AP Chemistry Name _____
Ms. Ye Date _____Block_____

First Law of Thermodynamics

- _____
- Therefore, the total energy of the universe is a constant.
- Energy can, however, _____ from one form to another or _____ from a system to the surroundings or vice versa

Spontaneous Processes

- Spontaneous processes _____
- Characteristics of spontaneity:
  1. _____
     - A nail will spontaneously rust but not spontaneously unrust
  2. _____
     - Above 0°C it is spontaneous for ice to melt.
     - Below 0°C the reverse process (freezing) is spontaneous.
     - At 0 °C both processes are in equilibrium and neither reaction is favored

Example: Determine whether the following processes are spontaneous:

a) when a piece of metal heated to 150°C is added to water at 40°C, the water gets hotter

b) water at room temperature decomposes into $H_2(g)$ and $O_2(g)$

c) Benzene vapor, $C_6H_6(g)$, at a pressure of 1atm, condenses to a liquid at the normal boiling point of benzene, 80.1°C

What is the driving force for reactions?

- Thought used to be just enthalpy – _____
  - **negative ΔH is "good" – more favorable**
  - leads to lower potential energy, which is more stable

BUT…….

- We do have reactions that are **endothermic** that occur **spontaneously**
- So another driving force could be **ENTROPY (S)!**

Units = J/mol x K

** NOTE THE UNITS! The standard for this is in J, while ΔH is in kJ/mol

Entropy

- _____in a system
- Described as the # of possible arrangements that are available to the system
- Reactions will **"**_____"
  - Entropy tends to increase with increases in
  - _____
  - _____
  - _____
    - State change
      - Entropy increases with the freedom of motion of molecules.
      - **Therefore,** _____
    - Solubility
      - **Generally, when a _____,**
        _____

Example:

1. Choose the sample of matter that has a greater entropy in each pair:
   a) 1mol NaCl(s) or 1mol HCl(g)

   b) 2mol HCl(g) or 1mol HCl(g)

   c) 1mol of HCl(g) or 1mol Ar(g)

2. Predict whether ΔS is positive or negative for each of the following processes:
   a) $H_2O(l) \rightarrow H_2O(g)$

   b) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

   c) $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

   d) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

Second Law of Thermodynamics

- _____
  and the entropy of the universe does not change for reversible processes.

Standard Changes in Entropy

- Standard entropy changes for a reaction can be estimated in a manner analogous to that by which ΔH is estimated: $\Delta S^\circ = \Sigma \Delta S^\circ(\text{products}) - \Sigma \Delta S^\circ(\text{reactants})$

Example:

1. Calculate the entropy of the following reaction: $2NiS(s) + 3O_2(g) \rightarrow 2SO_2(g) + 2NiO(s)$. The standard molar entropies for each substance is given below.

SO_2 = 248 J/mol K
O_2 = 205 J/mol K
NiO = 38 J/mol K
NiS = 53 J/mol K

2. Calculate the standard entropy change for the reaction below at 298K:

$$Al_2O_3(s) + 3H_2(g) \rightarrow 2Al(s) + 3H_2O(g)$$

S° values:
Al_2O_3 =51 J/mol K
H_2 = 130.58 J/mol K
Al = 28.32 J/mol K
H_2O = 188.83 J/mol K

Third Law of Thermodynamics

- _____
  - ONLY AT ABSOLUTE ZERO!
  - H_f of an element = 0, but the S of one is usually *NOT – be careful*

Gibbs Free Energy

- Can be thought of as the _____
- Mathematically combines enthalpy and entropy to predict whether a reaction at constant temperature and pressure will be spontaneous
- **$\Delta G = \Delta H - T \Delta S$**
  1. **If _____,** the forward reaction is spontaneous.
  2. **If _____,** the system is at equilibrium.
  3. **If _____,** the reaction is spontaneous in the reverse direction.

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

Problem with units:

ΔH = kJ/mole

ΔS = J / mole x K

T = K

*****Convert J to kJ******

Example:

1. Calculate the standard free energy change for the formation of NO(g) from $N_2(g)$ and $O_2(g)$ at 298K given that ΔH^o=180.7kJ and ΔS^o=24.7J/K. Is the reaction spontaneous under these conditions?

2. A particular reaction has a ΔH^o = 24.6kJ and ΔS^o =132J/K at 298K. Calculate ΔG^o. Is the reaction spontaneous under these conditions?

Standard Free Energy Changes

- Analogous to standard enthalpies of formation are standard free energies of formation, ΔG°: $\Delta G^\circ = \Sigma \Delta G^\circ(\text{products}) - \Sigma \Delta G^\circ(\text{reactants})$

Example:

1. Calculate the free-energy change for the following reaction at 298K:
   $P_4(g) + 6Cl_2(g) \rightarrow 4PCl_3(g)$. What is ΔG^o for the reverse reaction?

G° values:

P_4 = 24.4 kJ/mol

Cl_2 =0 kJ/mol

PCl_3= -269.6 kJ/mol

2. The ΔH^o for the combustion of propane is -2220kJ : $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
   a) Predict whether ΔG^o for this reaction is more or less negative than ΔH^o

   b) Calculate ΔG^o. Was your prediction correct?

G° values:

C_3H_8 = -23.47 kJ/mol

O_2 = 0 kJ/mol

CO_2 = -394.4 kJ/mol

H_2O = -237.13 kJ/mol

Spontaneity: Free Energy and Temperature $\Delta G = \Delta H - T\Delta S$

ΔH	ΔS	ΔG	Reaction Characteristics
-	+	-	
+	-	+	
-	-	+ or -	
+	+	+ or -	

Example:

1. The Haber process is used for the production of ammonia: N_2 (g) + 3 H_2 (g) → 2 NH_3 (g)

Assume ΔH^o and ΔS^o for this reaction do not change with temperature.

a) Predict the direction in which ΔG^o for this reaction changes with increasing temperature

b) Calculate the ΔG^o values for the reaction at 25°C and 500°C.

	H °	S °
H_2	0 kJ/mol	130.58 J/mol K
N_2	0 kJ/mol	191.50 J/mol K
NH_3	-46.19 kJ/mol	192.5 J/mol K

Spontaneity HW

Entropy-Spontaneity

1. Which of the following processes are spontaneous (circle all that apply)?
   a. Salt dissolves in H_2O
   b. A clear solution becomes a uniform color after a few drops of dye are added
   c. Iron rusts
   d. You clean your bedroom

2. When the environment is contaminated by a toxic or potentially toxic substance (for example, from a chemical spill or the use of insecticides), the substance tends to disperse. How is this consistent with the second law of thermodynamics?

Entropy – Qualitative

3. Predict the sign of ΔS for each of the following:
   a. the evaporation of alcohol

   b. the freezing of water

   c. compressing an ideal gas at constant temperature

4. For each of the following pairs, circle the substance that has the larger standard entropy:
   a. 1 mol of $P_{4\,(g)}$ at 300°C, 0.01 atm or 1 mol of $As_{4\,(g)}$ at 300°C, 0.01 atm

   b. 1 mol of $H_2O_{\,(g)}$ at 100°C, 1 atm or 1 mol of $H_2O_{\,(l)}$ at 100°C, 1 atm

   c. 1 mol of $Ne_{\,(g)}$ in 15.0 L or 1.0 mol of $Ne_{\,(g)}$ in 1.50 L

   d. 0.5 mol of $N_{2\,(g)}$ at 298 K, 20.0 L or 0.5 mol of $N_{2\,(g)}$ at 498 K, 20.0 L

5. Predict the sign of the entropy change of the system for each of the following reactions:
   a. $N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g)$

   b. $CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$

   c. $3\,C_2H_2\,(g) \rightarrow C_6H_6\,(g)$

   d. $2\,H_2S\,(g) + SO_2\,(g) \rightarrow 3\,S(s) + 2\,H_2O\,(g)$

   e. $2\,SO_3\,(g) \rightarrow 2\,SO_2\,(g) + O_2\,(g)$

Entropy – Quantitative

6. Predict the sign of ΔS° expected for the following reactions. Then calculate the exact value of ΔS° for each reaction that follows.

Substance	S° Values (J/mol K)
C_2H_6 (g)	229.5
C_6H_6 (l)	172.8
H_2 (g)	130.58
O_2 (g)	205.0
H_2O (l)	69.91
H_2O (g)	188.83
CH_3OH (g)	237.6
CO_2 (g)	213.6

a. $3\ C_2H_{6\,(g)} \rightarrow C_6H_{6\,(l)} + 6\ H_{2\,(g)}$

b. $H_{2\,(g)} + ½\ O_{2\,(g)} \rightarrow H_2O_{\,(l)}$

c. $2\ CH_3OH_{\,(g)} + 3\ O_{2\,(g)} \rightarrow 2\ CO_{2\,(g)} + 4\ H_2O_{\,(g)}$

GIBBS FREE ENERGY

Free Energy Concepts

1. Given the values of ΔH and ΔS, which of the following changes will be spontaneous at constant T and P?
   a. ΔH = + 25 kJ, ΔS = + 5.0 J/K, T = 300. K

   b. ΔH = + 25 kJ, ΔS = + 100. J/K, T = 300. K

   c. ΔH = - 10.0 kJ, ΔS = + 5.0 J/K, T = 298 K

   d. ΔH = - 10.0 kJ, ΔS = -40. J/K, T = 200. K

2. Classify the following reactions as <u>spontaneous at all temperatures</u>, <u>nonspontaneous at all temperatures</u>, <u>spontaneous at low T</u>, or <u>spontaneous at high T</u>:
   a. $N_{2\,(g)} + 3\ F_{2\,(g)} \rightarrow 2\ NF_{3\,(g)}$ ΔH° = - 249 kJ; ΔS° = - 278 J/K

   b. $N_{2\,(g)} + 3\ Cl_{2\,(g)} \rightarrow 2\ NCl_{3\,(g)}$ ΔH° = + 460 kJ; ΔS° = - 275 J/K

   c. $N_2F_{4\,(g)} \rightarrow 2\ NF_{2\,(g)}$ ΔH° = + 85 kJ; ΔS° = 198 J/K

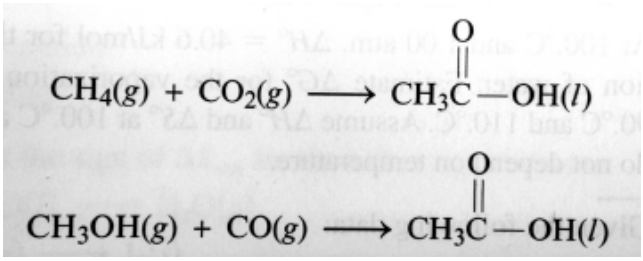
Free Energy Calculations

3. For the reaction at 298 K, **$2\ NO_{2\,(g)} \leftrightarrows N_2O_{4\,(g)}$**, the values of ΔH° and ΔS° are -58.03 kJ and -176.6 J/K, respectively.
   a. What is the value of ΔG° at 298 K?

   b. Assuming that ΔH° and ΔS° do not depend on temperature, at what temperature is ΔG° = 0?

   c. Is ΔG° negative or positive above this temperature?

4. Using thermodynamic data, calculate ΔH°, ΔS°, and ΔG° for the following reactions that produce acetic acid:



Which reaction would you choose as a commercial method for producing acetic acid ($HC_2H_3O_2$) under standard conditions? What temperature conditions would you choose for the reaction?

	H° (kJ/mol)	S° (J/mol K)
CH_4 (g)	-74.8	186.3
CO_2 (g)	-393.5	213.6
CH_3COOH (l)	-487.0	159.8
CH_3OH (g)	-201.2	237.6
CO (g)	-110.5	197.9