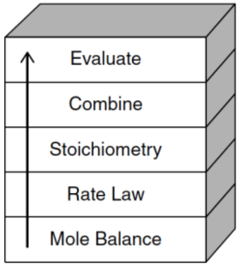
$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

$$\text{Choose limiting reactant A as basis of calculation}$$

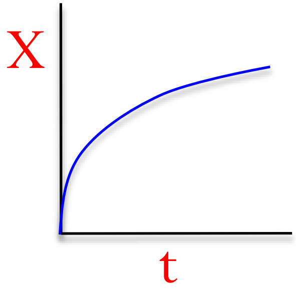
$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D$$

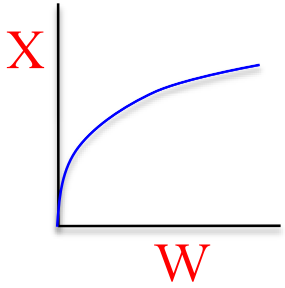
$$X = \frac{\text{moles A reacted}}{\text{moles A fed}}$$

Building Block 1: Mole Balance In terms of Conversion

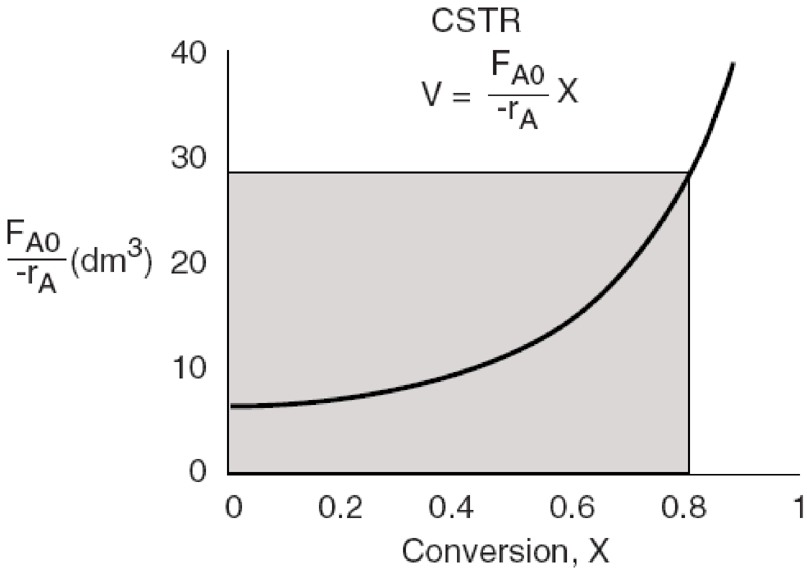

Evaluate
Combine
Stoichiometry
Rate Law
Mole Balance

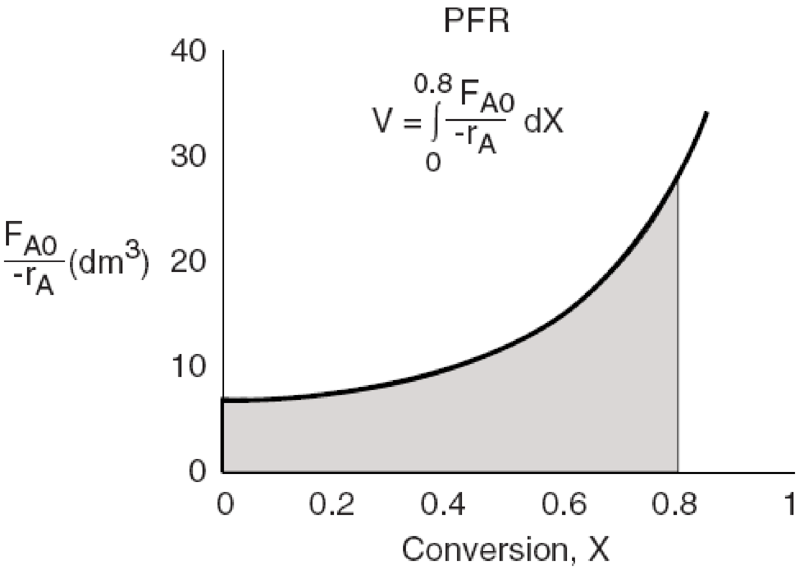
Reactor	Differential	Algebraic	Integral
Batch	$N_{A0}\frac{dX}{dt}=-r_A V$		$t=N_{A0}\int_0^X \frac{dX}{-r_A V}$
CSTR		$V=\frac{F_{A0}X}{-r_A}$	
PFR	$F_{A0}\frac{dX}{dV}=-r_A$		$V=F_{A0}\int_0^X \frac{dX}{-r_A}$
PBR	$F_{A0}\frac{dX}{dW}=-r'_A$		$W=F_{A0}\int_0^X \frac{dX}{-r'_A}$



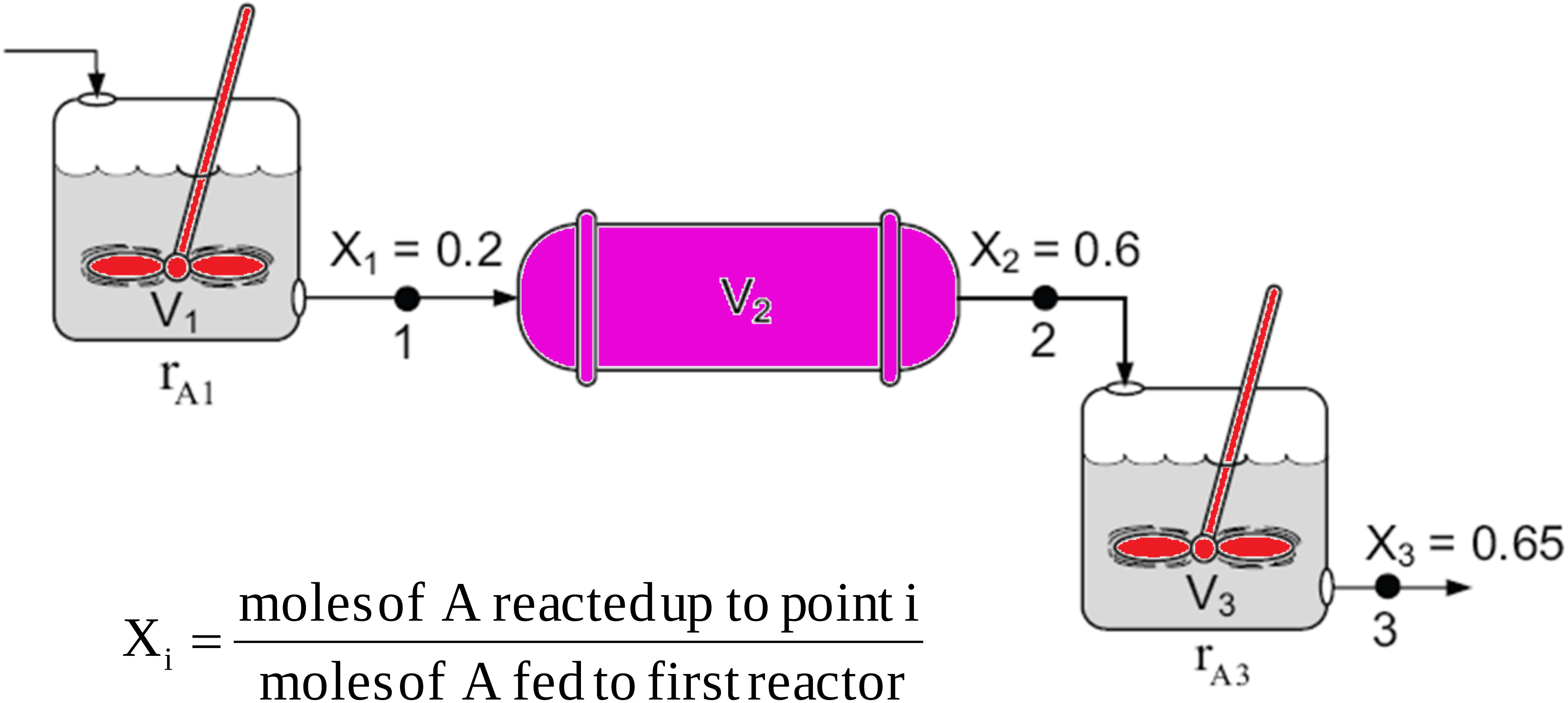


Levenspiel Plots





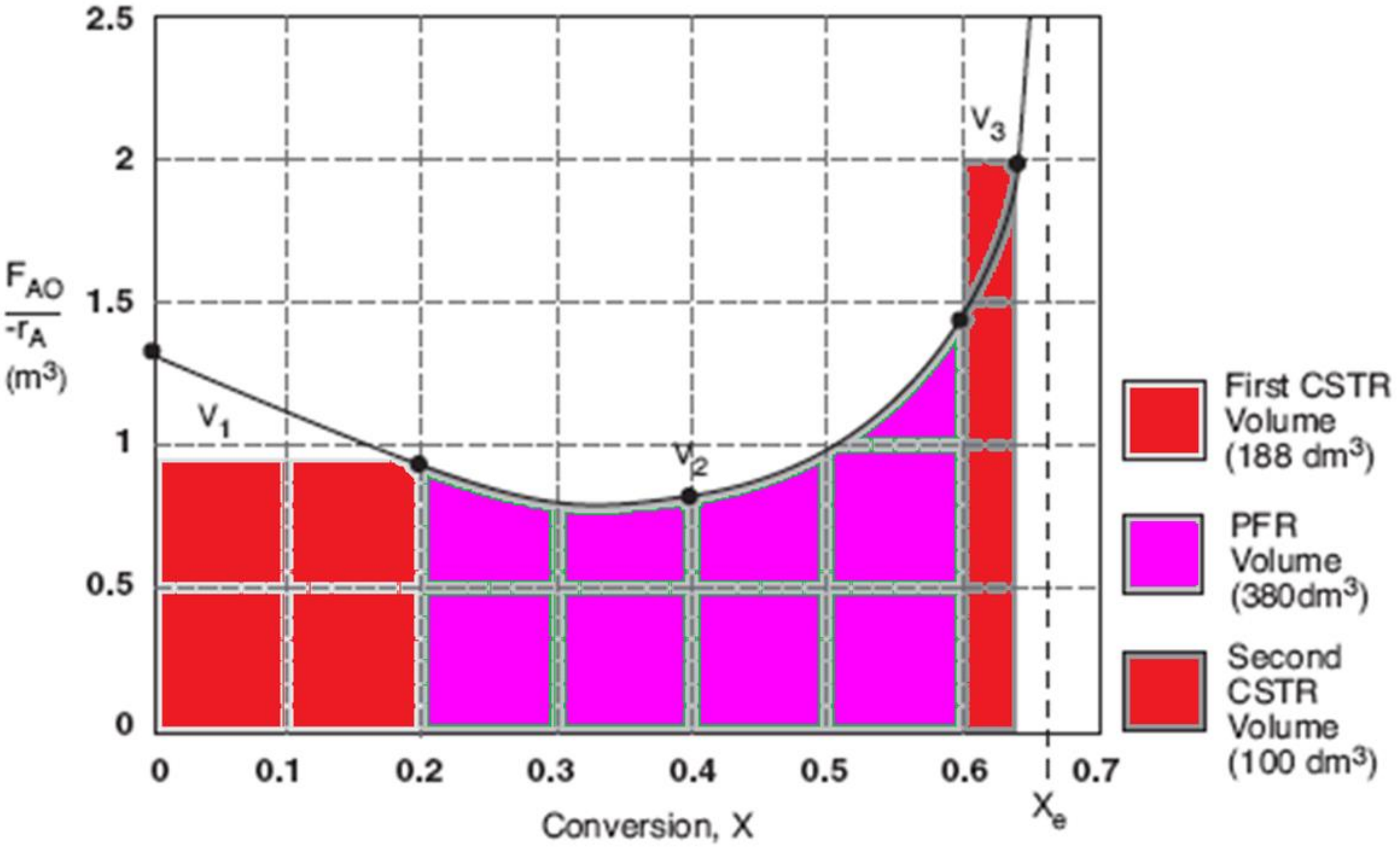
Reactors in Series

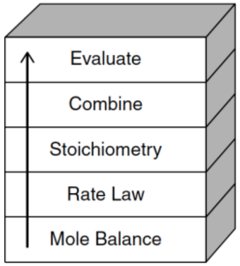


$$X_i = \frac{\text{moles of A reacted up to point i}}{\text{moles of A fed to first reactor}}$$

Only valid if there are no side streams

Reactors in Series





Building Block 2: Rate Laws

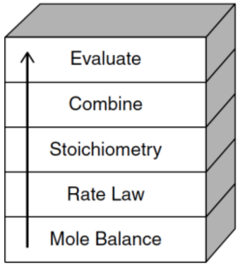
Power Law Model:

$$-r_A = kC_A^{\alpha}C_B^{\beta}$$

$$\alpha \text{ order in A}$$

$$\beta \text{ order in B}$$

$$\text{Overall Rection Order} = \alpha + \beta$$



Building Block 2: Rate Laws

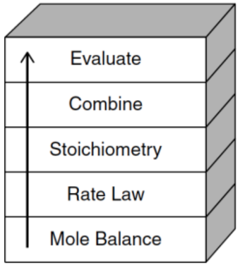
$$2\mathrm{A}+\mathrm{B}\rightarrow 3\mathrm{C}$$

A reactor follows an elementary rate law if the reaction orders just happens to agree with the stoichiometric coefficients for the reaction as written.

e.g. If the above reaction follows an elementary rate law

$$-r_A = k_A C_A^2 C_B$$

2nd order in A, 1st order in B, overall third order



Evaluate

Combine

Stoichiometry

Rate Law

Mole Balance

Building Block 2: Rate Laws

- Rate Laws are found from Experiments

  2A+B→3C

- Rate Laws could be non-elementary. For example, reaction could be:
  - Second Order in A
  - Zero Order in B
  - Overall Second Order

$$-r_A = k_A C_A^2$$

$$-r_B = k_B C_A^2$$

$$r_C = k_C C_A^2$$

Relative Rates of Reaction

$$aA + bB \rightarrow cC + dD$$

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

$$\boxed{\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}}$$

Relative Rates of Reaction

$$2\mathrm{A} + \mathrm{B} \rightarrow 3\mathrm{C}$$

Given $-r_A = 10 \dfrac{mol}{dm^3 \cdot s}$

Then $\dfrac{r_A}{-2} = \dfrac{r_B}{-1} = \dfrac{r_C}{3}$

$$-r_{\mathbf{B}} = \frac{-r_A}{2} = 5 \frac{mol}{dm^3 \cdot s}$$

$$r_C = \frac{-3}{2} r_A = 15 \frac{mol}{dm^3 \cdot s}$$

Reversible Elementary Reaction

$$\mathrm{A+2B} \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} \mathrm{3C}$$

$$-r_A = k_A C_A^2 C_B - k_{-A} C_C^3 = k_A \left[C_A^2 \, C_B - \frac{C_C^3}{k_A / k_{-A}} \right]$$

$$= k_A \left[C_A{}^2 C_B - \frac{C_C^3}{K_e} \right]$$

Reversible Elementary Reaction

$$A+2B \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} 3C$$

Reaction is: First Order in A
Second Order in B
Overall third Order

$$\left[-r_A\right]=\frac{moles}{dm^3 s}$$

$$C_A=\frac{moles}{dm^3}$$

$$\left[k\right]=\left[\frac{-r_A}{C_A C_B^2}\right]=\frac{mole/dm^3/s}{\left(mole/dm^3\right)\left(mole/dm^3\right)^2}=\frac{dm^6}{mole^2 s}$$

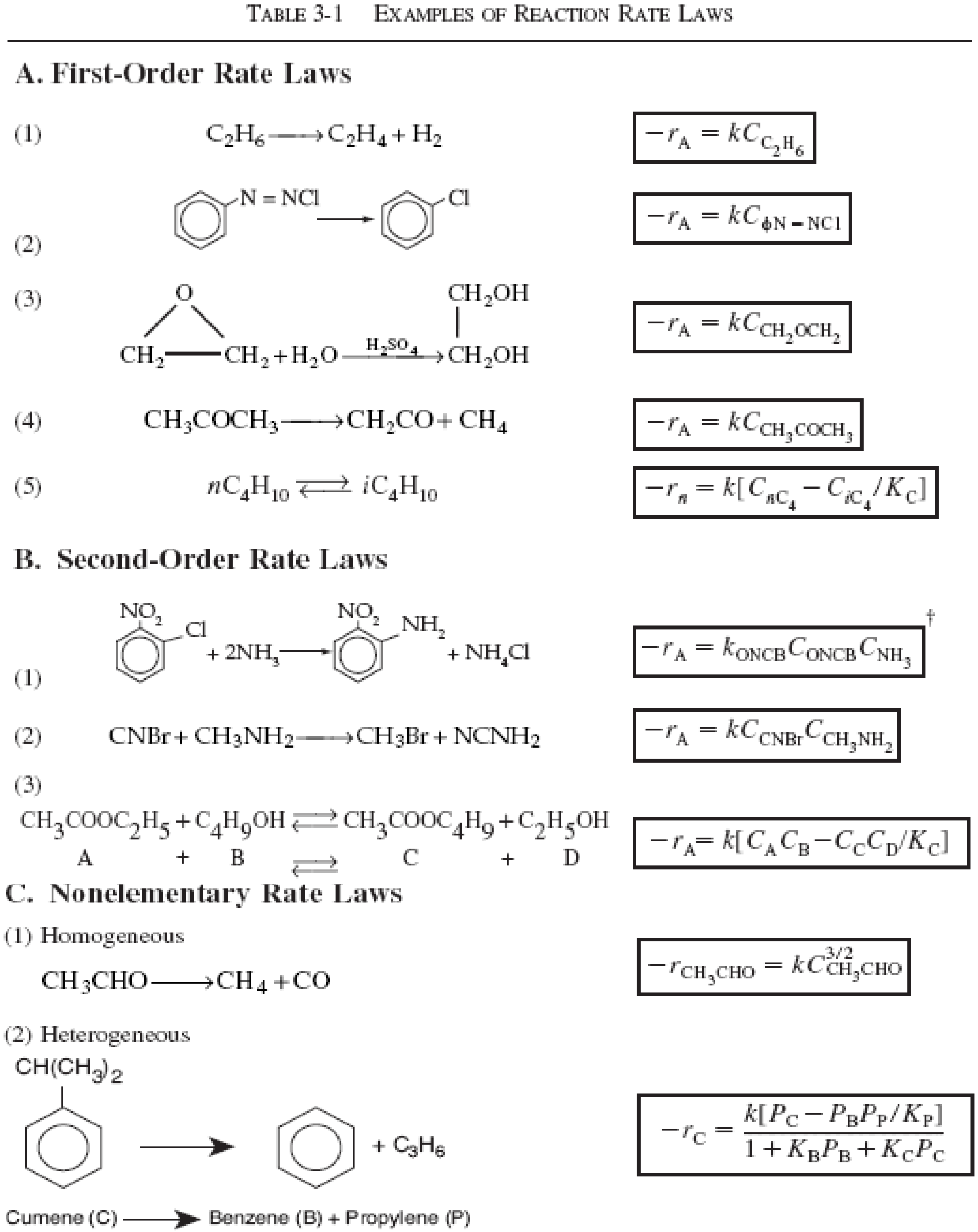


TABLE 3-1 EXAMPLES OF REACTION RATE LAWS

A. First-Order Rate Laws

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

B. Second-Order Rate Laws

(1)	$NO_2, Cl\text{-benzene} + 2NH_3 \longrightarrow NO_2, NH_2\text{-benzene} + NH_4Cl$	$\boxed{-r_A = k_{ONCB}C_{ONCB}C_{NH_3}}$ †
(2)	$CNBr + CH_3NH_2 \longrightarrow CH_3Br + NCNH_2$	$\boxed{-r_A = kC_{CNBr}C_{CH_3NH_2}}$
(3)	$CH_3COOC_2H_5 + C_4H_9OH \rightleftarrows CH_3COOC_4H_9 + C_2H_5OH$ $A + B \rightleftarrows C + D$	$\boxed{-r_A = k[C_AC_B - C_CC_D/K_C]}$

C. Nonelementary Rate Laws

(1) Homogeneous

$CH_3CHO \longrightarrow CH_4 + CO$

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

(2) Heterogeneous

$C_6H_5CH(CH_3)_2 \longrightarrow C_6H_6 + C_3H_6$

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

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

Algorithm

How to find $-r_A = f(X)$

Step 1: Rate Law $-r_A = g(C_i)$

Step 2: Stoichiometry $(C_i) = h(X)$

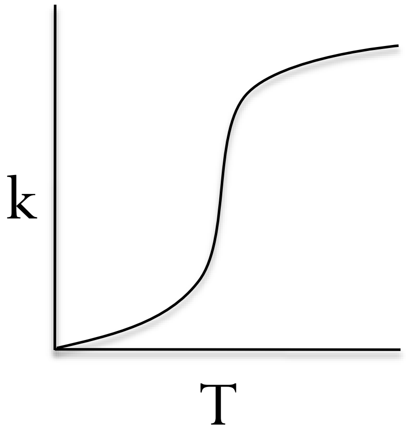
Step 3: Combine to get $-r_A = f(X)$

Arrhenius Equation

k is the specific reaction rate (constant) and is given by the Arrhenius Equation.

where:

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



$$T \to \infty \quad k \to A$$

$$T \to 0 \quad k \to 0$$

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

Arrhenius Equation

where:

E = Activation energy (cal/mol)

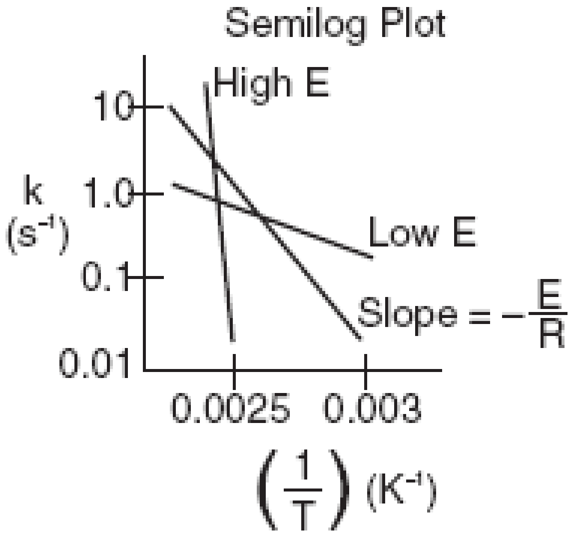
R = Gas constant (cal/mol*K)

T = Temperature (K)

A = Frequency factor (same units as rate constant k)

(units of A, and k, depend on overall reaction order)

$$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right)$$



Activation Energy

Concept 1. Law of Mass Action

The rate of reaction increases with increasing concentration of reactants owing to the corresponding increase in the number of molecular collisions.

The rate of disappearance of A, $-r_A$, depends on temperature and concentration. For many irreversible reactions, it can be written as the product of a *reaction rate constant*, k_A, and a function of the concentrations (activities) of the various species involved in the reaction:

$$-r_A = \left[k_A(T)\right]\left[fn(C_A, C_B \ldots)\right] \tag{3-2}$$

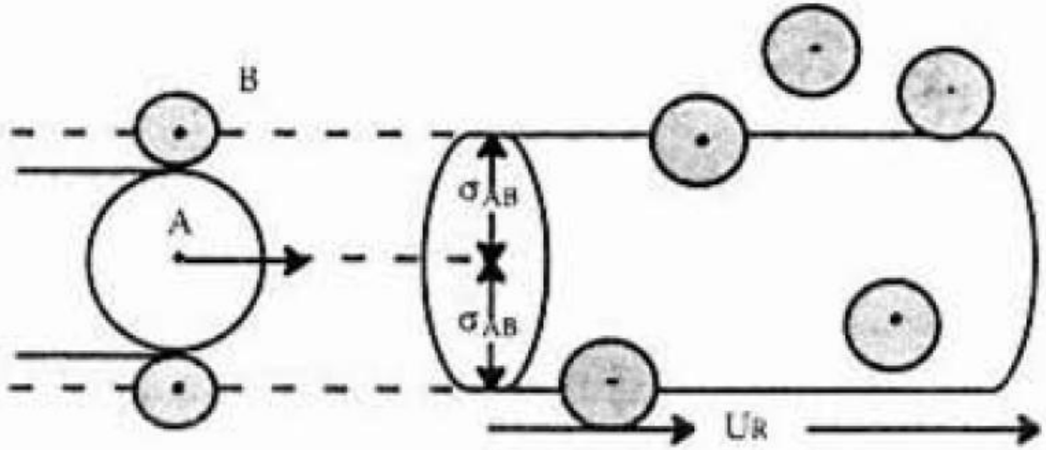
For example for the elementary reaction

$$AB + C \rightleftarrows A + BC$$

$$-r_{AB} = k_{AB}C_{AB}C_C = A_{AB}e^{-E/RT}C_{AB}C_C$$

E = Activation Energy, (kJ/mol)

Collision Theory



Schematic of collision cross section

Why is there an Activation Energy?

We see that for the reaction to occur, the reactants must overcome an energy barrier or activation energy E_A. The energy to overcome their barrier comes from the transfer of the kinetic energy from molecular collisions to internal energy (e.g. Vibrational Energy).

1. The molecules need energy to disort or stretch their bonds in order to break them and thus form new bonds
2. As the reacting molecules come close together they must overcome both stearic and electron repulsion forces in order to react.

Activation Energy

Concept 2. Potential Energy Surfaces and Energy Barriers

$$AB + C \rightleftarrows A\backslash\ \ B\backslash\ \ C \rightleftarrows A + BC$$

As two molecules, say AB and C, approach each other, the potential energy of the system (AB, C) increases owing repulsion of the molecules. The *reaction coordinate* is a measure of progress of the reaction as we go form AB and C to A and BC as shown in Figure 3-2 below.

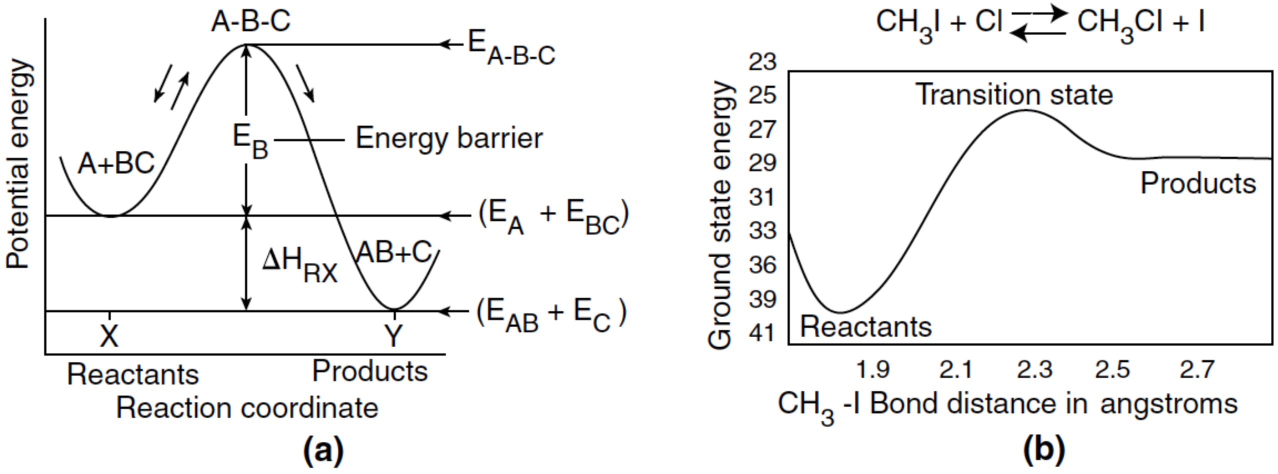


Figure 3-2 Progress along reaction path. **(a)** Symbolic reaction; **(b)** Calculated from computational software on the CRE Web site, Chapter 3 Web Module.

Activation Energy

Concept 2. Potential Energy Surfaces and Energy Barriers

The figure below shows a 3-dimensional energy surface and barrier over which the reaction must pass

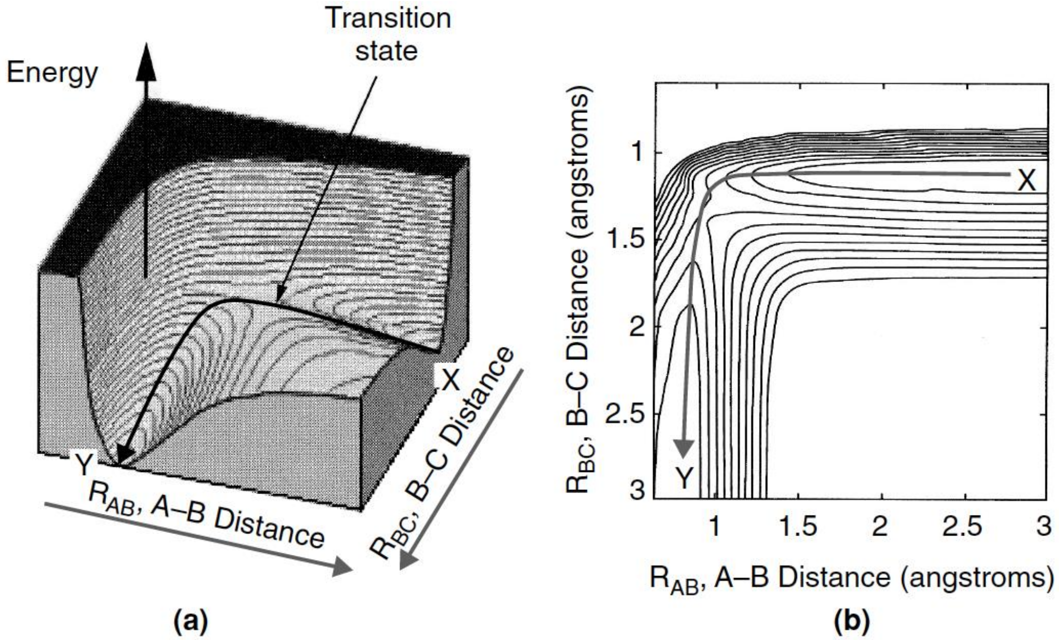


Figure 3-1 A potential energy surface for the H + $CH_3OH \longrightarrow H_2 + CH_2OH$ from the calculations of Blowers and Masel. The lines in the figure are contours of constant energy. The lines are spaced 5 kcal/mol. Richard I. Masel, *Chemical Kinetics and Catalysis*, p. 370, Fig.7.6 (Wiley, 2001).

Activation Energy

Concept 2. Potential Energy Surfaces and Energy Barriers

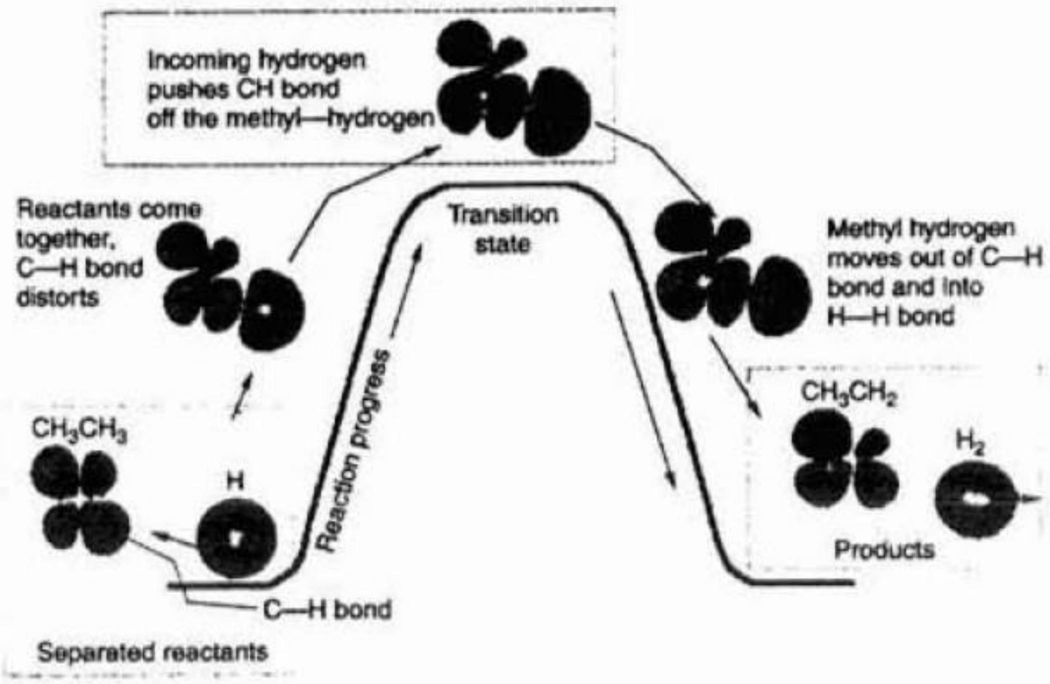


Figure 3-2 A diagram of the orbital distortions during the reaction

$$H\bullet + CH_3CH_3 \rightarrow H_2 + CH_2CH_3\bullet$$

The diagram shows only the interaction with the energy state of ethane (the C–H bond). Other molecular orbitals of the ethane also distort. [Courtesy of R. Masel, *Chemical Kinetics* (McGraw Hill, 2002), p. 594.]

Activation Energy

Concept 3. Fraction of Molecular Collisions That Have Sufficient Energy to React

The kinetic energy of the molecule must be transferred to potential energy to distort bonds and overcome steric forces in order for the reacting molecules to pass over the energy barrier.

The distribution of velocities of the reacting molecules relative to one another is given by the Boltzmann distribution

$$f\left(U,T\right)=4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} exp\left[\frac{-mU^2}{2k_B T}\right]U^2$$

Where

k_B = Boltzmann's constant = 3.29 x 10^{-24} cal/molecule/K

m = Reduced mass, *g*

U = Relative velocity, *m/s*

T = Absolute Temperature, K

e = Energy = $mU^{2,}$ kcal/molecule

E = Kinetic energy, kcal/mol

$f(U,T)$ = Fraction of relative velocities between U and U + dU

Activation Energy

Concept 3. Fraction of Molecular Collisions That Have Sufficient Energy to React

Distribution of Velocities

We will use the Maxwell-Boltzmann Distribution of Molecular Velocities. For a species of mass m, the Maxwell distribution of velocities (relative velocities) is:

$$f\left(U,T\right)dU = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mU^2/2k_B T}U^2 dU$$

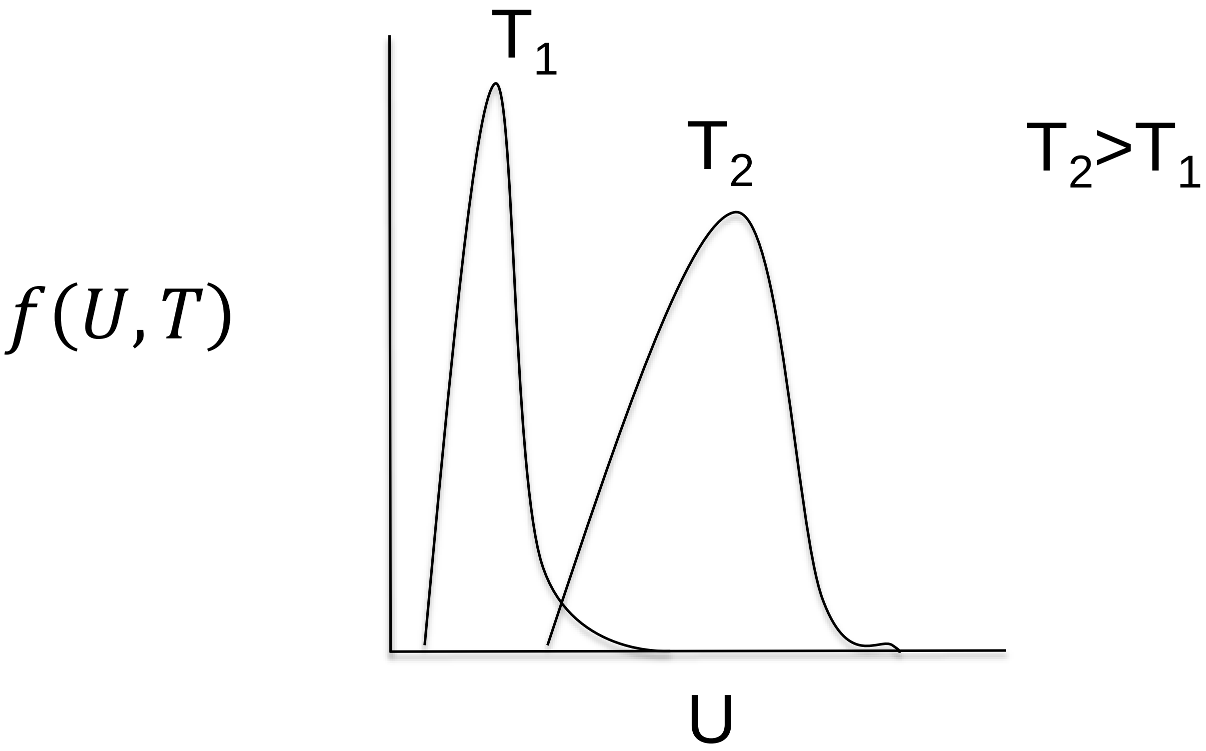
f(U,T)dU represents the fraction of velocities between U and (U+dU).

Activation Energy

Concept 3. Fraction of Molecular Collisions That Have Sufficient Energy to React

Distribution of Velocities

A plot of the distribution function, *f*(U,T), is shown as a function of U:



Maxwell-Boltzmann Distribution of velocities.

Activation Energy

Concept 3. Fraction of Molecular Collisions That Have Sufficient Energy to React

Distribution of Velocities

Given $f(U,T)\,dU = 4\pi\left(\dfrac{m}{2\pi k_B T}\right)^{3/2} e^{-mU^2/2k_BT}U^2\,dU$

Let $E = \dfrac{1}{2}mU^2$

$$f(E,T)\,dE = \frac{2\pi}{\left(2\pi k_B T\right)^{3/2}}E^{1/2}e^{\frac{-E}{k_BT}}\,dE$$

f(E,T)dE represents the fraction of collisions that have energy between E and (E+dE)

Activation Energy

Concept 3. Fraction of Molecular Collisions That Have Sufficient Energy to React

In terms of energy per mole, *E, instead* of energy per molecule, *e*, we have

$$f\left(E,T\right)=2p\left(\frac{1}{pRT}\right)^{3/2}E^{1/2}\,exp\left[\frac{-E}{RT}\right] \qquad (3\text{-}20)$$

where *E* is in (cal/mol) or (J/mole), *R* is in (cal/mol/K), and *f*(*E,T*) is in mol/cal.

The distribution function *f*(*E,T*) is most easily interpreted by recognizing that [*f*(*E,T*) *dE*] is the fraction of collisions with energies between *E* and *E* + *dE*.

$$f\left(E,T\right)dE=2p\left(\frac{1}{pk_BT}\right)^{3/2}E^{1/2}\,exp\left[\frac{-E}{k_BT}\right]dE \qquad (3\text{-}21)$$

This distribution is shown as a function of E for two temperatures in the next slide.

Activation Energy

Concept 3. Fraction of Molecular Collisions That Have Sufficient Energy to React

$$\left(\text{Fraction with energies between } (0.25) \text{ and } 0.35) \ \frac{kcal}{mol}\right) = \int_{0.25}^{0.35} f\left(E,T\right)dE$$

This fraction is shown by the shaded area in Figure 3-4(a) and is approximated by the average value of *f*(*E,T*) at *E* = 0.3 kcal/mole is 0.81 mol/kcal.

$$f\left(E,T\right)dE = f\left(0.3, 300K\right)\Delta E = \frac{0.81 \ \text{mol}}{\text{kcal}}\left(0.35\frac{\text{kcal}}{\text{mol}} - 0.25\frac{\text{kcal}}{\text{mol}}\right) = 0.081$$

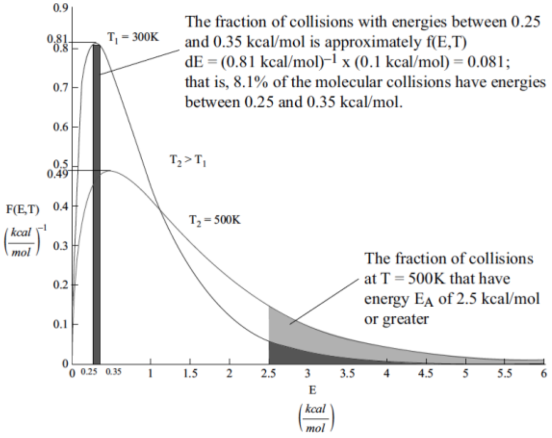


Figure 3-4(a) Energy distribution of reacting molecules.

We see 8.1% of the collisions have energies between 0.25 and 0.35 kcal/mol

Activation Energy

Concept 3. Fraction of Molecular Collisions That Have Sufficient Energy to React

Fraction of Molecules with Energy Greater than E_A

We can also determine the fraction of collision that have energies greater than a certain value, E_A

$$\left(\text{Fraction of Molecules with } E > E_A\right) = F\left(E > E_A, T\right) = \int_{E_A}^{\infty} f\left(E, T\right) dE \qquad (3\text{-}22)$$

For $E_A > 3RT$, we can obtain an analytical approximation for the fraction of molecules of collision with energies greater than E_A by combining Equations (3-21) and (3-22) and integrating to get

$$\left(\begin{matrix}\text{Fraction of collision with} \\ \text{energies greater than } E_A\end{matrix}\right) = F\left(E > E_A, T\right) \cong \frac{2}{\sqrt{\pi}}\left(\frac{E_A}{RT}\right)^{1/2} exp\left(-\frac{E_A}{RT}\right) \qquad (3\text{-}23)$$

Equation (3-23) is plotted in Figure 4-4(b) as a function of activation energy, E_A, as shown in the next slide.

Activation Energy

Concept 3. Fraction of Molecular Collisions That Have Sufficient Energy to React

Fraction of Molecules with Energy Greater than E_A

One observes for an activation energy E_A of 20 kcal/mol and a temperature of 300 K the fraction of collisions with energies greater than 20 kcal/mol is 1.76×10^{-14} while at 600 K, the fraction increases to 2.39×10^{-7}, **which is a 7 orders of magnitude difference**.

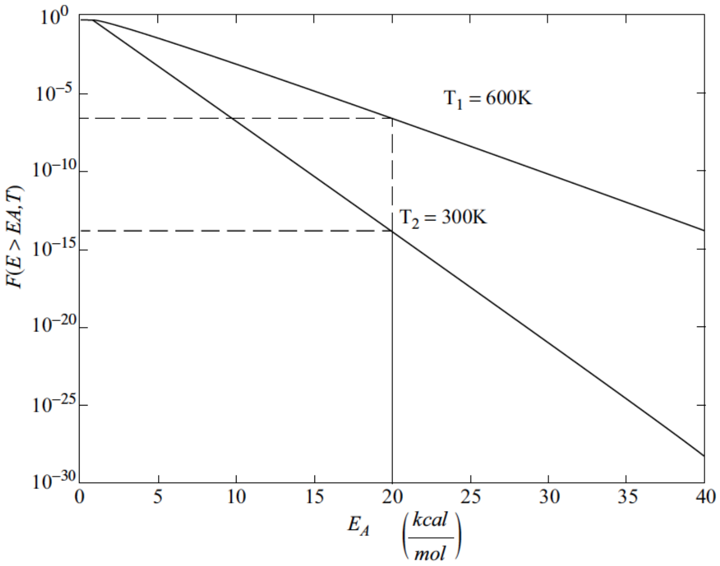
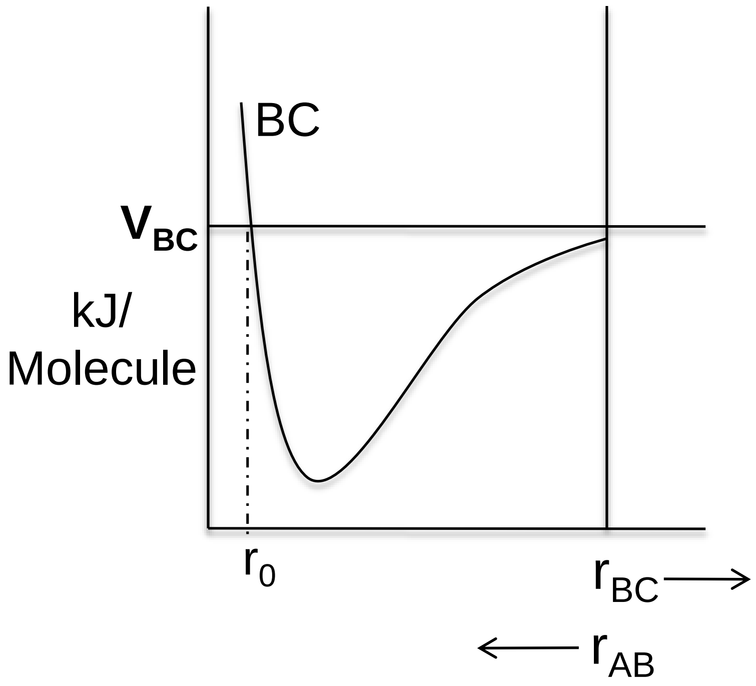
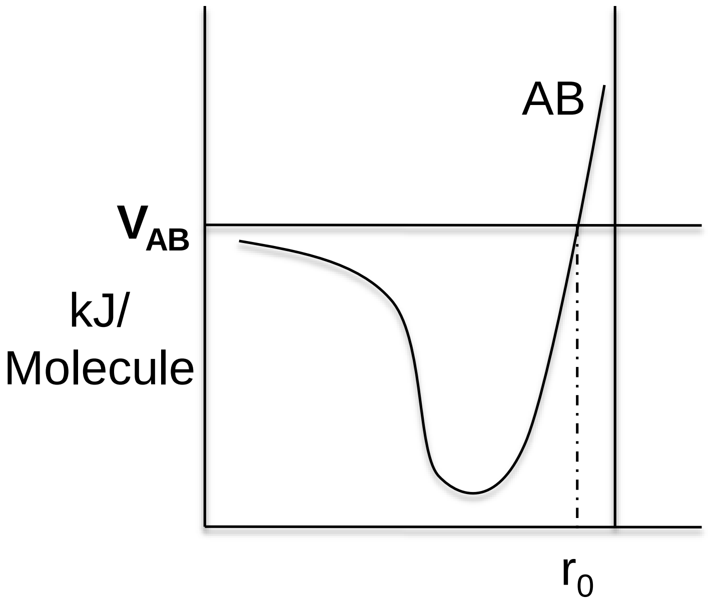


Figure 3-4(b) Fraction of collision with energies greater than E_A.

End of Lecture 3

Supplementary Material





Potentials (Morse or Lennard-Jones)

Supplementary Material

One can also view the reaction coordinate as variation of the BC distance for a fixed AC distance:

$$\overbrace{\left| A \;\underset{r_{AB}}{\leftarrow}\; B \;\underset{r_{BC}}{\rightarrow}\; C \right|}^{l} \qquad \overbrace{\left| A \qquad\qquad BC \right|}^{l} \qquad \overbrace{\left| AB \qquad\qquad C \right|}^{l}$$

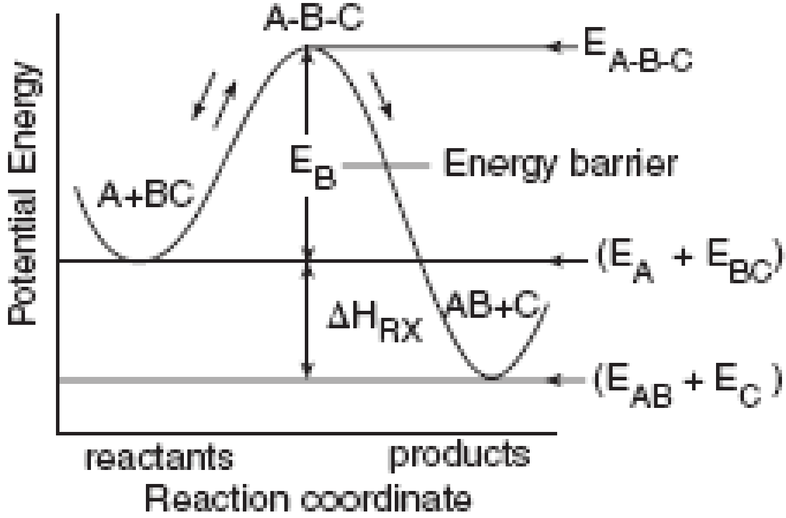
For a fixed AC distance as B moves away from C the distance of separation of B from C, r_{BC} increases as N moves closer to A. As r_{BC} increases r_{AB} decreases and the AB energy first decreases then increases as the AB molecules become close. Likewise as B moves away from A and towards C similar energy relationships are found. E.g., as B moves towards C from A, the energy first decreases due to attraction then increases due to repulsion of the AB molecules as they come closer together. We now superimpose the potentials for AB and BC to form the following figure:

Reaction Coordinate

The activation energy can be thought of as a barrier to the reaction. One way to view the barrier to a reaction is through the reaction coordinates. These coordinates denote the energy of the system as a function of progress along the reaction path. For the reaction:

$$A+BC \Leftrightarrow A:::B:::C \rightarrow AB+C$$

The reaction coordinate is:



Supplementary Material