

These Notes are to **SUPPLIMENT** the Text, They do NOT Replace reading the Text Book Material.  
Additional material that is in the Text Book will be on your tests! To get the most information, **READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes.**  
**These notes alone are NOT enough to pass any test!**

**NOTE THESE ARE DRAFT LECTURE NOTES!**

**1<sup>st</sup> Law of Thermodynamics:** Energy cannot be created or destroyed. The change in the internal energy of a system is the sum of the energy transferred into or out of the system as heat and/or as work,  $\Delta U = q + w$

**2<sup>nd</sup> Law:** Energy goes from being more concentrated to being more dispersed in the Universe  
It is not possible to have 100% of the energy in a process be transferred as work.  
A spontaneous process is one that results in an increase of the Entropy of the Universe.

**3<sup>rd</sup> Law:** A perfect crystal at 0 K will have zero entropy,  $S = 0$ .

**System:** The part of the Universe under study

**Surroundings:** The rest of the universe excluding the system, it is capable of exchanging energy and/or matter with the System

**Exothermic:** Energy transfers as heat from the system to the surroundings

**Endothermic:** Energy transfers as heat from the surroundings to the system

**Enthalpy change:**  $\Delta H$ , The energy transferred as heat under conditions of constant pressure

**Entropy Change:**  $\Delta S$

**State function:** The quantity whose value depends only on the state of the system

**Standard conditions:** Pressure – 1 bar, solution concentration = 1 M

**Standard Enthalpy of Formation:**  $\Delta_f H^\circ_f$  = the enthalpy change when one mol of a compound is formed from its elements in their standard state

### **Change is Central to Chemistry**

Spontaneous represents a change that occurs without outside intervention

Spontaneous changes occur only in the direction that leads to Equilibrium

Systems never change spontaneously in a direction that takes them farther from equilibrium

## **19.1 Spontaneity and Energy Transfer as Heat**

## **Exothermic Examples:**

1. A piece of hot metal is placed in a beaker of cold water → energy is transferred spontaneously as heat from hot to cold until both objects are at the same temperature. It will never happen that the metal will heat up and the water will get colder!
2. H<sub>2</sub> (gas) + O<sub>2</sub> (gas) will burn to form water
3. HCl + NaOH forms water via neutralization
5. Methane (CH<sub>4</sub>) will burn in air to produce CO<sub>2</sub> and Water.
6. Sodium and Chlorine will react to form NaCl

## **Non-Exothermic Reactions**

1. If the valve on a two container flask, where one container has a gas and the other a vacuum is opened, the gas will evenly be distributed between the two containers. It will never happen that the gas will all go into only one container.
2. Dissolving Ammonium Nitrate in water, the NH<sub>4</sub>NO<sub>3</sub> dissolves spontaneously but  $\Delta H = + 25.7 \text{ kJ/mol}$  or Endothermic
3. Phase changes: The melting of ice is endothermic, above 0°C it melts spontaneously, below 0°C it is not spontaneously, at 0°C no net change will occur – temperature can determine spontaneity!
4. A cold can of soda sitting outside (in Florida Summer), the temperature will rise until the can and contents reaches the ambient temperature. Energy transfers as heat from a hot object to a colder object.

**Conclusion:** The evolution of heat cannot be a sufficient criterion in determining spontaneity.

## **19.2 Dispersal of Energy: Entropy (S)**

You drop a book, it hits the floor. Potential Energy is converted to Kinetic Energy and then to thermal, acoustic and other forms of energy. The book WILL spontaneously fall to the ground. The book on the ground, WILL NOT jump back up onto the desk!

Energy has gone from concentrated to being more dispersed.

**Therefore:** In a spontaneous process, energy goes from being more concentrated to being more dispersed.

This is called the Entropy (S) and in a spontaneous process,  $\Delta S$  is greater than zero, or energy is being dispersed in the process.

$$\Delta S = q_{\text{rev}} / T \text{ in units of J/K}$$

$q_{\text{rev}}$  = the reaction must return to the starting point along the same path without altering the surroundings – and

1. At every step along a reversible pathway between the two states, the system remains at equilibrium
2. Spontaneous processes often follow irreversible pathways and involve non-equilibrium conditions.

Melting of ice and freezing of water at 0°C is an example of a reversible process

**Dispersal of Energy** – See description if the book, but as a summary of the discussion:  
As the number of particles increases, therefore, the number of microstates available increases dramatically, and the fraction of microstates in which the energy is concentrated rather than dispersed goes down dramatically. It is more likely that the Energy will be dispersed rather than concentrated!

### **S = k ln (W)**

Entropy of a system = Boltzmann's Constant ( $1.381 \times 10^{-23}$  J/K) \* ln (the number of accessible microstates)

**Dispersal of Matter** – the Entropy of the System Increases

Gas Expands: just open the valve on a container of gas, the gas has a larger volume thus a larger number of microstates

Dissolve KMnO<sub>4</sub> in water, drop in some KMnO<sub>4</sub> crystals, with time the water will turn purple as the KMNO<sub>4</sub> dissolves, the KMNO<sub>4</sub> is dispersed.

Per the 3<sup>rd</sup> Law – a perfect crystal at 0 K has S = 0. And since  $\Delta S = q/T$ , as you add energy to this crystal (q),  $\Delta S$  is a positive value so all substances have positive entropy values at T > 0 K.

$S^\circ$  = Standard Molar Entropy = the entropy gained by converting 1 mole of a perfect crystal at 0 K to standard state conditions.

Large molecules generally have larger entropies than smaller molecules

More complex molecular structures have larger entropies than simpler structures

Gases have larger entropies than liquids

Liquids have larger entropies than solids

A change of state produces a large increase in entropy

For a reaction:  $\Delta S = \Sigma nS^\circ$  (Products) -  $\Sigma nS^\circ$  (Reactants)

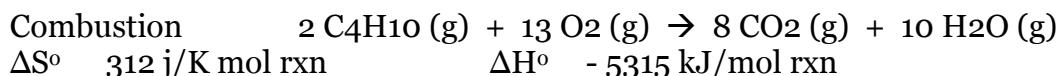
There are examples in the text book

A reaction where  $\Delta S$  is Positive = a spontaneous process and one that results in an increase of entropy in the universe

Other examples of increase of Entropy are where the number of moles of a gas are more for the product than the reactant.

### **Prediction of Spontaneous Reactions**

| <b>React</b> | $\Delta H^\circ$         | $\Delta S^\circ$       | <b>Is it Spontaneous</b>        |
|--------------|--------------------------|------------------------|---------------------------------|
| <b>Type</b>  | <b>System</b>            | <b>System</b>          |                                 |
| 1            | <b>Exothermic &lt; 0</b> | <b>Positive &gt; 0</b> | Spontaneous at all temperatures |



|   |                          |                        |   |
|---|--------------------------|------------------------|---|
| 2 | <b>Exothermic &lt; 0</b> | <b>Negative &lt; 0</b> | Depends on magnitude of $\Delta S^\circ$ and $\Delta H^\circ$<br>Spontaneous at Lower T |
|---|--------------------------|------------------------|---|

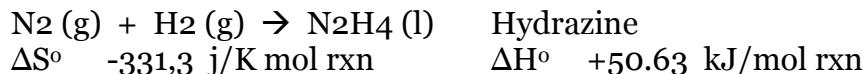
$$\Delta S = q_{\text{rev}} / T \quad \text{So the lower the temperature, the larger } \Delta S$$

An Exothermic Process with  $\Delta S$  negative,  $\Delta S$  will be smaller at higher temperatures

|   |   |  |
|---|---|--|
| 3 | <b>Endothermic &gt; 0 Positive &gt; 0</b> | Depends on magnitude of $\Delta S^\circ$ and $\Delta H^\circ$<br>Spontaneous at Higher T |
|---|---|--|

$\Delta S = q_{rev} / T$  So the higher the temperature, the smaller  $\Delta S$   
An Exothermic Process with  $\Delta S$  negative,  $\Delta S$  will be smaller at higher temperatures

|   |   |                                    |
|---|---|------------------------------------|
| 4 | <b>Endothermic &gt; 0 Negative &lt; 0</b> | Not spontaneous at any temperature |
|---|---|------------------------------------|



|                               |   |
|-------------------------------|---|
| <b>19.6 Gibbs Free Energy</b> | $G = H - TS$  |
|                               | $G = \text{Gibbs Free Energy}, H = \text{Enthalpy}, T \text{ is temp in K}, S \text{ is Entropy}$ |

Free energy is the Maximum Energy available to do useful work.

We will be concerned about the Change of G or  $\Delta G = \Delta H - T\Delta S$

Since G and S are related

- $\Delta G < 0$  Process is spontaneous in the direction written under standard conditions
- $\Delta G = 0$  Process is at equilibrium
- $\Delta G > 0$  Process is NOT spontaneous in the direction written under standard conditions

$\Delta G^\circ$  is the change in free energy accompanying the chemical reaction in which the reactants are converted completely to the products under standard conditions.

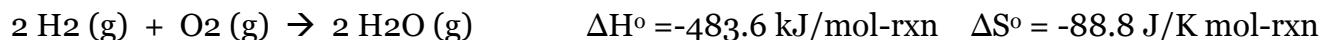
It is the difference in the free energy of the products minus the free energy of the reactants.

$$\Delta G = \Sigma nG^\circ (\text{Products}) - \Sigma nG^\circ (\text{Reactants})$$

Based on the Equilibrium Constant:

$$\Delta G^\circ = -RT \ln K$$

Note: When  $K > 1$ , then  $-RT \ln(10) = -RT 2.3$  then  $\Delta G^\circ$  is negative and the reaction is spontaneous



$$\Delta G^\circ = \Delta H - T\Delta S = -483.6 \text{ kJ/mol-rxn} - (298 \text{ K} \times -88.8 \text{ J/K mol-rxn}) = -457.2 \text{ kJ/mol-rxn}$$

Negative  $\Delta S^\circ$  means product energy is more dispersed than the reactants

And even though  $\Delta H^\circ = -483.6 \text{ kJ/mol-rxn}$ , only  $\Delta G^\circ = -457.2 \text{ kJ/mol-rxn}$  is available as heat

Free Energy and Temperature  $\quad G = H - TS$

Free Energy is a function of Temperature and this can effect equilibrium depending on the values of  $\Delta H^\circ$  and  $\Delta S^\circ$