Thermodynamics and Equilibrium

Chemical thermodynamics is concerned with energy relationships in chemical reactions.

In addition to enthalpy (*H*), we must consider the change in randomness or disorder that accompanies a chemical reaction.

The First Law of Thermodynamics: Energy is conserved

$$\Delta E = q + w$$

Any process that occurs without outside intervention is a spontaneous process. When two eggs dropped, they break spontaneously.

A process that is spontaneous in one direction, is not spontaneous in the opposite direction. Two eggs leaping in your hand with their shells back intact is not spontaneous.

Temperature may also affect the spontaneity of a process.

Reversible and Irreversible Processes.

Whenever a chemical reaction is in **equilibrium,** reactants and products can interconvert reversibly (**reversible process**).

In a **spontaneous** process, the path between reactants and products is **irreversible**.

Entropy, S

Entropy, S, is a thermodynamic term that reflects the disorder or randomness of the system.

The more disordered or random the system, the larger the value of S (increase the degree of ***FREEDOM***).

The Molecular Interpretation of Entropy

A gas is less ordered (molecules move **freely**) than a liquid, which is less ordered than a solid.

A process that increases the number of gas molecules leads to an increase in entropy.

$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

Reactants have 3 molecules of gas. Product have 2 molecules of gas. The number of gas molecules decreases. Therefore, entropy decreases.

The formation of the new N-O bonds 'ties up" more of the atoms in the products than in the reactant. The degree of freedom associated with the atoms is less.

When we lower the temperature, the entropy of the system decreases. The degree of freedom associated with motions within the molecule have decreased.

Entropy is a state function. It is independent of the path.

For a system:

$$\Delta S = S_{final} - S_{initial}$$

If $\Delta S > 0$, the randomness increases
If $\Delta S < 0$, the randomness decreases.

Suppose the system changes reversibly between state 1 and state 2. The change in entropy is given by

$$\Delta S = q / T$$

q: heat transferred
T: temperature at which change occurs in K

The Second Law of Thermodynamics

In any spontaneous process, the entropy of the universe increases. The change of the entropy of the universe is the sum of the change in entropy of the system and the change of entropy of the surrounding.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$$

For a **spontaneous process (irreversible)**:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$$

Entropy is not conserved: ΔS universe is continually increasing.

For a **reversible process:**

$$\Delta S \text{ universe} = \Delta S \text{ system} + \Delta S \text{ surrounding} = 0$$

Spontaneous = Thermodynamically Favored

The Third Law of Thermodynamics

The entropy of a perfect pure crystal at 0 K (absolute zero) is zero.

Entropy will increase as we increase the temperature of the perfect crystal from absolute 0 (0 K). Molecules gain vibrational motion. The degrees of freedom increase.

In general entropy will increase when:

liquids or solutions are formed from solids.

Gases are formed from solids or liquids.

The number of gas molecules increases.

Entropy Changes in Chemical Reactions

Standard molar entropy S: molar entropy of a substance in its standard state.

Similar in concept ΔS Units: J/mole K

The units of ΔH kJ/mole

Some observations about S values:

Standard molar entropies of elements are not zero.

S^o gas > S^o liquid or S^o solid

S^o tends to increase with increasing molar mass of the substance.

S^o tends to increase with the number of atoms in the formula of the substance.

For a chemical reaction which produces n products from m reactants.

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

Example:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

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

$$\Delta S^o_{rxn} = 2\, S^o(NH_3) - [S^o(N_2) + 3\, S^o(H_2)]$$

Gibbs Free Energy

$$G = H + T\,S$$

Free energy is a state function

For a process occurring at constant temperature, the free energy change is:

$$\Delta G = \Delta H + T\,\Delta S$$

The sign is is important in predicting the spontaneity (thermodynamically favorable) of the reaction.

If $\Delta G < 0$ then the forward reaction is spontaneous.

If $\Delta G = 0$ then the reaction is at equilibrium and not net reaction will occur.

If $\Delta G > 0$ then the forward reaction is not spontaneous. Work must be applied from the surrounding to drive the reaction. However, the reverse reaction is spontaneous.

Standard Free-Energy Changes

We can tabulate standard free energies of formation:

Standard states are: pure solid, pure liquid, 1 atm (gas), 1M concentration (solution) and $\Delta G^o = 0$ for elements.

We most often use 25^{o}C or 298 K as the temperature.

The standard free energy change for a precess is given by

$$\Delta G^o = \Sigma n\, \Delta G^o\,(\text{products}) - \Sigma m\, \Delta G^o\,(\text{reactants}).$$

The quantity of ΔG^o for a reaction tells us whether a mixture of substance will spontaneously react to produce more reactants ($\Delta G^o > 0$) or more products ($\Delta G^o < 0$)

Predicting the entropy of a system is based on physical evidence:

1) The greater the dispersal of matter and/or energy in a system, the larger the entropy.

2) The entropy of a substance always increases as it changes from solid to liquid to gas.

3) When a pure solid or liquid dissolves in a solvent, the entropy of the substance increases (Carbonates are an exception! Carbonates interact with water and actually bring MORE order to the system.)

4) When a gas molecule escapes from a solvent, the entropy increases

5) Entropy generally increases with increasing molecular complexity (crystal structure: KCl vs. CaCl2) since there are more MOVING electrons!

6) Reactions increasing the number of moles of particles often increase entropy.

In general, the greater the number of arrangements, the higher the entropy of the system!