Chapter 19: Chemical Thermodynamics

Key Terms and Concepts:

Section I: Spontaneous Processes

Spontaneous Process: A process that occurs without outside intervention (e.g. An egg falling and breaking).

Reversible Process: A process where the change in the system can be completely restored by exactly reversing the change (e.g. Ice melting at 0°C). All spontaneous processes and processes at equilibrium are reversible.

Irreversible Process: A process where the change cannot be restored by simply reversing the change (e.g. the expansion of a gas in a vacuum).

Section II: Entropy and the Second Law of Thermodynamics

Entropy (S): A thermodynamic state function that expresses the randomness of a system. The more random or disordered the system, the greater the entropy of that system. The change in entropy, (ΔS) is equal to $S_{final}-S_{initial}$. In a reversible process at constant temperature, and q_{rev} represents the heat transferred in that process, $\Delta S=q_{rev}/T$.

Isolated System: A system that does not exchange energy or matter with it's surroundings. Most of the time, we use isolated systems, and thus, unless otherwise indicated, ΔS is equivalent to ΔS_{sys}.

The Second Law of Thermodynamics: If ΔS_{univ} denotes the total change in entropy of the universe, and ΔS_{sys} and ΔS_{surr} represent the change in entropy of the system and surroundings respectively, then the second law is as follows:

- For a reversible process, $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$. (in an isolated system, $\Delta S_{univ} = \Delta S_{sys} = 0$).
- For an irreversible process, $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$. (in an isolated system, $\Delta S_{univ} = \Delta S_{sys} > 0$).

This means that entropy is *not* conserved, and ΔS_{univ} is continually increasing.

Section III: The Molecular Interpretation of Entropy

Molecular Motion:

- Translational – The entire molecule moves in space
- Vibrational – The atoms in the molecule move towards and away from each other periodically.
- Rotational – The molecules spin like a top.

  The greater the molecular motion, the greater the entropy of a substance. As less energy is stored in the molecules, the entropy of those molecules decreases.

The Third Law of Thermodynamics: The entropy of a pure crystalline solid at 0K is 0. As the temperature increases, the entropy also increases, as shown. If W represents the number of possible arrangements for a substance, then $S = k*\ln(W)$, where k is Boltzmann's constant, or 1.38×10^{-23}.
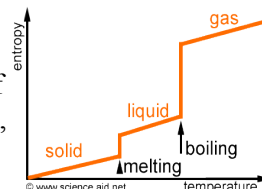
Section IV: Calculations of Entropy Changes

Standard Molar Entropy (S°): The molar entropy value of substances in their standard state (pure substance at 1 atm).

- They usually increase with number of atoms in the formula unit and molar mass
- S° of gases are greater than those of solids and liquids
- $\Delta S° = \Sigma S°(products) – \Sigma S°(reactants)$

Section V: Gibbs Free Energy

Gibbs Free Energy: A state function defined as G = H-TS, or $\Delta G = \Delta H - T\Delta S$ for a reaction at constant temperature. For such a reaction at constant pressure; if $\Delta G<0$, the reaction is spontaneous; if $\Delta G=0$, the reaction is at equilibrium; if $\Delta G>0$, the reverse reaction is spontaneous, but the surroundings must provide work for the forward reaction to occur. Free energy can also be defined as the energy available that a substance has to do work.

Standard Free Energy of Formation (G°): The free energy for a substance at a predefined state.

- $\Delta G° = \Sigma G°(products) – \Sigma G°(reactants)$ and $\Delta G° = \Delta H° - T\Delta S°$

Section VI: Free Energy and Temperature

Effect of Temperature on Free Energy: Enthalpy and Entropy are relatively unaffected by temperature, but depending on the reaction, the temperature could change the spontaneity of a reaction.

ΔH	ΔS	ΔG	Example
+	+	+ at low temperature, - at high temperature	$2HgO_{(s)} \rightarrow 2Hg_{(l)} + O_{2(g)}$
+	-	+ at all temperature	$3O_{2(g)} \rightarrow 2O_{3(g)}$
-	+	- at all temperature	$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + 2O_{2(g)}$
-	-	- at low temperature, + at high temperature	$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$

Section VII: Free Energy and the Equilibrium Constant
- For all systems, $\Delta G = \Delta G^{\circ} + RT*\ln(Q)$. ΔG° can be found through the calculated values, and Q is the reaction quotient for a system. The sign of ΔG shows which reaction is spontaneous, the forward or the backward reaction
- If the system is at equilibrium, then the equation reduces to $\Delta G^{\circ} = -RT*\ln(K)$, because $\Delta G = 0$, and $Q = K$ at equilibrium.

Sample Calculations:

-What is the entropy change when 50.0g of $Hg_{(l)}$ freezes at normal freezing temperature (-38.9° C), if it's molar enthalpy is 2.331 kJ/mol?

q = (50.0g Hg)*(1 mol Hg/200.59g Hg)*(1000J/1kJ)*(-2.331kJ/mol Hg) = -581J

$\Delta S = q/T$ = (-581 J)/(243.3 K) = -2.48 J/K (Since the process is reversible)

- Calculate ΔS° for $N_{2(g)}+3H_{2(g)} \rightarrow 2NH_{3(g)}$

ΔS° = $2S^{\circ}(NH_3) - [S^{\circ}(N_2) + 3S^{\circ}(H_2)]$ = (2 mol)(192.5J/mol-K) – [(1 mol)(191.5 J/mol-K) + (3 mol)(130.6 J/mol-K)] = -198.3 J/K

- Calculate ΔG° for $N_{2(g)}+3H_{2(g)} \rightarrow 2NH_{3(g)}$ at standard conditions

ΔG° = $2G^{\circ}(NH_3) - [G^{\circ}(N_2) + 3G^{\circ}(H_2)]$ = (2 mol)(-16.66 kJ/mol) – [(1 mol)(0 kJ/mol) + (3 mol)(0 kJ/mol)] = -33.32 kJ

- Calculate ΔG° for $N_{2(g)}+3H_{2(g)} \rightarrow 2NH_{3(g)}$ at 500°C

ΔH° = -92.38kJ ; ΔS° = -198.3 J/K (calculated from the tables)

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ = -92.38kJ - (773K)(-198.3 J/K)(1kJ/1000J) = 61kJ

- Calculate the boiling point of CCl_4 using the values in the tables.

ΔH° = 32.6kJ ; ΔS° = 95.0 J/K (calculated from the tables)

$\Delta G^{\circ} = \Delta H^{\circ} - T_b\Delta S^{\circ} = 0$ (since the system is at equilibrium if it is boiling)

$T_b = \Delta H^{\circ}/\Delta S^{\circ}$ = (32.6 kJ/95.0J/K)(1000J/1kJ) = 343 K = 70°C

- Calculate ΔG° for $N_{2(g)}+3H_{2(g)} \rightarrow 2NH_{3(g)}$ at 1.0 atm N_2, 3.0 atm H_2, and 0.50 atm NH_3 and 298K

$Q = (P_{NH3})^2/(P_{N2})(P_{H2})^3$ = 9.3 x 10^{-3}

ΔG° = -33.32kJ

$\Delta G = \Delta G^{\circ} + RT*\ln(Q)$ = -33.32kJ + (8.314J/mol-K)(298 K)(1kJ/1000 J)(ln 9.3 x 10^{-3}) = -44.9 kJ/mol

- Calculate the equilibrium constant for $N_{2(g)}+3H_{2(g)} \rightarrow 2NH_{3(g)}$ using the standard free energies of formation

ΔG° = -33.32kJ

$\Delta G^{\circ} = -RT*\ln(K)$

$- \Delta G^{\circ}/RT$ = -(-33,320 J/mol)/[(8.314 J/mol-K)(298 K)] = 13.4

$K = e^{-\Delta G/RT} = e^{13.4}$ = 7 x 10^5