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5.60 Thermodynamics & Kinetics
Spring 2008

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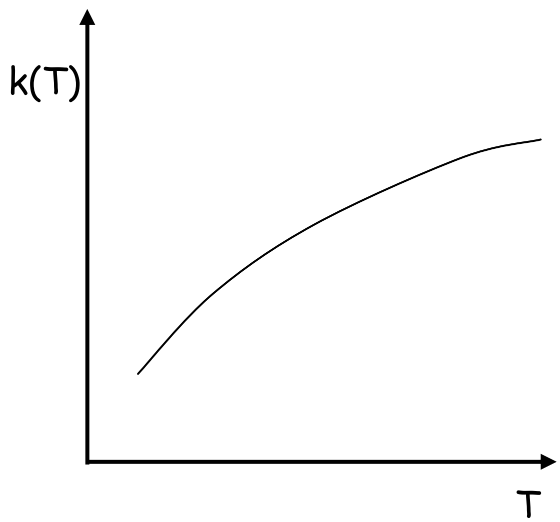
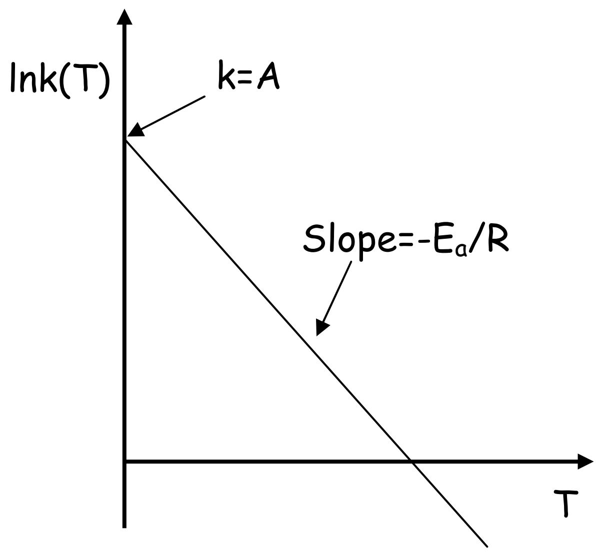
Temperature Dependence of Rate Constant

Arrhenius Law

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

where $E_a \equiv$ Activation Energy
$A \equiv$ Pre-Exponential Factor





Typically: E_a ~ 50-300 kJ/mole

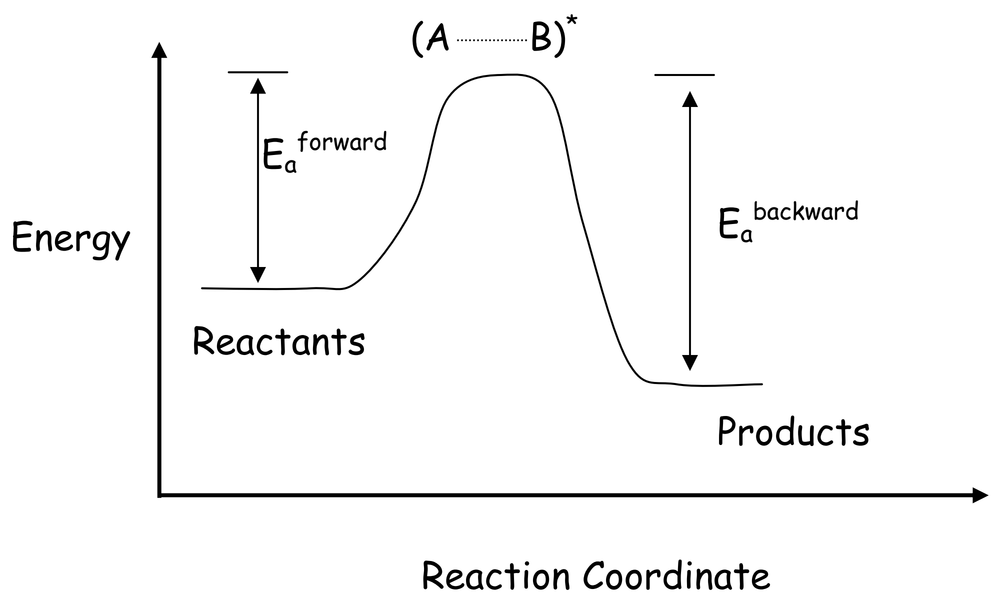
A (unimolecular) ~ 10^{12}–10^{15} sec^{-1}
(bimoledular) ~ 10^{11} liter/(mole sec)

Physical Interpretation of E_a

Consider $A + B \rightarrow C$

$A \rightarrow \; \leftarrow B \quad \Rightarrow \quad (A \cdots\cdots B)^* \quad \Rightarrow \quad C$

Reactants Activated Complex Product



Small E_a $\Rightarrow$ Weak T dependence $\Rightarrow$ Fast reaction

Large E_a $\Rightarrow$ Strong T dependence $\Rightarrow$ Slow reaction

Catalysis

A catalyst speeds up a reaction but is NOT destroyed or used up in the process

Consider $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$ (k_1, k_{-1}) both slow

Let C be a catalyst

$$A + C \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} B + C \qquad (k_2, k_{-2}) \text{ both fast}$$

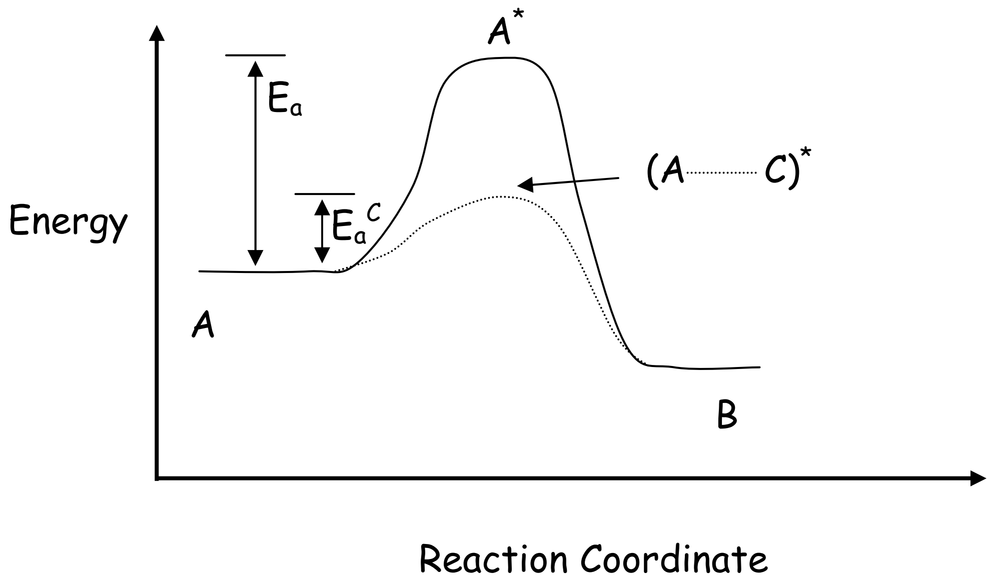
C acts to LOWER the E_a for the reaction, often altering the mechanism.

$$A \Rightarrow A^* \Rightarrow B$$

Uncatalyzed

$$A + C \Rightarrow (A \cdots C)^* \Rightarrow B + C$$

Catalyzed



The Equilibrium $K_{eq} = [B]_{eq}/[A]_{eq}$ is unaltered

Only the <u>rate</u> is changed through a lowering of E_a.