

Chapter Summary: Thermodynamics

Spontaneous change: a change that occurs without external action.

If the forward reaction is spontaneous then reverse is non spontaneous.

(note: spontaneous does not mean fast)

Entropy: degree of orderliness of a system. (Represented by ΔS). E.g. entropy increases when ice melts to liquid and liquid vaporizes to steam.

Second Law of Thermodynamics: all spontaneous process increase the entropy of the universe.

Third Law of Thermodynamics: entropy of a pure, perfect crystal can be taken to be 0 at 0K.

Standard Molar Entropy (S°): entropy of a mole of substance in its standard state.

Standard entropy of a reaction (ΔS°) can be calculated by:

$$\Delta S = \sum n_p S_f^\circ (\text{products}) - \sum n_r S_f^\circ (\text{reactants})$$

Free Energy and Free Energy Change (ΔG): Gibbs free energy determines the spontaneity of a process.

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

hence

if $\Delta G < 0$ then process is spontaneous

if $\Delta G > 0$ then non spontaneous and

if $\Delta G = 0$ then process is in equilibrium.

Standard free energy of a system (ΔG°) is when all reactants and products are in their standard states ($P = 1$ atm, solids and liquids are pure, etc.). It predicts the direction of the equilibrium.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

– ΔG° indicates large K value (products favored)

+ ΔG° indicates small K value (reactants favored)

Standard free energy of formation (ΔG_f°) is free energy change that occurs in the formation of one mole of substance in their standard state.

Standard free energy of a reaction can be calculated by:

$$\Delta G^\circ = \sum n_p G_p^\circ (\text{products}) - \sum n_r G_r^\circ (\text{reactants})$$

Relationship between ΔG and ΔG°

$$\Delta G = \Delta G^\circ + RT \ln Q$$

(R = gas constant = 8.314 J/K, T = temp in K, Q = reaction quotient)

Use this equation to figure out if reaction is spontaneous at a particular temp. at specific concentrations of reactants and products.

Relationship between ΔG and K

$\Delta G = 0$ at equilibrium and $Q = K$ at equilibrium

So the equation above becomes:

$$\Delta G^\circ = - RT \ln K$$

Value of ΔG° still predicts direction of reaction not spontaneity of reaction.