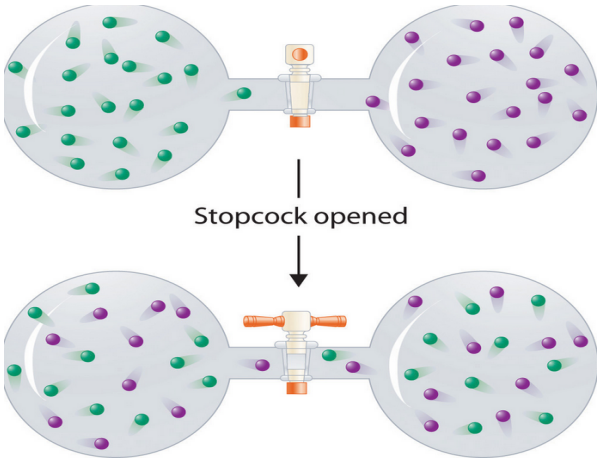
Ch 17 - Spontaneity, Entropy, and Free Energy

ENTROPY: (S) a thermodynamic function that describes the number of arrangements (positions and/ or energy levels) that are available to the system.

- it is a measure of molecular order and disorder
  lower entropy = more order
  higher entropy = less order (more disorder)

- Nature spontaneously proceeds to states with highest probability of existing



ENTROPY:

1) *Phase changes*:
melting, vaporization, and sublimation result in an increase in entropy. Likewise, freezing, condensing, and deposition result in a decrease in entropy.

2) T*emperature changes*:
raising the temperature results in an increase in entropy due to increase in motion (either translational or vibrational)

3) *Volume Changes*:
an increase in volume results in more available space for the particles to occupy. Thus there is an increase in entropy.

4) *Mixing of substances*:
The mixing of 2 or more substances results in an increases in entropy. Examples is the dissolving of a solid into water or mixing 2 liquids.

5) *Increase in the number of particles:*
Any process in which the number of particles increases results in an increase in entropy.

6) *Changes in the number of moles of gaseous substances:*
Processes that result in an increase in the number of moles of gaseous substances result in an increase in entropy.

7) *Size of the particle:*
Larger molecules have higher entropies than smaller molecules and molecules with more complex structures have higher entropies than simpler molecules

Spontaneity - ability/likelihood of a reaction proceeding without outside intervention

1st Law of Thermodynamics: energy cannot be created or destroyed, only transferred

2nd Law of Thermodynamics: In any spontaneous process there is an increase in the entropy of the universe

$$\Delta S = \Delta S_{system} + \Delta S_{surroundings}$$

$\Delta S_{universe}$ + = Increase ↑ entropy, spontaneous
$\Delta S_{universe}$ - = Decrease ↓ entropy, non-spontaneous
ΔS = 0 = no tendency to occur (system is at equilibrium)

Temperature and entropy:

Add heat to a system = endothermic (heat in from the surroundings)

= a increase in energy of system (↑ entropy)

= a decrease in energy of surroundings (↓ entropy)

Remove heat from a system = exothermic (heat to surroundings)

= a decrease in energy of system (↓ entropy)

= a increase in energy of surroundings (↑ entropy)

Choose the sample that has the greater entropy in each pair:

a) 1 mol NaCl(s) or 1mol of HCl(g)
b) 2 mol HCl(g) or 1 mol HCl(g)
c) 1 mol HCl(g) or 1 mol Ar(g)
d) 1 mol N_2 at 24K or 1 mol N_2 at 298K
e) 1mol N_2O_4 or 1 mol NO_2

Predict whether the entropy change of the system in each of the following isothermal reactions is positive or negative:

a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
c) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

Predict the sign of ΔS^0 for each of the following changes:

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

b) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

c) $NaCl(s) \rightarrow NaCl(l)$

d) $HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$

e) $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$

f) $N_2O(g)$ (at 1-atm, 25°C) or He (at 1-atm, 25°C)

g) 1 mole $H_2(g)$ (1-atm, 0°C) or 1 mole $H_2(g)$ (1-atm, 25°C)

Calculating S:

$$\Delta S = \frac{-\Delta H}{\text{Temp}}$$

Determine the entropy value of each reaction at 25 C:

$Sb_3S_{3(s)}$ + 3 $Fe_{(s)}$ ---> 2 $Sb_{(s)}$ + $3FeS_{(s)}$ H = -125 kJ

$Sb_4O_{6(s)}$ + $6C_{(s)}$ ---> $4Sb_{(s)}$ + $6CO_{(g)}$ H = +778 kJ

Now calculate ΔS for the reaction of the following at 25 C:

$2NiS(s) + 3O2(g) \rightarrow SO2(g) + 2NiO(s)$

- Use your equation: $S^0_{rxn} = \sum n_p S^0_{prod} - \sum n_r S^0_{react}$

-Look up your ΔS values (in appendix A19 - A22)

Calculate the ΔS° for the synthesis of ammonia from $N_2(g)$ and $H_2(g)$ at 298K Which equation should you use?

Determining if change is spontanteous:

S_{sys} and S_{surr} are + = $S_{universe}$ + (yes it is spontaneous)

S_{sys} and S_{surr} are - = $S_{universe}$ - (not spontaneous in forward direction BUT IS SPONTANEOUS IN REVERSE DIRECTION)

S_{sys} + and S_{surr} - = only spontaneous if $S_{sys} > S_{surr}$

S_{sys} - and S_{surr} + = only spontaneous if $S_{surr} > S_{sys}$

FREE ENERGY: A thermodynamic function relating enthalpy and entropy at various temperatures

STANDARD FREE ENERGY CHANGE: ΔG^o:

___The change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states.

Under certain conditions the change in the free energy of a process is equal to the maximum useful work

The more negative the value of ΔG, the more the rxn will proceed to products (to the right) to reach equilibrium

- equilibrium position represents the lowest achievable energy of the system

$$\Delta G = \Delta H - T * \Delta S$$

H = enthalpy

T = kelvins

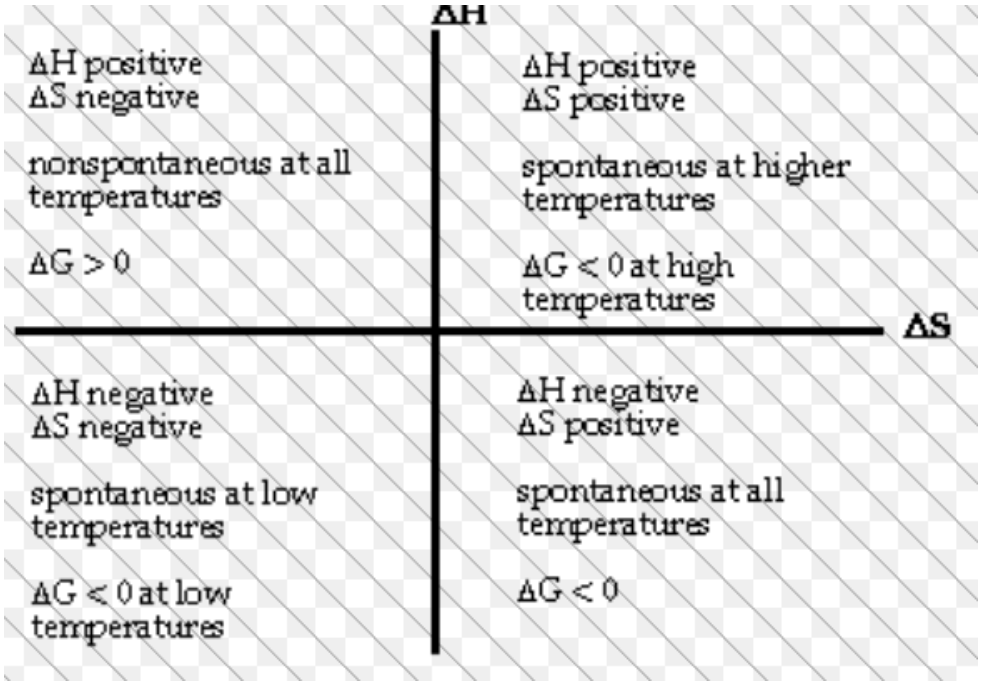
S = entropy

At constant P: $\Delta S = \frac{-\Delta G}{T}$

Use of ΔG:

A) Reaction will be spontaneous when -Δ G, (because this causes + spontaneity)

B) Possible ΔS and Δ H combinations:



	$H_f^o \Delta$	S_f^o
$Ba(OH)_2 * 8H_2O(s)$	-3342	427
$NH_4Cl(s)$	-314.4	94.6
$NH_3(g)$	-80.29	111
$H_2O(l)$	-285.83	69.91
$BaCl_2 * 2H_2O(s)$	-1460.1	203

$Ba(OH)_2 * 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2 * 2H_2O(s) + 2NH_3(g) + 8H_2O(l)$

Determine the ΔG^0 for the above reaction

Multiple steps:

a) Find ΔH ($H^0_{rxn} = \sum n_p H^0_{prod} - \sum n_r H^0_{react}$)

b) Find ΔS ($S^0_{rxn} = \sum n_p S^0_{prod} - \sum n_r S^0_{react}$)

c) Plug into ΔG equation

1) Calculate the standard free energy change for the following reaction by 2 different methods

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$$

Standard Free energy formation equation:

$$G^0_f = \sum n_p G^0_{f(prod)} - \sum n_r G^0_{f(react)}$$

Notes:

ΔG^0_f values = appendix A19-A22

Must use moles * G for each compound

ΔG^0_f for an ELEMENT in its standard state = 0

Ex: Calc ΔG^0 for

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

How spontaneous are each?

$C_2H_{4(g)} + H_2O_{(l)} \rightarrow C_2H_5OH_{(l)}$

2) Estimate the boiling point of water (Hint: What must ΔG be to be spontaneous?)

3) Estimate the temperature range over which

$2HgO(s) \rightarrow 2Hg(l) + O_2(g)$ is spontaneous.

A practice AP problem:

1) Propane, C_3H_8, is a hydrocarbon that is commonly used as fuel for cooking.

A) Write a balanced equation for the complete combustion of propane gas, which yields $CO_2(g)$ and $H_2O(l)$.

B) Calculate the volume of air at 30°C and 1 atm that is needed to burn completely 10.0-g of propane. Assume air is 21% O_2 by volume.

C) The heat of combustion of propane is -2220.1 kJ/mol. Calculate the heat of formation of propane given that ΔH_f^o of $H_2O(l)$ = -285.3 kJ/mol and ΔH_f^o of $CO_2(g)$ = -393.5 kJ/mol.

D) Assuming all of the heat evolved in burning 30.0-g of propane is transferred to 8.00-kg of water, calculate the increase in temperature of the water.

Another practice AP problem

1) $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

The reaction represented above is spontaneous at 25° C. Assume that all reactants and products are in their standard state

A) Predict the sign of ΔS^o for the reaction and justify your prediction.

B) What is the sign of ΔG^o for the reaction? How would the sign and magnitude of ΔG^o be affected by an increase in temperature to 50° C? Explain your answer.

C) What must be the sign of ΔH^o for the reaction at 25° C? How does the total bond energy of the reactants compare to that of the products?

D) When the reactants are placed together in a container, no change is observed even though the reaction is known to be spontaneous. Explain this observation.