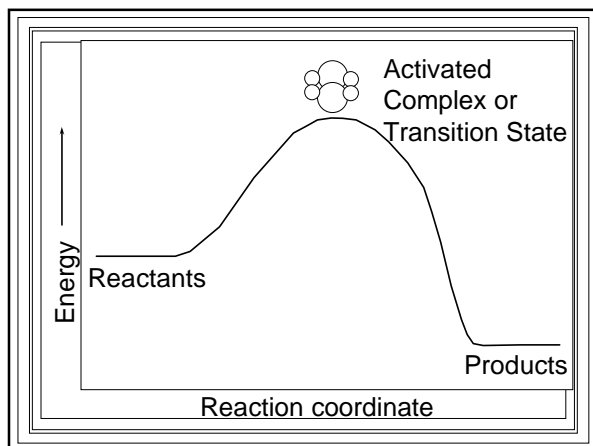
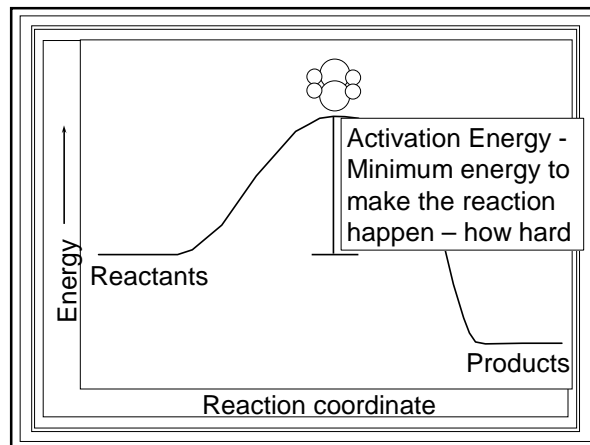
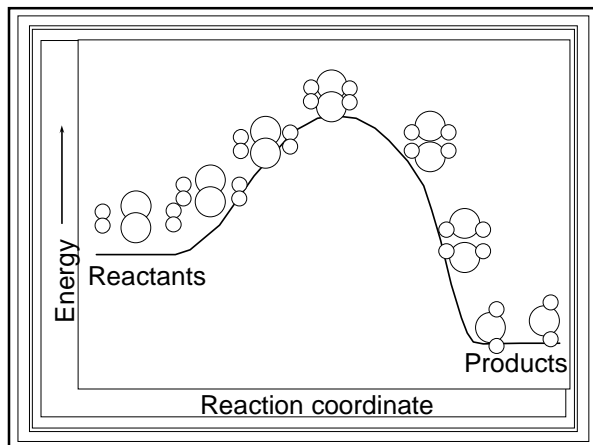


## Reaction Rate

How Fast Does the Reaction Go?

## Collision Theory

- In order to react molecules and atoms must touch each other.
- They must hit each other hard enough to react.
  - Must break bonds
- Anything that increases how often and how hard will make the reaction faster.

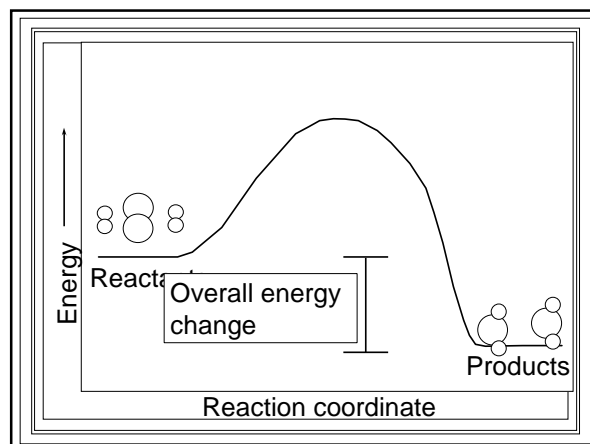


## Activation Energy

- Must be supplied to start the reaction
- Low activation energy
  - Lots of collision are hard enough
  - fast reaction
- High Activation energy
  - Few collisions hard enough
  - Slow reaction

### Activation energy

- If reaction is endothermic you must keep supplying heat
- If it is exothermic it releases energy
- That energy can be used to supply the activation energy to those that follow



### Things that Affect Rate

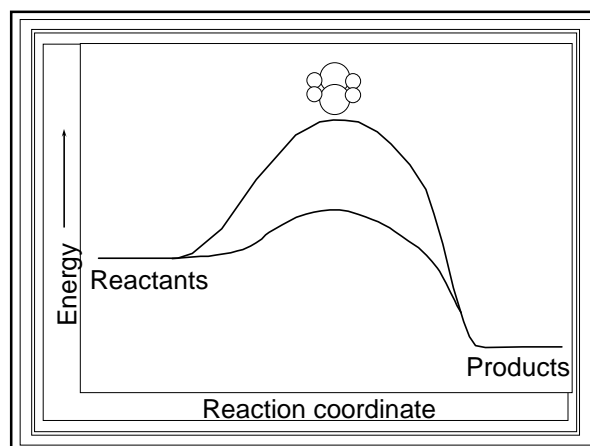
- Temperature
  - Higher temperature faster particles.
  - More and harder collisions.
  - Faster Reactions.
- Concentration
  - More concentrated molecules closer together
  - Collide more often.
  - Faster reaction.

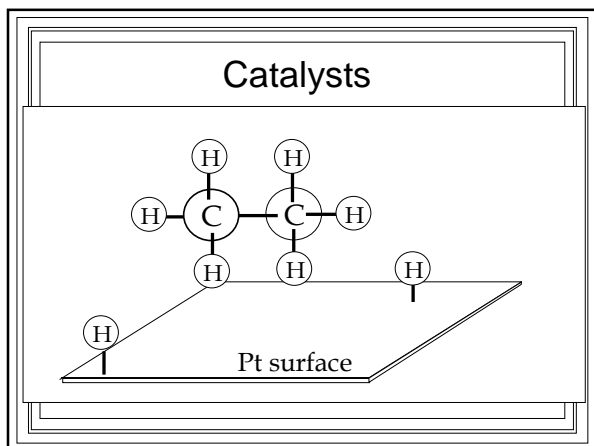
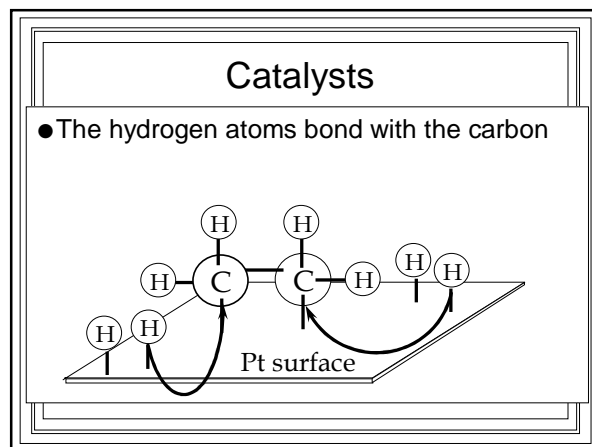
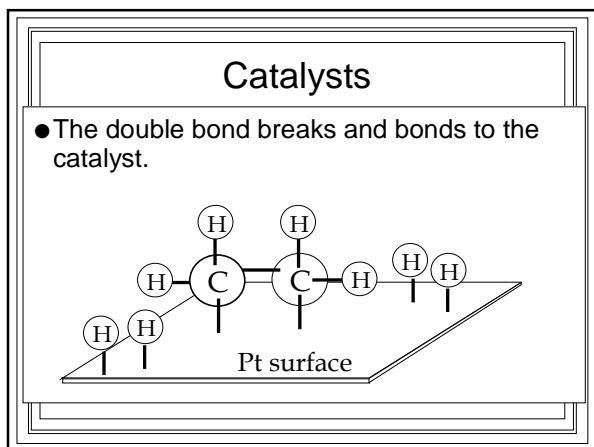
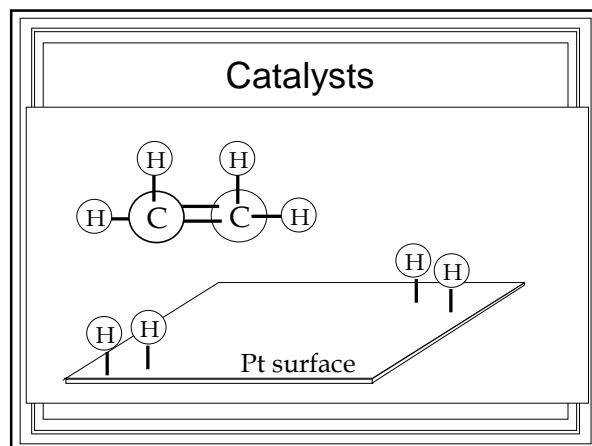
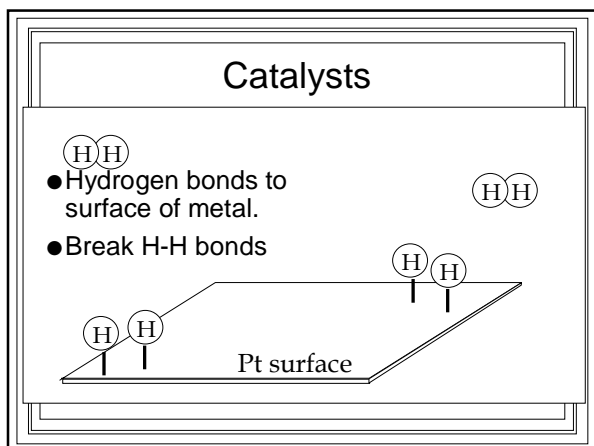
### Things that Affect Rate

- Particle size
  - Molecules can only collide at the surface.
  - Smaller particles bigger surface area.
  - Smaller particles faster reaction.
  - Smallest possible is molecules or ions.
  - Dissolving speeds up reactions.
  - Getting two solids to react with each other is slow.

### Things that Affect Rate

- Catalysts- substances that speed up a reaction without being used up.(enzyme).
- Speeds up reaction by giving the reaction a new path.
- The new path has a lower activation energy.
- More molecules have this energy.
- The reaction goes faster.
- Inhibitor- a substance that blocks a catalyst.





Reversible Reactions  
and  
Equilibrium

## Reversible Reactions

- Reactions are spontaneous if  $\Delta G$  is negative.
- If  $\Delta G$  is positive the reaction happens in the opposite direction.
- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{energy}$
- $2\text{H}_2\text{O}(\text{g}) + \text{energy} \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) + \text{energy}$

## Equilibrium

- When I first put reactants together the forward reaction starts.
- Since there are no products there is no reverse reaction.
- As the forward reaction proceeds the reactants are used up so the forward reaction slows.
- The products build up, and the reverse reaction speeds up.

## Equilibrium

- Eventually you reach a point where the reverse reaction is going as fast as the forward reaction.
- This is dynamic equilibrium.
- The rate of the forward reaction is equal to the rate of the reverse reaction.
- The concentration of products and reactants stays the same, but the reactions are still running.

## Equilibrium

- Equilibrium position- how much product and reactant there are at equilibrium.
- Shown with the double arrow.
- $\leftarrow \rightleftharpoons$  Reactants are favored
- $\rightleftharpoons \rightarrow$  Products are favored
- Catalysts speed up both the forward and reverse reactions so don't affect equilibrium position.

## Equilibrium

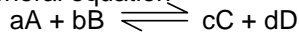
- Catalysts speed up both the forward and reverse reactions so don't affect equilibrium position.
- Just get you there faster

## Measuring equilibrium

- At equilibrium the concentrations of products and reactants are constant.
- We can write a constant that will tell us where the equilibrium position is.
- $K_{\text{eq}}$  equilibrium constant
- $K_{\text{eq}} = \frac{[\text{Products}]^{\text{coefficients}}}{[\text{Reactants}]^{\text{coefficients}}}$
- Square brackets [ ] means concentration in molarity (moles/liter)

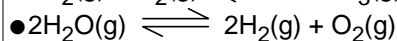
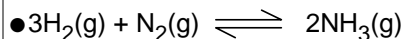
## Writing Equilibrium Expressions

- General equation



- $K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

- Write the equilibrium expressions for the following reactions.



## Calculating Equilibrium

- $K_{eq}$  is the equilibrium constant, it is only effected by temperature.
- Calculate the equilibrium constant for the following reaction.  
 $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$  if at 25°C there 0.15 mol of  $N_2$ , 0.25 mol of  $NH_3$ , and 0.10 mol of  $H_2$  in a 2.0 L container.

## What it tells us

- If  $K_{eq} > 1$  Products are favored
  - More products than reactants at equilibrium
- If  $K_{eq} < 1$  Reactants are favored

## LeChâtelier's Principle

Regaining Equilibrium

## LeChâtelier's Principle

- If something is changed in a system at equilibrium, the system will respond to relieve the stress.
- Three types of stress are applied.
  - Changing concentration
  - Changing temperature
  - Changing pressure

## Changing Concentration

- If you add reactants (or increase their concentration).
- The forward reaction will speed up.
- More product will form.
- Equilibrium "*Shifts to the right*"
- Reactants  $\rightarrow$  products

### Changing Concentration

- If you add products (or increase their concentration).
- The reverse reaction will speed up.
- More reactant will form.
- Equilibrium "*Shifts to the left*".
- Reactants  $\leftarrow$  products

### Changing Concentration

- If you remove products (or decrease their concentration).
- The reverse reaction will slow down.
- More product will form.
- Equilibrium reverse "*Shifts to the right*".
- Reactants  $\rightarrow$  products

### Changing Concentration

- If you remove reactants (or decrease their concentration).
- The forward reaction will slow down.
- More reactant will form.
- Equilibrium "*Shifts to the left*".
- Reactants  $\leftarrow$  products
- Used to control how much yield you get from a chemical reaction.

### Changing Temperature

- Reactions either require or release heat.
- Endothermic reactions go faster at higher temperature.
- Exothermic go faster at lower temperatures.
- All reversible reactions will be exothermic one way and endothermic the other.

### Changing Temperature

- As you raise the temperature the reaction proceeds in the endothermic direction.
- As you lower the temperature the reaction proceeds in the exothermic direction.
- Reactants + heat  $\rightarrow$  Products at high T
- Reactants + heat  $\leftarrow$  Products at low T
- $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{s}) + \text{heat}$

### Changes in Pressure

- As the pressure increases the reaction will shift in the direction of the least gases.
- At high pressure  
 $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$
- At low pressure  
 $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \leftarrow 2\text{H}_2\text{O}(\text{g})$
- Low pressure to the side with the most gases.

### Three Questions

- How Fast?
  - Depends on collisions and activation energy
  - Affected by
    - Temperature
    - Concentration
    - Particle size
    - Catalyst
- Reaction Mechanism – steps

### Three Questions

- Will it happen?
  - Likely if
    - $\Delta H$  is negative – exothermic
    - Or  $\Delta S$  is positive – more disorder
  - Guaranteed if  $\Delta G$  is negative
    - $\Delta G^\circ_f$  Products – Reactants
    - Or  $\Delta G = \Delta H - T \Delta S$

### Three Questions

- How far?
  - Equilibrium
    - Forward and reverse rates are equal
    - Concentration is constant
  - Equilibrium Constant
    - One for each temperature
  - LeChâtelier's Principle

## Thermodynamics

Will a reaction happen?

## Energy

- Substances tend to react to achieve the lowest energy state.
- Most chemical reactions are exothermic.
- Doesn't work for things like ice melting.
- An ice cube must absorb heat to melt, but it melts anyway. Why?

## Entropy

- The degree of randomness or disorder.
- Better – number of ways things can be arranged
- S
- The First Law of Thermodynamics - The energy of the universe is constant.
- The Second Law of Thermodynamics - The entropy of the universe increases in any change.
- Drop a box of marbles.
- Watch your room for a week.

Entropy

Entropy of a solid < Entropy of a liquid < Entropy of a gas

- A solid has an orderly arrangement.
- A liquid has the molecules next to each other but isn't orderly
- A gas has molecules moving all over the place.

Entropy increases when...

- Reactions of solids produce gases or liquids, or liquids produce gases.
- A substance is divided into parts -so reactions with more products than reactants have an increase in entropy.
- The temperature is raised -because the random motion of the molecules is increased.
- a substance is dissolved.

Entropy calculations

- There are tables of standard entropy (pg 407).
- Standard entropy is the entropy at 25°C and 1 atm pressure.
- Abbreviated  $S^\circ$ , measure in J/K.
- The change in entropy for a reaction is  $\Delta S^\circ = S^\circ(\text{Products}) - S^\circ(\text{Reactants})$ .
- Calculate  $\Delta S^\circ$  for this reaction  
 $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

- Calculate  $\Delta S^\circ$  for this reaction  
 $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$
- For  $\text{CH}_4$   $S^\circ = 186.2 \text{ J/K-mol}$
- For  $\text{O}_2$   $S^\circ = 205.0 \text{ J/K-mol}$
- For  $\text{CO}_2$   $S^\circ = 213.6 \text{ J/K-mol}$
- For  $\text{H}_2\text{O}(\text{g})$   $S^\circ = 188.7 \text{ J/K-mol}$

Spontaneity

Will the reaction happen, and how can we make it?

Spontaneous reaction

- Reactions that will happen.
- Nonspontaneous reactions don't.
- Even if they do happen, we can't say how fast.
- Two factors influence.
- Enthalpy (heat) and entropy (disorder).



### Two Factors

- Exothermic reactions tend to be spontaneous.
  - Negative  $\Delta H$ .
- Reactions where the entropy of the products is greater than reactants tend to be spontaneous.
  - Positive  $\Delta S$ .
- A change with positive  $\Delta S$  and negative  $\Delta H$  is always spontaneous.
- A change with negative  $\Delta S$  and positive  $\Delta H$  is never spontaneous.

### Other Possibilities

- Temperature affects entropy.
- Higher temperature, higher entropy.
- For an exothermic reaction with a decrease in entropy (like rusting).
- Spontaneous at low temperature.
- Nonspontaneous at high temperature.
- Enthalpy driven.

### Other Possibilities

- An endothermic reaction with an increase in entropy like melting ice.
- Spontaneous at high temperature.
- Nonspontaneous at low temperature.
- Entropy driven.

### Gibbs Free Energy

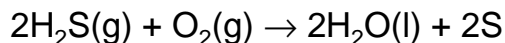
- The energy free to do work is the change in Gibbs free energy.
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  (T must be in Kelvin)
- All spontaneous reactions release free energy.
- So  $\Delta G < 0$  for a spontaneous reaction.

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G$	$\Delta H$	$\Delta S$	Spontaneous?
-	-	+	At all Temperatures
?	+	+	At high temperatures, "entropy driven"
?	-	-	At low temperatures, "enthalpy driven"
+	+	-	Not at any temperature, Reverse is spontaneous

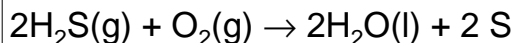
### Problems

- Using the information on page 407 and pg 190 determine if the following changes are spontaneous at 25°C.
- $2\text{H}_2\text{S}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{S}(\text{rhombic})$



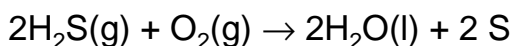
- From Pg. 190 we find  $\Delta H_f^\circ$  for each component
 

-H <sub>2</sub> S = -20.1 kJ	O <sub>2</sub> = 0 kJ
-H <sub>2</sub> O = -285.8 kJ	S = 0 kJ
- Then Products - Reactants
- $\Delta H = 2(-285.8 \text{ kJ}) + 2(0 \text{ kJ}) - 2(-20.1 \text{ kJ}) - 1(0 \text{ kJ}) = -531.4 \text{ kJ}$



- From Pg. 407 we find  $S^\circ$  for each component
 

-H <sub>2</sub> S = 205.6 J/K	O <sub>2</sub> = 205.0 J/K
-H <sub>2</sub> O = 69.94 J/K	S = 31.9 J/K
- Then Products - Reactants
- $\Delta S = 2(69.94 \text{ J/K}) + 2(31.9 \text{ J/K}) - 2(205.6 \text{ J/K}) - 205 \text{ J/K} = -412.5 \text{ J/K}$



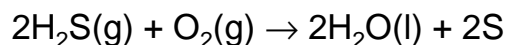
- $\Delta G = \Delta H - T \Delta S$
- $\Delta G = -531.4 \text{ kJ} - 298\text{K}(-412.5 \text{ J/K})$
- $\Delta G = -531.4 \text{ kJ} - -123000 \text{ J}$
- $\Delta G = -531.4 \text{ kJ} - -123 \text{ kJ}$
- $\Delta G = -408.4 \text{ kJ}$
- Spontaneous
- Exergonic- it releases free energy.
- At what temperature does it become spontaneous?

### Spontaneous

- It becomes spontaneous when  $\Delta G = 0$
- That's where it changes from positive to negative.
- Using  $0 = \Delta H - T \Delta S$  and solving for T
- $0 - \Delta H = -T \Delta S$
- $-\frac{\Delta H}{\Delta S} = -T$
- $T = \frac{\Delta H}{\Delta S} = \frac{-531.4 \text{ kJ}}{-412.5 \text{ J/K}} = \frac{-531400 \text{ J}}{-412.5 \text{ J/K}} = 1290 \text{ K}$

### There's Another Way

- There are tables of standard free energies of formation compounds. (pg 414)
- $\Delta G_f^\circ$  is the free energy change in making a compound from its elements at 25° C and 1 atm.
- for an element  $\Delta G_f^\circ = 0$
- Look them up.
- $\Delta G^\circ = \Delta G_f^\circ(\text{products}) - \Delta G_f^\circ(\text{reactants})$



- From Pg. 414 we find  $\Delta G_f^\circ$  for each component
 

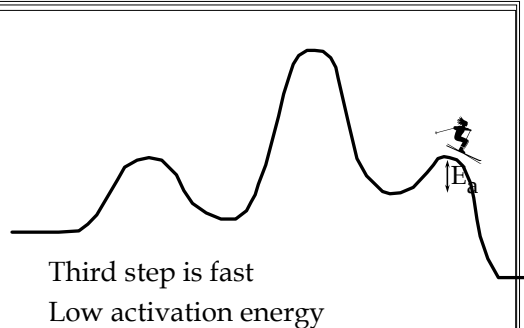
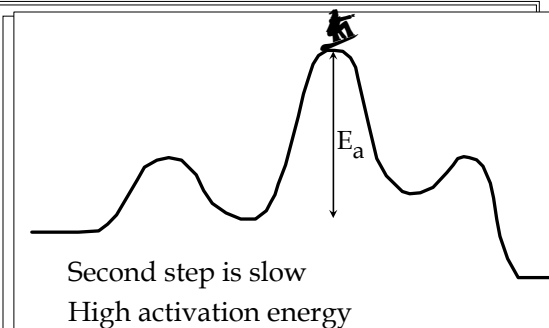
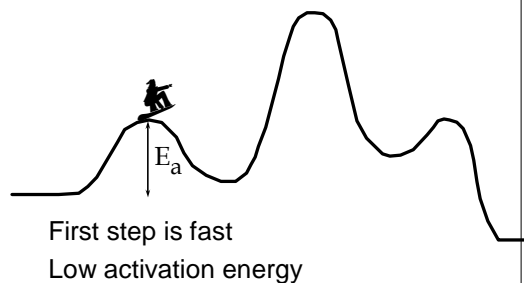
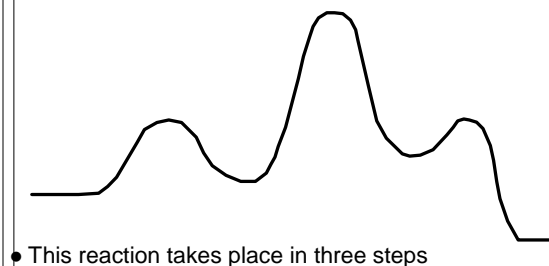
-H <sub>2</sub> S = -33.02 kJ	O <sub>2</sub> = 0 kJ
-H <sub>2</sub> O = -237.2 kJ	S = 0 kJ
- Then Products - Reactants
- $\Delta G = 2(-237.2) + 2(0) - 2(-33.02) - 1(0) = -408.4 \text{ kJ}$

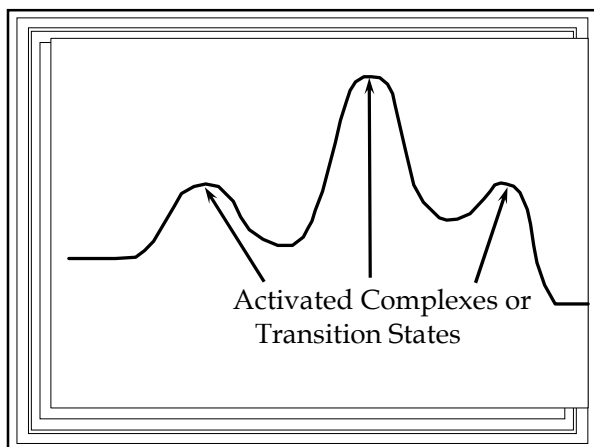
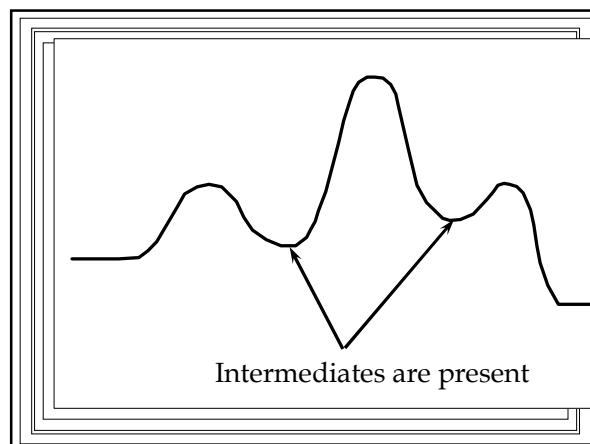
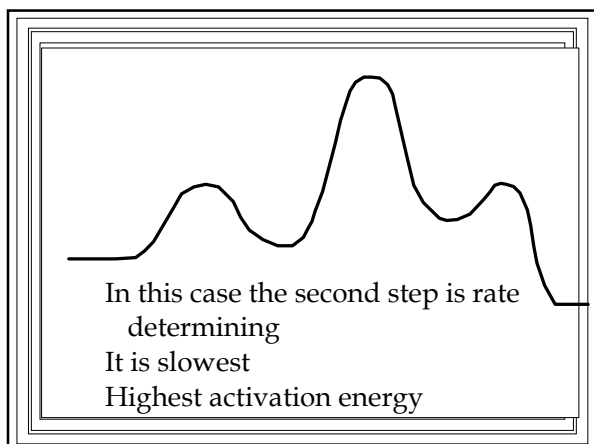
### Does ice melt?

- For the following change  
 $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$   
 $\Delta H^\circ = 6.03 \text{ kJ}$  and  
 $\Delta S^\circ = 22.1 \text{ J/K}$   
At what temperature does ice melt?

### Reaction Mechanism

- Elementary reaction- a reaction that happens in a single step.
- Reaction mechanism is a description of how the reaction really happens.
- It is a series of elementary reactions.
- The product of an elementary reaction is an intermediate.
- An intermediate is a product that immediately gets used in the next reaction.





- ### Mechanisms and rates
- Intermediates are stable -they last for a little time
  - Activated complexes don't
  - There is an activation energy for each elementary step.
  - Slowest step (rate determining) must have the highest activation energy.

- The mechanism for the decomposition of hydrogen peroxide is
 

<b>Slow</b>
<b>Fast</b>
<b>Fast</b>
- Which is the rate determining step?
- What are the intermediates?
- Sketch the potential energy diagram.