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

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

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

    - or the rate of disappearance of benzene

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

    - or with in equilibrium constant

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

2. The Rxn Order and the Rate Law X

- **Rate Law Test**

  - What is the reaction rate law for the reaction

  $A + \frac{1}{2}B \rightarrow C$

  if the reaction is elementary? $-r_A = k_A C_A C_B^{1/2}$

  What is r_B? $r_B = \frac{1}{2} r_A = -\frac{1}{2} k_A C_A C_B^{1/2}$

  What is r_C? $r_C = -r_A = k_A C_A C_B^{1/2}$

  Calculate the rates of A, B, and C in a CSTR where the concentrations are C_A = 1.5 mol/dm^3, C_B = 9 mol/dm^3 and k_A = 2 (dm^3/mol)$^{(1/2)}$(1/s).

$$-r_A = k_A C_A C_B^{1/2} = (2)(1.5)(9)^{1/2} = 9 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

3. Rate Constant, k (p 91)

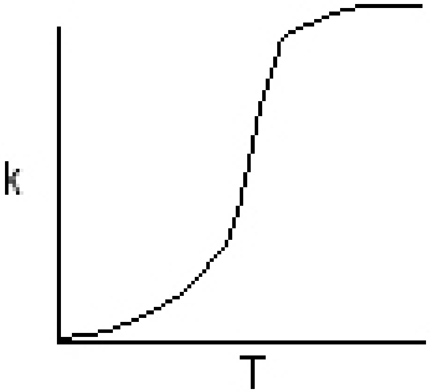
- **Specific reaction rate**
  - **k is the specific reaction rate (constant) and is given by the Arrhenius Equation:**

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

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

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

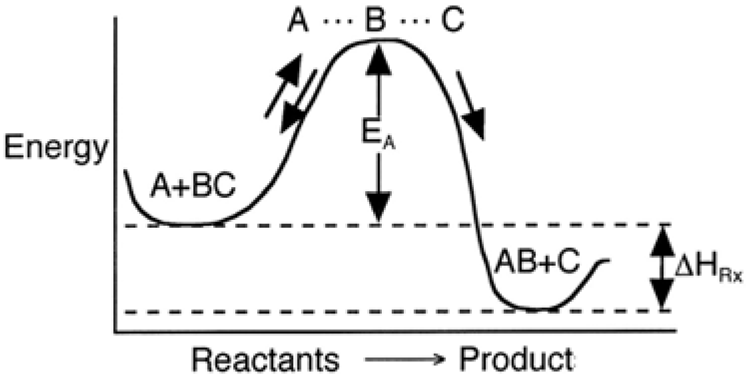
$$A \approx 10^{13}$$



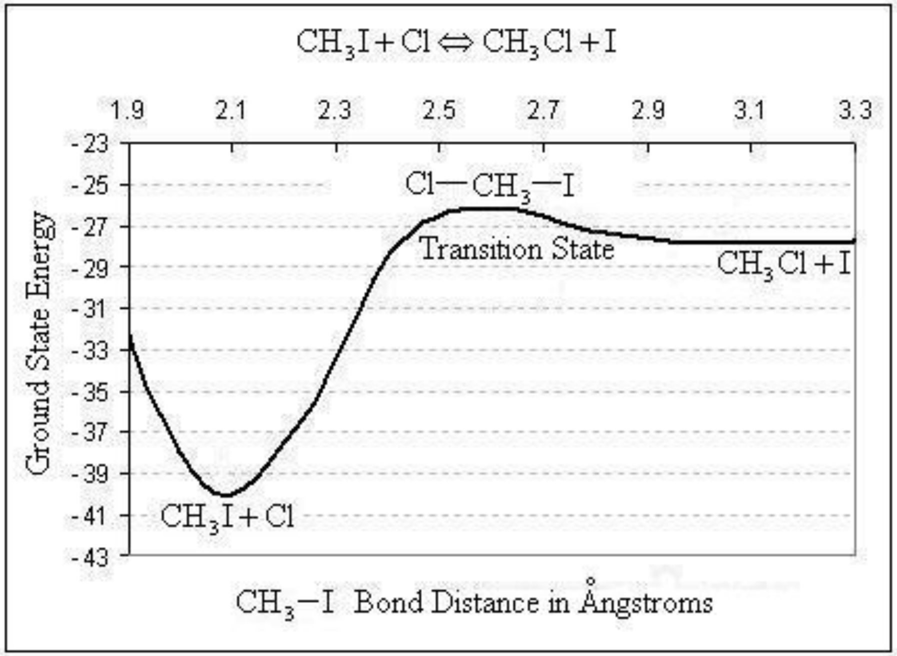
Where: E = activation energy (cal/mol)
R = gas constant (cal/mol*K)
T = temperature (K)
A = frequency factor (units of A, and k, depend on overall reaction order)

3. Rate Constant II

- **Activation energy 1**
  - **The height of the energy barrier separating two minima of potential energy of the reactants and products of a reaction)**



$$E_B = E^{\circ}_{fA\text{-}B\text{-}C} - (E^{\circ}_{fA} + E^{\circ}_{fB\text{-}C})$$



3. Rate Constant III

○ **Activation energy 2**

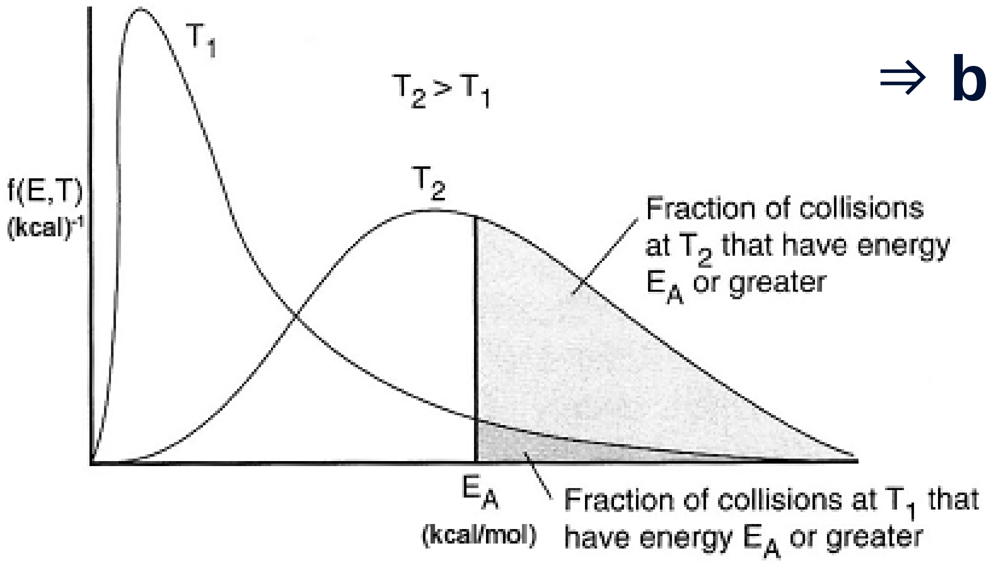
- Collision theory

- **T ↑, E_k of reactant ↑ , molecular collision ↑**

⇒ internal energy (stretching, bending) ↑

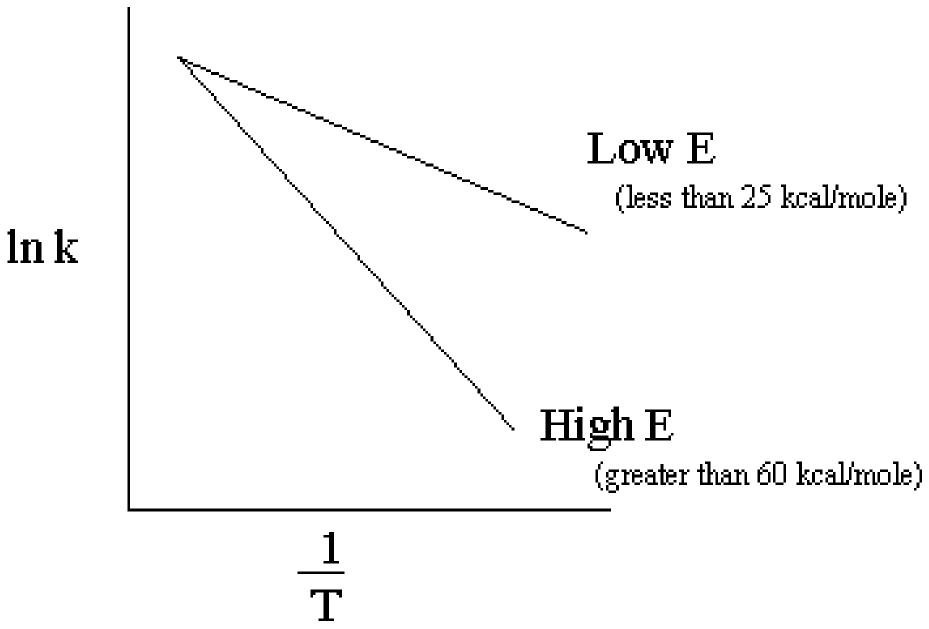
⇒ causing them to reach an activated state

⇒ bond breaking & rxn



3. Rate Constant IV

- **Activation energy 3**
  - **Rearrangement** $k = Ae^{-E/RT}$



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

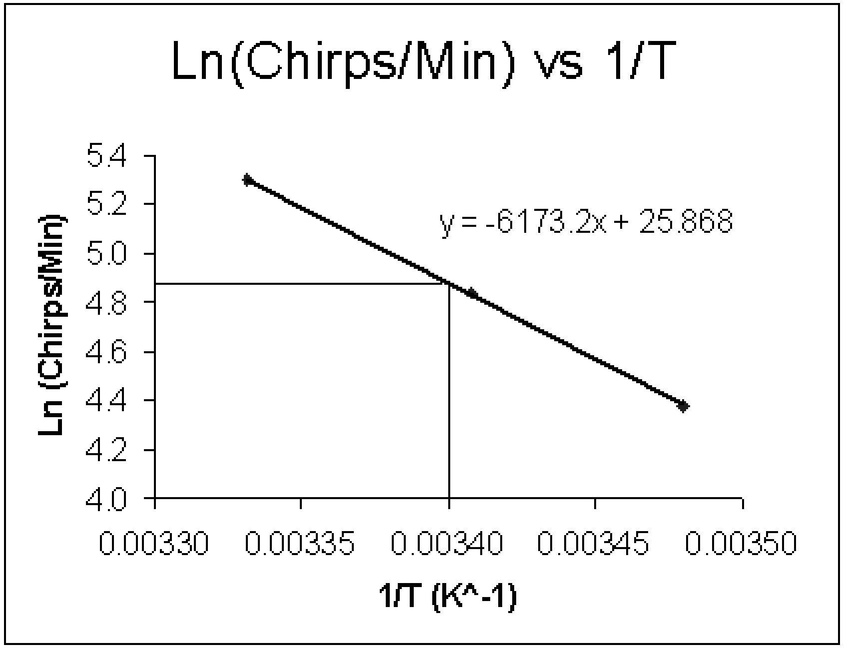
$$k(T) = k(T_0)e^{\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}$$

3. Rate Constant V

- **Activation energy 4 (p 132 p 3-4)**

  - The following sound of chirping crickets was recorded in the woods during the summer evening

T(°C)	**14.2**	**20.3**	**27.0**
Chirps/min	**80**	**126**	**200**



3. Rate Constant VI

- **Activation energy 5**

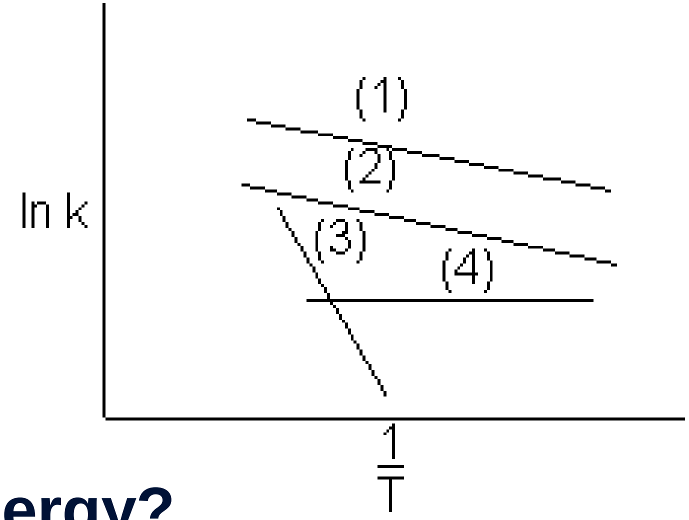
  - Consider the following elementary reactions

$$1)\ A \xrightarrow{k_1} B$$

$$2)\ A \xrightarrow{k_2} D$$

$$3)\ A \xrightarrow{k3} Y$$

$$4)\ A \xrightarrow{k4} U$$



- **The higher activation energy?**
- **The same activation energy?**
- **Virtually temperature insensitive?**
- **Which reaction will dominate (i.e. take place the fastest) at high temperatures?**

3. Rate Constant VII

- **Examples of Rate Laws**

- First order reactions

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

$$\boxed{-r_A = k \quad C_{C_2H_6}} \text{ with } \quad k = 0.072 \ s^{-1} \ e^{\frac{82 \cdot \text{kcal}}{\text{mol}}\left(\frac{1}{1000} - \frac{1}{T}\right)}$$

$$\phi N = NCl \longrightarrow \phi Cl + N_2$$

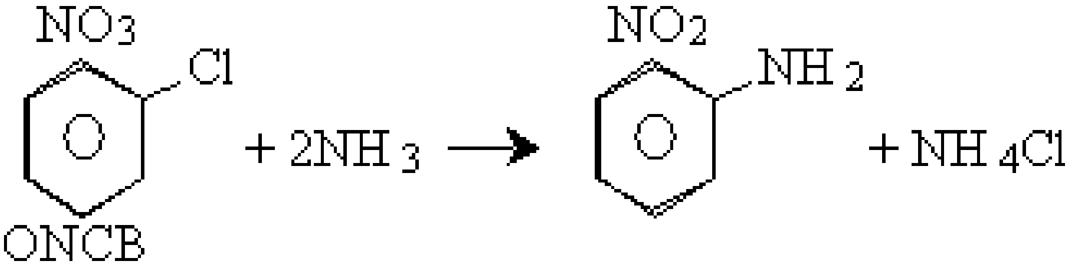
$$\boxed{-r_A = k \quad C_{\phi N = NCl}} \text{ with } \quad k = 0.00717 \ s^{-1} \ e^{-\frac{28.7}{R}\frac{\text{kcal}}{\text{mol}}\left(\frac{1}{333} - \frac{1}{T}\right)}$$

$$CH_3COCH_3 \longrightarrow CH_2CO + CH_4$$

$$\boxed{-r_A = k \quad C_{CH_3COCH_3}} \text{ with } \quad \ln \ k = 34.34 - \frac{34,322}{T}$$

3. Rate Constant VIII

- **Examples of Rate Laws**
  - **Second order reactions**



$$\boxed{-r_A = k\, C_{ONCB} C_{NH_3}} \quad \text{with} \quad k = 0.0017 \frac{m^3}{kmol \cdot min} \quad \text{at} \quad 188°C$$

$$\text{and} \quad E = 11{,}273 \frac{cal}{mol}$$

This reaction is first order in ONCB, first order in ammonia and overall second order

4. Reactor Sizing & Design

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

5. Batch Systems (p.100)

- **Limiting reactant A**

  - Basis of calculation

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

  - Define

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

$$N_T = N_{T0} + \delta N_{\mathrm{A}0} X$$

5. Batch Systems II

Species	Initial (mol)	Change (mol)	Remaining (mol)
A	N_{A0}	$-(N_{A0}X)$	$N_A = N_{A0} - N_{A0}X$
B	N_{B0}	$-\frac{b}{a}(N_{A0}X)$	$N_B = N_{B0} - \frac{b}{a}N_{A0}X$
C	N_{C0}	$\frac{c}{a}(N_{A0}X)$	$N_C = N_{C0} - \frac{c}{a}N_{A0}X$
D	N_{D0}	$\frac{d}{a}(N_{A0}X)$	$N_D = N_{D0} - \frac{d}{a}N_{A0}X$
Inert	$\underline{N_{I0}}$	$---$	$\underline{N_I = N_{I0}}$
Totals	N_{T0}		$N_T = N_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)N_{A0}X$

5. Batch Systems III

- Eqns for batch conc'n

  - Concentration of batch system (= number/volume)

$$C_\mathrm{A} = \frac{N_\mathrm{A}}{V}$$

  - Define

$$\boxed{\Theta_i = \frac{N_{i0}}{N_\mathrm{A0}} = \frac{C_{i0}}{C_\mathrm{A0}} = \frac{y_{i0}}{y_\mathrm{A0}}}$$

$$C_\mathrm{A} = \frac{N_\mathrm{A}}{V} = \frac{N_\mathrm{A0}(1-X)}{V}$$

$$\left.\begin{aligned}
C_\mathrm{B} &= \frac{N_\mathrm{B}}{V} = \frac{N_\mathrm{B0} - (b/a)N_\mathrm{A0}X}{V} \\
C_\mathrm{C} &= \frac{N_\mathrm{C}}{V} = \frac{N_\mathrm{C0} - (c/a)N_\mathrm{A0}X}{V} \\
C_\mathrm{D} &= \frac{N_\mathrm{D}}{V} = \frac{N_\mathrm{D0} - (d/a)N_\mathrm{A0}X}{V}
\end{aligned}\right\}
\begin{aligned}
C_\mathrm{B} &= \frac{N_\mathrm{A0}[\Theta_\mathrm{B} - (b/a)X]}{V} \\
C_\mathrm{C} &= \frac{N_\mathrm{A0}[\Theta_\mathrm{C} - (c/a)X]}{V} \\
C_\mathrm{D} &= \frac{N_\mathrm{A0}[\Theta_\mathrm{D} - (d/a)X]}{V}
\end{aligned}$$

5. Batch Systems IV

○ **Constant Volume Batch**

- if the reaction occurs in the liquid phase or if a gas phase reaction occurs in a rigid (e.g., steel) batch reactor

Then $V = V_0$

$$C_\mathrm{A} = \frac{N_\mathrm{A0}(1-X)}{V} = C_\mathrm{A0}(1-X)$$

$$C_\mathrm{B} = \frac{N_\mathrm{A0}[\Theta_\mathrm{B} - (b/a)X]}{V} = C_\mathrm{A0}\left(\Theta_\mathrm{B} - \frac{b}{a}X\right)$$

$$C_\mathrm{C} = \frac{N_\mathrm{A0}[\Theta_\mathrm{C} - (c/a)X]}{V} = C_\mathrm{A0}\left(\Theta_\mathrm{C} - \frac{c}{a}X\right)$$

$$C_\mathrm{D} = \frac{N_\mathrm{A0}[\Theta_\mathrm{D} - (d/a)X]}{V} = C_\mathrm{A0}\left(\Theta_\mathrm{D} - \frac{d}{a}X\right)$$