Thermodynamic basis of chemical changes, Enthalpy, Entropy and free energy change during a chemical change

Enthalpy change of a chemical reaction:

As we know that internal energy (E) of a system is the energy that the system posses internally and it is the sum of potential and kinetic energy of all its components. Any change in internal energy produces work and heat. From first law of thermodynamics we know

$\Delta E = Q + W$, Where Q is heat supplied to the system and W is the work done to the system.

Chemical reaction involves energy (heat) change with the surroundings where either heat is evolved (exothermic reaction) or heat is absorbed (exothermic reaction). To measure this energy changes, chemists usually use a thermodynamic quantity called enthalpy (H). The enthalpy or heat content of a system is defined as
$$H = E + PV \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Since E, pressure (P), volume (V) are all state functions, enthalpy is also a state function.

Suppose a system at constant pressure (P) undergoes a chemical change, then enthalpy change

ΔH can be written as

$\Delta H = H_{final} - H_{initial} = (E_2 + PV_2) - (E_1 + PV_1) = (E_2 - E_1) + P(V_2 - V_1)$

$\Delta H = \Delta E + P\,\Delta V$

$\Delta H = \Delta E - W$.........................(2)

Substituting, $\Delta E = Q_p + W$ in eqn(2) we get $\Delta H = Q_p$,where Q_p is the heat change at constant pressure.

So, the enthalpy change is defined as the heat change at constant pressure. Generally, all chemical reactions occur under constant atmospheric pressure (1 atm pressure) and hence heat change for a chemical reaction is measured in terms of enthalpy.

$\Delta H_{rxn} < 0$ for an exothermic reaction, and

$\Delta H_{rxn} > 0$ for an endothermic reaction.

The energy change in chemical reaction originates from the breaking and formation of bonds. In chemical reactions where bond breaking requires an input of energy is therefore an endothermic process and whereas bond making releases energy, which is an exothermic process.

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants. if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants.

Enthalpy of a gaseous reaction

Suppose n_1 moles of reactant gases react to form n_2 moles of gaseous products. The reaction occur at constant temperature and pressure and the volume changes from V_1 to V_2.

We know for ideal gas
$PV = nRT$,   then $P(V_2-V_1) = (n_2-n_1)RT$
$P\Delta V = \Delta nRT$
Using first law of thermodynamics we can write
$\Delta H = \Delta E + P\Delta V = \Delta E + \Delta nRT$

The heat change in chemical reaction is governed by two general laws, which are basically consequence of the first law of thermodynamics.
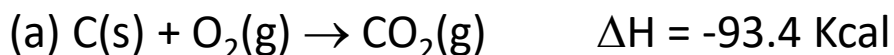
(i) Law of Lavoisier and Laplace:

This law states that the heat change associated with a chemical process in one direction is equal in magnitude but opposite in sign to that associated with the same process taking place in opposite direction.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = \text{-93.4 Kcal}$$

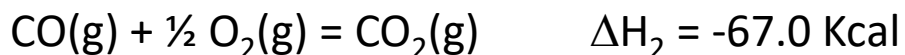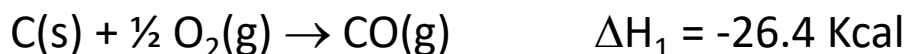$$CO_2(g) \rightarrow C(s) + O_2(g) \qquad \Delta H = \text{93.4 Kcal}$$
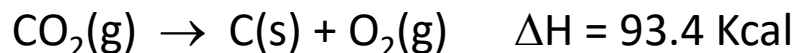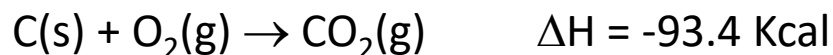
(ii) Hess's law (law of constant heat summation):

This law states that for a chemical reaction the amount of heat evolved or absorbed is the same whether the chemical reaction occurs through a single or multi steps. Let us take an example of formation of CO_2 in one step (a) or in several steps (b).

(a) $C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = \text{-93.4 Kcal}$

(b)
$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g) \qquad \Delta H_1 = \text{-26.4 Kcal}$
$CO(g) + \frac{1}{2} O_2(g) = CO_2(g) \qquad \Delta H_2 = \text{-67.0 Kcal}$

Addition of $\Delta H_1 + \Delta H_2 = \text{-(26.4 + 67.1) Kcal} = \text{-93.4 Kcal}$ which is equal to ΔH.

The main advantage of this law is that thermochemical equation can be treated as simple algebraic equation and the heat of formation, heat of transition etc. which are difficult to measure experimentally can be easily determined by simple addition, subtraction or multiplication of the quantities.

Heat of reaction

Heat of reaction is defined as the difference between the heat content of the product and the heat contents of the reactants when molar quantity react and indicated by a balanced chemical reaction.

$H_2 + Cl_2 = 2HCl$ +43.6 Kcal
For this reaction, heat of formation of 2 moles of HCl is 43.6 Kcal which is exothermic.

Heat of combustion

Heat of combustion (ΔH_{comb}) is defined as the heat change for complete combustion of 1 gm mole of the substance at a given temperature under normal pressure.

Combustion reactions are always exothermic. Heat of combustion is determined in bomb calorimeter.
$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$ $\Delta H = -325$ Kcal
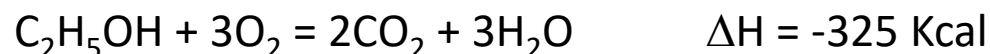
Heat of neutralization

Heat of neutralization of an acid is defined as the amount of heat released when 1 gm equivalent of an acid is neutralized by 1 gm equivalent of base in large excess of water.

$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O$ -13.7 Kcal
Heat of neutralization is actually heat of formation of 1 gm mole of water from 1 gm eq. of H^+ and OH^-.

Heat of formation

It is defined as the amount of heat evolved or absorbed when one mole of compound is formed from its constituent elements where all the elements are in their respective standard state at a reference temperature and pressure.

Usually the conditions at which the compound is formed are taken to be at a temperature of 25 °C (77 °F) and a pressure of 1 atmosphere, in which case the heat of formation can be called the standard heat of formation or standard enthalpy of formation.

The standard enthalpy of formation of any element in its most stable form is zero by definition.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

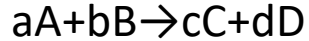$$6C(s, graphite) +6H_2(g)+3O_2(g) \rightarrow C_6H_{12}O_6(s) \qquad \Delta H°_f = -1273.3 kJ$$
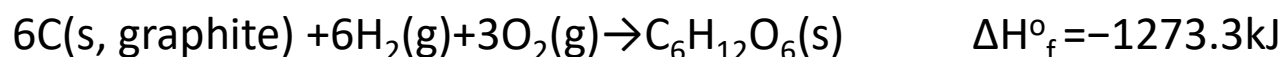
Heat of solution and dilution

The heat change occurs when 1 gm mole of solute is completely dissolved in a solvent is called heat of solution.

The heat of solution is highly dependent on the concentration of the solute; one gm mole of KCl dissolves in 50 moles of water and in 200 moles of water will produce different heat change.

$KCl(s) + 50 H2O = KCl(50H) \qquad$ -4.27 Kcal

$KCl(s) + 100H_2O = KCl(100H) \qquad$ -4.40 Kcal

Consider the general reaction

aA+bB→cC+dD

where A, B are reactant and C, D are product., a, b, c, and d are their stoichiometric coefficients.

The magnitude of ΔH^o is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$\Delta H^o_{rxn} = [c\Delta H^0_f (C) + d\Delta H^0_f (D)] - [a\Delta H^0_f (A) + b\Delta H^0_f (B)]$

Entropy change of chemical reaction

The second law of thermodynamic gives birth to state function entropy denoted by S and its change determine the spontaneity of a process. The requirement for a real or spontaneous transformation in an isolated system is that the total entropy change must be positive.

Any spontaneous change that occurs within an isolated system is attended by an increase in entropy of the system. The entropy of an isolated system has its maximum value at equilibrium.

In case of nonisolated system, the system plus its immediate surroundings can be considered as a composite isolated system where the entropy changes as natural process occurs.

So to predict the spontaneity of a change in a non-isolated system, we always need to calculate the total entropy change, ΔS_{total} that includes entropy change of system and its surrounding. If that ΔS_{total} is positive then the change will be spontaneous.

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

Mathematically, S is defined as

$$dS = \frac{dq_{rev}}{T}$$

for a measurable change between two states i and f, the integration results

$$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$

Physically, entropy is measure of randomness of a system or it is measure of unavailable energy.

From third law of thermodynamics we know that the entropy of a pure, perfectly crystalline substance is zero at the absolute zero temperature. Using third law, we can write

$$S_T = \int_0^T \frac{C_p}{T} dT$$

Where C_p specific heat at constant pressure and S_T is the entropy of the solid at temperature T and pressure p. If the pressure is 1 atm, then the entropy is also a standard entropy S^0_T.

The standard entropy of a liquid can be calculated using the below equation.

$$S^\circ_T = \int_0^{T_m} \frac{C^\circ_p(s)}{T} dT + \frac{\Delta H^\circ_{fus}}{T_m} + \int_{T_m}^{T} \frac{C^\circ_p(l)}{T} dT.$$

Where ΔH^0_{fus} is the standard enthalpy of fusion and T_m is the melting point.

Similarly for gas the standard entropy can be written as

$$S^\circ_T = \int_0^{T_m} \frac{C^\circ_p(s)}{T} dT + \frac{\Delta H^\circ_{fus}}{T_m} + \int_{T_m}^{T_b} \frac{C^\circ_p(l)}{T} dT + \frac{\Delta H^\circ_{vap}}{T_b} + \int_{T_b}^{T} \frac{C^\circ_p(g)}{T} dT$$

Where ΔH^0_{vap} is the standard enthalpy of vaporization and T_b is the boiling point.

The entropy change in a chemical reaction at 1 atm presuure pressure and 25^0C is given by the sum of the standard entropies of the products minus the sum of the standard entropies of the reactants. As with other calculations related to balanced equations, the coefficients of each component must be taken into account in the entropy calculation (the n, and m, terms below are there to indicate that the coefficients must be accounted for)

$$\Delta So = \sum_n nS^0(products) - \sum_m mS^0(products)$$

Let consider the reaction

$$Fe_2O_3(s) + 3\ H_2(g) \rightarrow 2\ Fe(s) + 3\ H_2O(l)$$
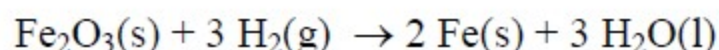
The value of the entropy of each element at 25 °C and 1 atm pressure is known from the third law. Then

$$\Delta S^\circ = 2\bar{S}^\circ(Fe, s) + 3\bar{S}^\circ(H_2O, l) - \bar{S}^\circ(Fe_2O_3, s) - 3\bar{S}^\circ(H_2, g)$$

Using the supplied standard entropy value for different substance, we can calculate entropy for this reaction at 25^0C as

$$\Delta S^\circ = R[2(3.28) + 3(8.4131) - 10.51 - 3(15.7041)]$$

$$= -25.82R = -25.82(8.314\ J/K\ mol) = -214.7\ J/K\ mol.$$

Knowing the value of entropy change $(\Delta S_{T_0}^0)$ for a reaction at a particular temperature T_0, the entropy change at other temperature $(\Delta S\ ^0_T)$ can be calculated using the following equation

$$\int_{T_0}^{T} d(\Delta S^\circ) = \int_{T_0}^{T} \frac{\Delta C_p^\circ}{T} dT;$$

$$\Delta S_T^\circ = \Delta S_{T_0}^\circ + \int_{T_0}^{T} \frac{\Delta C_p^\circ}{T} dT,$$

Where $\quad \dfrac{\Delta C_p^\circ}{T} = \dfrac{C_p^\circ(\text{products})}{T} - \dfrac{C_p^\circ(\text{reactants})}{T}$

$\Delta S_{T_0}^0$ and $\Delta S\ ^0_T$ are the entropy change of the reaction at temperature T_0 and T and for both the cases pressure is maintained at 1 atm.

Free energy change in a chemical reaction:

Two thermodynamic state functions which are very useful for physicochemical studies are (a) Gibb's Free energy and (b) Helmholtz free energy or work function.

Gibb's free energy is related to enthalpy and entropy by the following equations

$G = H-TS$

$\Delta G = \Delta H - T\Delta S$, at constant pressure

Using thermodynamic relations, it can be shown that

$$-\Delta G = W_{a, rev},$$

So the decrease in Gibbs energy (-ΔG) for a change in state at constant T and p is equal to the maximum work available ($W_{a,,rev}$) except expansion work, which is obtainable in the transformation. For any real transformation, the work obtained over and above expansion work is less than the decrease in Gibbs energy that accompanies the change in state at constant T and p.

At constant temperature and pressure always system tends to attain a position of minimum free energy which is the position of equilibrium. For a natural or spontaneous process ΔG must be negative. If ΔG is negative that transformation or change will occur spontaneously. If $\Delta G = 0$, the system is in equilibrium with respect to the transformation. If ΔG is positive, the process will not occur spontaneously in the direction; we are studying but may be spontaneous in opposite direction.

Chemical Potential: Chemical potential (μ) of a pure substance is defined as free energy per mole at a given temperature and pressure.

$$\mu = \frac{G}{n} \text{ (for a pure substance)}$$

For a species i which is a component of mixture, the chemical potential of the i_{th} component μ_i can be defined as

$$\mu_i = \left(\frac{\partial G}{\partial n}\right)_{T, P, n_j}$$

Where n_j represents the composition of the other components except i. chemical potential is an intensive property.

Mater flows spontaneously from a region of high chemical potential to a region of low chemical potential just as electric current flows spontaneously from a region of high electrical potential to one of lower electrical potential, or as mass flows spontaneously from a position of high gravitational potential to one of low gravitational potential.
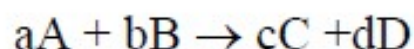
The Gibbs free energy or chemical potential of the ideal gas at any temperature and pressure can be written as

$$\mu = \mu_a^0 + RT \ln P$$

$$G = G^0 + RT \ln P$$

Where G^0 is the standard Gibbs energy or μ^0 is the standard chemical potential of the gas standard pressure (P = 1 atm). μ^0 and G^0 are both function of temperature but not function of pressure.

For a chemical reaction

$$aA + bB \rightarrow cC + dD$$

Free energy change ΔG can be written as

$$\Delta G = G_{products} - G_{reactants} = (c\mu_C - d\mu_D) - (a\mu_A - b\mu_B)$$

The chemical equilibrium constant (K_{eq}) is related to standard free energy change ΔG^0 of a chemical reaction by the relation

$$\Delta G^0 = -RT \ln K_{eq}$$

where ΔG^0 is the standard free energy change of the reaction where both reactant and products were in their standard state (1 atm pressure).

$$\Delta G^0 = G^0{}_{products} - G^0{}_{reactants} = (c\mu^0{}_C - d\mu^0{}_D) - (a\mu^0{}_A - b\mu^0{}_B)$$

Having obtained the values of ΔG^0 from measurements of equilibrium constants, it is possible to calculate conventional values of the standard molar Gibbs energy μ^0 of individual compounds.

Just as in the case of the standard enthalpies of substances, the Gibbs energy of the elements in their stable state of aggregation at 25 °C and 1 atm pressure is taken as zero.

For example, at 25 °C, μ^0 (Cl_2, g) = 0, μ^0 (S, rhombic) = 0 .

Gibbs Helmholtz Equation

In a natural change at constant temperature and pressure, ΔG must be negative. By definition, G = H - TS, so that at constant temperature,

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

Or $\Delta G = \Delta H - T\left(\frac{\partial \Delta G}{\partial T}\right)_P$

This equation is called Gibbs Helmholtz Equation. We know that any reaction will be spontaneous if ΔG is negative. When $\Delta G = 0$, the free energy of reactants and products are equal and the reaction attains equilibrium.

(i) for an exothermic reaction, ΔH is negative and if ΔS is positive , then ΔG is always negative and the reaction become spontaneous.

(ii) For an endothermic reaction, ΔH is positive and if $T\Delta S$ is positive and greater than ΔH, then ΔG is negative and the reaction become spontaneous.

(iii) when ΔH is negative and ΔS is also negative, the process will be spontaneous only when ΔH is greater than $T\Delta S$.