Chapter 19 Chemical Thermodynamics

Review
Spontaneous Processes
Second Law of Thermodynamics: Entropy
Gibbs Free Energy
Free Energy, Enthalpy, Entropy and Temperature
Free Energy and the Equilibrium Constant

I. Review from Chapter 5

A. Internal Energy (E), heat (q) and work (w)

1. The ΔE is the change in the internal energy (energy inside the molecule which is translational, vibrational and rotational of the molecule and energy in the bonds).

$\Delta E = q + w$ First Law of Thermodynamics

Energy can be transformed into heat, into work or some combination of both. 2. Heat stored = (mass)(specific heat capacity)(change in temperature). Used to calculate the heat when something is warmed or cooled. **$q = mc(\Delta T)$**

3. Work is **$w = -P\,\Delta V = -P(V_f - V_i)$**

where the P is the opposing pressure.

4. Type of experimental processes.

a. At constant pressure (open container) the **$q = \Delta H$,** the change in enthalpy.

b. At constant volume (closed container) the **$q = \Delta E$,** the change in internal energy.

B. To calculate the heat associated (either released-exo or absorbed-endo) for a chemical reaction done at constant pressure use Hess' Law.

1. Add or substract reactions (reverse-change sign, etc)
2. Use the equation:

$$\Delta H^o_{rxn} = \Sigma n\,[\Delta H^o_f(\text{products})] - \Sigma n\,[\Delta H^o_f(\text{reactants})]$$

The Σ is the mathematical symbol telling us to sum up all the reactants or all the products and the "n" is the number of moles of each reactant or product. **Learn this very important equation.** Recall that Table 5.3 and Appendix C has tabulated values for ΔH^o_f. Remember that the physical state (s, l, g, aq) is important and that ΔH^o_f(elements) = 0.

C. The first law of thermodynamics tells us how the change in internal energy is divided between the work and the heat associated with a process. Nature wants to minimize the energy of a system and will proceed in that direction spontaneously.

1. If the process is spontaneous that means it is irreversible.
2. If a process is at equilibrium it is reversible.

The tendency to minimize energy is only part of nature's desire.

II. Entropy.

A. A measure of the disorder in a system and nature wants to maximize the disorder, the entropy.

S = entropy

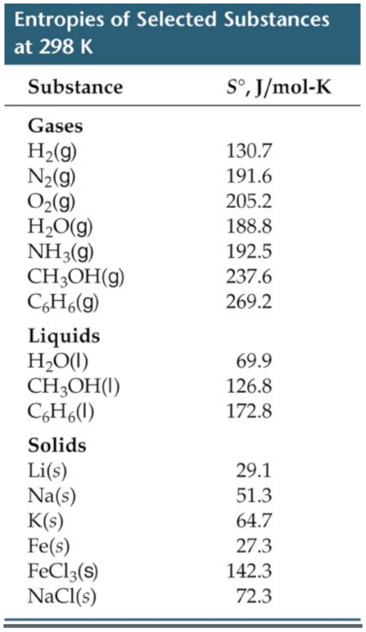
The next three slides show a change in disorder of the system, ΔS. The first is the expansion of a gas into a vacuum, a process that is spontaneous and irreversible. Note the huge increase in disorder upon expansion.

We know the melting of ice is an endothermic process and nature wants to minimize energy so the energy portion tends to keep water as ice. But we also realize that as ice melts there is a large increase in disorder of the water molecules, large increase in entropy. Because the entropy portion is dominant over the enthalpy portion the ice melts spontaneously at temperatures above its melting point. As it melts $\Delta S > 0$.

We know that many salts spontaneously dissolve at room temperature. In this case the water molecules become more ordered when they solvate the ions ($\Delta S < 0$), but the salt becomes less ordered when the very ordered crystal structure is lost as the ions move into solution ($\Delta S > 0$).

B. Third Law of Thermodynamics: At 0K a system is usually a perfectly ordered as possible and the S = 0. As T increases above 0K the entropy will increase as the material becomes more disordered.

1. In general, gases are more disordered than liquids and gases would have the higher entropy. (H-bonding)
2. In general, liquids are more disordered than solids and liquids would have the higher entropy.
3. In general, the more freedom of movement a molecule has the greater the disorder. A molecule with more atoms would then have greater disorder than a molecule with fewer atoms. (H-bonding)



Entropies of Selected Substances at 298 K

Substance	S°, J/mol-K
Gases	
$H_2(g)$	130.7
$N_2(g)$	191.6
$O_2(g)$	205.2
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.3
$K(s)$	64.7
$Fe(s)$	27.3
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

The freedom of movement is associated with translational (in three dimensions), rotational (in two or three dimensions) and vibrational motion (three vibrational motions for water). Of course, water can form strong intermolecular attractions (hydrogen-bonds) in the gas phase which will decrease the entropy compared to a molecule (methane) that cannot form hydrogen bonds.

Symmetric stretch	Bend	Asymmetric stretch	Rotations (in 3-D)

C. Units for entropy.

1. For a compound the units are J/(mol-K) or cal/(mol-K) or e.u. (entropy units).
2. For a chemical reaction the units will be J/K.
3. If the entropy is measured at “Standard State” conditions a superscript o is added, S^o. (Standard state is pure solids, P = 1 atm for gases, and 1.0M concentration for solutions). Standard state entropies are in the Appendix.

D.Entropy change, ΔS^o.

1. In general, $\Delta S^o = S^o_{\text{final state}} - S^o_{\text{initial state}}$.
2. For a chemical reaction: (learn this equation)

$$\boldsymbol{\Delta S^o_{rxn} = \Sigma n\,[S^o(\text{products})] - \Sigma n\,[S^o(\text{reactants})]}$$

a. Calculate the change in entropy for the vaporization of 150.0g of bromine liquid. $Br_2(l) \rightarrow Br_2(g)$

DO Look up the S^o for each of these:

$S^o(Br_2 l)$ = 152.3J/mol-K and $S^o(Br_2 g)$ = 245.3J/mol-K

$$\begin{aligned}\Delta S^o_{rxn} &= \Sigma n\,[S^o(\text{products})] - \Sigma n\,[S^o(\text{reactants})]\\ &= 1\text{mole}[S^o(Br_2 g)] - 1\text{ mole}[S^o(Br_2 l)]\\ &= 1\text{ mole}(245.3\text{J/mol-K}) - 1\text{ mole}(152.3\text{J/mol-K}) = 93.0\text{ J/K}\end{aligned}$$

and we can make unit factors

93.0 J/K / 1mole $Br_2(l)$ or 93.0 J/K / 1mole $Br_2(g)$

{93.0 J/K/1mole $Br_2(l)$}{1mole $Br_2(l)$/159.8g $Br_2(l)$}{150g $Br_2(l)$} = 87.3 J/K.

The next slide shows the ΔS^o for several phase changes.

b. Calculate the entropy change for the production of ammonia gas from gaseous hydrogen and nitrogen. $S^o(H_2)$ = 130.58 J/mol-K $S^o(N_2)$ = 191.50 J/mol-K $S^o(NH_3)$ = 192.5 J/mol-K Write the balanced equation and DO

ANS: -198.24J/K (a decrease in disorder) Is this reasonable? Explain.

Make unit factors: -99.12J/K /mole NH_3 or -66.08J/K/mole H_2

E. Second Law of Thermodynamics (see # 2 and 3 below):

1. The entropy change is related to the amount of heat transferred and it also depends on the temperature. For example, the transfer of a specific amount of heat a lower T would lead to a large increase of S as solid is converted into a liquid or even a gas. At a much higher T, where the substance is a gas, the transfer of the same amount of heat would lead to a small increase in S as the gas molecules only move faster. For a reversible process at constant T,

$$\mathbf{\Delta S_{system} = q_{rev}/T}$$

As an example, consider the vaporization of an ideal gas at its boiling point. This occurs at constant pressure (the opposing pressure of the atmosphere is constant) and at constant P the heat associated with a process is the enthalpy change. Notice that the process also is isothermal, constant T, because it is occurring at the boiling point temperature.

$$\Delta S_{vaporizaton} = \Delta H_{vaporization}/T_{boiling\ temp}.$$

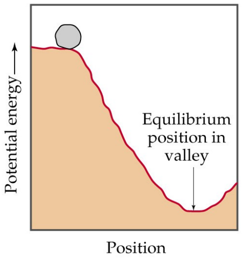
In this case the "system" is the liquid that is vaporizing and the heat comes from the surrounding (a Bunsen burner or hot plate). The total change in entropy is the sum of the change in the system and in the surroundings and is called the change in entropy in the universe.

$$\mathbf{\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}.}$$

2. **For a reversible process: $\Delta S_{universe} = 0$**

3. **For a irreversible process (spontaneous): $\Delta S_{universe} > 0$.** In other words, the entropy of the universe is continually increasing. These two statements are the Second Law of Thermodynamics.

III. Gibbs Free Energy.



(a)

A. J. Willard Gibbs proposed that a reaction will be spontaneous only if it is capable of doing useful work he defined the Gibbs Free Energy, G, as the following:

$$G = H - TS$$

1. We are interested in the change in Gibbs Free Energy as a process occurs at constant T,

$$\Delta G = \Delta H - T\Delta S - S\Delta T$$ but a constant T the $\Delta T = 0$ so,

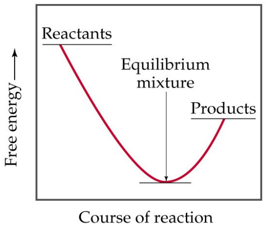
$$\mathbf{\Delta G = \Delta H - T\Delta S}$$

2. Possible results for ΔG

a. Negative, spontaneous process. This is a decrease in enthalpy (minimize the energy and ΔH is negative, exothermic) and an increase in entropy (maximize the disorder the ΔS is positive so that $-T\Delta S$ is negative).

b. Positive: Not spontaneous

c. Zero: equilibrium.



(b)

The following picture illustrates these ideas. As the reaction progresses from reactants toward products, we see the following: On the left-hand side the slope of G, ΔG is negative, so the reaction is spontaneous. On the right-hand side the slope is positive, ΔG is positive, so the reaction is non-spontaneous.

At the bottom of the curve the ΔG = 0 so this is equilibrium.

B. Both the enthalpy and entropy contribute to the Gibbs Free Energy,
$\Delta G = \Delta H - T\Delta S$. Not necessarily standard state conditions.
A process can be endothermic (ΔH is positive) or exothermic (ΔH is negative) and the change in entropy can result in an increase in disorder (ΔS is positive) or a decrease in the disorder (ΔS is negative). We also notice that the temperature will influence whether the TΔS is bigger than the ΔH term. Let us consider these four possibilities in more detail.

C. Calculate of the ΔG for a reaction, there are two possible methods.
1. Calculate the enthalpy and entropy change using

$$\mathbf{\Delta H^o_{rxn} = \Sigma n\, [\Delta H^o_f(products)]\ - \Sigma n\, [\Delta H^o_f(reactants)]}$$

$$\mathbf{\Delta S^o_{rxn} = \Sigma n\, [S^o(products)]\ - \Sigma n\, [S^o(reactants)]}$$

and then use $\mathbf{\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn}}$.

2. Use the Gibbs Free Energy of formation (Appendix) and use

$$\mathbf{\Delta G^o_{rxn} = \Sigma n\, [\Delta G^o_f(products)]\ - \Sigma n\, [\Delta G^o_f(reactants)]}$$

D. Sample Problems:

1. Is the absorption of 1000kJ of heat and an increase in disorder of 5.00 kJ/K a spontaneous process at 300 K? The ΔH = + 1000 kJ and ΔS = + 5.00 kJ/K.

$$\Delta G = \Delta H - T\Delta S = 1000\text{ kJ} - 300\text{K}(5.00\text{ kJ/K}) = -500\text{ kJ.}$$

2. Can the following reaction be spontaneous at any temperature?
$MgO(s) + CO_2(g) \text{ ---> } MgCO_3(s)$ given the following: $\Delta H^o_{rxn} = -117.2$ kJ and $\Delta S^o_{rxn} = -174.9$ J/K
At some T the TΔS term in the ΔG = ΔH - TΔS equation will equal the value of the ΔH term and then ΔG will be zero, equilibrium. At higher T the TΔS term will be positive and larger then the value of the ΔH term and the reaction will not be spontaneous. Let us find the T when equilibrium exists.

$\Delta G = \Delta H - T\Delta S$
$0 = -117.2\text{ kJ} - T(-174.9\text{ J/K})$
T = 670K. T > 670K not spontaneous
T < 670K spontaneous

3. Natural gas, CH_4, can be produced by the gasification of coal.
$2\ C(s) + 2\ H_20(g) \text{ ---> } CO_2(g) + CH_4(g)$
a. Is the reaction spontaneous at 298K?
$\Delta G^o_f(CH_4(g)) = -50.75$kJ/mol $\Delta G^o_f(H_20(g)) = -228.6$kJ/mol $\Delta G^o_f(CO_2(g)) = -394.4$kJ/mol
$\Delta G^o_f(C(g)) = -0$kJ/mol because all elements have a value of zero for ΔG^o_f. DO
ANS: 12.0kJ.

b. Could the reaction be spontaneous at any T? $\Delta H^o_{rxn} = 15.3$ kJ and $\Delta S^o_{rxn} = 0.0169$ kJ/K
Yes, at high T.

c. Find that temperature when it could be spontaneous. DO
ANS: T = 905K (superheated steam)

IV. The Equilibrium Constant and ΔG^o_{rxn} and ΔG_{rxn}.

A. We have calculated the ΔG^o_{rxn} at standard state conditions. What would happen at non-standard state conditions.

1. Equation **$\Delta G_{rxn} = \Delta G^o_{rxn} + RT \ln Q$** where Q is the reaction quotient, same form as the K_{eq}.

2. Would the above gasification of coal reaction be spontaneous at 298K if $P_{water} = 10.0$atm, $P_{methane} = P_{carbon\ dioxide} = 0.01$atm? Recall that $\Delta G^o_{rxn} = 12$kJ/mol and

$2\ C(s) + 2\ H_20(g) \text{ ---> } CO_2(g) + CH_4(g)$ DO

ANS: Yes, because the $\Delta G_{rxn} = -22.2$ kJ/mol.

B. At equilibrium the $\Delta G_{rxn} = 0$ and the $Q = K_{eq}$.

1. Then the equation is

$$\boldsymbol{\Delta G^o_{rxn} = -RT \ln} K_{eq}$$

and this allows us to calculate the K_{eq} from thermodynamic data.

This shows the following:

ΔG^o_{rxn} = negative	$K_{eq} > 1$
ΔG^o_{rxn} = zero	$K_{eq} = 1$
ΔG^o_{rxn} = positive	$K_{eq} < 1$

2. Calculate the K_{eq} for the above reaction at 298K.

$\Delta G^o_{rxn} = -RT \ln K_{eq}$ DO

$12.0\text{ kJ/mol} = -(8.314\text{J/mol-K})(298\text{K})(1.0\text{kJ/1000J}) \ln K_{eq}$

$-4.84 = \ln K_{eq}$

$7.9 \times 10^{-3} = K_{eq}$

3. At 1000K the $\Delta G^o_{rxn} = -1.6$kJ.mol and $K_{eq} = 1.91$.

The slide on the right shows this for the production of ammonia.