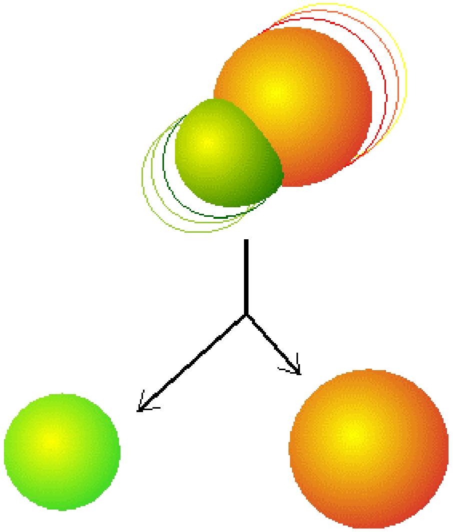
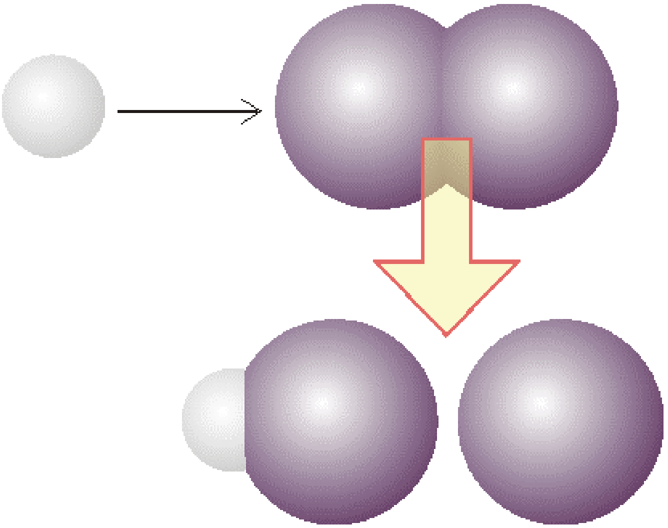
For elementary reaction steps the rate law can be inferred



unimolecular elementary step

A → products

$$\textbf{Rate} = -\frac{d[A]}{dt} = k[A]$$



bimolecular elementary step

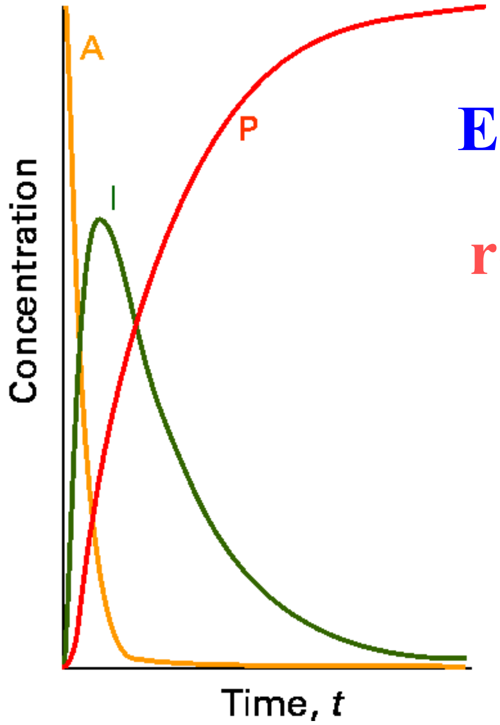
A + B → products

$$\textbf{Rate} = -\frac{d[A]}{dt} = k[A][B]$$

Molecularity: Number of particles coming together to react in an elementary step

An overall reaction often consists of consecutive elementary steps

A → I → P



Example: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Elementary steps: 1.) $2NO(g) \rightarrow N_2O_2(g)$

$$\frac{d[N_2O_2]}{dt} = k_1[NO]^2$$

reverse steps

2.) $N_2O_2(g) \rightarrow 2NO(g)$

$$-\frac{d[N_2O_2]}{dt} = k_{-1}[N_2O_2]$$

3.) $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$

$$-\frac{d[N_2O_2]}{dt} = k_2[N_2O_2][O_2]$$

and $-\frac{d[N_2O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$

problem: intermediate

$$\Rightarrow \boxed{\frac{d[NO_2]}{dt} = 2k_2[N_2O_2][O_2]}$$

The steady-state approximation

$$\frac{d[N_2O_2]}{dt} = k_1[NO]^2 \qquad -\frac{d[N_2O_2]}{dt} = k_{-1}[N_2O_2] \qquad -\frac{d[N_2O_2]}{dt} = k_2[N_2O_2][O_2]$$

Overall: $\Sigma =$ $\frac{d[N_2O_2]}{dt} = k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][O_2]$ **$= 0$**

Steady-state approximation =
[intermediate] remains small and constant

$$\Rightarrow [N_2O_2] = \frac{k_1[NO]^2}{k_{-1}+k_2[O_2]} \quad \textbf{and} \quad \frac{d[NO_2]}{dt} = 2k_2[N_2O_2][O_2]$$

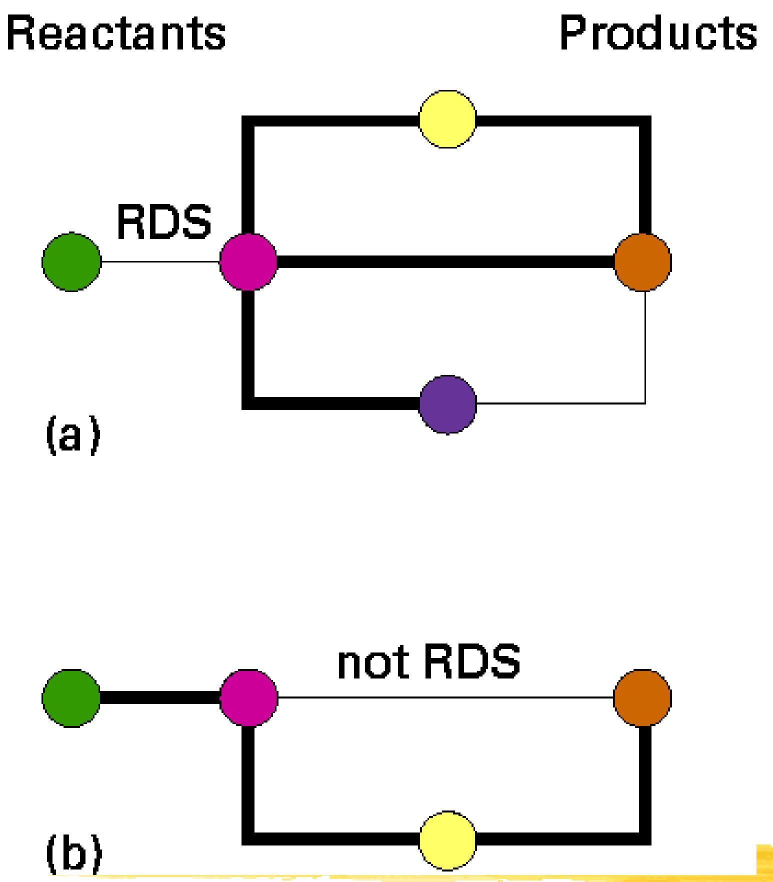
$$\Rightarrow \frac{d[NO_2]}{dt} = \frac{2k_1k_2[NO]^2[O_2]}{k_{-1}+k_2[O_2]}$$ **and** $k_{-1} \gg k_2[O_2]$ **2nd approximation**

$$\Rightarrow \frac{d[NO_2]}{dt} = \frac{2k_1k_2}{k_{-1}}[NO]^2[O_2] = \boxed{k[NO]^2[O_2]}$$

Indeed observed ⇒ the proposed reaction mechanism is correct!

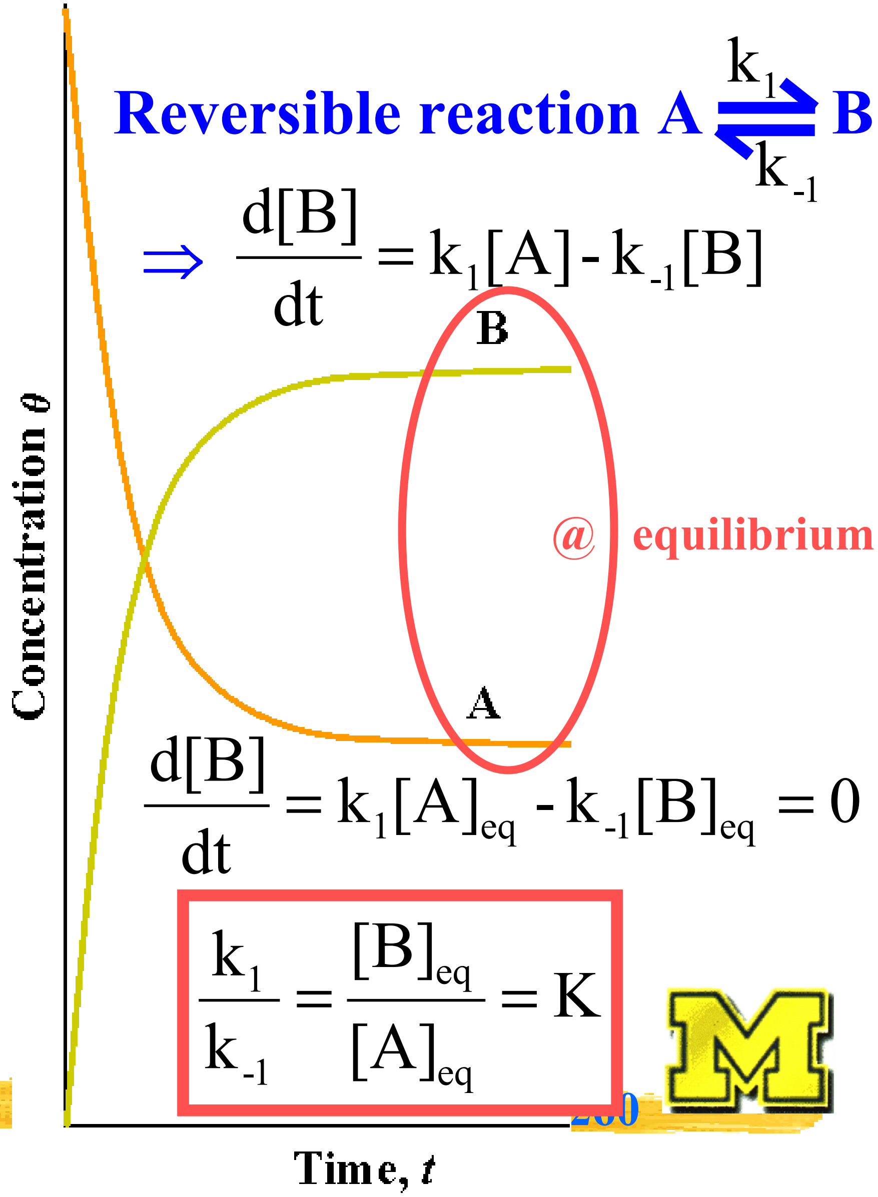
The rate-determining step (RDS) and reaching equilibrium

The RDS is the slow bottleneck in consecutive elementary steps



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

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

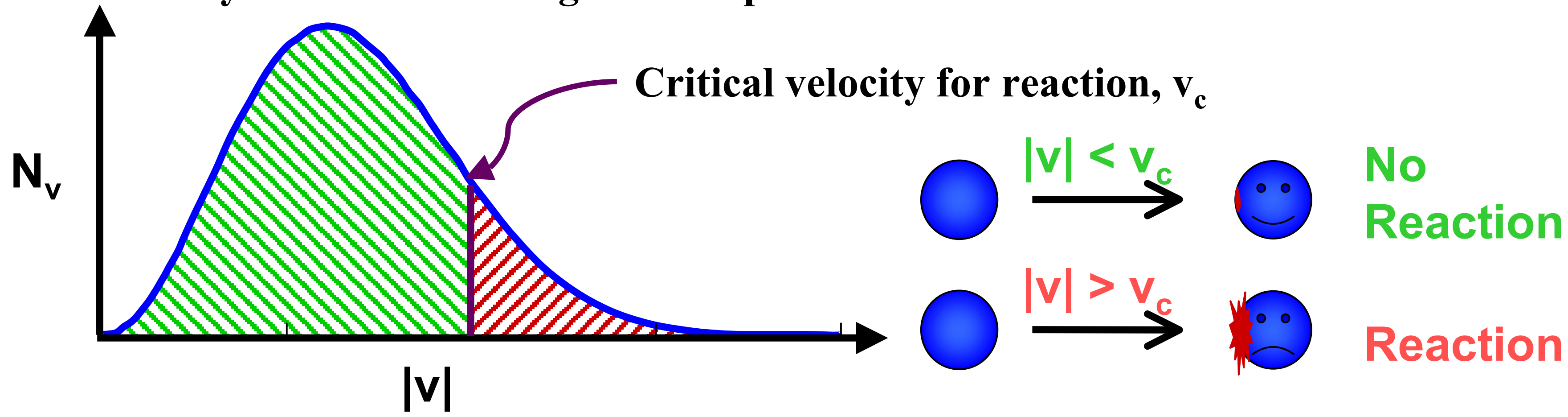


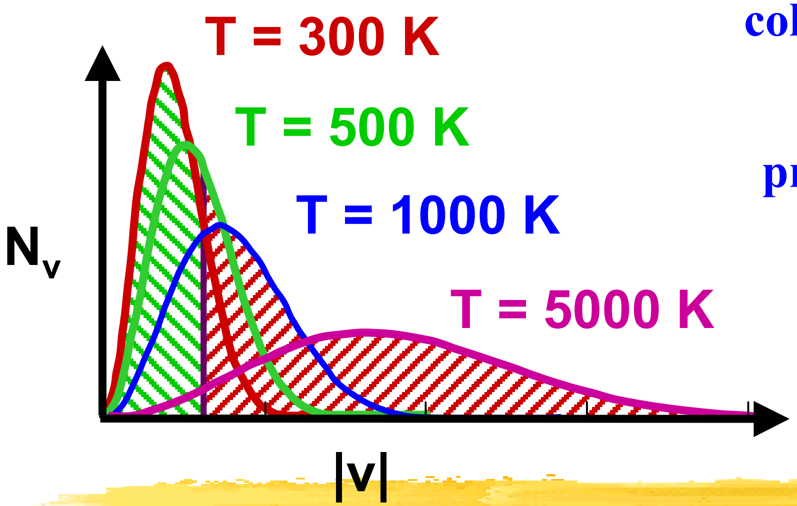
$$\frac{d[B]}{dt} = k_1[A]_{eq} - k_{-1}[B]_{eq} = 0$$

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

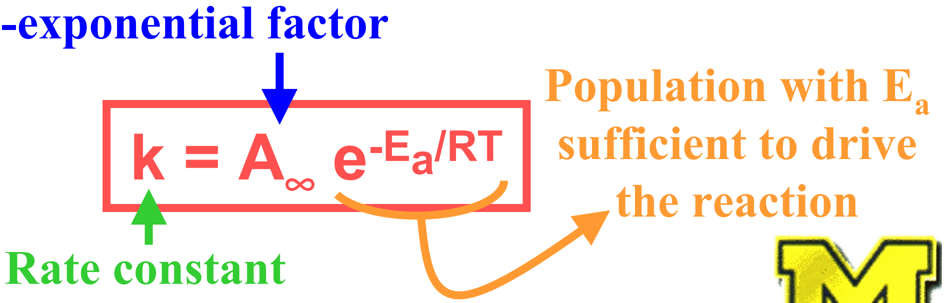
Temperature dependence of the reaction rate constant

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

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

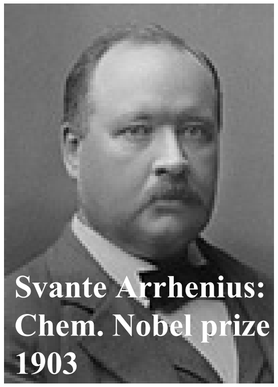
Rate constant

Population with E_a sufficient to drive the reaction

The Arrhenius equation

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

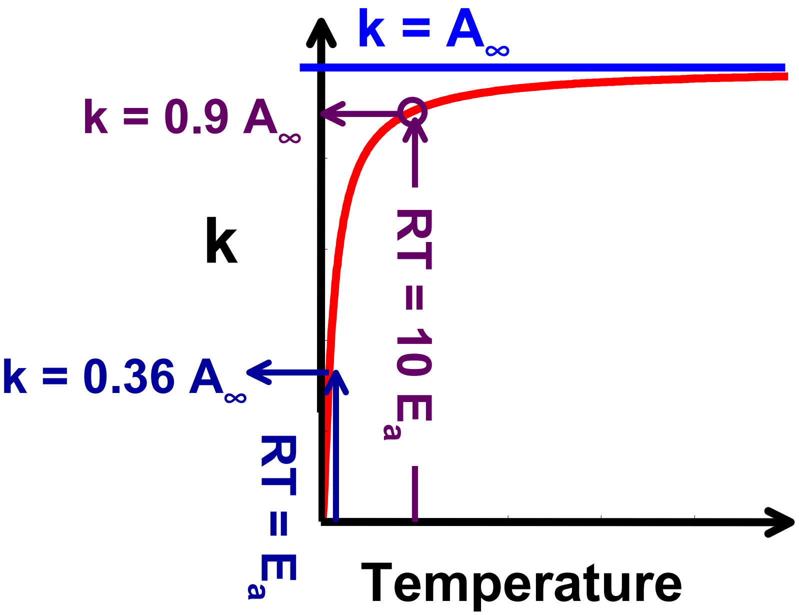
A_∞ = maximum possible rate at infinite temperature

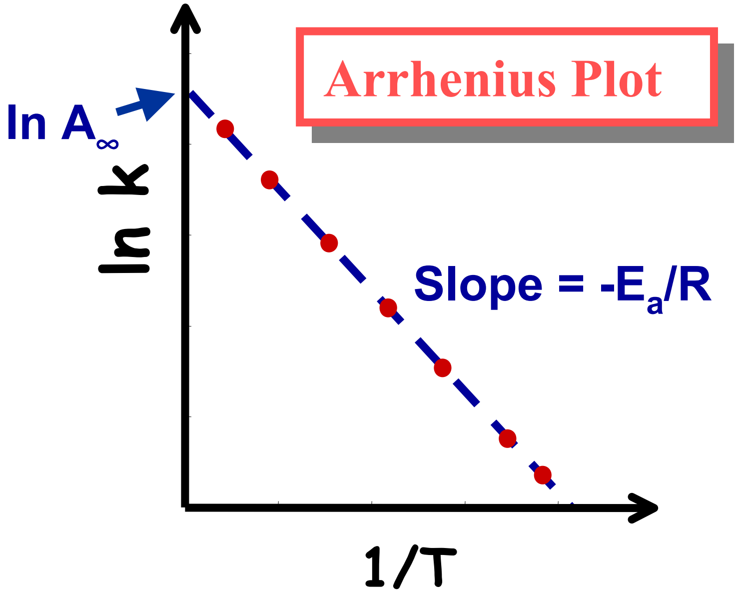


Svante Arrhenius: Chem. Nobel prize 1903

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

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

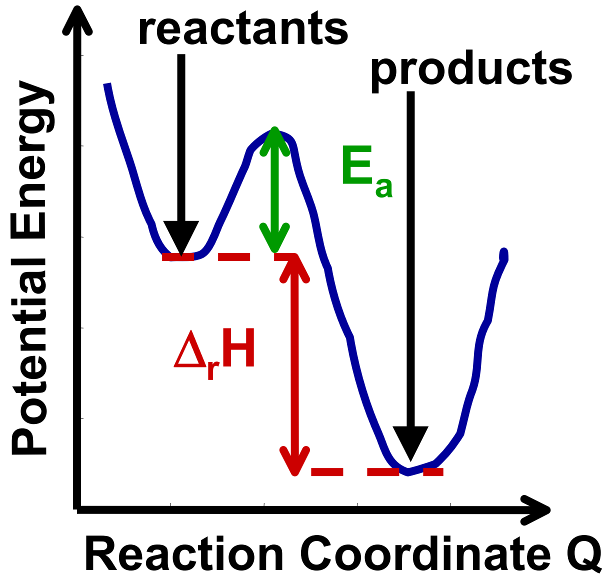




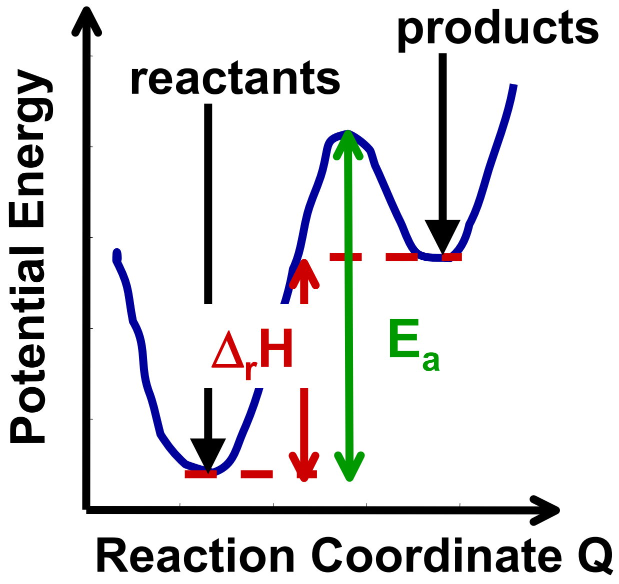
Activation energies are determined experimentally by measuring the rate over as large a range of T as possible

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



What is catalysis?

Consider: $2\ H_2O_2(l) \rightarrow 2\ H_2O\ (l) + O_2(g)$

$$\Delta_r G^{\ominus} = 2(-237.13) + 0 - 2(-120.35) = -233.56\ \text{kJ}$$

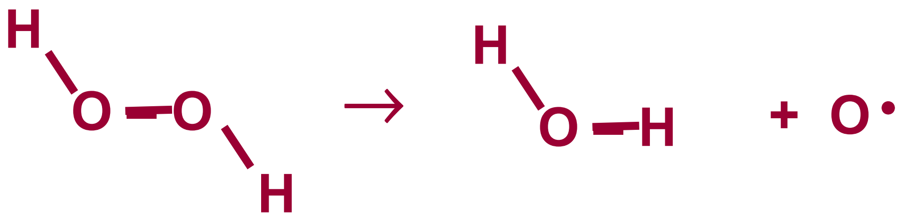
$$\Delta_r H^{\ominus} = 2(-285.83) + 0 - 2(-187.78) = -196.10\ \text{kJ}$$

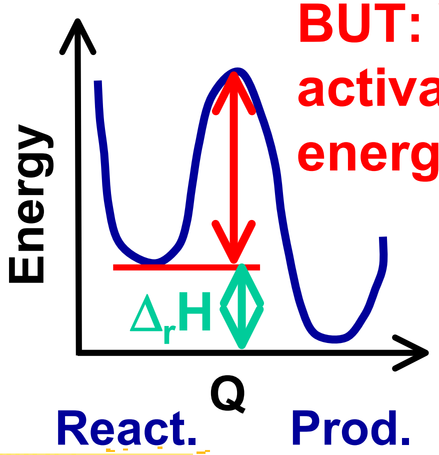
This reaction is exothermic and spontaneous!

In fact the equilibrium constant is huge:

$$K = e^{-\Delta_r G^{\ominus}/RT}$$

$$K = \exp\left[\frac{233.56 \times 10^3\ \text{J}}{8.31451\ \text{J K}^{-1} \times 298\ \text{K}}\right] = 1.15 \times 10^{41}$$





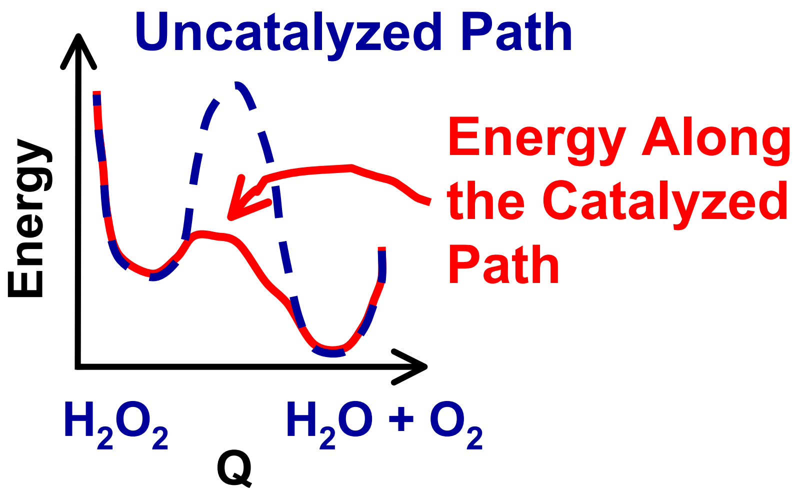
BUT: Very high activation energy ⇒ slow

Adding a catalyst

$$2\,H_2O_2(l) \xrightarrow{MnO_2} 2\,H_2O\,(l) + O_2(g)$$

Add MnO_2:
The reaction becomes very fast

MnO_2 acts as a catalyst – that is, it provides a mechanism with a much smaller activation energy



Initial and final states are unaffected by catalyst; but the nature of the reaction coordinate is changed, reducing E_a