Chemical inermodynamics

waws of Thermodynamics.

1. Zeroth law:

When two bodies are in thermal equilibrium with a third body, then all the three are in thermal equilibrium with each other. Or

If a body A is in thermal equilibrium with a body C and a body B is also in thermal equilibrium with C then A, B and C are in thermal equilibrium with each other.

ie. Every thermodynamic system must possess a temperature.

2. First Law :

Energy can neither be created nor destroyed although it can be converted from one form to other. Or The total energy and mass of an isolated system remain constant. Or Whenever a quantity of one kind of energy is produced, an exactly equivalent amount of other kinds must disappear.

3. Second Law:

The entropy of universe is constantly increasing. Or

Heat cannot be transferred from a cold body to a hot body or

It is impossible to convert heat into work without loss. Or

All natural processes (or spontaneous) are irreversible and leads to equilibrium. Or

No engine can work with 100% efficiency.

3. Third Law:

The entropy of all perfectly pure crystalline solids is zero at absolute zero of temperature.

Important terms in Thermodynamics

1. Internal Energy U

Every substance is associated with a definite amount of energy called internal energy E. Internal energy depends on the chemical nature of the substance, temperature, pressure and volume. It is the sum of all translational, rotational, vibrational motions and the kinetic and potential energies of nuclei and electrons present in the system.

By first law of thermodynamics

 $\Delta U = q + w$ (where q=heat and w= work) (w -ve when work is done by the system, +ve when work is done on the system)

or dU = dq +dw (differential form)

In a constant pressure process $w = P\Delta V$ (when work is done by the system)

Hence $\Delta U = q - P\Delta V$ or $\Delta U + P\Delta V = q$

In a constant Volume process ΔV=0,w=0

Hence $\Delta U = q$ at constant volume

2. Enthalpy H

Enthalpy is the energy of the system at constant pressure.

$$H = U + PV$$
, $\Delta H = \Delta U + P\Delta V = q$.

or
$$\Delta H = q$$

It is a measure of remoun ness का कि कुप्रस्कृत Furtaoba os For a reversible process

$$\Delta S = \underbrace{q_{rev}}_{T}$$
 or $T\Delta S = q_{rev}$

4. Free energy G: This is the available energy for doing work (capacity to do useful work) The decrease in its value is equal to the weful work done in the system. $\Delta G = \Delta H - T\Delta S$ Spontaneous process: is a process that takes place without any external compulsion.

All natural processes are spontaneous processes and it proceeds in one direction only ie . irreversible in nature. Spontaneous process continues up to equilibrium. All spontaneous processes tend towards a decrease in energy and an increase in entropy of the system. AG should be -ve for spontaneous processes. Possibility of a spontaneous process can be decided by using the expression $\Delta G = \Delta H - T\Delta S$.

Sign of ΔS	Sign of ΔG	Possibility of reaction
+ve	-ve	Always spontaneous.
-ve	-ve at low temp	spontaneous at low temp
+ ve	-ve at high temp	spontaneous at high temp
—ve	+ve	Non spontaneous at all temp
	+ve -ve + ve	+ve —ve —ve at low temp + ve —ve at high temp

Mathematical derivation of first law of Thermodynamics:

For a change A → B

Let U_A be the internal energy of A and q be the heat absorbed by the system, then net amount of energy of the system be $U_A + q$. During this transformation, w be the work done by the system. If U_B be the internal energy of system in B state, then the net energy of system after the change would be U_B + w.

By first law,
$$U_A + q = U_B + w$$

or
$$U_B - U_A = \Delta U = q - w$$
 —(1) (this is the first law equation)

In the differential form: dU = dq - dw ----(2)

In an isolated system, no heat exchange with the surrounding, hence dq=0 ie dU= — dw.

In a non-isolated system, the system gains heat and perform work dw.

Hence internal energy of system is dU = dq - dw.

Surrounding loses dq amount of heat and receives dw work.

Hence internal energy of Surrounding is dU' = dw - dq = -dU

Net internal energy change of system and surrounding taken together would be nil

le.
$$dU = -dU'$$
 or $dU + dU' = 0$

Enthalpy of a reaction is the enthalpy change when number of moles of the reactants as indicated by the balanced chemical equation react to form products. ΔH= ΣEnthalpy of products – ΣEnthalpy of reactants

Enthalpy of formation is the enthalpy change when one mole of a compound is formed from its elements.

Enthalpy of fusion is the enthalpy change when one mole of a solid changes into liquid at its boiling point.

Enthalpy of sublimation is the enthalpy change when one mole of a solid changes directly into vapour.

Enthalpy of neutralization is the change in enthalpy when one gram equivalent of an acid is completely neutralized by one gram equivalent of a base; $H^+ + OH^- \rightarrow H_2O$

Standard Enthalpy of formation: Enthalpy change when one mole of a compound is formed from its elements in their standard state. (1atm pressure and 298K)

Hess's Law of constant heat summation: The total enthalpy change of a given chemical reaction will be the same whether the reaction takes place in one step or in several steps

Molecular relation between △ H and Æ △ U

by first law

$$\Delta U = q + w$$

Pressure-volume work occurs in constant pressure process ie. $w = -P\Delta V$ (when work is done by the system)

$$\Delta U = q - P\Delta V \dots (1)$$

Let us consider a reaction involving gases, A → B

If V_A and n_A be the volume and number of moles of gaseous reactants and V_B and n_B be that of the products, then at constant temperature and pressure

$$PV_A = n_A RT$$
 and $PV_B = n_B RT$ (gas law)

$$P(V_B - V_A) = (n_B - n_A) RT$$

or
$$P\Delta V = \Delta n RT$$

substituting in (1)

$$\Delta U = q - \Delta n RT$$

At constant pressure $q = \Delta H$

$$\Delta U = \Delta H - \Delta n RT$$

or

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

The difference between ΔH and ΔU is not significant for solids and liquids.

Problems: refer class notes.

Heat Capacity is the heat required to raise the temperature of a substance through 1° C.

at constant pressure
$${}^{4}C_{p} = \left(\frac{\partial H}{\partial T}\right)_{P}$$

at constant volume
$$C_v = \left(\frac{\partial U}{\partial T}\right)_U$$

Specific heat capacity s is the heat required to raise the temperature of 1gm of a substance through 1°C.

Molar heat capacity C_m is the heat required to raise the temperature of 1mole of a substance through 1°C.

1. Kirchoff's equation- Relation between enthalpy and Heat capacity with temperature.

Consider the reaction A → B

Let H₁ be the enthalpy of the reactant and H₂ be the enthalpy of product respectively. The change in enthalpy is given by

$$\Delta H = H_2 - H_1 - 1$$

Case 1: If pressure is kept constant

Differentiating (1) w.r.to temperature at constant pressure

$$\begin{bmatrix} \frac{\partial (\Delta H)}{\partial T} \end{bmatrix}_{p} = \begin{pmatrix} \frac{\partial H_{2}}{\partial T} \end{pmatrix}_{p} - \begin{pmatrix} \frac{\partial H_{1}}{\partial T} \end{pmatrix}_{p}$$
But $\begin{pmatrix} \frac{\partial H_{2}}{\partial T} \end{pmatrix}_{p} = Cp_{1}$ and $\begin{pmatrix} \frac{\partial H_{1}}{\partial T} \end{pmatrix}_{p} = Cp_{1}$

Therefore
$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_{P} = Cp_2 - Cp_1 = \Delta Cp$$

or
$$d\Delta H = \Delta Cp \times dT$$

on Integration we get

$$\int_{T_i}^{2} d\Delta H = \Delta C p \int_{T_i}^{T_2} dT$$

$$\Delta H_2 - \Delta H_1 = \Delta Cp (T_2 - T_1) = \Delta Cp (T_2 - T_1) - --2$$

Case 2: If volume is kept constant

If U₁ and U₂ are the internal energies of reactant and product respectively $\Delta U = U_2 - U_1$

Differentiating w.r.to temperature at constant volume

$$\begin{bmatrix} \frac{\partial(\Delta U)}{\partial T} \end{bmatrix}_{V} = \begin{pmatrix} \frac{\partial U_{2}}{\partial T} \end{pmatrix}_{V} - \begin{pmatrix} \frac{\partial U}{\partial T} \end{pmatrix}_{V}$$

But
$$\left(\frac{\partial U_2}{\partial T}\right)_V = Cv_2$$
 and $\left(\frac{\partial U_1}{\partial T}\right)_V = Cv_1$

Therefore
$$\left[\frac{\partial(\Delta U)}{\partial T}\right]_V = Cv_2 - Cv_1 = \Delta Cv$$

or
$$d\Delta U = \Delta Cv \times dT$$

on Integration we get

$$\int_{0}^{\infty} d\Delta U = \Delta C v \int_{0}^{\infty} dT$$

$$\Delta U_2 - \Delta U_1 = \Delta Cv (T_2 - T_1) = \Delta Cv \times \Delta T$$
 ——3 Equations (2) and (3) are the Kirchoff's equations.

This equation gives the influence of temperature on enthalpy change in a reaction

We have

$$H = U + PV - 1$$

Substituting (1) in (2)

Upon differentiation

From first law of thermodynamics, at constant pressure

$$dq = dU + dw = dU + PdV ----- 5$$

And for a reversible process

$$dS = \underline{dq}$$

or
$$dq = TdS -------6$$

Substituting in (4)

$$dG = TdS + VdP - TdS - SdT = VdP - SdT -----8$$

This equation gives the dependence of free energy on temperature and pressure.

When pressure kept constant dP = 0, VdP = 0

Then
$$dG = -SdT - 9$$

or
$$\left(\frac{dG}{dT}\right) = -S ----10$$

When temperature kept constant dT =0, SdT=0

Or
$$\left| \frac{dG}{dQ} \right| = V$$
 ---12

These equations show that G is a function of pressure and temperature. It combines

first and second law and makes it suitable for chemical applications.

From (9) and (10) it follows that G decreases when T increases.

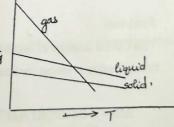
Since gases have higher entropy than liquids and solids,

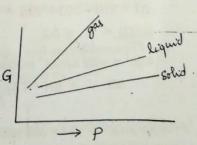
G of gases is more sensitive to changes in temperature.

From (11) and (12) ,since V is +ve, G always increases when pressure is increased at constant temperature.

Since molar volume of gases are very large,

free energy G of gases is more sensitive as indicated by the figure.





Gibbs - Helmholtz Equation

It is a mathematical relation connecting the free energy change, enthalpy change and entropy change absolute temperature of the system.

At constant pressure

$$dG = -SdT$$

If G_1 and G_2 are the free energies & S_1 and S_2 are the entropies of the system in the initial and final states, then

$$dG_1 = -S_1 dT$$
 , $dG_2 = -S_2 dT$ $d(G_2 - G_1) = -(S_2 - S_1) dT$

or
$$d(\Delta G) = -\Delta S dT$$

or
$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_{p} = -\Delta S$$
 ----1.

we know
$$\Delta G = \Delta H - T\Delta S$$
 ----2.

Substituting (1) in (2) we get

$$\Delta G = \Delta H + T \left[\frac{\partial (\Delta G)}{\partial T} \right]_{P}$$

This equation is known as Gibbs - Helmholtz Equation

Application: 1. To calculation of EMF of electrochemical cell. Suppose e.m.f of cell is E, and if nF coulombs of electricity is produced by the cell, then

Electrical work obtained = nFE

 $\Delta G = -nFE$ (-ve sign indicate that work is done by the cell)

2.Gibbs – Helmholtz Equation helps us to determine spontaneity of a reaction.

If ΔG is negative, the reaction is spontaneous.

Problem .

The Gibbs energy change for a reaction at 300K is $-86kJ \text{ mol}^{-1}$ and at 310K it is -84 kJmol^{-1} . Calculate the enthalpy change for the reaction at the average temperature of 305K if ΔG at 305K is -85 kJmol^{-1} .

$$\Delta G = (-84+86) \text{kJ mol}^{-1} = 2 \text{ kJ mol}^{-1}$$

$$\Delta T = 310 - 300 = 10K$$

$$\frac{\partial(\Delta G)}{\partial T} = \frac{2}{10} = 0.2$$

$$\Delta G = -85 \text{ kJmol}^{-1} \text{ at} 305 \text{ K}$$

$$\Delta G = \Delta H + T \left[\frac{\partial (\Delta G)}{\partial T} \right]_{p}$$

$$-85 \text{ kJmol}^{-1} = \Delta H + 305 \times 0.2 \text{ kJmol}^{-1}$$

$$\Delta H + 61.0 \text{ kJmol}^{-1}$$
, $\Delta H = -85 - 61.0 \text{ kJmol}^{-1} = -146 \text{ kJmol}^{-1}$

Van't Hoff reaction isotherm - (relation between free energy change and equilibrium constant we know, at constant temperature

For one mole of an ideal gas, PV=RT or V = RT

Substituting in (1) we get $dG = RT \underline{dP}$

$$\int dG = RT \int dP$$

On integration
$$\int dG = RT \int \frac{dP}{P}$$

$$G = G^{0} + RT \ln P - 2.$$

Where Go is the integration constant. It is the standard free energy and is a constant for a given reaction. Consider a general reaction

Let GA and GB be the free energy per mole of the reactant and the product at pressures PA and PB and G⁰_A and G⁰_B be their standard free energies respectively.

Then eqn (2) becomes

$$G_A = G_A^0 + RT \ln P_A ----4$$

$$G_B = G^0_B + RT \ln P_B - - 5$$

Subtracting 4 from 5 we get

$$(G_B - G_A) = (G^0_B - G^0_A) + RT \ln \frac{P_B}{P_A}$$
since
$$\frac{P_B}{P_A} = K_P$$

$$\Delta G = \Delta G^{\circ} + RT \ln K_{P}$$

At equilibrium $\Delta G = 0$, $\Delta G^0 = -RT \ln K_P$

$$\Delta G^0 = -RT \ln K_P$$

This equation is known as Van't Hoff reaction isotherm

this expression gives a quantitative relation for free energy change accompanying a chemical reaction.

K_P is related to K_c as

$$K_P = K_c(RT)^{\Delta n}$$

$$\Delta n = (n_{products} - n_{reactants})$$

n is the number of moles

When number of moles of reactants equals the number of moles of the products, then $K_{\text{P}} = K_{\text{c}}$

Trouton's rule

The entropy of vaporization of liquids at their boiling points is a constant and approximately equal to 85 Jmol⁻¹K⁻¹. This is known as Trouton's rule and may be expressed as

$$\Delta S = \Delta H_{y} \sim 85 \text{ Jmol}^{-1} \text{K}^{-1}$$

Where ΔH_{ν} is the molar heat of vaporization (enthalpy of vaporization) and T_b is boiling point of liquid on absolute scale. The quantity ΔH_v is called entropy of vaporization. In phase transitions like melting,

aling etc heat absorbed is used to increase the entropy while temperature remains constant. Deviations: 1. In water, methanol, ethanol and ammonia etc, intermolecular hydrogen bonding is presen in the liquid state. Much heat is required to break these hydrogen bonds. Therefore entropy of vaporization is much higher than 85Jmql⁻¹K⁻¹.

- Mercury has a higher value because of metallic bonding between atoms.
- 3. Acetic acid has a low value of molar entropy of vaporization due to dimer formation even in vapour state.

Liquid	ΔH _v Jmol ⁻¹ K ⁻¹
Water	T _b 109.
Ethyl	- 112.8
alcohol	97.4
Ammonia	62.2
Acetic acid /	94.2
Mercury /	1,1

Nernst Heat theorem

According to Nernst heat theorem ΔG and ΔH tend to approach each other asymptotically (ie gradually) as the temperature is lowered and at absolute zero $\Delta G = \Delta H$.

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

. When $T \rightarrow 0$, $\Delta G = \Delta H$. This can be seen from the graph.

When T→ 0the curve becomes more and more horizontal.

Therefore the slope of the curve $\partial(\Delta G) = 0$ as $T \rightarrow 0$,

Gibbs- Helmholtz equation is

$$\Delta G = \Delta H + T \left[\frac{\partial (\Delta G)}{\partial T} \right]_{P}$$
, at T=0, $\Delta G = \Delta H$.

Mathematically it is written as

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4H

This means that at absolute zero, heat capacities and entropies of products and reactants in solid state are identical. Similarly heat capacities and entropies of solids become zero at absolute zero.

AG

AH

This is the basis of third law of thermodynamics which states that entropy of solids become zero at absolute zero.

Entropy changes in different processes.

Entropy change at constant temperature

Entropy of a system varies with the state of the system

From first law of thermodynamics $\Delta U = q + w$

In an isothermal expansion of an ideal gas in a reversible process, there will be no change in internal energy ie. $\Delta U = 0$. or

In such cases, work done in the expansion of n moles of a gas from volume V1 to V2 at constant -w = PdVtemperature is given by

1 - V-1111/

dividing by T,
$$\underline{q}_{rey} = \frac{nRT}{T} \ln \frac{V_2}{V_1}$$

since
$$\underline{q}_{rev} = \Delta S$$

entropy change at constant temperature is given as

$$\Delta S = 2.303 \, \text{nR log} \, \frac{V_2}{V_1}$$

Entropy change

Entropy change at constant pressure

From first law of thermodynamics dq = dU +dw = dU + PdV

we have
$$C_v = \left(\frac{dU}{dT}\right)_v$$
 and $P = \frac{RT}{V}$

or dq =
$$C_v$$
 dT + $mRT \frac{dV}{V}$
Dividing by T we get, $\frac{d_{rev}}{T} = C_v \frac{dT}{T} + \frac{nRT}{V} \frac{dV}{V}$ or dS = $C_v \frac{dT}{T} + r_v R \frac{dV}{V}$ (since $\frac{dV}{V} = C_v \frac{dV}{V} + r_v R \frac{dV}{V}$)

For a change from state1 to 2, the total entropy change is given by

$$\int_{1}^{2} dS = nC_{v} \int_{1}^{T_{2}} \frac{dT}{T} + nR \int_{v}^{T} \frac{dV}{V} \quad \text{or} \quad \Delta S = C_{v} \ln \frac{T_{2}}{T_{1}} + nR \ln \frac{V_{2}}{V_{1}}$$

or
$$\Delta S = 2.303 \, \text{a} \, \text{C}_v \log \frac{\text{T}_2}{\text{T}_1} + 2.303 \, \text{nR} \, \log \frac{\text{V}_2}{\text{V}_1}$$
(1)

$$\Delta S = 2.303 \text{ nC}_v \log \frac{T_2}{T_1} + 2.303 \text{ nR} \log \frac{P_1}{P_2} \qquad (\text{since } \frac{V_2}{P_2} = \frac{P_1}{P_2}) \qquad \frac{V_2}{V_l} = \frac{P_l}{P_2}$$

At constant pressure $P_1 = P_2$, equation becomes

$$\Delta S = 2.303 \text{ n C}_p \log \frac{T_2}{T_1}$$

Entropy change at constant volume For an isochoric process $V_1 = V_2$ equation (1) becomes $\Delta S = 2.303 \text{ nC}_v \log \frac{T_2}{T_1}$

Problem: One mole of an ideal gas expands reversibly from a volume of 1dm³ to 10dm³ at 25°C. Calculate the change in entropy.

soln:
$$\Delta S = 2.303 \text{ nR log } \frac{V_2}{V_1}$$

$$V_1 = 1 dm^3$$
 $V_2 = 10 dm^3$, n = 1 mole, R= 8.314JK⁻¹mol⁻¹

$$\Delta S = 2.303 \text{ x1 mole x8.314 JK}^{-1} \text{mol}^{-1} \log \frac{10}{1} = 19.147 \text{ JK}^{-1}$$

Micai Potentiai Mi

Chemical potential is defined as the free energy change of a system when one mole of a component added to such a large quantity of the system at constant temperature and pressure so that there is not much change in composition of the system.

$$M_{i} = \left(\frac{\partial G}{\partial n_{i}}\right)^{i}$$
 where n is the number of moles and M_{i} is the chemical potential of the ith component.

The matter tends to flow spontaneously from a region of high chemical potential to region of low potential. This flow continue till the substance acquires the same chemical potential in both regions.

At this stage dG =0 and so the system will be in equilibrium. Therfore chemical potential of a component in a system is directly proportional to its escaping tendency.

Different ways of defining chemical potential are

$$\mathbf{M}_{i} = \left(\frac{\partial G}{\partial n_{i}}\right)_{T, P, n_{i} \cdots n_{j}} = \left(\frac{\partial H}{\partial n_{i}}\right)_{S, P, n_{i} \cdots n_{j}} = \left(\frac{\partial E}{\partial n_{i}}\right)_{S, V, n_{i} \cdots n_{j}}$$

The chemical potential may be considered to be proportional to concentration.

Fugacity f.

Fugacity is 'pressure" of real gases. Fugacity represents the actual behavior of real gases. It is represented as

$$G = G^0 + nRT \ln f$$

Where G^0 is the free energy for n moles of a real gas. (for ideal gases the eqn is $G = G^0 + nRT \ln P$) The fugacity function is defined as

Limit
$$\underline{f}$$
 = 1 where P is ideal gas pressure or actual pressure.

When P approaches zero, a real gas approximates ideal behavior.

At low pressures fugacity is equal to pressure. Fugacity of a real gas can be both less or more than the pressure.

It is positive at low pressures and negative at very high pressures.

At o^o C fugacity of Nitrogen gas at 50atm is 48.9atm and at 400atm it is 424.4atm. For hydrogen and helium fugacity is always greater than the pressure.

Fugacity
$$f = \frac{P^2V}{RT}$$

This equation is used for calculating fugacity at moderately low pressures.

Thermodynamics of Biochemical reactions ?

Thermodynamically favoured reactions involve decrease in free energy ie. $\Delta G = -ve$. Several reactions in biological systems are spontaneous ($\Delta G = -ve$) while several others are non-spontaneous

in which $\Delta G = +ve$. Still they occur in living systems .Cellular reactions requiring energy is "coupled another reactions in which $\Delta G = -ve$. This <u>coupled reactions</u> become energetically favoured basic principle behind all enzymatic actions in biological organisms.

Glucose + Fructose \rightarrow Sucrose $\Delta G = +5.5 \text{ k cal mol}^{-1}$ ATP \rightarrow ADP + Phosphate $\Delta G = -7.3 \text{ k cal mol}^{-1}$ Coupling these two equations gives Glucose + Fructose + ATP \rightarrow Sucrose + ADP + Phosphate. $\Delta G = \Delta G_1 + \Delta G_2 = +5.5 \text{ k cal mol}^{-1} -7.3 = -1.8 \text{k cal mol}^{-1}$

The hydrolysis of ATP provides energy in the cells. This energy is used for different kinds of work like contraction of muscles, up take of nutrients, movement of cells, transmitting nerve impulses etc.

Thus ATP can be considered as the centre to all activities of a cell.

For the synthesis of ATP, cells obtain energy from photosynthesis (in plants) and account

like carbohydrates and lipids in animals.

Food undergo aerobic oxidation and releases energy and is stored in the body as ATP.

For example, oxidation of glucose

 $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ $\Delta G = -2880 \text{ kJmol}^{-1}$

One mole of glucose gives 38 moles of ATP.

ATP undergo hydrolysis to give ADP

ATP + $H_2O \rightarrow ADP + H_2PO4^- + H^+ \Delta H = -20 \text{ kJ mol-1}, \Delta G = -30.5 \text{ kJmol}^{-1}$ at body temperature. ie. when one mole of ATP is formed 30.5 kJmol $^{-1}$ of energy is stored. When 38 moles of ATP are formed 1160kJ of energy is stored. When one mole of glucose is burned 1720kJ of energy is utilized for doing work and the remaining 1160kJ is stored for further purpose (1720+1160=2880 kJmol $^{-1}$).