# 5.111 Principles of Chemical Science
Fall 2008

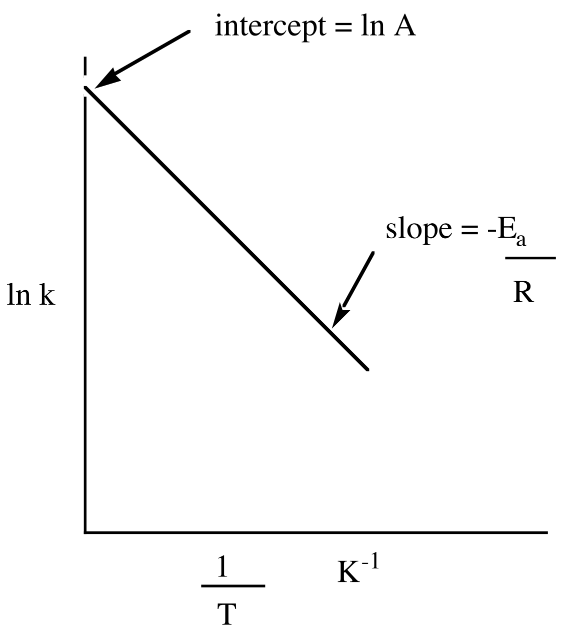
5.111 Lecture 34
Kinetics Topics: Effect of Temperature, Collision Theory, Activated Complex Theory.
Chapter 13.11-13.13

## Effect of Temperature on Reaction Rates

### Gas-Phase

A qualitative observation is that reaction rates tend to increase with increased temperature. Now we will consider the quantitative effect.

In 1889, Svante Arrhenius plotted rate constants (k) versus temperature. He found that plotting ln k versus inverse temperature gave a straight line.



k = rate constant

T = temperature

A = factor A or pre-exponential factor (same units as k)

$E_a$ = activation energy

R = gas constant

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$y \;=\; mx \;+ b$$

Rate constants vary ____________________ with inverse temperature

A and $E_a$ depend on the reaction being studied.

Is factor A temperature dependent?

Is $E_a$ temperature dependent?

$\ln k = \frac{-E_a}{RT} + \ln A$ can also be written $\boxed{\ln k = \ln A - \frac{E_a}{RT}}$ Arrhenius equation

or $\boxed{k = Ae^{-E_a/RT}}$

<u>What is $E_a$, activation energy?</u>

Consider $CH_3\,(g) + CH_3\,(g) \rightarrow C_2H_6\,(g)$

2 molecules collide to form product (bimolecular) but every two molecules that collide won't form product. Why?

Only those collisions for which the collision energy exceeds some critical energy

(_________________ energy) result in a reaction.

At low temperatures, a small fraction will have this much energy.

At higher temperatures, a larger fraction will have this much energy.

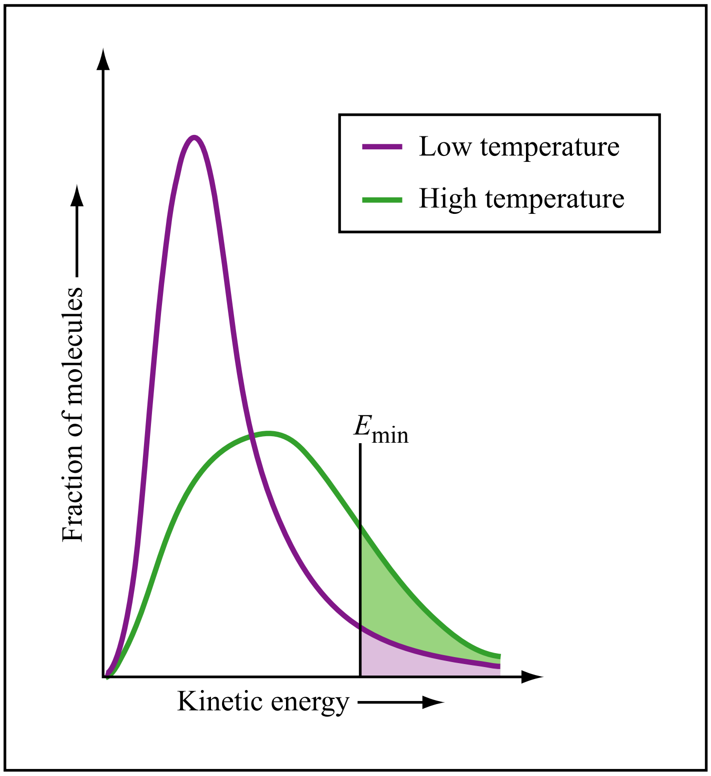


Figure by MIT OpenCourseWare.

Example: Using the activation energy to predict a rate constant

The hydrolysis of sucrose to form a molecule of glucose and a molecule of fructose is part of the digestive process.

$E_a$ = 108 kJ/mol
$k_{obs} = 1.0 \times 10^{-3}\ M^{-1}s^{-1}$ at 37°C (normal body temperature)

What is $k_{obs}$ at 35°C?

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \qquad \ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln k_2 - \ln k_1 = \ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_2}{1.0 \times 10^{-3}\ M^{-1}\ s^{-1}}\right) = \frac{-108 \times 10^3\ J\ mol^{-1}}{8.315\ JK^{-1}\ mol^{-1}}\left(\frac{1}{308K} - \frac{1}{310\ K}\right)$$

$$k_2 = 7.6 \times 10^{-4}\ M^{-1}\ s^{-1}$$

A large activation energy means that the rate constant is ________ sensitive to changes in temperature.

What do you think happens to the rate of an enzymatic reaction at liquid $N_2$ temperatures?

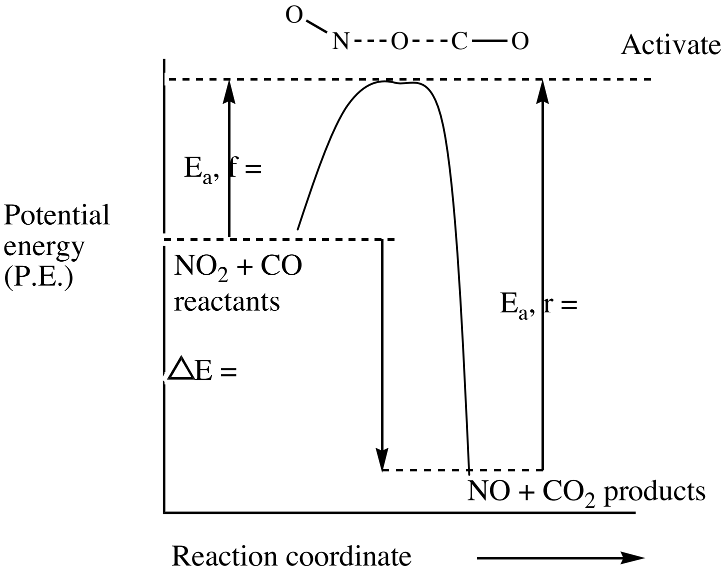
<u>The Reaction Coordinate and the Activation Complex</u>

Why is there a critical collision energy, $E_a$, for the reaction between two molecules?

As two reactant molecules approach each other along a reaction path, their potential energy increases as the bonds within them distort. The encounter results in the formation of an activated complex or transition state, a combination of molecules that can either go on to form products or fall apart again into unchanged reactants.

Only molecules with sufficient energy can overcome the activation energy barrier.

Example $NO_2\,(g) + CO\,(g) \rightleftharpoons NO\,(g) + CO_2\,(g)$



$\Delta E = E_a, f - E_a, r$

change in internal energy

$E_a$ for forward reaction

$E_a$ for reverse reaction

thermodynamic quantity
calorimetric measurements

Recall from Lecture #17, $\Delta H = \Delta E + \Delta(PV)$

For gases, these quantities differ by 1-2% and for liquids and solids, there is a negligible difference.

For elementary reactions, the activation energy barrier is always positive (some barrier to overcome).

Therefore increasing the temperature __________________the rate of an elementary reaction.

<u>For overall reactions, increasing temperature can decrease or increase the overall rate.</u>

<u>Example</u> $2NO + O_2 \rightarrow 2NO_2$ with proposed mechanism:

1st step
(Fast, reversible)

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

2nd step
slow

$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$$

rate of product formation = $2k_2\,\underset{\substack{\uparrow\\ \text{intermediate}}}{[N_2O_2]}\,[O_2]$

Since first step is fast and reversible and the second step is slow, we can solve for $[N_2O_2]$ by setting up an equilibrium expression:

$K_1 =$ $[N_2O_2] =$

Substituting:

rate of product formation $= 2k_2 [N_2O_2] [O_2] =$

$$\text{rate} = 2k_2K_1 [NO]^2 [O_2]$$

| $k_2$ | $K_1$ |
|---|---|
| elementary rate constant | equilibrium constant |
| rate increases with temperature | effect of temperature on an equilibrium constant depends on whether the reaction is endothermic or exothermic |

Here the reaction is exothermic, so increasing temperature ___________the equilibrium constant

$k_{obs} = 2k_2K_1$ with increased temperature / the rate constant increases and the equilibrium constant decreases

(Magnitude of change depends on $E_a$ (for rate constant) and $\Delta H$ (for equilibrium constant.)

For $2NO + O_2 \rightleftharpoons 2NO_2$, $E_a$ is a small number and $\Delta H$ is a big number

Since $E_a$ is small, the rate constant increases only a little

Since $\Delta H$ is big, the equilibrium constant decreases a lot with temperature

Thus, increasing the temperature actually decreases $k_{obs}$.

$$\ln\left[\frac{k_{Temp2}}{k_{Temp1}}\right] = \frac{-E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \ln\left[\frac{K_{Temp2}}{K_{Temp1}}\right] = \frac{-\Delta H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

A large $E_a$ means that k is very sensitive to changes in temperature.

A large $\Delta H$ means that K is very sensitive to changes in temperature.

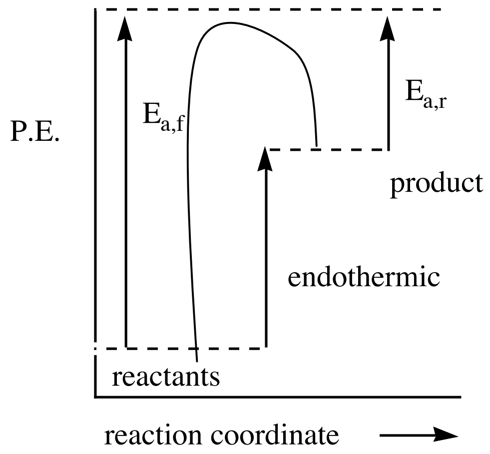
Rate constants always increase with temperature, since $E_a$ is always ______________.

Equilibrium constants can increase or decrease with temperature, since $\Delta H$ can be (-) or (+).

The magnitude of $\Delta H$ indicates the magnitude of the change, and the sign of $\Delta H$ indicates the direction of the change.

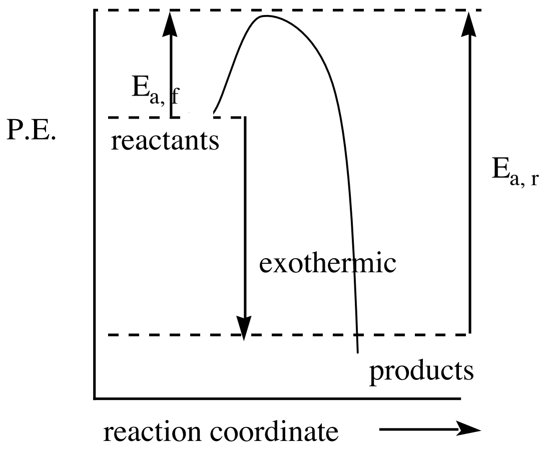
Le Chatelier's Principle - when a stress is applied to a system in equilibrium, the equilibrium tends to adjust to _____________the effect of the stress.

Increasing the temperature...



$\Delta E = E_{a,f} - E_{a,r}$
+ (endo) = big number - small number

increase temperature, easier to overcome $E_{a,f}$. Equilibrium shifts toward products for endothermic reaction.



$\Delta E = E_{a,f} - E_{a,r}$
- (exo) = small number - large number

increase temperature, easier to overcome $E_{a,r}$. Equilibrium shifts toward reactants in the exothermic reaction.

most molecules have enough energy to overcome small barriers
increasing temperature allows more molecules to overcome larger barriers

Recall, a large $E_a$ means that the rate constant is very sensitive to changes in temperature.

Big $E_a$ - increasing the temperature makes a ________ difference

Small $E_a$ - increasing the temperature does not make much of a difference.