Name ______________________ **Honors Chemistry** ___/___/___

Entropy & Free Energy

Entropy (ΔS°) is defined as the amount of disorder or positional probability in a system. For example, a messy room has greater entropy than a clean organized room. Yes, rooms are fun, but this is chemistry and we use molecules, not rooms. Anyway here are a couple of things to understand when thinking about the entropy of molecules:

1. For a given substance, the entropy of the gas is greater than the entropy of the liquid. And, the entropy of the liquid is greater than that of the solid. This makes sense if you think about the movement of the particles at each state. At solid they are nicely organized in a structure, vibrating, but organized. As they become liquid, movement increases. And as they become gases, the movement is out of control…so to speak.

2. In a chemical reaction entropy generally increases where a solid reactant produces a liquid or gaseous product or a liquid reactant produces a gaseous product. Entropy would decrease if the reverse were true. Treat aqueous as it were a liquid. To summarize this one:

s → l or g (increase in entropy) l → g (increase in entropy)
g → l or s (decrease in entropy) l → s (decrease in entropy)

3. Entropy increases when a substance is divided into parts. For example, when sodium chloride decomposes or dissociates, entropy increases. Think of it this way, a compound, sodium chloride is two parts put together. If it is broken into two separate parts, those two parts are a lot more disorganized than if it were neatly put together into one part.

Calculating Entropy

Ok, now we will also calculate the entropy of a reaction in a similar way to how we calculated the enthalpy of a reaction. The formula you need to know is: $\Delta S^\circ_{rxn} = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$

Example #1: Calculate the entropy change when calcium reacts with water. Don't forget to balance!!!

Ca (s) + H_2O (l) → $Ca(OH)_2$ (s) + H_2 (g)

Substance	S° (J/K mol)
Ca (s)	41.4
H_2O (l)	69.9
$Ca(OH)_2$ (s)	75.9
H_2 (g)	130.5

First Balance It:

Ca (s) + **2** H_2O (l) → $Ca(OH)_2$ (s) + H_2 (g)

Determine the entropy for the products and the reactants:

Ca (s) + **2** H_2O (l) → $Ca(OH)_2$ (s) + H_2 (g)
41.4 + **2** (69.9) → 75.9 + 130.5
41.4 + 139.8 → 75.9 + 130.5
181.2 → 206.4

Calculate the ΔS° for the reaction using the formula from above:

$\Delta S^\circ_{rxn} = S^\circ_{products} - S^\circ_{reactants}$
$\Delta S^\circ_{rxn} = 206.4 - 181.2$
$\mathbf{\Delta S^\circ_{rxn} = 25.2\ J/K}$

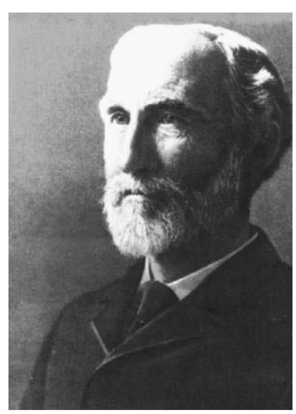
Spontaneous Reactions

Although we can write any chemical reaction on paper, not all chemical reactions will occur. A **spontaneous reaction** is a chemical reaction that will occur because of the nature of the system, once it is initiated. Note that just because a reaction is called spontaneous, does not necessarily mean that the reaction will happen instantly or quickly. It simply means that the chemical reaction will occur once it is started (once it gets enough activation energy).

ΔH°	ΔS°	Spontaneous Reaction
- favorable	+ favorable	yes
+ unfavorable	- unfavorable	no
- favorable	- unfavorable	only if effect of ΔH° > effect of ΔS° **low temperatures**
+ unfavorable	+ favorable	only if effect of ΔS° > effect of ΔH° **high temperatures**

The information referred to in the chart above can be calculated using the Gibbs Free Energy Equation. The Gibbs Equation is: $\mathbf{\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ}$

ΔH° = the change in enthalpy (heat energy)
T = the Kelvin temperature (you **MUST** convert Celsius to Kelvin, **K = ºC + 273**)
ΔS° = the change in entropy



G represents a quantity called **free energy**. The letter G is used in honor of the American mathematician J. Willard Gibbs (1839 – 1903) who first showed that the effect of entropy is dependent upon temperature. What you need to know is:

ΔG° = - (negative), the reaction will occur spontaneously as it is written
ΔG° = + (positive), the reaction will NOT occur spontaneously as it is written

Consider the likelihood of the following two reactions and relate it to their ΔG° values. In the first equation, iron reacts with oxygen to form rust. You know this happens (ΔG° is -). In the second example, rust decomposes to release oxygen and return to pure iron. It would be really cool but this does not happen (ΔG is +).

$4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$ **ΔG° = -1482 kJ (spontaneous)**

$2\ Fe_2O_3(s) \rightarrow 4\ Fe(s) + 3\ O_2(g)$ **ΔG° = 1482 kJ (NOT spontaneous)**

Consider the reaction below:

$Ca(s) + 2H_2O\ (l) \rightarrow Ca(OH)_2(s) + H_2\ (g)$ ΔH° = -414.6 kJ; ΔS° = 25.2 J/K

Determine if the reaction is spontaneous at 25°C.

ΔG° = ΔH° - TΔS°

ΔG° = (-414.6) – (298 x 0.0252)

ΔG° = -422 kJ. The reaction is spontaneous.

Homework:

1. Decide for each of the following whether the ΔS° is increasing (+) or decreasing (-).
   a. __________ $2\ KClO_3\ (s) \rightarrow 2\ KCl\ (s) + 3\ O_2\ (g)$
   b. __________ $2Ag\ (s) + Cl_2\ (g) \rightarrow 2AgCl\ (s)$
   c. __________ $CO_2\ (s) \rightarrow CO_2\ (g)$
   d. __________ $NaCl\ (s) \rightarrow Na^+\ (aq) + Cl^-\ (aq)$
   e. __________ $2C_8H_{18}\ (l) + 25O_2\ (g) \rightarrow 16CO_2\ (g) + 18H_2O\ (g)$
   f. __________ $H_2O\ (g) \rightarrow H_2O\ (l)$

For each of the following reactions you must solve for each:

a. ΔH°
b. ΔS°
c. ΔG° at 25°C
d. Is the reaction spontaneous?
e. At what temperature would the reaction become spontaneous or stop being spontaneous?

2. $K_2O(s) + H_2O(l) \rightarrow 2KOH(aq)$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
$K_2O(s)$	-361	98
$H_2O(l)$	-286	70.
KOH(aq)	-481	9.2

3. $Pb(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2\ (g)$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
Pb(s)	0	65
$H_2SO_4(aq)$	-909	20.
$PbSO_4(s)$	-920	149
$H_2(g)$	0	131

4. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/K mol)
$SO_2(g)$	-297	248
$SO_3(g)$	-396	257
$O_2(g)$	0	205

5. $4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g)$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
$NH_3(g)$	-46	193
$O_2(g)$	0	205
$NO_2(g)$	34	240
$H_2O(g)$	-242	189

6. $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
$CH_3OH(l)$	-239	127
$O_2(g)$	0	205
$CO_2(g)$	-393.5	214
$H_2O(l)$	-286	70

7. $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
$C_6H_{12}O_6(s)$	-1275	212
$O_2(g)$	0	205
$CO_2(g)$	-393.5	214
$H_2O(l)$	-286	70

8. $CH_3OH(l) \rightarrow CH_3OH(g)$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
$CH_3OH(l)$	-239	127
$CH_3OH(g)$	-201	240

9. $H_2SO_4(aq) \rightarrow SO_3(g) + H_2O(l)$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
$H_2SO_4(aq)$	-909	20
$SO_3(g)$	-396	257
$H_2O(l)$	-286	70

10. $C_{graphite}(s) + O_2(g) \rightarrow CO_2(g)$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
$C_{graphite}(s)$	0	6
$O_2(g)$	0	205
$CO_2(g)$	-393.5	214

11. NaCl(s) + H_2O(l) → NaOH(aq) + HCl(g)

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
NaCl(s)	-411	72
H_2O(l)	-286	70.
NaOH(aq)	-470	50
HCl(g)	-92	187

12. Sn(s) + 4HNO_3(l) → SnO_2(s) + 4NO_2(g) + 2H_2O(l)

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/mol K)
Sn(s)	0	52
HNO_3(l)	-174	156
SnO_2(s)	-581	52
NO_2(g)	34	240
H_2O(l)	-286	70