

## Chapter 16

### Thermodynamics



## Calculating $\Delta H^\circ_{\text{rxn}}$

- $\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_f \text{ products} - \sum \Delta H^\circ_f \text{ reactants}$ 
  - ♦ Heat of formation values, Appendix B
  - ♦  $\Delta H^\circ_f$  is reported as kJ/mol
- The  $^\circ$  symbol refers to the standard state, 1.00 atm pressure, 25.0°C, 1.00 M for solutions
- Review heat of formation reactions (making 1 mole of substance from its elements in the standard state)
  - ♦  $\Delta H^\circ_f$  for elements is 0 (no energy needed!)
- Write heat of formation rxn for  $\text{MgCl}_2(\text{s})$ ,  $\text{H}_2\text{O}(\text{l})$ .

## Thermodynamics

- Study of energy changes in chemical reactions
  - ♦ useful to understand the nature of chemical changes
- Recall thermochemistry (study of heat changes) from Chapter 8
- You are responsible for information from CHM 151, specifically sections 2, 5, 7, 9, and 10 (except "work").

## Thermodynamics

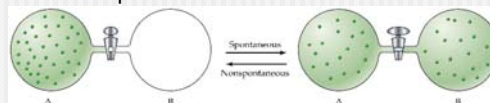
- How do we know if a chemical reaction will occur?
- How can we tell how far a reaction will go?
- Thermodynamics helps to answer these questions.
- Enthalpy is only one part of the equation.
- Entropy is another.

## Thermochemistry Review

- 1st Law of Thermodynamics: Energy is conserved, it cannot be created or destroyed
  - ♦ If the system gives off heat, the universe must absorb it.
  - ♦ Heat flow (enthalpy,  $\Delta H$ ) always defined with reference to the system
    - System absorbs heat,  $\Delta H > 0$ , endothermic
    - System gives off heat,  $\Delta H < 0$ , exothermic

## Spontaneous Processes

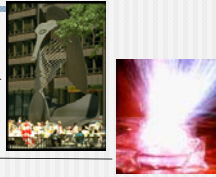
- In chemistry, we define a spontaneous process as one that proceeds on its own without any external influence.
  - ♦ Consider the expansion of a gas into a vacuum. This happens spontaneously. The reverse process does not!



• Figure 16.1

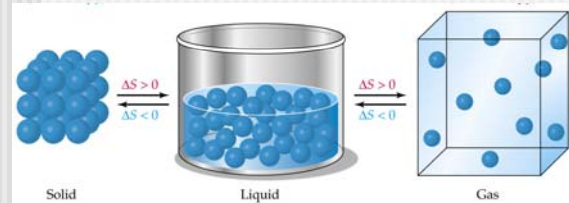
## Spontaneous Chemical Reactions

- Spontaneous processes
  - hot object cools
  - gases expand
  - iron rusts
  - Cs reacts with  $\text{H}_2\text{O}$
- What do all these processes have in common?
- They happen with no external intervention.
  - Nature tends toward lower energy! **Usually** exothermic reactions are spontaneous (but not always)!!



## Which has the greater entropy?

- Solid, liquid or gas? (ice, water, or steam)



## Spontaneous Processes

- Spontaneous does not mean the same thing as "fast"
  - Rusting of iron is slow but spontaneous
- Thermodynamics just tells us whether or not a reaction will occur, not how fast it will occur
  - Kinetics (Ch. 12) looks at that!
- Problem 16.1

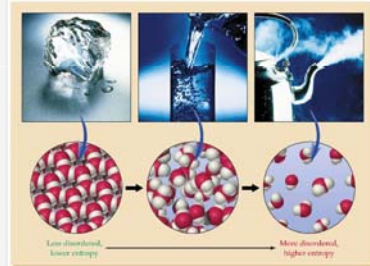


## Enthalpy & Entropy: $\Delta H$ & $\Delta S$

$S(s) < S(l) < S(g)$ , Section 10.4

**Melting:**  
 $\Delta H ?$ ,  $\Delta S ?$

**Boiling:**  
 $\Delta H ?$ ,  $\Delta S ?$



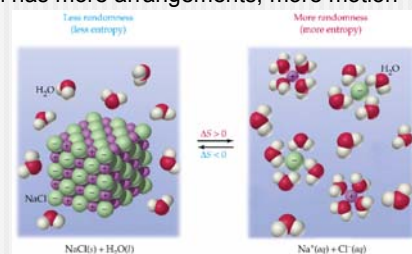
Example 10.4  
Problem 10.7, 10.8

## Entropy (S)

- Section 8.13: Nature tends toward disorder (increase in entropy).
  - Who wants to play 52 card pick-up?
- Entropy is a measure of disorder or randomness.
  - A process is usually spontaneous if it increases the disorder (change in entropy is positive:  $\Delta S > 0$ )
  - S: J/K

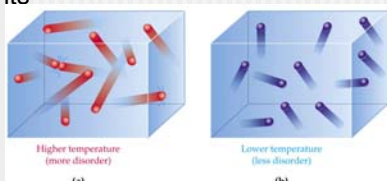
## Which has the greater entropy?

- Solute and solvent or solution?
- Solution has more arrangements, more motion

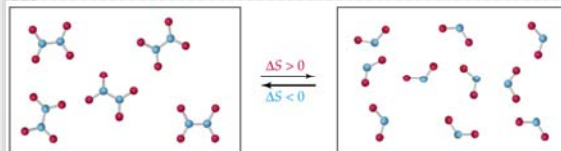


## Which has the greater entropy?

- Low temperature or high temperature?
- Consider gases at different temperatures
- High T: more motion, more possible arrangements
- Figure 16.7

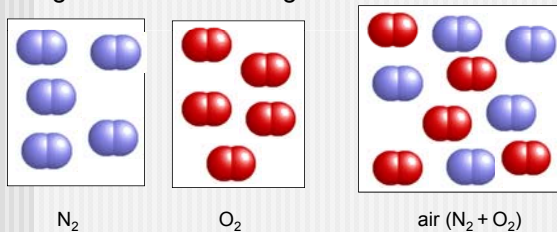


## Which has greater entropy?

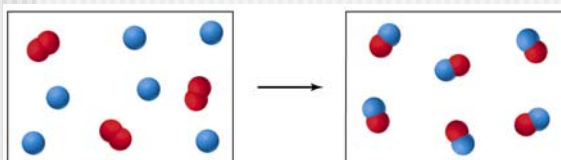


## Group Quiz #11

- Which has the greater entropy, separate gases or mixture of gases?

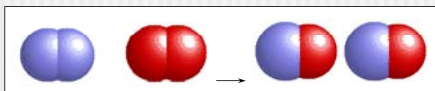


## Which has greater entropy?



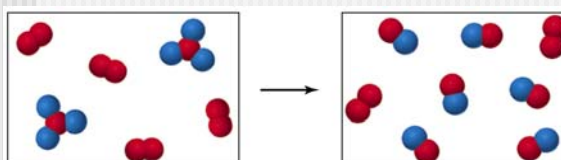
## Which has the greater entropy?

- Elements or compounds?
- $$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$



- The compound has more arrangements.
- Worked example 16.1, Problem 16.2, Key Concept 16.2, 16.3

## Which has greater entropy?



## Entropy Summary

- Phase changes
  - Boiling:  $\Delta H > 0$ ,  $\Delta S > 0$
  - Melting:  $\Delta H > 0$ ,  $\Delta S > 0$
- Salts dissolving
  - $\Delta H < \text{or} > 0$  (depends),  $\Delta S > 0$  (usually)
- Temperature changes
  - Increase:  $\Delta S > 0$ , more energy, more positions, more possible arrangements

## What makes a process spontaneous?



- Tendency to go to a state of lower energy.
  - Enthalpy:  $\Delta H < 0$  (exothermic), but can be endothermic
- Tendency to become more disordered or random
  - Entropy:  $\Delta S > 0$  (increase in randomness)
- Randomness increases when particles become further apart.
- Spontaneous:  $\Delta H < 0$ ,  $\Delta S > 0$**
- Non-spontaneous:  $\Delta H > 0$ ,  $\Delta S < 0$**



## Changes in Entropy

- Does entropy increase or decrease for the following?
  - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
  - $2\text{O}_3(\text{g}) \rightleftharpoons 3\text{O}_2(\text{g})$
  - $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$
  - $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightleftharpoons \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
  - $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{CH}_3(\text{g})$
  - $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- More motion, more arrangements for the substances that have more particles
- Worked example 8.11, Problem 8.21, 8.22

## Entropy and Temperature

- 3rd Law of Thermodynamics: The entropy of a perfectly ordered crystalline substance at 0 K is zero.
- This allows us to calculate S values and changes in entropy ( $\Delta S$ )
- We can calculate S values and  $\Delta S$  values; unlike enthalpy - can only measure **change!**
- Use Standard Molar Entropies (Table 16.1) - entropy of 1 mole of the pure substance at 1 atm pressure and 25.0°C (in units of J/mol·K)
  - Calculate like  $\Delta H^\circ_{\text{rxn}}$  (products - reactants)

## Spontaneity

- Which tendency for spontaneity predominates, enthalpy or entropy?
  - They can oppose one another, or they can work together.
- For example, freezing of water at -10°C is exothermic and spontaneous, even though  $\Delta S < 0$ .
- If we change the entropy of the system, we also change the surroundings, so we must consider the total entropy change.

## Standard Molar Entropies

- Notice which phases have lowest values? Highest?

Substance	Formula	S° [J/(K·mol)]	Substance	Formula	S° [J/(K·mol)]
<b>Gases</b>			<b>Liquids</b>		
Acetylene	C <sub>2</sub> H <sub>2</sub>	200.8	Acetic acid	CH <sub>3</sub> CO <sub>2</sub> H	160
Ammonia	NH <sub>3</sub>	192.3	Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	161
Carbon dioxide	CO <sub>2</sub>	213.6	Methanol	CH <sub>3</sub> OH	127
Carbon monoxide	CO	197.6	Water	H <sub>2</sub> O	69.9
Ethylene	C <sub>2</sub> H <sub>4</sub>	219.5	<b>Solids</b>		
Hydrogen	H <sub>2</sub>	130.6	Calcium carbonate	CaCO <sub>3</sub>	92.9
Methane	CH <sub>4</sub>	186.2	Calcium oxide	CaO	39.7
Nitrogen	N <sub>2</sub>	191.5	Diamond	C	2.4
Nitrogen dioxide	NO <sub>2</sub>	240.0	Graphite	C	5.7
Dinitrogen tetroxide	N <sub>2</sub> O <sub>4</sub>	304.2	Iron	Fe	27.3
Oxygen	O <sub>2</sub>	205.0	Iron(III) oxide	Fe <sub>2</sub> O <sub>3</sub>	87.4

- Predict and calculate  $\Delta S^\circ$  for the combustion of methanol.

## Entropy Changes

- Calculate  $\Delta S^\circ_{\text{rxn}}$  for:
- $2\text{Na(s)} + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NaCl(s)}$ 
  - ♦ Given:  $\text{Na(s)} = 51.05 \text{ J/mol}\cdot\text{K}$ ,  $\text{Cl}_2(\text{g}) = 223.0 \text{ J/mol}\cdot\text{K}$ ,  $\text{NaCl(s)} = 72.38 \text{ J/mol}\cdot\text{K}$
- Ans:  $\Delta S^\circ_{\text{rxn}} = -180.34 \text{ J/K}$
- Not spontaneous with respect to entropy.
- What about in the dissolution direction?

## Entropy

- $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- $\Delta S_{\text{total}} > 0$ , the reaction is spontaneous
- $\Delta S_{\text{total}} < 0$ , the reaction is nonspontaneous
- $\Delta S_{\text{total}} = 0$ , the reaction is at equilibrium
- All reactions proceed spontaneously in a direction that increases the entropy of the system plus the surroundings.

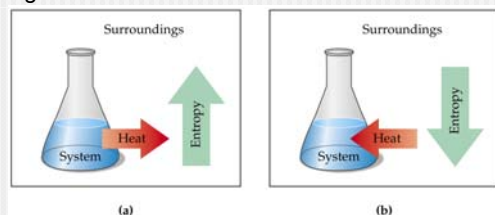
## Individual Quiz #2

- Calculate  $\Delta S^\circ$  for the following two reactions:
- $2\text{S(s)} + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
- $\text{SO}_3(\text{g}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{SO}_4(\text{aq})$

$S^\circ$ in J/mol K	
S(s)	31.8
O <sub>2</sub>	205.03
H <sub>2</sub> O(l)	69.91
2SO <sub>3</sub> (g)	256.6
H <sub>2</sub> SO <sub>4</sub> (aq)	20

## 2<sup>nd</sup> Law of Thermodynamics

- We know how to calculate  $\Delta S_{\text{system}}$  (previous calculations); now calculate  $\Delta S_{\text{surr}}$
- Figure 16.9



## Entropy, 2<sup>nd</sup> Law of Thermo.

- The **Second Law of Thermodynamics** states that in any spontaneous process, the *total* entropy of a system and its surroundings always increases. (Spontaneous Reactions will Occur)
  - ♦ The system is the chemical reaction itself.
- $\Delta S_{\text{tot}}$  is positive for a spontaneous process;  $\Delta S_{\text{tot}}$  is 0 at equilibrium
  - ♦  $\Delta S_{\text{tot}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

## Calculating $\Delta S_{\text{surr}}$

- Exothermic: heat leaves system, enters surroundings, surroundings have more energy which gives them more disorder ( $\Delta S_{\text{surr}} > 0$  when  $\Delta H < 0$ )
- Endothermic: heat enters system, leaves surroundings, surroundings have less energy which gives them more order ( $\Delta S_{\text{surr}} < 0$  when  $\Delta H > 0$ )
- $\Delta S_{\text{surr}} \propto -\Delta H_{\text{rxn}}$  and  $\Delta S_{\text{surr}} \propto 1/T$
- $\Delta S_{\text{surr}} = -\Delta H_{\text{rxn}}/T$

## 2<sup>nd</sup> Law of Thermodynamics

- Calculate  $\Delta S_{\text{tot}}$  for  $2\text{CuO(s)} \rightarrow 2\text{Cu(s)} + \text{O}_2\text{(g)}$  at 25°C.
- Find  $\Delta S^{\circ}_{\text{rxn}}$  using molar entropy values.
- Find  $\Delta H^{\circ}_{\text{rxn}}$  using standard enthalpy values.
- Find  $\Delta S^{\circ}_{\text{surr}}$  using  $\Delta H^{\circ}_f$  and T.
- $\Delta S_{\text{tot}} = (184.6 \text{ J/K}) + (-1042 \text{ J/K}) = -857 \text{ J/K}$
- Not spontaneous!
- Entropy decreased! But what about enthalpy? Also part of the equation.

## Change in Gibbs Free Energy

- Gibbs free energy change or free energy change =  $\Delta G$ ; maximum amount of energy available to do work on the **surroundings**
- $\Delta E$  or  $\Delta H$ : some is used to do work within the system (rearrange particles, new bonds, ...) and the rest is available to do work on the surroundings ( $\Delta G$ )
- $\Delta G < 0 \rightarrow$  Spontaneous process
- $\Delta G > 0 \rightarrow$  Nonspontaneous process
- $\Delta G = 0 \rightarrow$  Process is at equilibrium

## Free Energy

- Go Back to Section 8.14
- Gibbs Free Energy Change ( $\Delta G$ )
  - ♦ Takes into account enthalpy and entropy to predict spontaneity of a reaction.
- $\Delta G = \Delta H - T\Delta S$  ( $\Delta G = \text{kJ/mol}$ )
  - ♦  $\Delta H$  is enthalpy (kJ/mol)
  - ♦ T is temperature (K)
  - ♦  $\Delta S$  is change in entropy (J/mol·K)

## Free Energy

- Notice that the  $T\Delta S$  term is temperature dependent. Temperature plays a part in predicting spontaneity.
  - ♦ For endothermic processes, they are spontaneous at higher temps ( $T\Delta S > \Delta H$ )
  - ♦ For exothermic processes, they are spontaneous at lower temps ( $T\Delta S < \Delta H$ )

## Change in Gibbs Free Energy

- Exothermic ( $\Delta H < 0$ ) reactions tend to be spontaneous.
- Increases in entropy ( $\Delta S > 0$ ) tend to be spontaneous.
- What will the sign of  $\Delta G$  be under these conditions?
  - ♦  $\Delta G = \Delta H - T\Delta S$

## Decomposition of CuO(s)

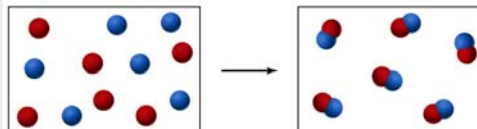
- $2\text{CuO(s)} \rightleftharpoons 2\text{Cu(s)} + \text{O}_2\text{(g)}$ 
  - ♦  $\Delta H^{\circ}_{\text{rxn}} = +310.4 \text{ kJ}$
  - ♦  $\Delta S^{\circ}_{\text{rxn}} = +184.6 \text{ J/K}$
- At room temperature (300 K), is the reaction spontaneous or nonspontaneous?
- At what temperature will the reaction become spontaneous? Temperatures above this occur spontaneously.
- Examples 8.12-13, 16. 5; Problems 8.23-8.25, 16.7-16.9

## Free Energy and Spontaneity

- Calculate the temperature at which the reaction of nitrogen and chlorine becomes spontaneous.  $\Delta H = 460 \text{ kJ}$ ;  $\Delta S = -275 \text{ J/K}$

## Gibbs Free Energy Changes

- What are the signs (+, -, or 0) of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  for the following **spontaneous** reaction of A atoms (red) and B atoms (blue)?



## Free Energy

- Using  $\Delta G = \Delta H - T\Delta S$ , we can predict the sign of  $\Delta G$  from the sign of  $\Delta H$  and  $\Delta S$ .
  - If  $\Delta H$  is negative and  $\Delta S$  is positive,  $\Delta G$  will always be negative.
  - If both  $\Delta H$  and  $\Delta S$  are negative,  $\Delta G$  will be negative only when the temperature value is small.
  - If  $\Delta H$  is positive and  $\Delta S$  is negative,  $\Delta G$  will always be positive.
  - If both  $\Delta H$  and  $\Delta S$  are positive,  $\Delta G$  will be negative only when the temperature value is large.

## Entropy of Phase Changes

- Phase changes occur at equilibrium
  - $\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{O(l)}$
  - Solid and liquid are in equilibrium
  - Think phase diagrams from Section 10.11
  - $\Delta G = \Delta H - T\Delta S = 0$  (at equil.), solving for temperature tells us the boiling point!
- Melting Ice:
  - At  $-10^\circ\text{C}$  (263 K):  $\Delta G = 6.01 \text{ kJ/mol} - [(263\text{K})(0.0220 \text{ kJ/K}\cdot\text{mol})] = +0.22 \text{ kJ/mol}$
  - At  $0^\circ\text{C}$  (273 K):  $\Delta G = 6.01 \text{ kJ/mol} - [(273\text{K})(0.0220 \text{ kJ/K}\cdot\text{mol})] = 0.00 \text{ kJ/mol}$
  - At  $+10^\circ\text{C}$  (283 K):  $\Delta G = 6.01 \text{ kJ/mol} - [(283\text{K})(0.0220 \text{ kJ/K}\cdot\text{mol})] = -0.22 \text{ kJ/mol}$

## Free Energy

TABLE 17.2 Signs of Enthalpy, Entropy, and Free-Energy Changes and Reaction Spontaneity for a Reaction at Constant Temperature and Pressure

$\Delta H$	$\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Spontaneity
-	+	-	Spontaneous at all temperatures
-	-	- or +	Spontaneous at low temperatures where $\Delta H$ outweighs $T\Delta S$ Nonspontaneous at high temperatures where $T\Delta S$ outweighs $\Delta H$
+	-	+	Nonspontaneous at all temperatures
+	+	- or +	Spontaneous at high temperatures where $T\Delta S$ outweighs $\Delta H$ Nonspontaneous at low temperatures where $\Delta H$ outweighs $T\Delta S$

## Phase Change Calculations

- Calculate the boiling point of ethanol if entropy of vaporization is  $111.9 \text{ J/K}$  and  $\Delta H_{\text{vap}} = 39.3 \text{ kJ}$
- Convert to the right units...

## Group Quiz #12

- $\Delta H = -247 \text{ kJ}$ ,  $\Delta S = -109 \text{ J/K}$ ,  $T = 1350 \text{ K}$ . Is this process spontaneous?
- Calculate the temperature (in  $^{\circ}\text{C}$ ) at which this reaction becomes spontaneous.

## Standard Free Energy Changes

- Can get  $\Delta G^{\circ}$  from  $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ 
  - ♦ Use  $\Delta G^{\circ}$  to predict spontaneity in the standard state
- Can also get values of  $\Delta G^{\circ}$  from free energies of formation:  $\Delta G^{\circ}_f$  (formation from the elements)
- $\Delta G^{\circ}_f = 0$  for an element in its stable form
  - ♦ This should look familiar ( $\Delta H^{\circ}_f$ )
- What are the characteristics of a formation reaction?
  - ♦ 1 mole of product formed
  - ♦ Reactants are elements in standard state.

## Standard Free Energy Changes

- The free energy of a substance depends on temperature, pressure, and physical states (like enthalpy and entropy). We must look at standard-state conditions:
  - ♦ Solids, liquids, gases: pure form at 1 atm
  - ♦ Solutes at 1 M concentration, gases at 1 atm
  - ♦ Room temperature:  $25^{\circ}\text{C}$  (298 K)
- Standard free energy change ( $\Delta G^{\circ}$ ) is free energy change with reactants and products in their standard states.

## $\Delta G^{\circ}_f$

- Which one of these reactions corresponds to  $\Delta G^{\circ}_f$  of  $\text{H}_2\text{O}(\text{g})$ ?
- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$
- $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
- $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
- $\Delta G^{\circ} = \sum n \Delta G^{\circ}_f \text{ products} - \sum n \Delta G^{\circ}_f \text{ reactants}$

## Standard Free Energy

- $\Delta G^{\circ}_{\text{rxn}}$  tells us whether a reaction will favor reactants or products.
  - ♦  $\Delta G^{\circ}_{\text{rxn}} > 0$ : reactant favored. What is  $K_c$ ?
  - ♦  $\Delta G^{\circ}_{\text{rxn}} < 0$ : product favored. What is  $K_c$ ?
- Using  $\Delta H^{\circ}_{\text{rxn}}$  and  $\Delta S^{\circ}_{\text{rxn}}$  values to calculate  $\Delta G^{\circ}_{\text{rxn}}$ . (We've already done this!)

## $\Delta G^{\circ}_f$

- $\Delta G^{\circ} = \sum n \Delta G^{\circ}_f \text{ products} - \sum n \Delta G^{\circ}_f \text{ reactants}$
- Similarly,  
$$\Delta H^{\circ} = \sum n \Delta H^{\circ}_f \text{ products} - \sum n \Delta H^{\circ}_f \text{ reactants}$$
$$\Delta S^{\circ} = \sum n S^{\circ} \text{ products} - \sum n S^{\circ} \text{ reactants}$$
- Values of  $\Delta G^{\circ}_f$ ,  $\Delta H^{\circ}_f$ ,  $S^{\circ}$  are listed for standard state conditions in Table 16.3 and Appendix B
- Can use tables to predict the value of  $\Delta G^{\circ}$  and the spontaneity of chemical reactions, even ones that are not yet observed.

## Individual Quiz #3

$\Delta G_f^\circ$ in kJ/mol	
$\text{NO}_{2(g)}$	51.3
$\text{KClO}_{3(s)}$	-296.3
$\text{KCl}_{(s)}$	-409.2

- Calculate  $\Delta G^\circ$  and determine spontaneity for these reactions:
- $\text{N}_{2(g)} + 2\text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{2(g)}$
- $2\text{KClO}_{3(s)} \rightleftharpoons 2\text{KCl}_{(s)} + 3\text{O}_{2(g)}$

## $\Delta G^\circ$ and Equilibrium

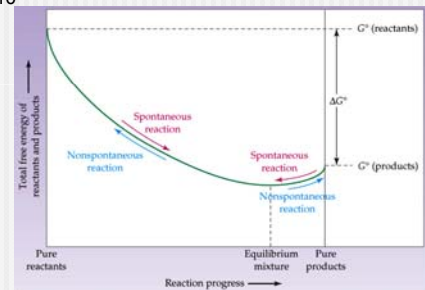
- $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$
- $Q = P_{\text{CO}_2} P_{\text{H}_2} / P_{\text{CO}} P_{\text{H}_2\text{O}}$
- Initially,  $Q = 0$ , but then it increases
- As the reaction progresses,  $\Delta G$  decreases until a minimum value of  $G$  is reached; at this point,  $\Delta G = 0$  and net reaction ceases (though the forward and reverse reactions still occur, but they offset one another).

## Relating $\Delta G^\circ$ to $\Delta G$ and $K$

- $\Delta G$  is not standard. It changes as a chemical reaction proceeds, as concentrations and/or temps change.
- $\Delta G^\circ$  **IS** standard and does **NOT** change during a reaction.
- $\Delta G = \Delta G^\circ + RT \ln Q$
- $Q$  (from Ch. 13, conc. not necessarily at equil.)
- $RT \ln Q$  is correction for non-standard condition;  $R = 8.314 \text{ J/mol}\cdot\text{K}$  (just unit conversions from  $0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$ )

## $\Delta G^\circ$ and Equilibrium

Figure 16.10



## $\Delta G$ and $\Delta G^\circ$

- Consider:  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
- $Q_p = (P_{\text{NH}_3})^2 / [(P_{\text{N}_2})(P_{\text{H}_2})^3]$
- If we're at equilibrium,  $\Delta G = 0$  and  $Q_p = K_p$ 
  - ♦  $\Delta G^\circ = -RT \ln K$
- If the reaction mixture is mostly reactants:
  - ♦  $Q \ll 1$ ,  $RT \ln Q \ll 0$
  - ♦  $\Delta G < 0$
- If the reaction mixture is mostly products:
  - ♦  $Q \gg 1$ ,  $RT \ln Q \gg 0$
  - ♦  $\Delta G > 0$

## $\Delta G^\circ$ and Equilibrium

- When  $\Delta G = 0 = \Delta G^\circ + RT \ln Q$ , we call this a state of equilibrium.
- At equilibrium,  $Q = K$ .
- Thus,  $\Delta G^\circ = -RT \ln K$
- $\Delta G^\circ > 0$  when  $K \ll 1$  (lies toward reactants)
- $\Delta G^\circ < 0$  when  $K \gg 1$  (lies toward products)
- $\Delta G^\circ = 0$  when  $K = 1$  (roughly equal amounts of reactants and products)

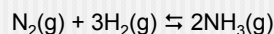
## $\Delta G^\circ$ and K

**TABLE 17.4** Relationship Between the Standard Free-Energy Change and the Equilibrium Constant for a Reaction:  $\Delta G^\circ = -RT \ln K$

$\Delta G^\circ$	$\ln K$	$K$	Comment
$\Delta G^\circ < 0$	$\ln K > 0$	$K > 1$	The equilibrium mixture is mainly products.
$\Delta G^\circ > 0$	$\ln K < 0$	$K < 1$	The equilibrium mixture is mainly reactants.
$\Delta G^\circ = 0$	$\ln K = 0$	$K = 1$	The equilibrium mixture contains comparable amounts of reactants and products ( $K = 1$ for 1 M concentrations and 1 atm partial pressures).

## Group Quiz #13

- $\Delta G^\circ = -RT \ln K$
- Calculate K (the equilibrium constant) for the following reaction at 25.0°C.



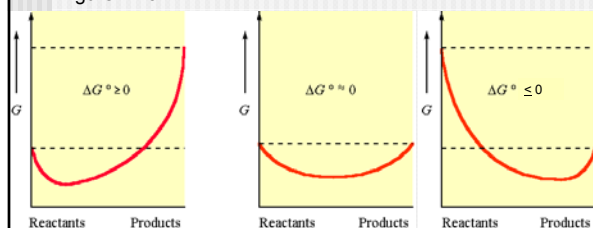
$$\Delta G^\circ_f (\text{HBr}) = -16.5 \text{ kJ/mol}$$

(Hint: This value goes with the formation reaction!!!!)

## $\Delta G^\circ$ and Equilibrium

- The position of equilibrium depends on the value of  $\Delta G^\circ$ .

Figure 12.9



## Calculations Practice

- Calculate K for  $2\text{CuO}(\text{s}) \rightleftharpoons 2\text{Cu}(\text{s}) + \text{O}_2(\text{g})$  at 25°C.
- Calculate  $\Delta G^\circ$  from Appendix B values.
  - $\Delta G^\circ_f (\text{CuO}(\text{s})) = -130 \text{ kJ/mol}$ ;  $\Delta G^\circ_f (\text{Cu}(\text{s})) = 0$ ;  $\Delta G^\circ_f (\text{O}_2(\text{g})) = 0$
- $\ln K = -104.94$
- $K = 2.66 \times 10^{-46}$

## Calculating K

- $\Delta G^\circ_{\text{rxn}}$  for the formation of ethanol is -24.7 kJ.
- $\text{CO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$
- Calculate the equilibrium constant, K, at 25°C for this reaction.
- $\ln K = \Delta G^\circ / -RT = -24,700 \text{ J} / -(8.314 \text{ J/mol}\cdot\text{K} \cdot 298\text{K})$
- $\ln K = 9.97$ ;  $K = 2.14 \times 10^4$

## Calculations Practice

- Calculate  $\Delta G^\circ$  for  $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
- This is a weak acid solution. Find  $\Delta G^\circ$  at 25°C.
  - $K_a = 1.8 \times 10^{-5}$
- $\Delta G^\circ = -RT \ln K$
- $\Delta G^\circ = 27.1 \text{ kJ}$

## Calculations Practice

- Calculate  $\Delta G$  for  $S(s) + O_2(g) \rightleftharpoons SO_2(g)$  when  $P_{O_2} = 0.140$  atm and  $P_{SO_2} = 1.24$  atm at  $25^\circ\text{C}$ .
- Need to calculate  $\Delta G^\circ$  and  $Q$ .
  - ♦  $\Delta G^\circ_f(S(s)) = 0$  kJ/mol;  $\Delta G^\circ_f(O_2(g)) = 0$  kJ/mol;  $\Delta G^\circ_f(SO_2(g)) = -300.2$  kJ/mol
- $Q = 1.24 \text{ atm} / 0.140 \text{ atm} = 8.8571$
- $\Delta G^\circ = -300.2$  kJ
- $\Delta G = -300.2 \text{ kJ} + (0.008314 \text{ kJ/molK})(298\text{K}) \ln(8.8571) = -295 \text{ kJ}$

## Calculations Practice

- $\Delta G^\circ$  for the reaction  $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$  is  $2.60$  kJ at  $25^\circ\text{C}$ .
- In one experiment, the initial pressures are  $P_{H_2} = 4.26$  atm,  $P_{I_2} = 0.024$  atm, and  $P_{HI} = 0.23$  atm.
- Calculate  $\Delta G$  and predict the direction that this reaction will proceed.
- Can compare  $Q$  &  $K$  values to predict.
- Examples 16.8-11, Problems 16.13-17

The End