Ch. 19: Chemical Thermodynamics (Thermochemistry II)

- Chemical thermodynamics is concerned with energy relationships in chemical reactions.
- We consider enthalpy... ΔH .
- We also consider randomness or disorder in the reaction.
- First, let's look at some vocabulary terms...

•Any process that occurs without outside intervention is a spontaneous process... *Example:* Drop an egg on the ground and it will break.

•A process that is spontaneous in one direction is not spontaneous in the opposite direction...*Example:* Dropping a broken egg on the ground will not make it spontaneously come back together.

• Temperature may also effect the spontaneity of a process... Example: $(a) \leftarrow \rightarrow (l)$. Water malts spontaneously above 0° C but

Reversible and Irreversible Processes

- A reversible process is one that can go back and forth between states along the same path. The reverse process restores the system to its original state.
- The path taken back to the original state is *exactly* the reverse of the forward process.
- There is no net change in the system or the surroundings when this cycle is completed...*Example:* At 0° C, water freezing and melting is reversible, but it is irreversible at other temperatures.
- Quick Facts:
- Chemical systems in equilibrium are reversible.
- <u>Completely</u> reversible processes are too slow to be attained in practice.
- In any spontaneous process, the path between reactants and products is irreversible.

An Example of Irreversible Processes



- In order for the system to go back to the way it was, the surroundings would have to do work on the system which changes the surroundings forever.
- This process is therefore irreversible.

Entropy

- Nature tends toward disorganization, a more random arrangement of molecules.
- This is because disordered arrangements are much more probable than ordered arrangements.
- Entropy (S): a measure of the <u>disorder</u> of a system.
- The higher the entropy, the greater the degree of disorder.

- Processes in which the disorder or entropy of the system increases tend to be spontaneous.

- Spontaneous reactions proceed to lower energy, $-\Delta H$, <u>or</u> higher entropy, $+\Delta S$.

 Entropy is a state function...(the path doesn't matter, only the initial and final states of the system make any difference.)

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

If Δ S > 0 the randomness increases, if Δ S < 0 the order

Entropy

Entropy Examples:

1) Consider the melting of ice...

- When it melts, the molecules have more freedom to move increasing degrees of freedom.

- The molecules are more randomly distributed and have more entropy.

2) Consider a KCI crystal dissolving in water...

- The solid KCI has ions in a highly ordered arrangement. When the crystal dissolves the ions have more freedom. They are more randomly distributed...more entropy.

- However, now the water molecules are more ordered. Some must be used to hydrate the ions. Thus this example involves both ordering and disordering. (The disordering usually predominates for most salts.)

In general: A gas is less ordered than a liquid which is less ordered

Entropy of Dissolving



Entropy



Things to note...

- Boiling corresponds to a much greater change in entropy than melting.
- Entropy will increase when... - liquids or solutions are formed from solids.
- gases are formed from solids or liquids.
- the number of gas molecules increase.

-the temp. is increased.

Relating Entropy to Heat Transfer and

• Suppose a system changes reversibly between state 1 and state 2...

<u>Example</u>: A phase change occurs at constant T with the reversible addition of heat such as freezing/melting equilibrium for water at 0° C.

• Then, the change in entropy at constant temperature is given by:

$$\Delta S_{sys} = q_{(rev)}/T$$

(...where $q_{(rev)}$ is the amount of heat added reversibly to the system.)

• The subscript "rev" reminds us that the path between states is reversible.

Entropy & the 2nd Law of

- 2nd Law of Thermody and points neous process, the entropy of the universe increases.
- The change in entropy of the universe is the sum of the change in entropy of the system and the change in entropy of the surroundings.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

• For a reversible process:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$$

• For a spontaneous process (i.e., irreversible):

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

Therefore, entropy <u>*is not*</u> conserved... ΔS_{univ} is continually increasing.

•Note: The second law states that the entropy of the universe

Entropy & the 3rd Law of

- In a perfect crystal **anex meets names**tion, rotation or vibration of molecules. Therefore, this is a state of perfect order.
- Third Law of Thermodynamics: the entropy of a perfect crystal at 0 K is zero.



Increasing temperature



Entropy Changes in Chemical Reactions

- Absolute entropy can be determined from complicated measurements.
- Standard molar entropy, S°: entropy of a substance in its standard state...(This is similar in concept to Δ H°.)
- **<u>Units</u>**: J/mol-K... (Note: units of Δ H are in kJ/mol.)
- Standard molar entropies of elements are <u>not</u> zero!
- For a chemical reaction:

$$\Delta S^{\circ} = \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}}$$

<u>Example</u>: Consider the reaction: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

$$\Delta S^{\circ} = 2S^{\circ}(NH_3) - [S^{\circ}(N_2) + 3S^{\circ}(H_2)]$$

• The values for standard entropies are in Appendix C in the textbook.

• We could just look them up and plug and chug!...(See

Gibbs Free Energy: Predicting

- We know that spontan Spontations the universe, and that exothermic reactions also tend to be spontaneous.
- But what's the deal with spontaneous endothermic reactions? Or how about a spontaneous exothermic reaction that decreases entropy?
- Both concepts, enthalpy and entropy, drive the spontaneity of chemical reactions.
- •How do we balance ΔS and ΔH to predict whether a reaction is going to be spontaneous?
- Gibbs Free Energy: G = H TS
- For a process occurring at constant temperature... $\Delta G = \Delta H T \Delta S$
- If ΔG is (–), the reaction is spontaneous in the forward direction.

Standard Free Energy Changes

- We can tabulate standard free energies of formation, Δ ${\it G^{o}}_{\rm f}$.
- <u>Standard states are</u>: pure solid, pure liquid, 1 atm (gas), 1 M for solutions, and $\Delta G^{o}_{f} = 0$ for elements.
- We most often use 25° C (or 298 K) as the temperature.
- The standard free-energy change for a process is given by:

$$\Delta G^{o} = \Sigma \Delta G^{o}_{f \text{ (products)}} - \Sigma \Delta G^{o}_{f \text{ (reactants)}}$$

Standard Free Energy and Temperature

Often times, temperature will determine if a reaction is spontaneous.

 $\bullet \Delta G = \Delta H + (-T\Delta S)$

Standard Free Energy and Temperature

TABLE 19.4		Effect of Temperature on the Spontaneity of Reactions			
ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T \Delta S$	Reaction Characteristics	Example
0	+	4 7	Always negative	Spontaneous at all temperatures	$2O_3(g) \longrightarrow 3O_2(g)$
+	-	+	Always positive	Nonspontaneous at all temperatures; reverse reaction always spontaneous	$3O_2(g) \longrightarrow 2O_3(g)$
—	-	+	Negative at low <i>T;</i> positive at high <i>T</i>	Spontaneous at low <i>T</i> ; becomes nonspontaneous at high <i>T</i>	$\mathrm{H}_{2}\mathrm{O}(l)\longrightarrow\mathrm{H}_{2}\mathrm{O}(s)$
+	+	-	Positive at low <i>T</i> ; negative at high <i>T</i>	Nonspontaneous at low <i>T</i> ; becomes spontaneous at high <i>T</i>	$\mathrm{H}_{2}\mathrm{O}(s) \longrightarrow \mathrm{H}_{2}\mathrm{O}(l)$

• If $\Delta H < 0$ and $\Delta S > 0$, then ΔG is always negative...(spontaneous.)

- If $\Delta H > 0$ and $\Delta S < 0$, then ΔG is always positive...(nonspontaneous)
- If $\Delta H < 0$ and $\Delta S < 0$, then ΔG is negative at low temperatures.
- If $\Delta H > 0$ and $\Delta S > 0$, then ΔG is negative at high temperatures.
- **<u>NOTE</u>**: Even though a reaction has a negative ΔG it may occur too slowly to be observed.

Free Energy and the Equilibrium

- It is useful to determine whether table tances <u>under any</u> <u>conditions</u> will react.
- •Here's a formula which will determine if a reaction will occur:

$\Delta \mathbf{G} = \Delta \mathbf{G}^{\mathbf{o}} + \mathbf{RT} \ln \mathbf{Q}$

...where Q is the reaction quotient which is similar to K_{eq} but it is not at standard conditions.

- "R" is the ideal gas constant, 8.314 J/mole·K, and "T" is the temperature in Kelvin.
- Again, (–) ΔG means the reaction will be spontaneous in the forward direction.
- When a reaction is at standard conditions, Q = 1, so... In Q = 0.
- See Practice Problems for all of the examples!

Free Energy and the Equilibrium

• At equilibrium, $Q = K_{eq} a Req Q C S t a, R t ...$

 $\Delta G^{o} = - RT \ln K_{eq}$

- From the above we can conclude the following:
- If $\Delta G^{\circ} < 0$, then K > 1...the reaction will go forward.
- If $\Delta G^{\circ} = 0$, then K = 1...the reaction is at equilibrium.
- If $\Delta G^{\circ} > 0$, then K < 1...the reaction will go in reverse.
- Here's the equation rearranged to solve for K_{eq} :

 $K_{eq} = e^{-\Delta G_0/RT}$

- Be sure ΔG° is in units of kJ/mol, and the values in the equilibrium expression are in atm or moles/L.
- Finally, if you want a nonspontaneous reaction to proceed, you have to supply energy to the system to "drive" it forward. Nature does this often. (See p. 765 for more details.)