Lecture 3

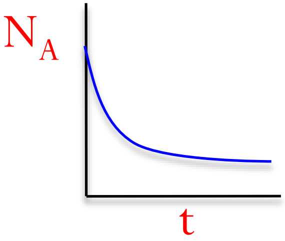
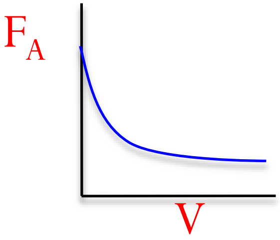
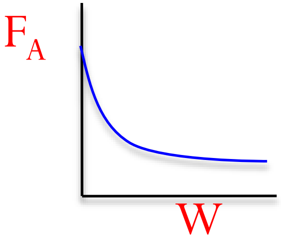
Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 3 – Thursday

- 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

Reactor Mole Balances Summary

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

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

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

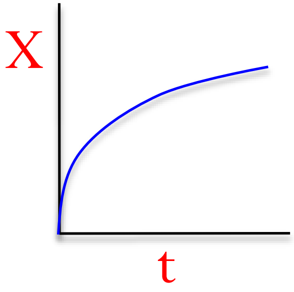
Choose limiting reactant A as basis of calculation

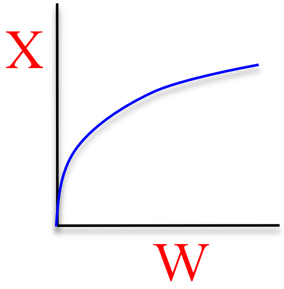
$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D$$

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

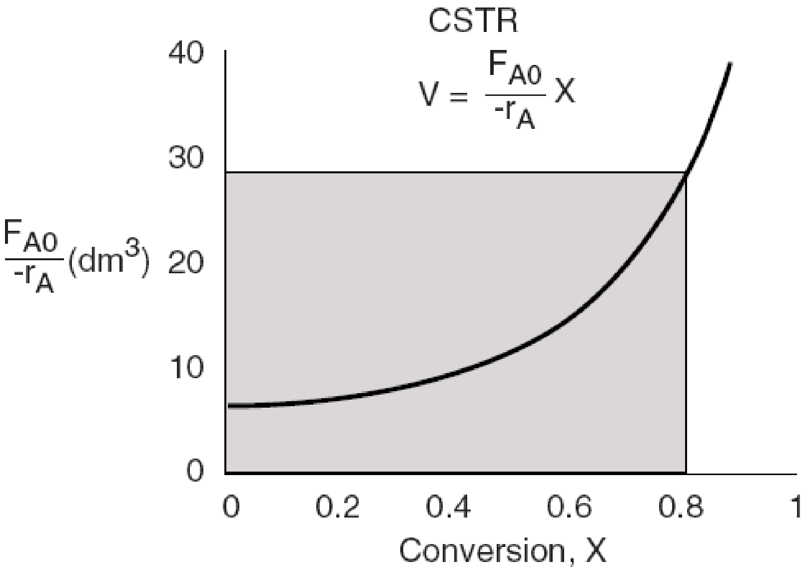
Reactor Mole Balances Summary In terms of Conversion

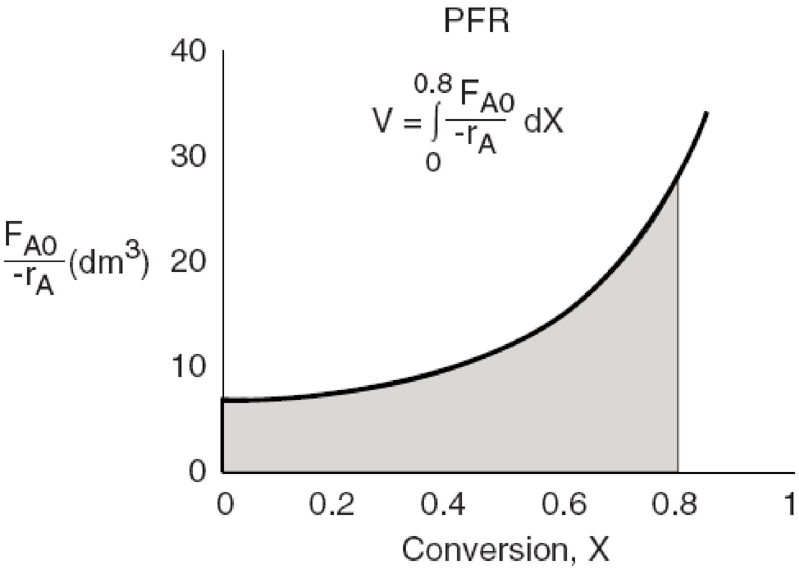
Reactor	Differential	Algebraic	Integral
Batch	$N_{A0}\dfrac{dX}{dt}=-r_AV$		$t=N_{A0}\displaystyle\int_0^X\frac{dX}{-r_AV}$
CSTR		$V=\dfrac{F_{A0}X}{-r_A}$	
PFR	$F_{A0}\dfrac{dX}{dV}=-r_A$		$V=F_{A0}\displaystyle\int_0^X\frac{dX}{-r_A}$
PBR	$F_{A0}\dfrac{dX}{dW}=-r'_A$		$W=F_{A0}\displaystyle\int_0^X\frac{dX}{-r'_A}$



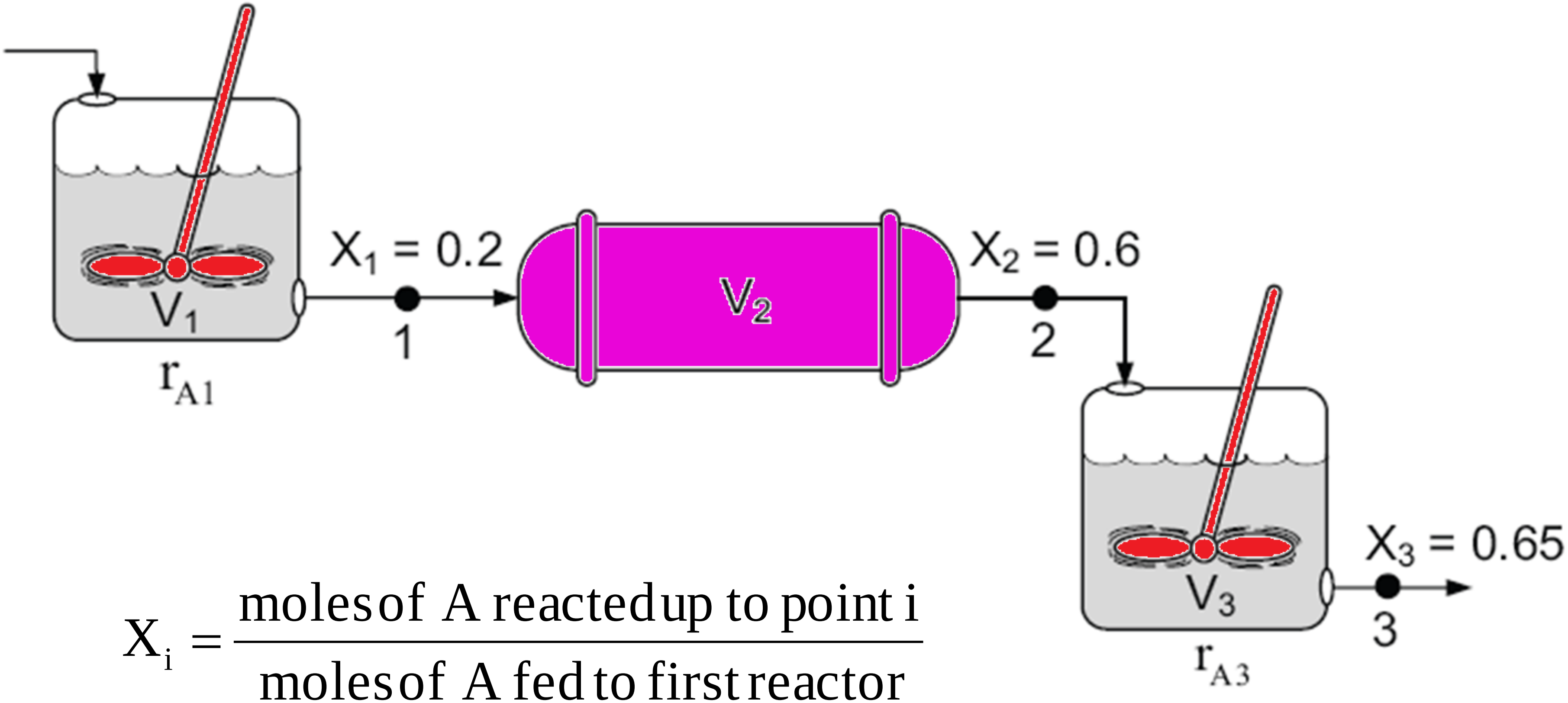


Levenspiel Plots





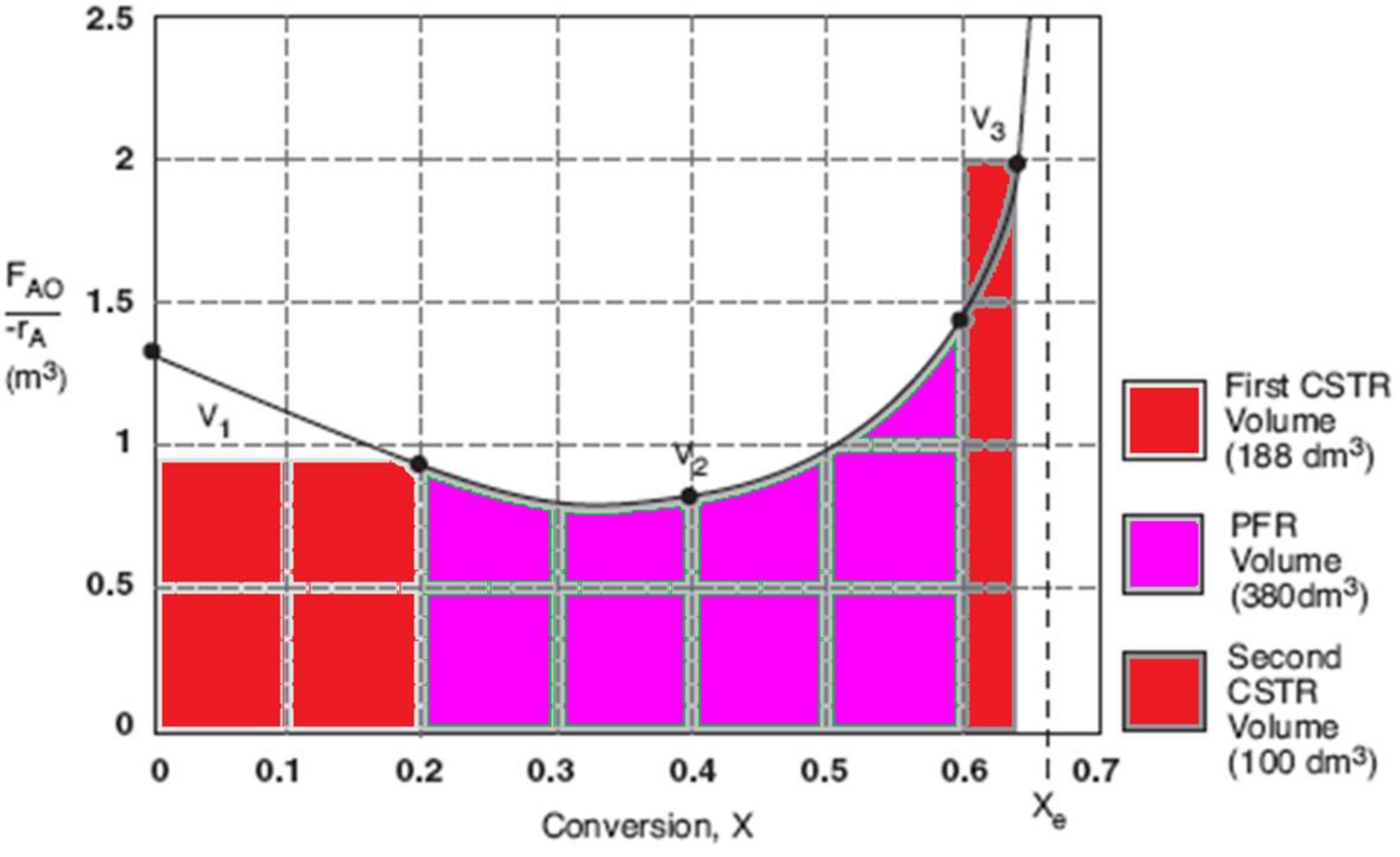
Reactors in Series



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

Only valid if there are no side streams

Reactors in Series



Building Block 2: Rate Laws

Power Law Model:

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

α order in A

β 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

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

$$2A + B \rightarrow 3C$$

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

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

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

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

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

$$[-r_A] = \frac{moles}{dm^3 s} \qquad C_A = \frac{moles}{dm^3}$$

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

TABLE 3-1 EXAMPLES OF REACTION RATE LAWS

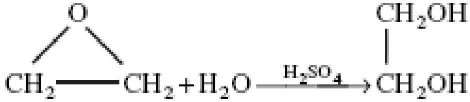
A. First-Order Rate Laws

(1) $C_2H_6 \longrightarrow C_2H_4 + H_2$ $\boxed{-r_A = kC_{C_2H_6}}$

(2)

$\boxed{-r_A = kC_{\phi N-NCl}}$

(3)



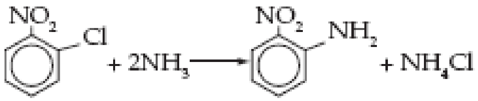
$\boxed{-r_A = kC_{CH_2OCH_2}}$

(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)



$\boxed{-r_A = k_{ONCB}C_{ONCB}C_{NH_3}}$ †

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

(3)

$CH_3COOC_2H_5 + C_4H_9OH \rightleftarrows CH_3COOC_4H_9 + C_2H_5OH$

$A + B \rightleftarrows C + D$

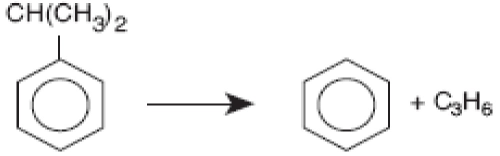
$\boxed{-r_A = k[C_AC_B - C_CC_D/K_C]}$

C. Nonelementary Rate Laws

(1) Homogeneous

$CH_3CHO \longrightarrow CH_4 + CO$ $\boxed{-r_{CH_3CHO} = kC_{CH_3CHO}^{3/2}}$

(2) Heterogeneous



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

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

Algorithm

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

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

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

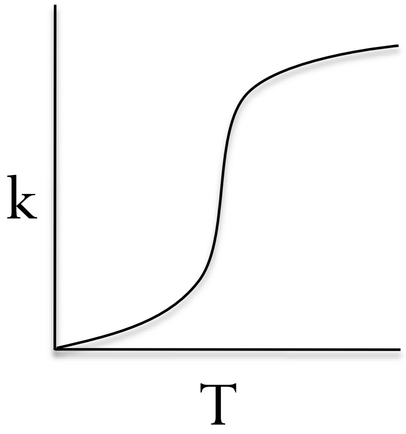
Step 3: Combine to get $-r_A = f(X)$

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)

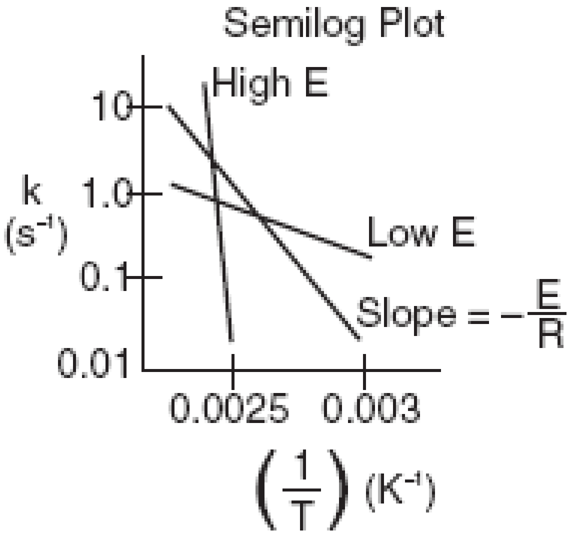
R = Gas constant (cal/mol*K)

T = Temperature (K)

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

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

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

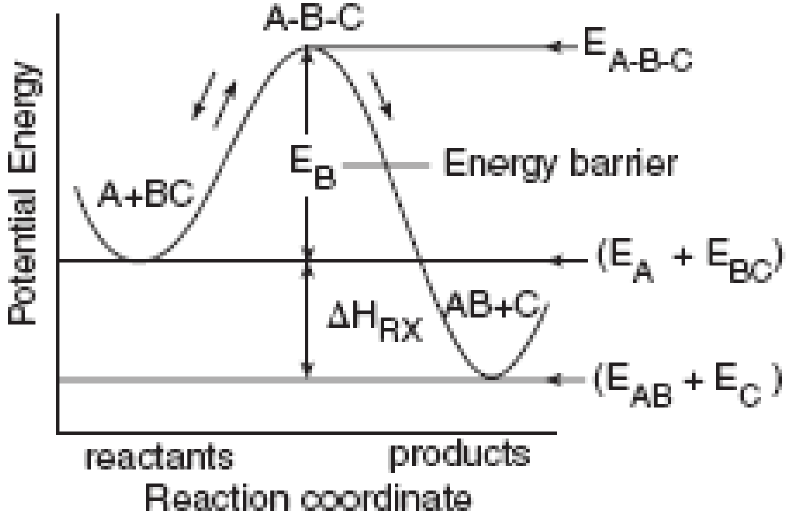


Reaction Coordinate

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:



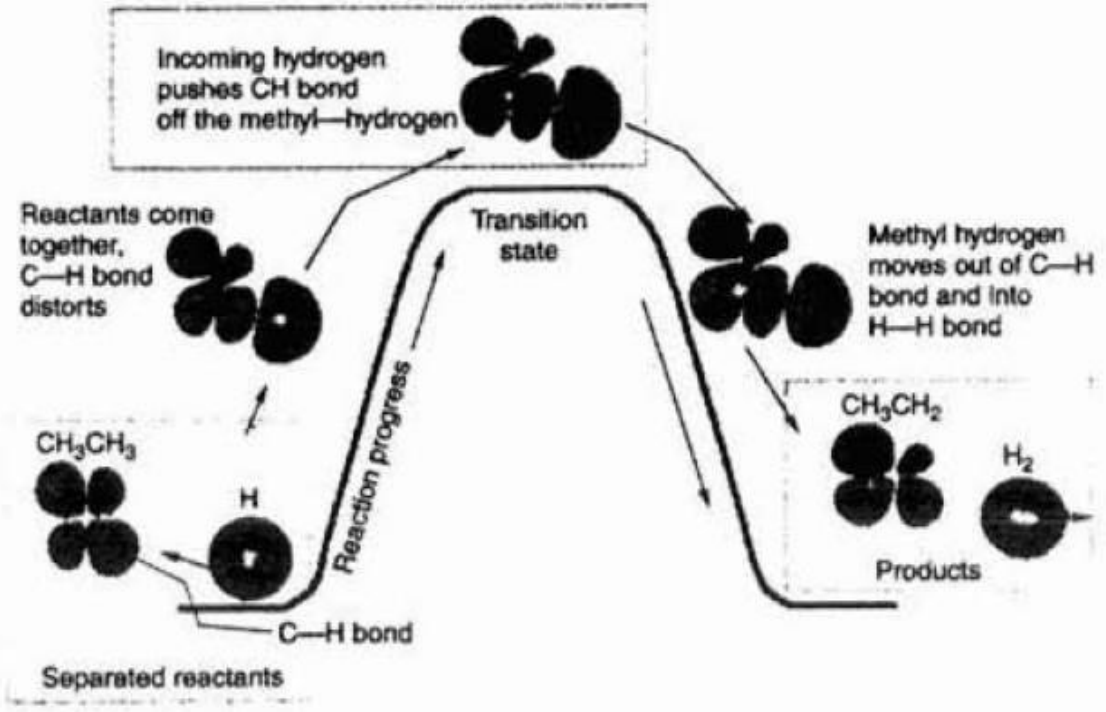
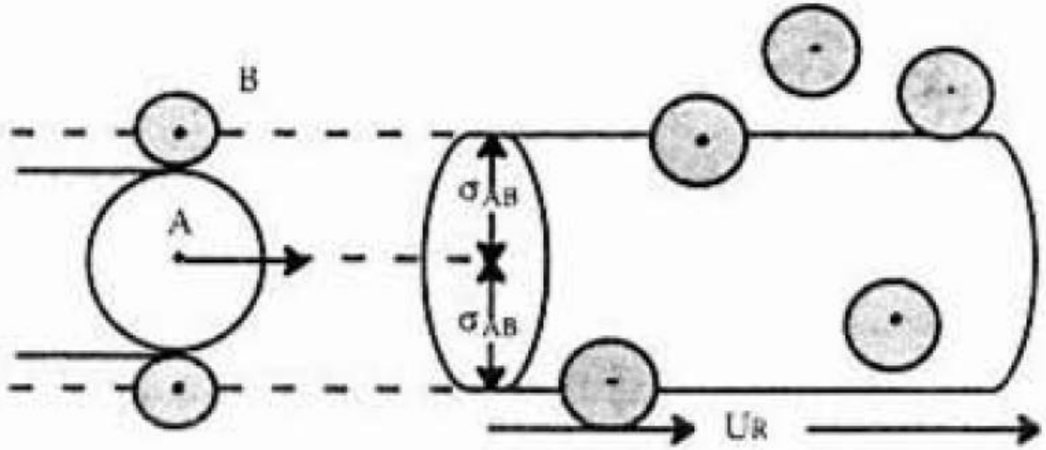


Figure 3-2 A diagram of the orbital distortions during the reaction

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

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.]

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.

Distribution of Velocities

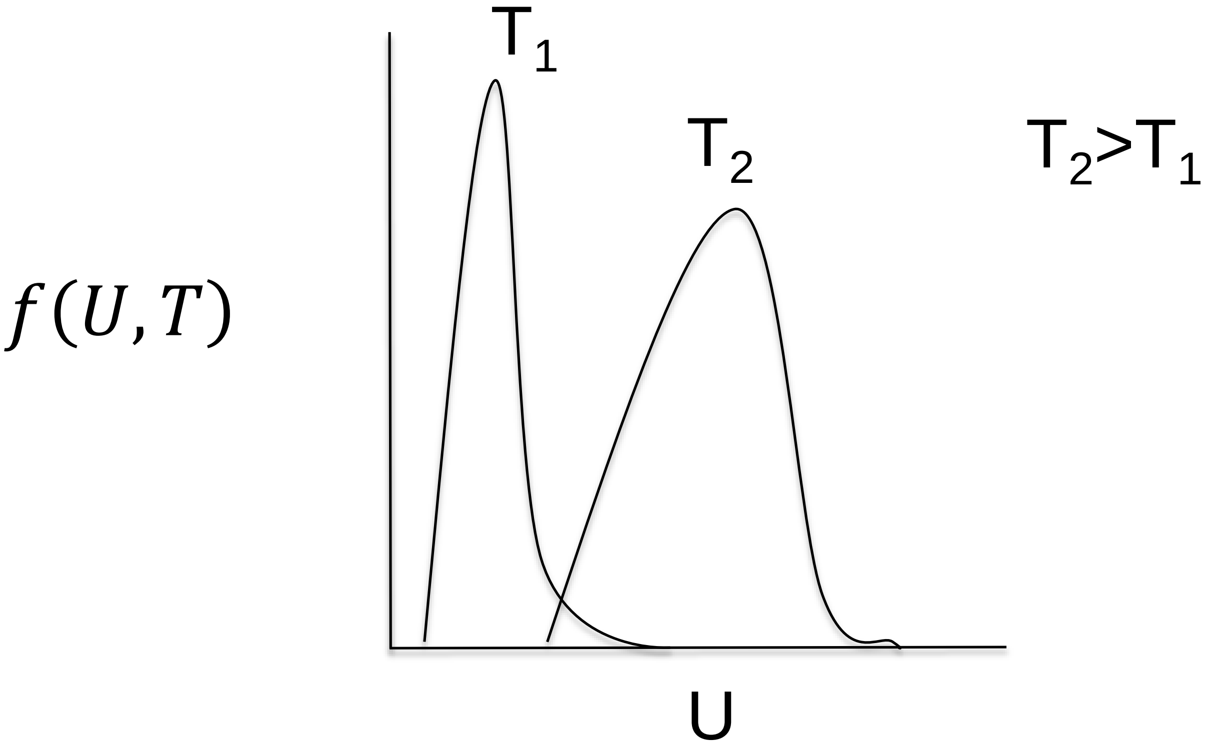
We will use the Maxwell-Boltzmann Distribution of Molecular Velocities. For a species af mass m, the Maxwell distribution of velocities (relative velocities) is:

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

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

Distribution of Velocities

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



Maxwell-Boltzmann Distribution of velocities.

Distribution of Velocities

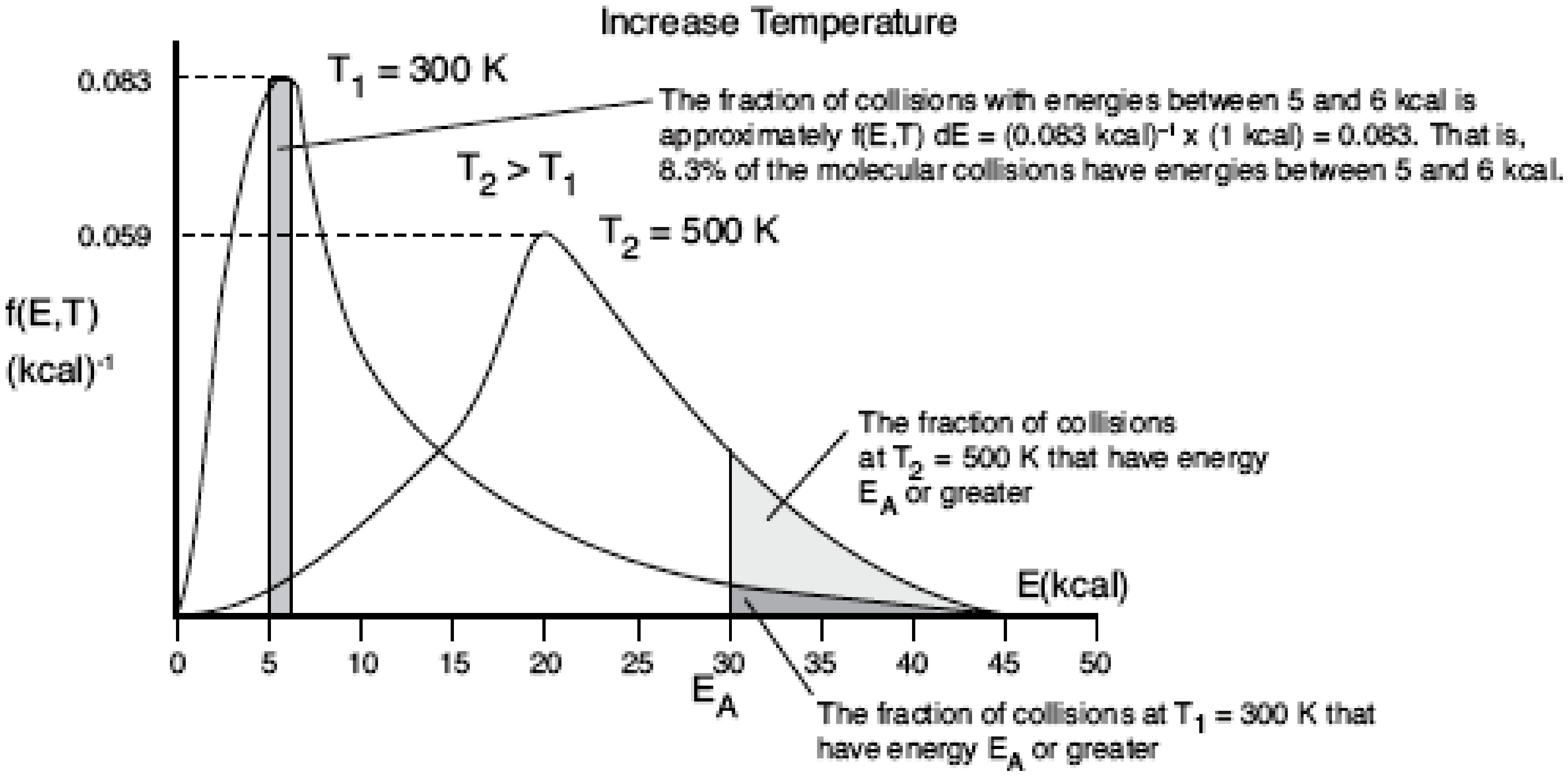
Given $f(U,T)dU = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mU^2/2k_BT}U^2 dU$

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

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

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

One such distribution of energies is in the following figure:



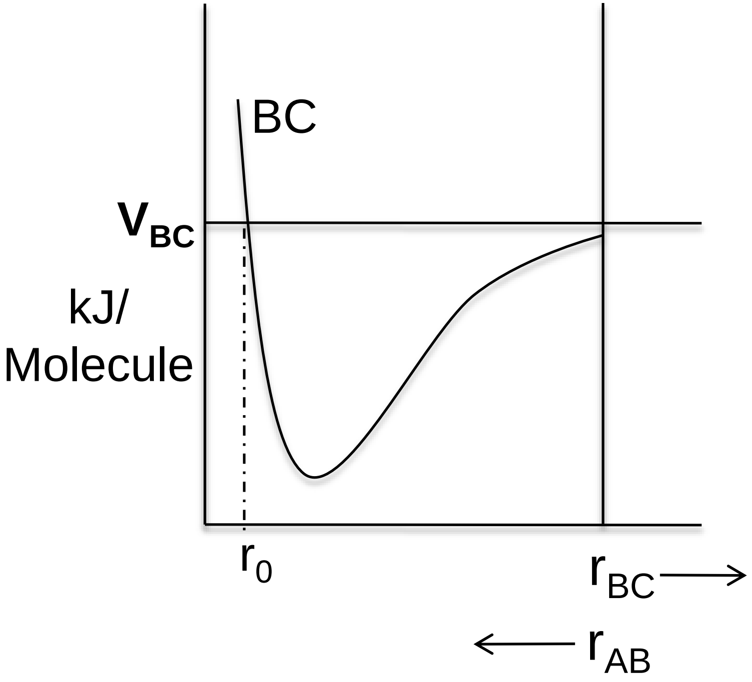
The fraction of collisions with energies between 5 and 6 kcal is approximately $f(E,T)\ dE = (0.083\ \text{kcal})^{-1} \times (1\ \text{kcal}) = 0.083$. That is, 8.3% of the molecular collisions have energies between 5 and 6 kcal.

The fraction of collisions at $T_2 = 500$ K that have energy E_A or greater

The fraction of collisions at $T_1 = 300$ K that have energy E_A or greater

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:

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

$$r_{AB} \qquad r_{BC}$$

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:

Supplementary Material