Lecture Notes DD: Chemical Kinetics III

Distributed on Monday, April 17, 1999

1. Steady-state approximation

Consider the reaction:

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

Consider the following proposed mechanism

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad \text{(slow)}$$

$$N_2O_2 + O_2 \xrightarrow{k_2} NO_2 + NO_2 \qquad \text{(fast)}$$

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad \text{(fast equilbrium)}$$

$$N_2O_2 + O_2 \xrightarrow{k_2} NO_2 + NO_2 \qquad \text{(slow)}$$

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad \text{(fast)}$$

$$N_2O_2 + O_2 \xrightarrow{k_2} NO_2 + NO_2 \qquad \text{(fast)}$$

2. Michaelis-Menton equation

$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$ S= Substrate P=Product E=enzyme

$ES \xrightarrow{k_2} E + P$

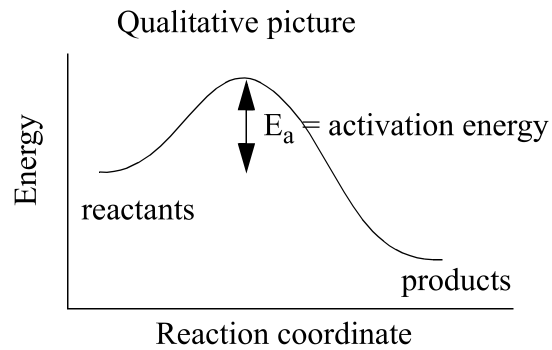
3. Activation energy

For many reactions (especially single-step) reactions, the temperature dependence of the rate constant is given by the Arrhenius expression,

$$k = Ae^{-\frac{E_a}{RT}}$$

A = prefactor

E_a = Arrhenius activation energy



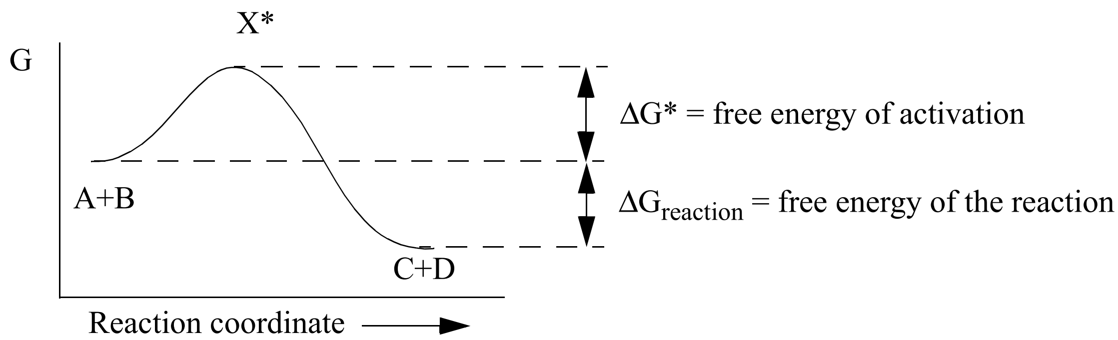
Arrhenius plot

At room temperature (25^{o}C), to raise the rate by a factor of 10, what must I do to the activation energy?

4. Transition State Theory

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^* \qquad \text{(fast equilibrium)}$$

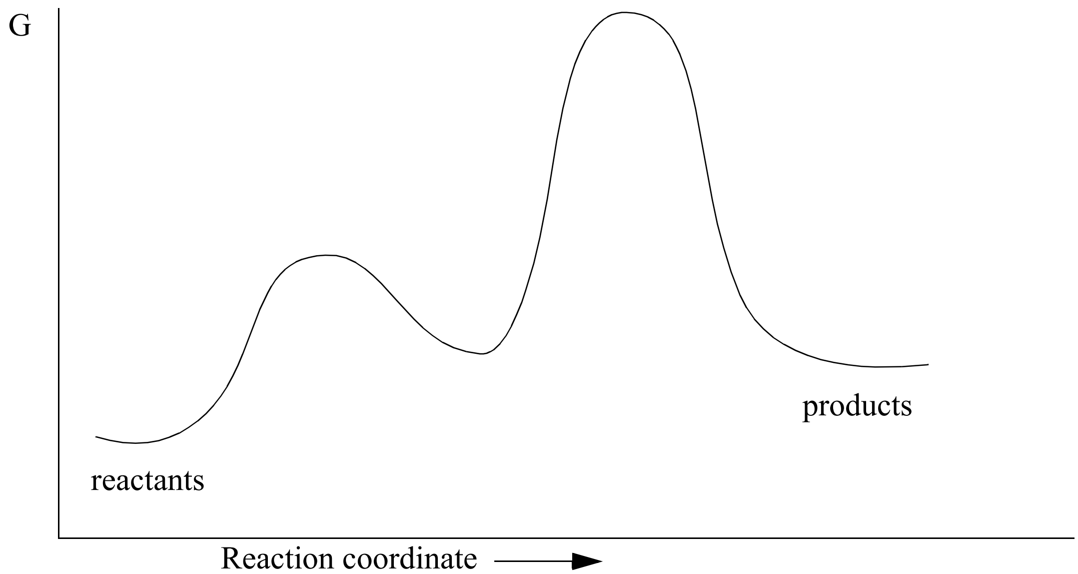
$$X^* \xrightarrow{k'} C+D$$ (slow) decomposition of the transition state to form products is rate limiting step



$$K = e^{-\frac{\Delta G_{reaction}}{RT}} \qquad k = k'e^{-\frac{\Delta G^*}{RT}}$$ k' has a weak temperature dependence

5. Concept test:

The following shows the free energy along the pathway for some reaction



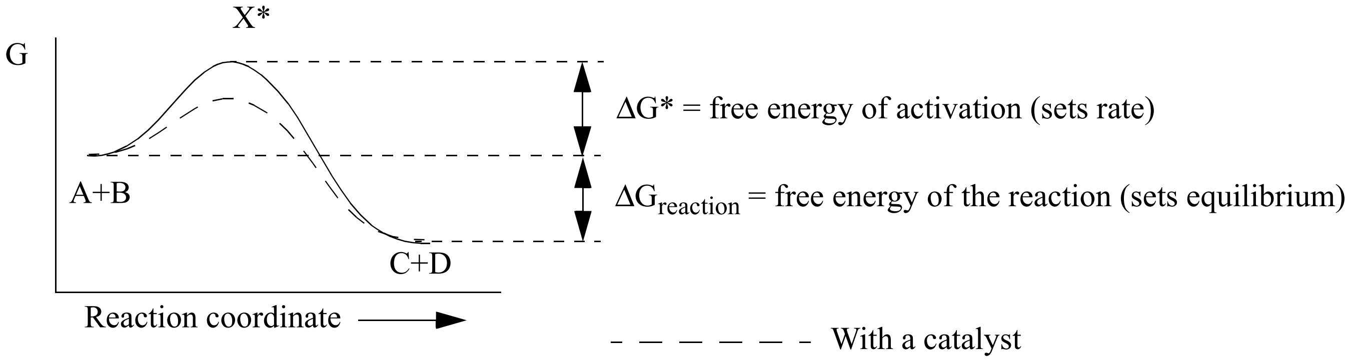
a) How many elementary steps are in this reaction: a) 0 b) 1 c) 2 d) 3

b) How many intermediates are in this reaction : a) 0 b) 1 c) 2 d) 3

c) What is the rate limiting step for this reaction?

d) Is this reaction spontaneous: a) yes b) no

6. Catalysis

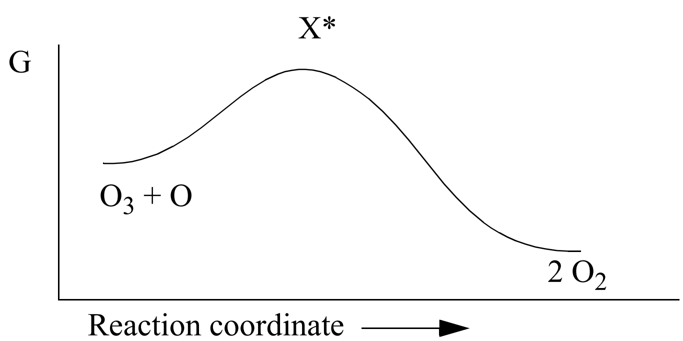


As we discussed earlier, the following is proposed as a mechanism for the “catalytic” destruction of ozone.

$Cl + O_3$ -- > $ClO + O_2$
$ClO + O$ --> $Cl + O_2$

$O_3 + O$ ---> $2\ O_2$

How would this look in terms of the above diagram for catalysis



Some enzymes catalyze a reaction by orienting the reactants in a way that makes them more likely to react. How do you think this catalytic mechanism appears in the above framework?

7. Surface Catalysis

Hydrogenation of ethylene

C_2H_4 + H_2 ---> C_2H_6