5.111 Lecture Summary #33 **Wednesday, December 3, 2014**

Reading for Today: 14.11-14.13 in 5^{th} ed and 13.11-13.13 in 4^{th} ed
Reading for Lecture #34: 14.14 & 14.16 in 5^{th} ed and 13.14 & 13.16 in 4^{th} ed

---

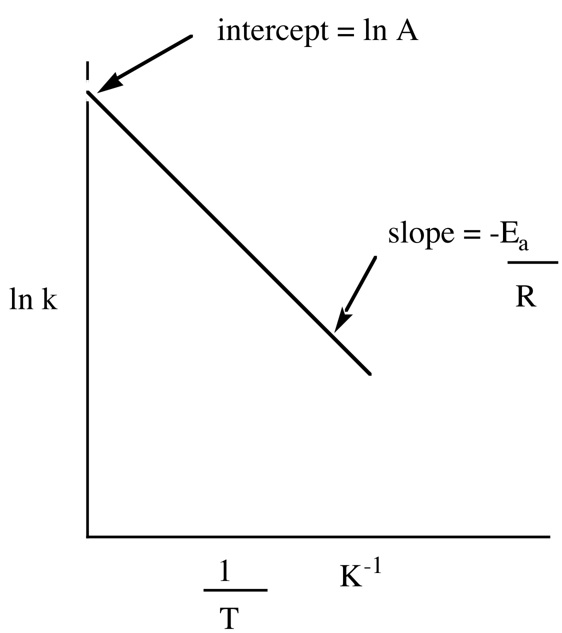
Topic: Kinetics
I. Effect of Temperature on Reactions Rates
II. The Reaction Coordinate and the Activation Complex

I. Effect of Temperature on Reaction Rates

Gas-Phase

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

In 1889, Svante Arrhenius plotted ln k versus inverse temperature and got 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

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

$$y \quad = \quad mx \quad + b$$

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

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)

Calculate k_{obs} at 35°C.

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

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

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

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

Equation to relate change in T to change in k

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

What about the rate of a non-enzymatic reaction at liquid N_2 temperatures?

II. The Reaction Coordinate and the Activation Complex

Consider CH_3 (g) + CH_3 (g) → 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 (E_{min}) (also known as ______________________ energy, E_a) result in a reaction.

Why is there a critical collision energy, E_{min} or E_a, for the reaction between two molecules?

As two reactant molecules approach each other along a reaction path, their potential energy________________________ as the bonds within them distort.

The encounter results in the formation of an activated complex or ____________________, 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.

This is where temperature becomes important.

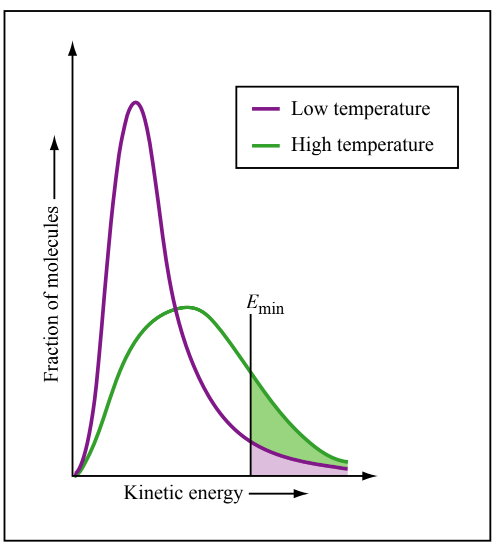


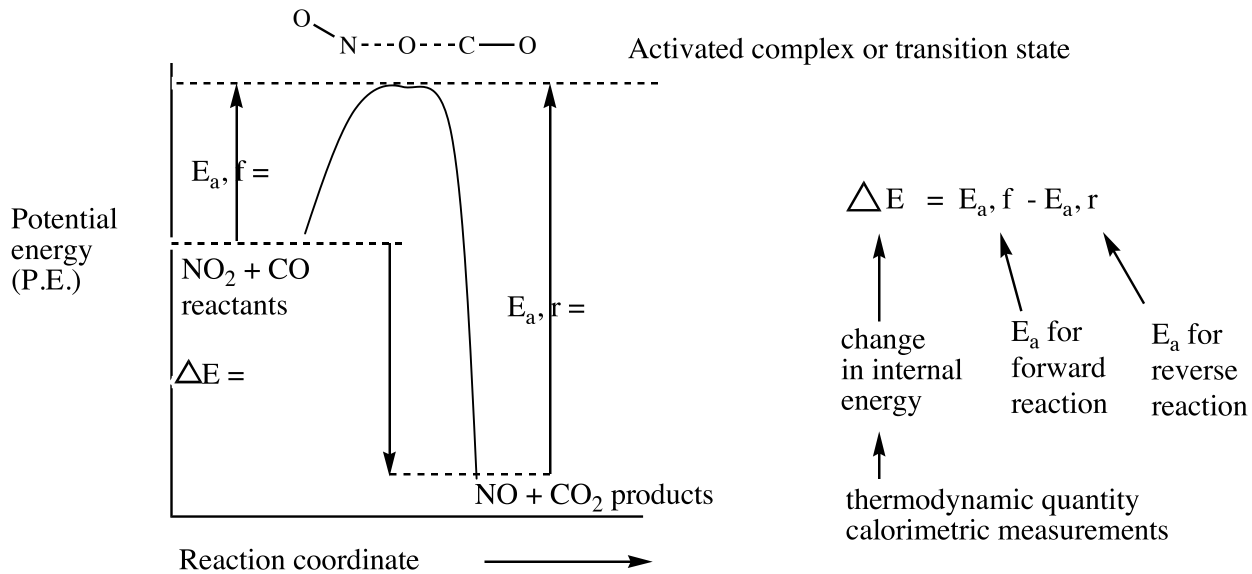
Figure by MIT OpenCourseWare.

At low temperatures, only a small fraction of molecules will have sufficient energy.

At higher temperatures, a larger fraction will have sufficient energy.

Reaction Coordination Diagrams

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



Recall $\Delta H = \Delta E + \Delta(PV)$

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.

For overall reactions, increasing temperature can decrease or increase the overall rate.

Example $2NO + O_2 \rightarrow 2NO_2$ 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 $= 2k_2\,[N_2O_2]\,[O_2]$

↑ intermediate ($[N_2O_2]$)

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 = $2k_2 [N_2O_2] [O_2]$ =

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

elementary rate constant (k_2) — rate increases with temperature

equilibrium constant (K_1) — effect of temperature on an equilibrium constant depends on whether the reaction is endothermic or exothermic

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

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

$k_{obs} = 2k_2K_1$ with increased temperature,
k increases (elementary rate constants always increase with T)
K ____________________(for exothermic reaction)

Magnitude of change depends on E_a (for rate constant) and ΔH (for equilibrium constant).

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

- Since E_a is a small positive, the rate constant increases only a little
- Since ΔH is a big negative, the equilibrium constant decreases a lot with temperature

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

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

A large ΔH means that K is very sensitive to changes in temperature.

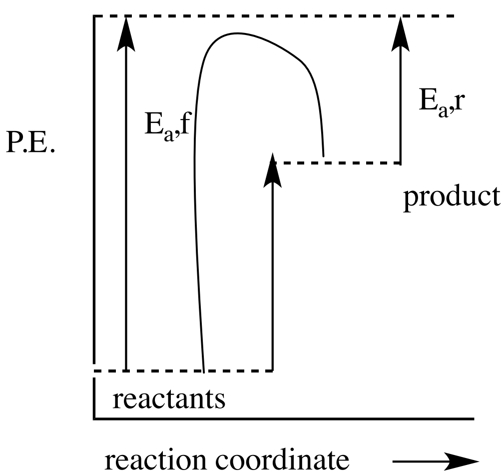
Rate constants always increase with temperature, since E_a is always _______________.

Equilibrium constants can increase or decrease with temperature, since ΔH can be (-) or (+).

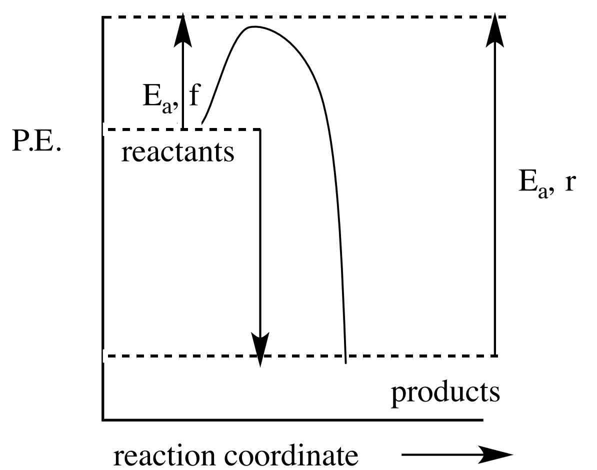
The magnitude of ΔH indicates the **magnitude** of the change, and the sign of ΔH indicates the ___________________ of the change.

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, shifts the reaction in the ________________________ direction.



$\Delta E = E_{a,f} - E_{a,r}$



$\Delta E = E_{a,f} - E_{a,r}$

Inc T, easier to overcome $E_{a,f}$
Equilibrium shifts toward products

Inc T, easier to overcome $E_{a,r}$
Equilibrium shifts toward reactants

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.