THERMODYNAMICS

Hess's law,second and third law of thermodynamics, entropy ,gibb's free energy.

1. Hess Law states that total heat change in a reaction is the same whether the chemical reaction takes place in one step or in several steps.

2. Hess law based on first law of thermodynamics

3. Hess law is useful to calculate:

    i)   Heat of formation of intermediate compounds

    ii)   Heat of transition like $S_\alpha \rightarrow S_\beta$ which is slow

    iii) Lattice energies of compounds (Eg. NaCl)

4. First law of themodynamics does not indicate the spontaneous nature or otherwise of process. It does not indicate whether a process occur in a specific direction without involving any external agency.

5. It does not indicate what fraction of one form of energy is converted into another form in any transformation.

6. Statements of Second law of thermodynamics: are

    i.   Second law of thermodynamics can be stated in different forms

    ii.   Heat can not flow from a colder body to hotter body of its own.

    iii. Heat can not be converted into work completely without causing some permanent changes in the system and surroundings

    iv.   All spontaneous processes are themodynamically irreversible

    v.   In all spontaneous process, the entropy of the universe increases.

    vi.   Second law of themodynamics rules out the existance of a perpetual motion machine of second kind. It is one which works in cycles and transforms heat from lower temperature region to higher temperature region without intervention of any external agency.

7   The degree of disorder of a system is called entropy. It is denoted by "S". Its units are joule K^{-1}. It is a state function and extensive property.

8. Entropy of a gas is greater than that of liquid which is greater than that of a solid.

    $S_{(g)} > S_{(l)} > S_{(S)}$

9. The entropy change $(\Delta S) = \dfrac{q_{rev}}{T}$

    [Where q_{rev} is the heat absorbed by the system isothermally and reversibly]

    T = Temperature during the state change

10. Absolute entropy of a substance at 298K and

1atm is called standard entropy and it is represented as S^0.

11. Phase transformation takes place at constant temparature and pressure. Thus $q_{rev} = \Delta H$

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_f} , \quad \Delta S_{evap} = \frac{\Delta H_{evap}}{T_b}$$

12. Spontaneous reaction is one which has a natural tendency to occur (or) a spontaneous reaction is one which will proceed to completion without any external agency.

13. Themodynamically a spontaneous reaction is an irreversible one

    eg :   a)   Heat flows from a hotter body to a colder body

    b)   Water flows from a higher level to lower level.

    c)   Movement of gas molecules from high pressure area to low pressure area.

    d)   Dissolution of glucose in water

    e)   Evaporation of water

    f)   Melting of ice.

    g) $2H_2 + O_2 \rightarrow 2H_2O$ (slow reaction)

    h) $NaOH + HCl \rightarrow NaCl + H_2O$ (fast reaction)

    Note : A spontaneous reaction can be slow (or) moderately slow (or) instantaeous.

14. Criteria for a reaction to be spontaneous.

    a.   Exothermic reactions are generally spontaneous, because the energy released increases the

    disorder of the surroundings, moreover the reaction proceeds from high energy state to low energy state. But some endothermic reactions are also spontaneous. eg:- Evaporation of water.

    Therefore it is concluded that exhother-micity is required condition for a reaction to be spontaneous but not necessry and sufficient condition.

    b.   Some times endothemic reactions also can be spontaneous if the heat flow into the system causes a greater disorderness of the system such that total entropy change is positive.

    c.   In general spontaneous reactions are accompanied by an increase in entropy $\Delta S = +ve$.

    eg : Evaporation of water is spontaneous as they involve an increase in entropy.

    d.   For a spontaneous process in an isolated system the entropy change is positive.

    e.   For a spontaneous process in a non isolated system the total entropy change is positive.

    $$\Delta S_{total} = \Delta S_{(sys)} + \Delta S_{(surr)} = +ve$$

f.   But it is observed that some reactions with

ΔS = –ve are also spontaneous. eg. some reactions involved in industries, metallurgy and in bio systems.

15.   In order to explain the spontaneous nature of a process, Gibb introduced a new themo-dynamic parameter called Gibbs energy (or) Gibbs function (G) that accounts for both exothermicity and entropy.

G = H – TS.

G is state function and extensive property.

For a process $\Delta G_{(sys)} = \Delta H_{(sys)} - T\Delta S_{(sys)}$

$\Delta G_{sys} = -T\Delta S_{Total}$

Note : ΔG= –ve, the process is spontaneous.

ΔG = +ve, the process is non spontaneous

If $\Delta G = 0$, the system is in equilibrium state

ΔH	ΔS	ΔG	Discription of the nature of reaction
Negative	Positive	Negative	Spontaneous at all temperature
Negative	Negative	Negative	Spontaneous at all temperature
Negative	Negative	Positive	Non - Spontaneous at high temperature
Positive	Positive	Negative	Spontaneous at high temperature
Positive	Positive	Positive	Non-Spontaneous at low temperature
Positive	Negative	Positive	Non-Spontaneous at all temperature

16.   Gibb's energy change calculated under standard condition is called standard Gibb's energy change .ΔG^0

$\Delta G = \Delta G^0 + RT$ ln K_C at equilirbrium $\Delta G = 0$

17.   The entropy of a pure and perfect crystalline substance is zero at absolute zero according to third law of thermodynamics. This is suggested by Planck. This is also known as Nernst Heat Theorm.

18. The absoulte value of entropy of a substance is calculated from heat capacity at constant pressure [C_p] by using $$\Delta S = S_T - S_0 = S_T = \int_0^T \frac{C_p}{T} . dt ......(1)$$

    S_T = absolute entropy at T.K

    S_0 = absolute entropy at 0 K

    C_p = heat capacity at constant pressure.

19. But C_p cannot be measured at absolute zero (or) near absolute zero. At very low temperature $C_p - C_v$ is negligible. C_v value at absolute zero is obtained by using the extra polating technique and Debye equation. The C_v values obtained are taken as C_p values and absolute entropies are calculated. $C_v = aT^3$ Debye's equation

20. For a reaction for the type xA + yB → mC + nD. The standard entropy change is calculated as

    $$\Delta S^0 = \left(mS_C^0 + nS_D^0\right) - \left(xS_A^0 + yS_B^0\right)$$