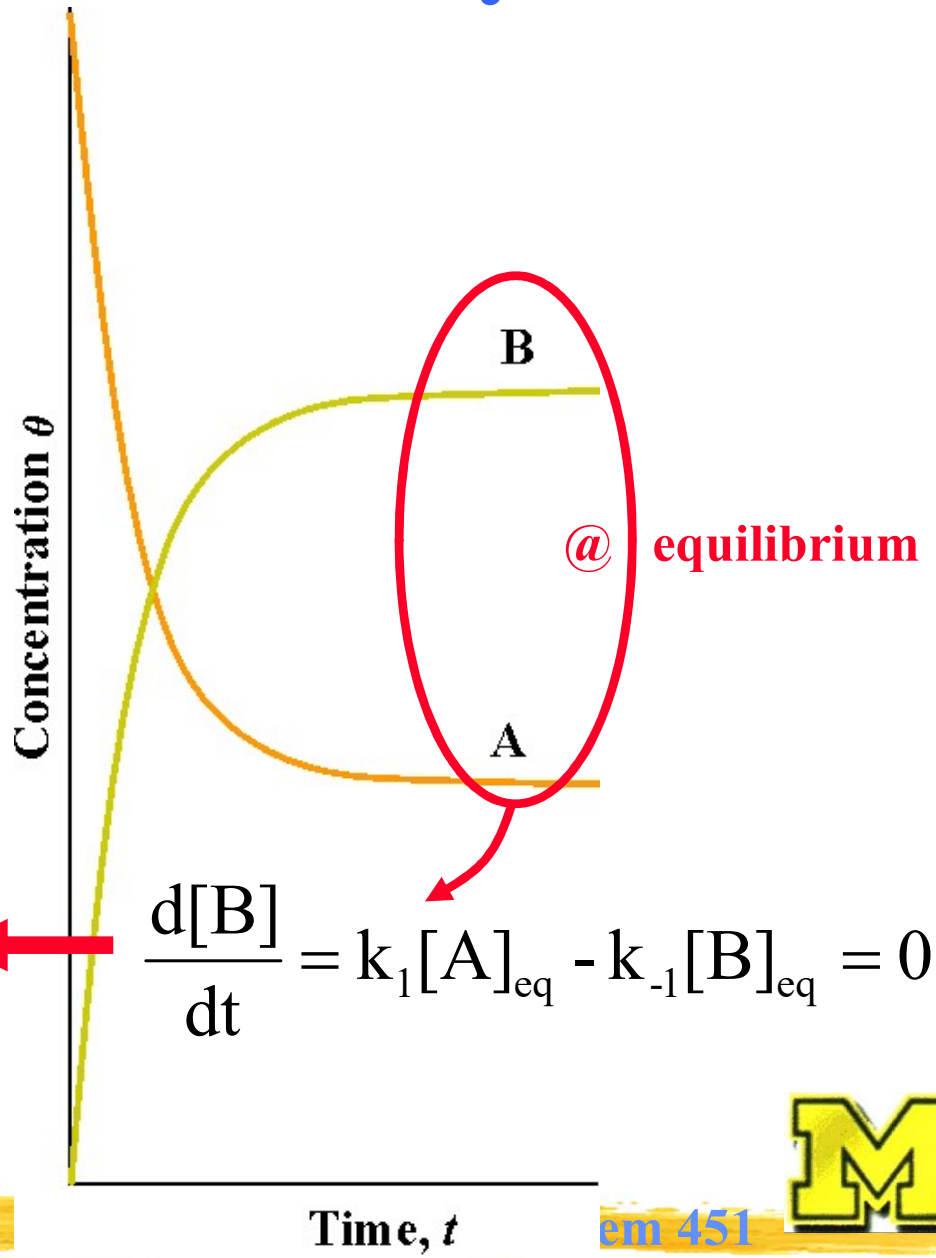
# Reaching equilibrium: Connection between kinetics and thermodynamics

**Reversible reaction A** $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ **B**

$$\Rightarrow \frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$$

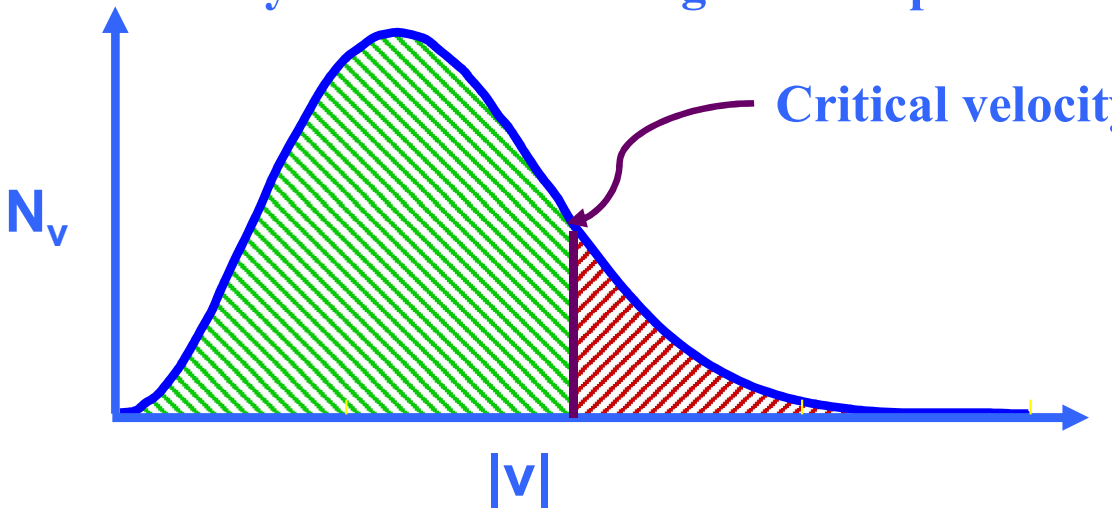


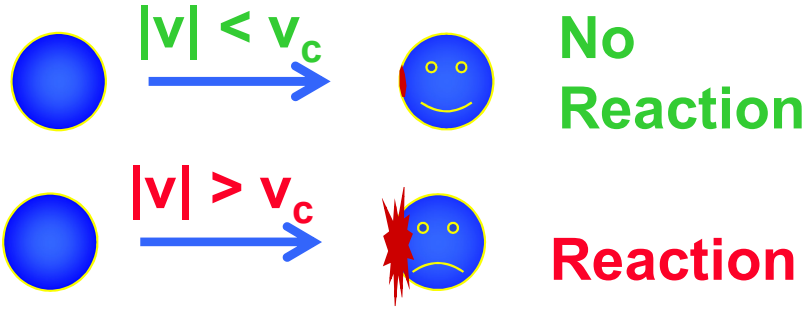

$$\frac{d[B]}{dt} = k_1[A]_{eq} - k_{-1}[B]_{eq} = 0$$

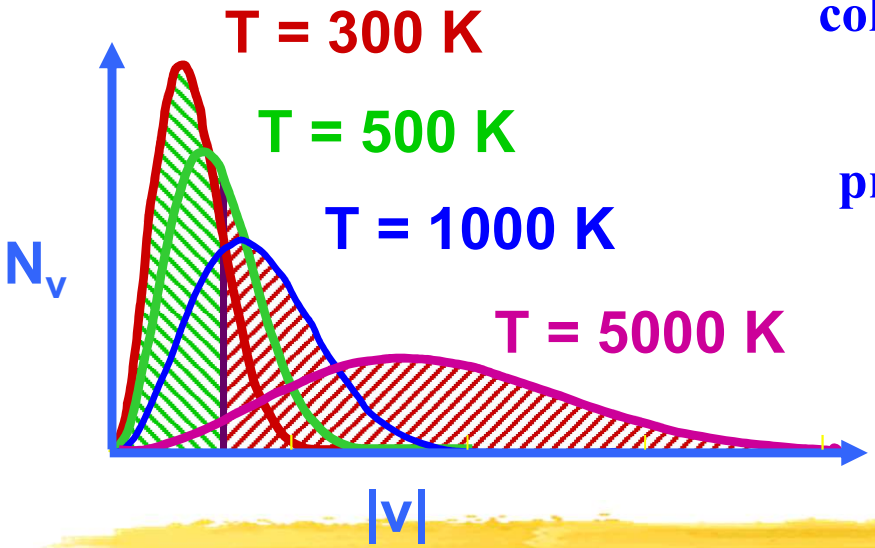
$$\frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}} = K$$

# Temperature dependence of the reaction rate constant

Maxwell velocity distribution of a gas at temperature T




**The minimum energy that must be supplied by a collision as $E_{kin}$ ($= {}^1/_2 mv^2$) per mole reaction is the activation energy $E_a$ [kJ/mol]**

pre-exponential factor

$$k = A_\infty \, e^{-E_a/RT}$$

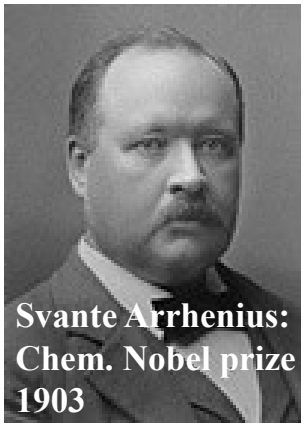
Rate constant

Population with $E_a$ sufficient to drive the reaction

# The Arrhenius equation

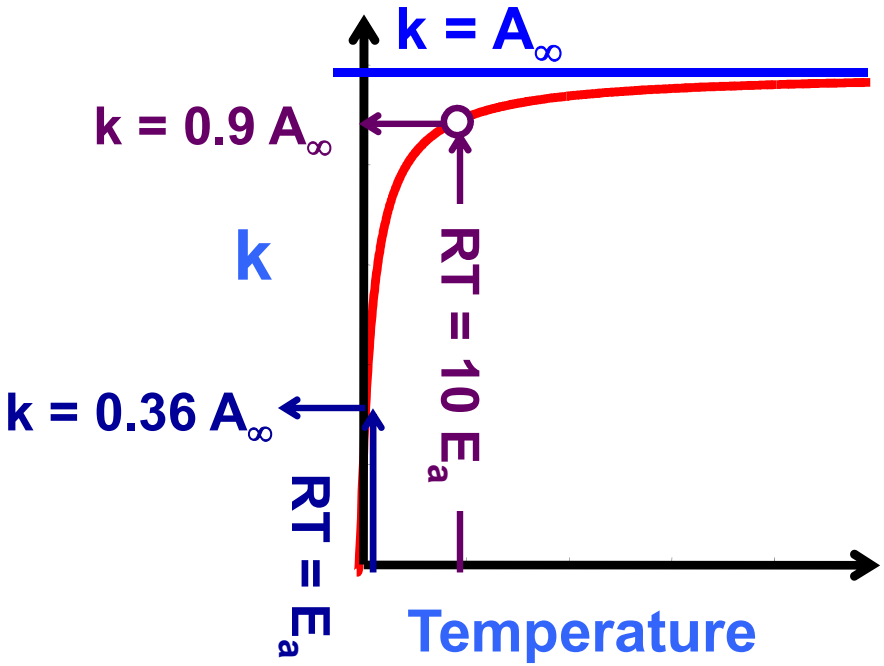
$k = A_\infty e^{-E_a/RT}$

$A_\infty$ = maximum possible rate at infinite temperature

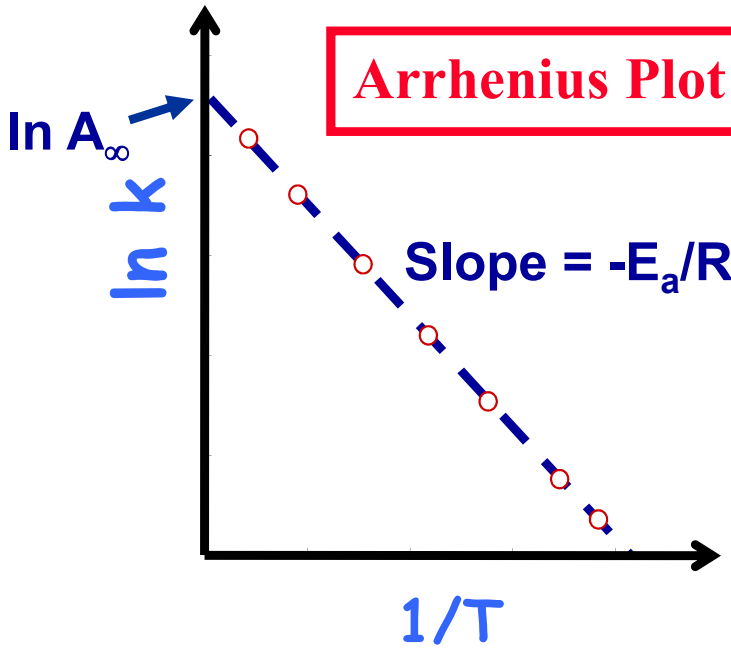



$$\Rightarrow \ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A_\infty$$

**A plot of ln k vs 1/T will be linear!**



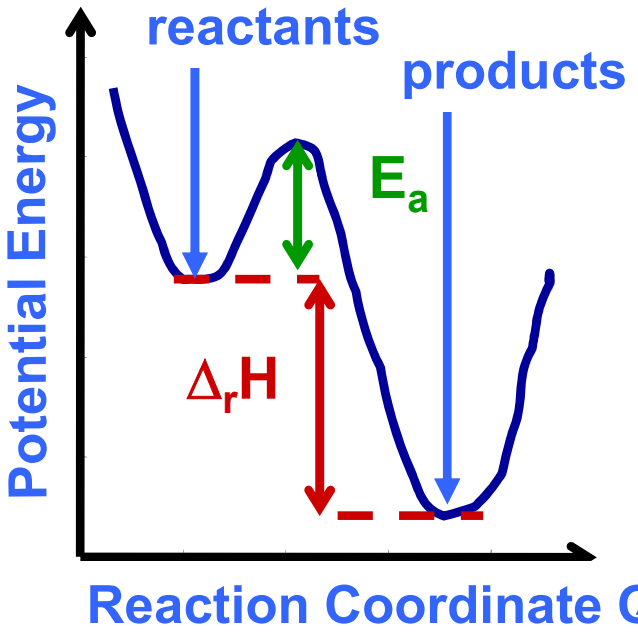

**Arrhenius Plot**



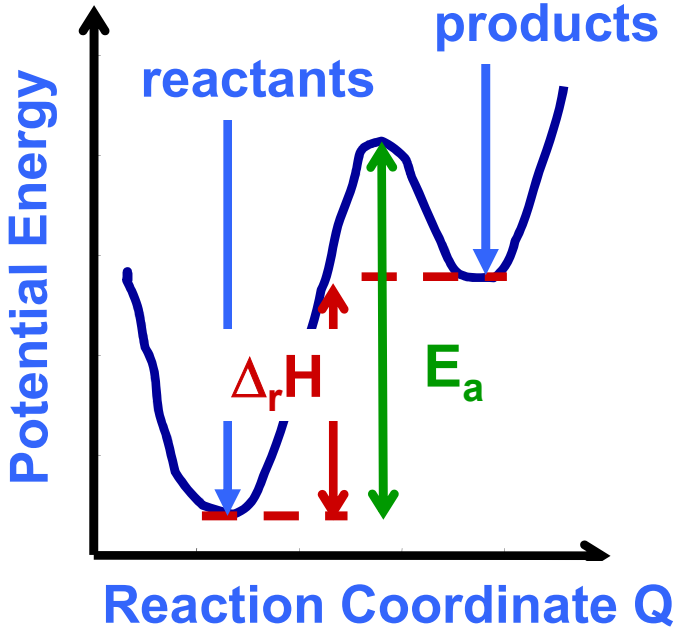

**Activation energies are determined experimentally by measuring the rate over as large a range of T as possible**

# Typical activation energies

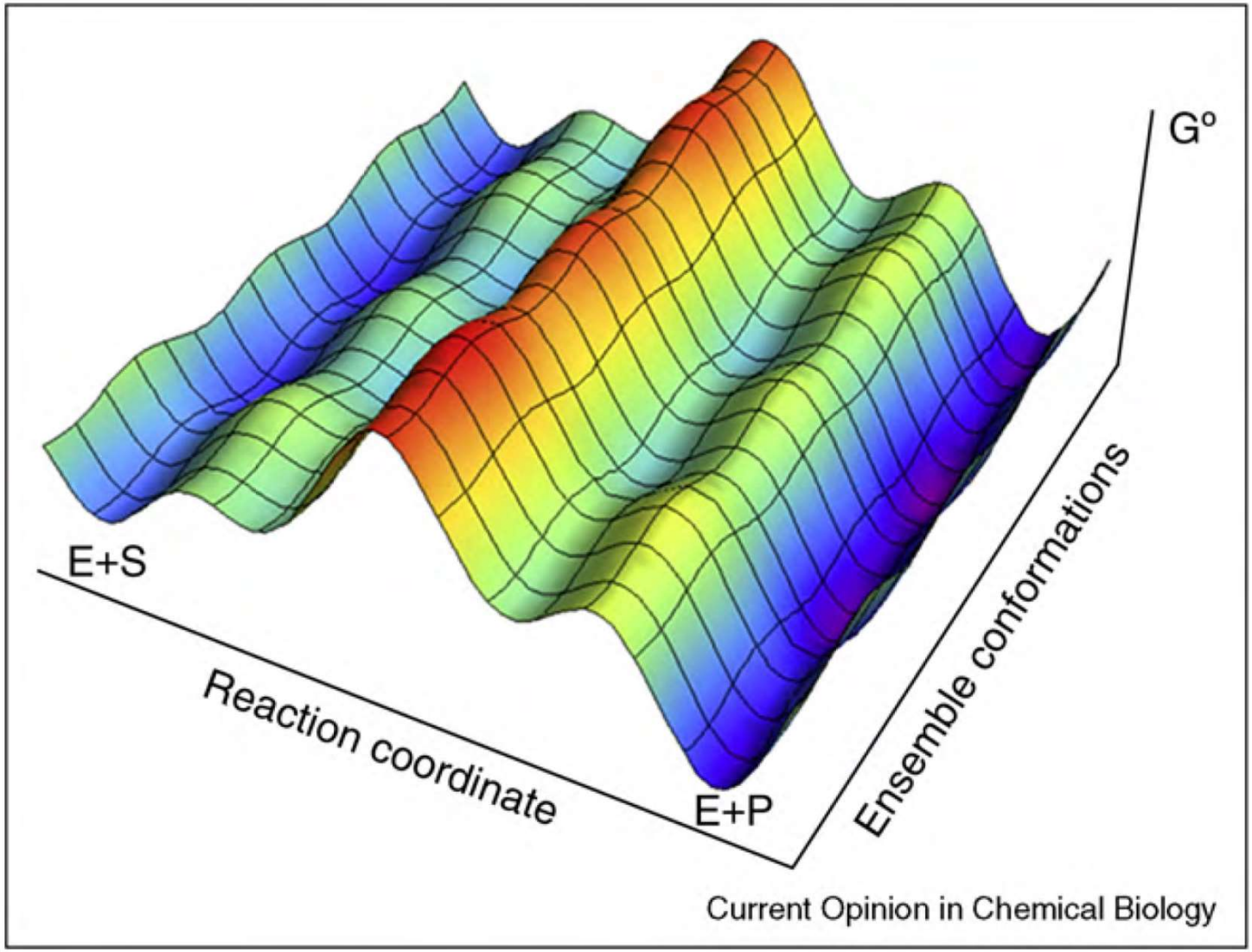
**An exothermic reaction will occur rapidly if $E_a < RT$ and only slowly if $E_a >> RT$**




**An endothermic reaction will normally have a large activation energy, $E_a$**



# Factoring in the multitude of enzyme conformations






Nashine, V.C., Hammes-Schiffer, S. and Benkovic, S.J. *Curr. Opin. Chem. Biol.* 14 (2010) 644-651

# Applying our knowledge to enzymes: Invertase (β-fructofuranosidase)