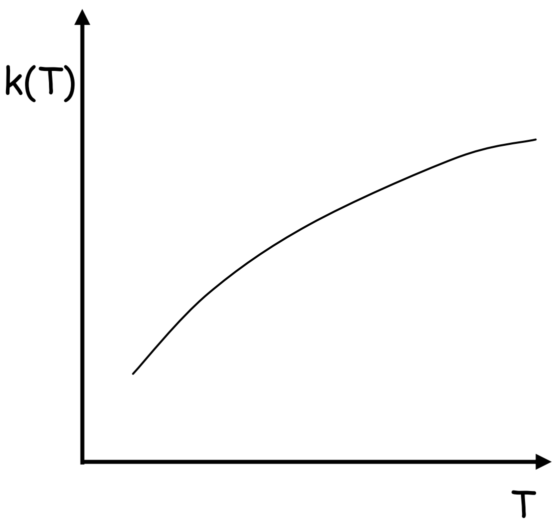
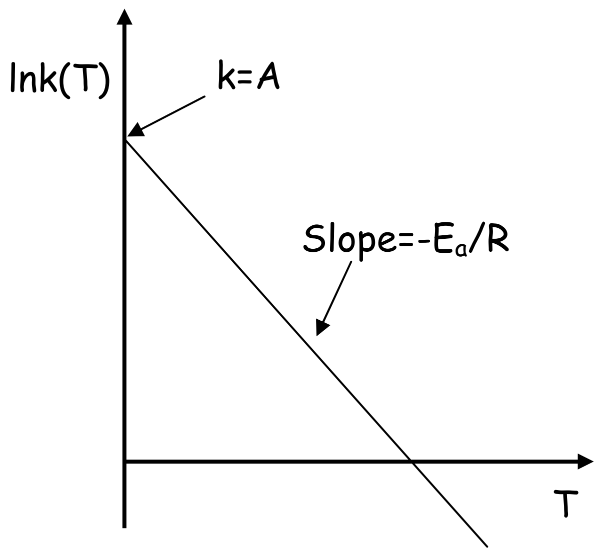
# Temperature Dependence of Rate Constant

## 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

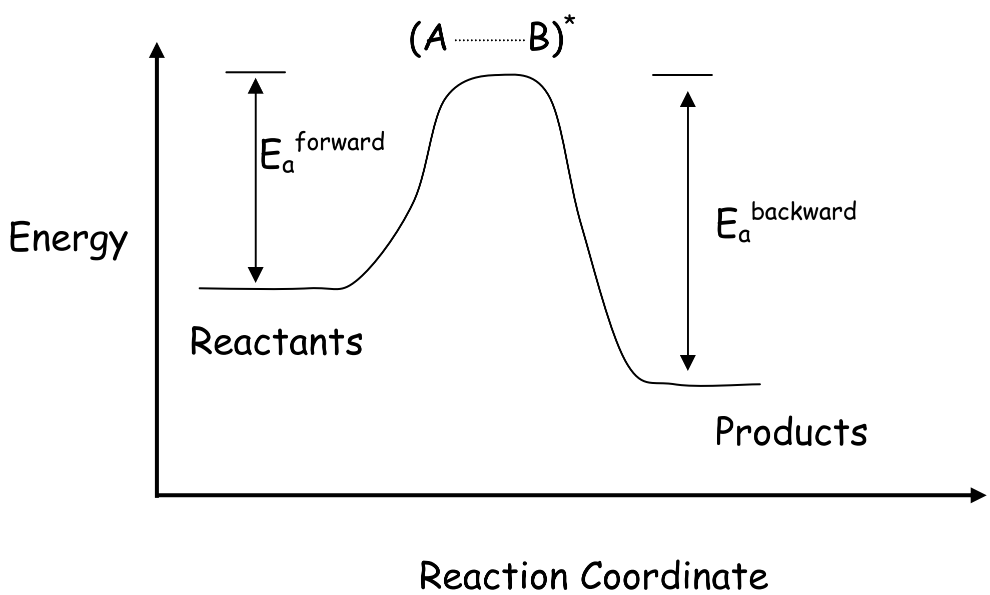
A (unimolecular) ~ $10^{12}$–$10^{15}$ $sec^{-1}$
(bimoledular) ~ $10^{11}$ liter/(mole sec)

## 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

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

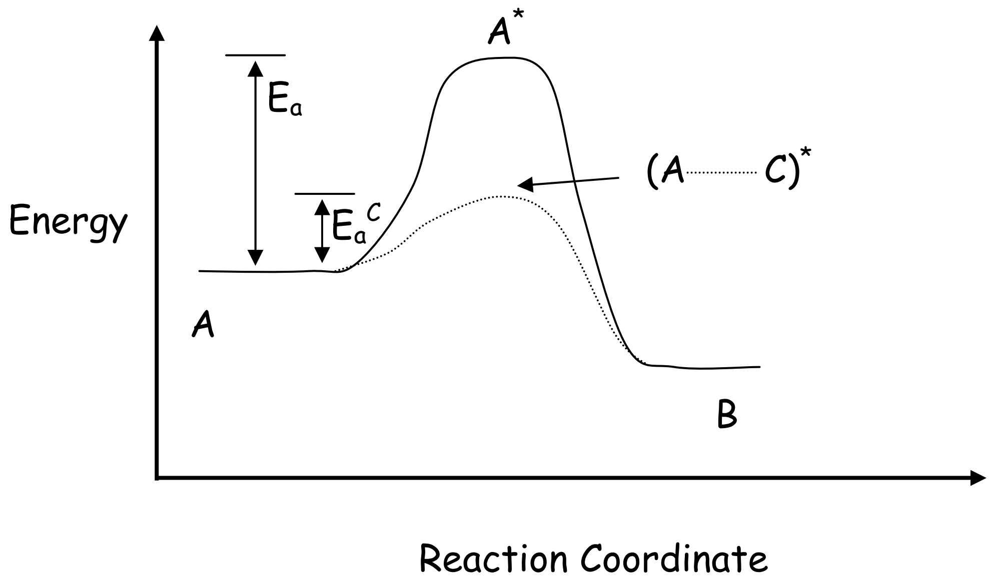
C acts to LOWER the $E_a$ for the reaction, often altering the mechanism.

$A \Rightarrow A^* \Rightarrow B$

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 $E_a$.