Thermodynamics and Chemical Energetics

TERMINOLOGY

System: Part of universe under observations.

Surrounding: Excluding system, entire universe is called as surrounding.

Types of Systems

(i) Open system : A system, which can exchange matter as well as energy with the surroundings, is called as open system.

(ii) Closed system : A system which can exchange energy but not matter with the surroundings is called as closed system.

(iii) Isolated system : A system which can neither exchange energy nor any matter with the surroundings is called as isolated system.

STATE OF A SYSTEM AND STATE FUNCTIONS

(i) State of a system (thermodynamic equilibrium state) : The condition of a system which is described by its measurable properties e.g. temperature (T), pressure(P), volume (V) etc. is called as state of the system.

(ii) State functions : A measurable property whose value depends only on the state of the system, and not on how that state was reached is called a state function or a state variable. Some state function commonly used in thermodynamics are internal energy (E or U), Enthalpy (H), Entropy (S), Free energy (G), Pressure (P), Temperature (T), Volume (V) etc.

EXTENSIVE AND INTENSIVE PROPERTIES

(i) Extensive properties : The property whose value depends upon the quantity of matter contained in any system is called extensive property. e.g. Mass, Volume of solid or liquid , Area, Energy, Heat capacity.

(ii) Intensive properties : The property whose value depends upon the nature of the substance, and is independent of its amount in the system is called an intensive property. e.g. Density, Temperature, Pressure, Concentration, Viscoisity, Refractive index, Surface tension.

Types of Process

(i) Isothermal process: When the temperature of the system remains constant the process is called an isothermal process i.e. $\Delta T = 0$.

(ii) Adiabatic process : When there is no exchange of heat between the system and the surrounding then the process is called an adiabatic process i.e. $q = 0$

(iii) Isobaric process : When the pressure on a system remains constant during any operation, then the process is termed isobaric i.e. $\Delta P = 0$

(iv) Isochoric process : When there is no change in the volume of the system during an operation, the process is termed isochoric. i.e. $\Delta V = 0$

(v) Cyclic process : If a system after having undergone a change returns back to its initial state, the process is called a cyclic process. The path of such a process is called a cycle. Change in the value of any state function for a cyclic process is 0.

(vi) Reversible Process : When a process is carried out so slowly such that the system and the surrounding are always in equilibrium, then the process is termed as reversible process.

(vii) Irreversible Process: A process which is carried out so rapidly that the system does not get a chance to attain equilibrium, then the process is termed as irreversible process.

HEAT (Q)

The energy transferred from hotter body to colder body is known as heat. If heat is given to the system $q > 0$. If heat is released from system $q < 0$.

WORK (w)

Work done by system $\Rightarrow$ $w < 0$, Work done on the system $\Rightarrow$ $w > 0$

INTERNAL ENERGY

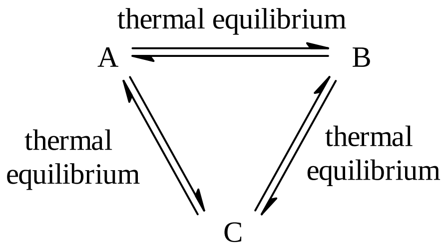
The total energy contained in a system is called its internal energy or intrinsic energy. This is denoted by a symbol E or U. Change in internal energy = ΔU

If internal energy is increased $\Rightarrow$ $\Delta U > 0$

If internal energy is decreased $\Rightarrow$ $\Delta U < 0$

ZEROTH LAW OF THERMODYNAMICS

The zeroth law of thermodynamics states that "the two systems in thermal equilibrium with a third system separately are also in thermal equilibrium with each other."



FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is also known as the law of conservation of energy. "The total energy of the universe (system + surroundings) remains constant".

Mathematical Formulation of the First Law of Thermodynamics

Let us consider a system in its initial state having internal energy U_1. If heat equal to 'q' is supplied to the system, and work equal to 'w' is done on the system, then the internal energy of the system in the final state (U_2) is given by,

$$U_2 = U_1 + q + w$$

$$U_2 - U_1 = q + w$$

$$\Delta U = q + w$$

Calculation of Work done (W): For any expansion against external pressure p_{ext};

$$w = -\int_{v_1}^{v_2} p_{ext} dv$$

Case 1: When V is constant (Isochoric process)

$w = 0, \Rightarrow Q_v = \Delta U$

Case 2: When p_{ext} is constant (isobaric process)

$w = -p_{ext}\ \Delta V \ \Rightarrow Q_p = \Delta U + p_{ext}\ \Delta V$

If process is reversible and isobaric i.e. $p_{ext} = P_{gas}$ = constant

$w = -p_{ext}\ \Delta V = -P_{gas}\ \Delta V \ \Rightarrow Q_p = \Delta U + P\Delta V$

Case 3: When T is constant (Isothermal expansion)

Case (a): When process is irreversible isothermal and p_{ext} is constant.

$w = -p_{ext}\,\Delta V$

Case (b): When process is reversible and isothermal.

$w = -2.303\ nRT \log V_2/V_1 = -2.303nRT \log P_1/P_2$

Note : During isothermal expansion for a sample of ideal gas $\Delta U = 0$

Case 4: When Q = 0 i.e. (adiabatic reversible process)

$$w = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

Enthalpy (H): It is total heat content of the system. It is state function as well as extensive property.

$H = U + PV$

Enthalpychange: $\Delta H + \Delta U + \Delta(PV) \Rightarrow \Delta H = \Delta U + (P_2V_2 - P_1V_1)$

Case 1: When P is constant

$\Delta H = \Delta U + P\Delta V$

Note: Heat supplied at constant pressure under reversible condition is equal to increase in enathalpy under ` that condition. $\Delta H_p = Q_p$

Case 2: When V is constant

$$\Delta H = \Delta U + V\Delta P$$

Case 3: When T is constant and chemical reaction takes place,

$$\Delta H = \Delta U + \Delta n_g RT$$

Case 4: When gaseous moles before and after reaction remain same, but temperature is changed.

$$\Delta H = \Delta U + n_g R\Delta T$$

Heat Capacity

The heat capacity (C) of a sample of a substance is defined as the quantity of heat energy required to raise its temperature by 1 K (or 1°C) from this definition.

$$Q = C.\,\Delta t$$

where Q is the quantity of heat given to the sample; Δt is the rise in the temperature of the substance. Heat capacity is an extensive property.

Specific Heat Capacity

The specific heat capacity of a substance is equal to the quantity of heat required to raise the temperature of 1 unit mass of the substance by 1°C or by 1 K. It is also called as specific heat.

Let the temperature of a body of mass 'm' and sp. heat S be raised by Δt^0C. Then heat required is given by

$$Q = m.S\,.\,\Delta t$$

It is intensive property.

Molar Heat Capacity

The molar heat capacity (c_m) of a substance is defined as the quantity of heat required to raise the temperature of one mole of a substance by 1 K (or 1 K (or 1°C). Thus

Molar heat capacity = Specific heat capacity ´ Molar mass

or $c_m = C \times M$

It is also intensive property

ENTHALPY OF REACTION

It is the enthalpy change measured during any reaction.

$$\Delta H_r = \sum H_{products} - \sum H_{reactants}$$

eq. $H_2(g) + Cl_2(g) = 2HCl(g) + 44.0$ k.cal. or $\Delta H = -44$ k.cal.

$C(s) + H_2O(l) = CO(l) + H_2(g) - 31.4$ k.cal $\Delta H = 31.4$ k.cal

STANDARD ENTHALPY OF REACTION (ΔH_r^o)

The enthalpy of reaction under standard state condition is called standard enthalpy of reaction.

Factors which influence the heat of reaction

(i) Physical state of reactants and Products

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g); \quad \Delta H = -57.8 \text{ k.cal}$$

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l); \quad \Delta H = -68.32 \text{ k.cal}$$

Thus the difference in the value of ΔH if water is obtained in gaseous or liquid stae.

(ii) Allotropic forms of the elements : Heat energy is also involved where one allotropic form of an element is converted into another

$$C_{(Diamond)} + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.3 \text{ kcal}$$

$$C_{(amorphous)} + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -97.6 \text{ kcal}$$

(iii) Way of presentation of reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}; \qquad \Delta H$$

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}; \qquad \Delta H_1 = \frac{\Delta H}{2}$$

$$3N_{2(g)} + 9H_{2(g)} \rightleftharpoons 6NH_{3(g)}; \qquad \Delta H_2 = 3\Delta H$$

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}; \qquad \Delta H_3 = -\Delta H$$

(iv) Temperature : Heat of reaction or enthalpy of reaction also depends on the temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature.

(v) Reaction carried out at constant pressure or constant volume

(vi) If two reactions are added then their ΔHr are added and when they are substracted, their ΔH_r are also substracted.

MOLAR ENTHALPY OF FUSION (ΔH_{fus})

"The change in enthalpy when one mole of a solid substance is melted at its melting temperature is called molar enthalpy of fusion." e.g.

$$\underset{(ice)}{H_2O(273\,K)} \longrightarrow \underset{(liquid)}{H_2O\,(273\,K)} \qquad \Delta_{fus}H^\circ = 6.0 \text{ kJ mol}^{-1}$$

MOLAR ENTHALPY OF VAPORISATION (ΔH_{vap})

"The change in enthalpy when one mole of a liquid is converted into vapours at its boiling temperture is called molar enthalpy of vaporization. (ΔH_{vap})" e.g.

$H_2O(l), (373\,K) \longrightarrow H_2O(v)\ 373\,K,$ $\Delta H_{vap.}$ H° = 40.7 kJ mol^{-1}

ENTHALPY OF SUBLIMATION (ΔH_{sub})

"The change in enthalpy when one mole of a solid substance is converted into its vapour, without melting at a temperature, below its melting point is called molar enthalpy of sublimation." e.g.

$$I_2(s) \xrightarrow{\Delta} I_2(v) \quad \Delta H_{sub} \text{ for } (I_2) = 62.4\ kJ\ mol^{-1}$$

ENTHALPY OF FORMATION

"The enthalpy change accompanying the formation of one mole of any substance from its element in their most stable physical state under that condition is called its enthalpy of formation." If ΔH_f is calculated under standard state condition it is called as ΔH_f^o.

Note: Enthalpy of formation of all elements in their most stable physical state is zero. e.g.

C (graphite) + $O_2(g) \longrightarrow CO_2(g)$. ΔH = –97.6 kcal/mol. ΔH_f of $CO_2(g)$ = –97.6 kcal m^{-1}

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$. ΔH = –44 kcal ΔH_f of HCl (g) = –22 kcal m^{-1}

Enthalpy of Combustion (ΔH_c)

The enthalpy of combustion of a substance is the enthalpy change accompanying complete combustion of one mole of that substance.

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l) \qquad \Delta H = -3268\ kJ$$

Thus, ΔH_c of (C_6H_6 (l) = –3268 kJ mol^{-1}

Enthalpy of Neutralization (ΔH_{neu})

"The enthalpy change when one mole of H^+ ions from any acid is completely neutralized by one mole of OH^- ions from any base in their dilute solution to forms one mole of water is defined as the enthalpy of neutralization."

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(r)}; \quad \Delta H = -57.1\ kJ\ mole^{-1} = -13.7\ kcal\ mol^{-1}$$

$$\Delta H_{neutralisation} = \left(-57.1 + \Delta H^{acid}_{ionisation} + \Delta H^{base}_{ionisation}\right) kJ$$

Enthalpy of Solution (ΔH_{sol})

"The change in enthalpy when one mole of a solute is dissolved in a specified quantity of a solvent at a given temperature is called enthalpy of solution."

KCl (s) + aq. = KCl (aq) ΔH = –4.4 kcal

Hess's Law of Constant Heat Summation

"The enthalpy change during a chemical reaction is independent of the manner in which the change is brought about."

This is illustrated by the following example, in which the reaction A ® B, can be made to proceed through two different routes,viz.

(i) Directed conversions of A into B

$A \longrightarrow B \qquad \Delta H_r = H_B - H_A$

(ii) Conversion of A into B via the formation of C.

$A \longrightarrow C \qquad \Delta H_1 = H_C - H_A$

$C \longrightarrow B \qquad \Delta H_2 = H_B - H_C$

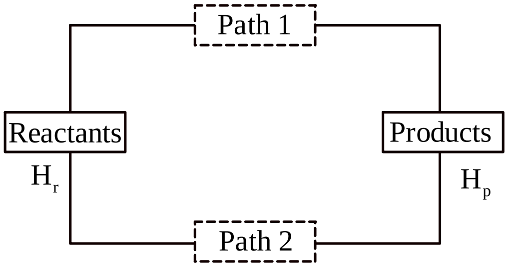
Then, according to the Hess's law,

$(H_B - H_A) = (H_C - H_A) + (H_B - H_C)$

or $\Delta H_r = \Delta H_1 + \Delta H_2$

i.e., the total enthalpy change in a reaction does not depend upon the route (path) by which the reaction is brought about.

$$\Delta H_r = \sum H_p - \sum H_r$$



Calculation of ΔH_r

(i) Using Hess's Law

(ii) $\Delta H_r = \sum \Delta H_f^{\text{product}} - \sum \Delta H_f^{\text{reactant}}$

(iii) $\Delta H_r = \sum \Delta H_C^{\text{reactant}} - \sum \Delta H_C^{\text{product}}$

(iv) $\Delta H_R = \sum \Delta H_{B-E}^{\text{reactant}} - \sum \Delta H_{B-E}^{\text{product}}$

INFLUENCE OF TEMPERATURE ON THE HEAT OF REACTION OR KIRCHOFF'S REACTION

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_p$$

This equation is called kirchoff's equation. This equation is used to calculate heat of reaction at a temperature provided it is known at another temperature.

Thus, $$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_V$$

Bond Energy of Bond Enthalpies

The amount of energy required to break one mole of bond of a particular type between the atoms in the gaseous state, i.e. to separate the atoms in the gaseous state under 1 atm. pressure and the specified temperature is called bond dissociation energy eq.

$H-H(g) \longrightarrow 2H(g), \qquad \Delta H = +433 \text{ kJ mole}^{-1}$

$Cl-Cl(g) \longrightarrow 2Cl(g), \qquad \Delta H = +242.5 \text{ kJ mole}^{-1}$

$H-Cl(g) \longrightarrow H(g) + Cl(g) \qquad \Delta H = +431 \text{ kJ mole}^{-1}$

The bond dissociation energy of a diatomic molecule is called bond energy. when more than one bond of the same kind are present in a compound, then the average bond dissociation energy required to break each bond in a compound is called bond energy.e.g.

Dissociation of H_2O molecule

$$H_2O(g) \longrightarrow H(g) + OH(g) \qquad \Delta H = 497.8 \text{ kJ mole}^{-1}$$

$$OH(g) \longrightarrow H(g) + O(g) \qquad \Delta H = 428.5 \text{ kJ mole}^{-1}$$

The average bond dissociation energy gives the value of O – H.

$$\text{Bond energy of O – H bond} = \frac{497.8 + 428.5}{2} = 463.15 \text{ kJ mole}^{-1}$$

Application of Bond Energy

1. Heat of Reactions : Enthalpy of reaction = $\sum$ Bond energy of reactants - $\sum$ Bond energy of products .
2. Determination of Resonance Energy : When a compound shows resonance there is considerable difference between the heat of formation as calculated from bond energies and that determined experimently. Resonance Energy = Experimental or actual heat of formation – Calculated heat of formation.

SECOND LAW OF THERMODYNAMICS

Spontaneous Process

A process which proceeds without any outside assistance, is termed as spontaneous or natural process. The reverse process which proceeds with the help of outside assistance does not proceed on its own, is referred as a nonspontneous or unnatural process.

In general, tendency of a process to occur naturally is called spontaneity.

Entropy

Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of the molecules of the system.

- Entropy was introduced by claussius
- It is the measure of the disorderness or randomness of the system
- It is an extensive property
- It is a state function
- It decreases with the increase of pressure or decrease in volume and vice-versa
- For any reversible cyclic process $\Delta S = 0$
- Unit of entropy is J mol^{-1} k^{-1}.

$$\Delta S = 2.303 \, nC_p \log \frac{T_2}{T_1} + 2.303 \, nRT \log \frac{P_1}{P_2}$$

$$\Delta S = 2.303 \, nC_V \log \frac{T_2}{T_1} + 2.303nRT \log \frac{V_2}{V_1}$$

Standard Entropy of formation

It is the entropy of formation of 1 mole of a compound from the elements under standard conditions. It is denoted by ΔS_f^o. $S_f^o = S^o(\text{compound}) - \sum S^o \text{elements}$

Entropy change for isothermal reversible process;

$$\Delta S = \frac{Q}{T}$$

When Q is heated supplied and T is temperature at which it is supplied

Second law of thermodynamic: Total entropy of entere universe for any spontaneous process is always increasing i.e. $\Delta S_{total} > 0$. At equilibrium $\Delta S_{total} = 0$.

GIBB’S FREE ENERGY AND FREE ENERGY CHANGE

The nature direction of physical and chemical changes is towards minimum energy (ΔH – ve) or towards maximum disorder (ΔS +ve). A spontaneous change take place without any continuing outside influence. When both ΔH and ΔS of a process are favourable then the process will be spontaneous but when both enthalpy and entropy are unfavourable the process will be nonspontaneous. However, when these driving forces oppose each other then it is to be seen that which predominates. Hence a new thermodynamic function called Gibb’s Free Energy was introduced.

Characteristics of Free Energy

- It is a thermodynamic state function
- It is represented by ‘G’.

  $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$
- It is related to enthalpy and entropy by the above expression
- It is an extensive property since its value depends upon the quantity of substance.
- Criteria of spontaneity based on constant T and P.
  - (a) If $\Delta G < 0$, the process is spontaneous
  - (b) If $\Delta G > 0$, the process is non-spontaneous
  - (c) If $\Delta G = 0$, the system is at equilibrium
- ΔG is equal to maximum possible useful work other than the P-V work that is obtainable from the system.
- $\Delta G = -nF\ E_{cell}$
- $\Delta G^0 = -nF\ E^o_{cell}$ where E^o_{cell} = standard cell potential.
- The relation between Gibb’s free energy change and equilibrium constant.

  $\Delta G^0 = \Delta G^0 + RT/\ln Q$

  at equilibrium $\Delta G = 0$

  $\therefore \quad \Delta G^0 = -RT\ \text{In}\ K = -2.303\ RT \log K \qquad \ldots (1)$

  Again $\therefore\ \Delta G^0 = \Delta H^0 - T\Delta S^0$
- At equilibrium $\Delta G = 0$

  So $\Delta H - T\Delta S = 0$ or $T\Delta S = \Delta H$

$$T = \frac{\Delta H}{\Delta S}$$

Standard Free Energy Change

The change in free energy which takes place when the reactants in their standard states are converted into the products also in their standard states.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta G^o = \sum \Delta G^o_{f\,(Products)} - \sum \Delta G^o_{f\,(reactants)}$$

Standard free energy of formation of a substance

- The free energy change which accompanies the form of one mole of a substance from its constituting elements in their standard states.
- The standard free energy of formation of all free elements is assumed to be zero.

COUPLED REACTIONS

When ΔG = –ve the reaction is spontaneous and when DG = +ve the reaction is non-spontaneous. A non spontaneous reaction can also be made spontaneous in case it is carried simultaneously with another reaction which is spontaneous and has a very large negative free energy. Such reactions are said to be coupled reactions. e.g. Biosynthesis of sucrose from glucose and fructose has +ve value of DG. It can be driven when coupled with hydrolyses at A.T.P.

$$\text{Glucose} + \text{Fructose} + \text{ATP} \longrightarrow \text{Sucrose} + \text{ADP}$$

$$\Delta G = -8\,\text{kJ mol}^{-1}$$

THIRD LAW OF THERMODYNAMICS (Given in 1906 by German Physical Chemist Nernst.)

The entropy of an ideal or perfect crystalline solid may be taken as zero at absolute zero of temperature.

Application of third law of thermodynamics

$\Delta S = S_T - S_0$ where, S_T = Entropy at TK, S_0 = Entropy at 0 K

Clausius – Clapeyron Equation

$$\log_{10}\frac{p_2}{p_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$