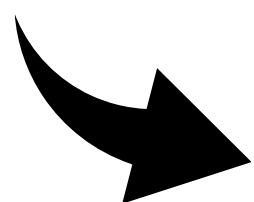


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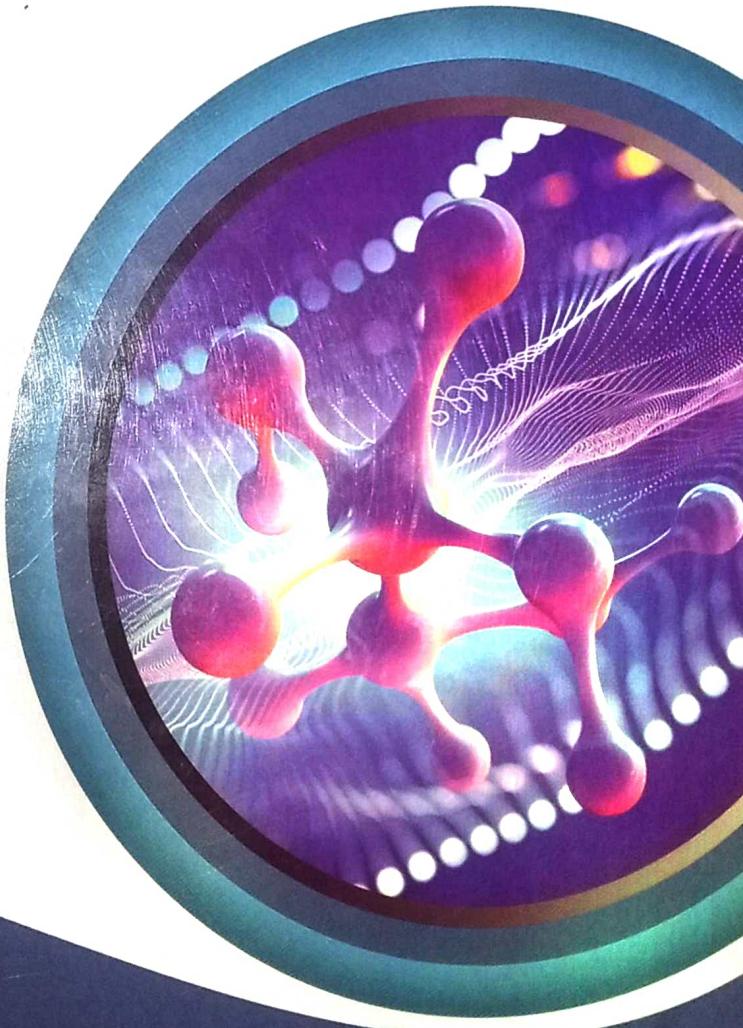
CHEMISTRY

FULL COURSE STUDY MATERIAL

Class XI

- Chemical Thermodynamics and Energetics
- Equilibrium
- Redox Reaction

Module-2





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Chemistry Module-2

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CHAPTER

4

Chemical Thermodynamics and Energetics

INTRODUCTION

Thermodynamics is related with energy and its transformation in various forms in different physical and chemical processes.

| | |
|----------------|---|
| Thermodynamics | \equiv Thermo + dynamics |
| Dynamics | \equiv Study of change due to a driving force |
| Thermo | \equiv Thermal which is related to temperature or energy. |

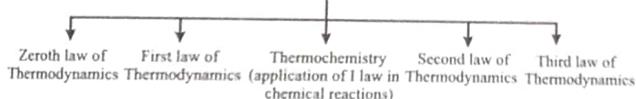
The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state.

CHEMICAL ENERGETICS

The branch of science which deal with the energy changes associated with chemical reactions is called chemical energetics. While the study of heat energy and its transformation is known as thermodynamics.

Thermodynamics: The branch of science which deals with different forms of energy & their interconversion.

Thermodynamics



Basic Terms

- ◆ **System:** Part of the universe which is under study for energy changes.



Ex. Air in a room, water in a bottle, any living body.

- ◆ **Surrounding:** Rest of the universe.

- ◆ **Universe:** Universe = System + Surroundings



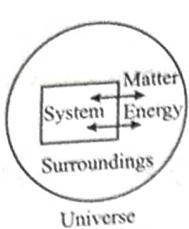
- ◆ **Boundary:** Anything which separates system & surroundings is called boundary.
- ◆ Boundary can be real or imaginary.
- ◆ Boundary can be flexible or rigid
 - e.g.: Air in a flexible balloon (flexible boundary) while air in a room (fixed boundary).
- ◆ Boundary can be adiabatic(non-conducting) or diathermic (conducting).

Classification of System on the Basis of Nature

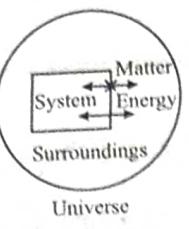
- (i) **Homogeneous systems:** A system having uniform nature throughout, made up of one phase only.
- (ii) **Heterogeneous system:** A system not uniform throughout, consists of more than one phase.

Classification of System on the Basis of Boundary

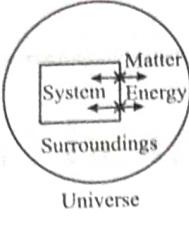
- ◆ **Open system:** System which can exchange energy & matter with the surroundings.
 - e.g.: Living systems (any living organism) are open systems, air in an open room.
- ◆ **Closed system:** System which can exchange only energy but cannot exchange matter with the surroundings is called closed system.
 - e.g.: Any matter in a closed container.
- ◆ **Isolated system:** System which cannot exchange energy and matter both with the surroundings.
 - e.g.: Water in thermos flask. (Though not a perfectly isolated system but can be taken as, for small interval of time as the energy exchanges are negligible).
- ◆ Whole of universe is a perfect isolated system.



Open System



Closed System



Isolated system

STATE OF A SYSTEM

- ❖ It means the condition in which the system is present.
- ❖ It can be specified/defined by measuring/specifying some observable/measurable properties of the system like pressure, volume, temperature, amount of substance, elasticity, heat capacity etc.
e.g.: For an ideal gaseous system state of the system can be defined by specifying volume, temperature and pressure.
- ❖ We may have to specify more properties of the system depending on the complexity of the system.

State Function

- ❖ Property of a system which is dependent only on the state of the system i.e. it is a point function.
- ❖ It is independent of the path followed to attain a particular state.

Condition for a function to be a state function:

$$(i) \text{ If } \phi \text{ is state function, } \int_A^B d\phi = \phi_B - \phi_A$$

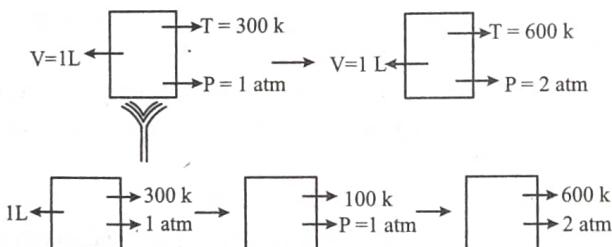
$$(ii) \text{ If } \phi \text{ is state function, } \oint d\phi = 0$$

e.g.: In Mechanics, Displacement of any object will be a state function but distance travelled by the object will be a path function.

For any thermodynamic system,

Temperature, Pressure, Volume, Total internal energy (E or U), Enthalpy(H), Gibbs free energy (G), Entropy (S) are all state functions.

e.g.:



In the above example the final temperature, pressure, and the volume will be same in both the above ways but the work involved and the heat exchanged during the processes will be different.

Note: $\Delta H, \Delta U, \Delta G, \Delta P, \Delta T$ etc. are not state function

Path function:

- ❖ Quantities which are dependent on the path/way the system has achieved a particular state.
e.g. Heat, work, Heat capacities(Molar heat capacities, specific heat capacities etc.).
- ❖ These quantities are defined when there is a process going on.
- ❖ These can not have any definite (particular) value in any particular state of the system.

TYPES OF PROPERTIES

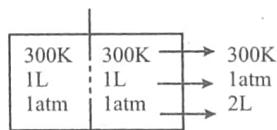
Extensive Properties

- ❖ Functions or properties of the system which are dependent on mass or size of the system are called Extensive Properties.
- ❖ Extensive functions are additive in nature e.g. The addition of the volumes of the two parts equals the volume of the whole of the room.
e.g.: Mass, Total heat capacity, Total internal energy (E), Enthalpy(H), Gibbs Free Energy(G), Entropy(S).

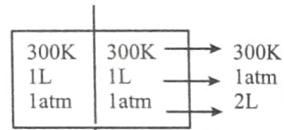
Intensive Properties

- ❖ Functions or properties which are not mass dependent or size dependent, are called intensive function.
- ❖ Intensive properties are not additive in nature.
e.g.: Temperature, pressure, molar heat capacity, specific heat capacity, density, concentration, vapour pressure.

How to identify extensive or intensive properties: If a system in a particular state is divided into two equal or unequal parts, the properties which have value equal to the original value of that property for the whole of the system is called an Intensive property. While the properties which have values different from the values for whole of the system are called Extensive Properties.



Room is divided into two equal halves



Room is divided into two equal halves

- ❖ For example consider air in a room at temp of 300K, 1 atm pressure. Now, if the room is divided by some boundary (imaginary or real) into two parts (equal or unequal) then in these two parts.
- ❖ Temperature, pressure, density of the gas, concentration of gaseous molecules etc. will have the same value as that of for whole of the system. (intensive)
- ❖ While the volume of two parts, mass of gas in two parts, total energy of the gaseous molecules in the two parts, entropy the two parts etc. will be different from the values of these properties as for the whole of the system initially. (extensive)



Train Your Brain

Example 1: Classify the following into open, closed or isolated systems:

- (i) Animals and plants
- (ii) A refrigerator or a fridge
- (iii) A solar cooker

Sol. (i) Open system
(ii) Closed system
(iii) Closed system

Example 2: Which of the following are open, closed or nearly isolated systems:

- (i) Human beings
- (ii) The Earth
- (iii) Can of tomato soup
- (iv) Ice-cube tray filled with water
- (v) A satellite in orbit
- (vi) Coffee in a thermos flask and
- (vii) Helium filled balloon.

Sol. Open: Human beings, Earth, Ice cube tray

Close: Can of Tomato soup, A satellite in an orbit, Helium filled balloon.

Isolated: Coffee in thermos flask.

Example 3: Separate out the following into extensive and intensive.

Volume, Temperature, Pressure, Boiling point, Free energy.

Sol. Volume and free energy are extensive, others, are intensive.

Example 4: Which of the following are state functions :

- (i) Height of hill
- (ii) Distance travelled in climbing the hill
- (iii) Energy change in climbing the hill.

Sol. (i) and (iii)

Example 5: A thermally isolated gaseous system can exchange energy with the surroundings. What is the mode of transference of energy?

Sol. Work

Concept Application

1. Which amongst the following is an extensive property of the system?
 - (a) Temperature
 - (b) Volume
 - (c) Viscosity
 - (d) Refractive index

2. Which of the following is not a state function of thermodynamic system?

- (a) Internal energy(E)
- (b) Free energy(G)
- (c) Enthalpy(H)
- (d) Work(W)

3. What is true for a cyclic process [E = internal energy]

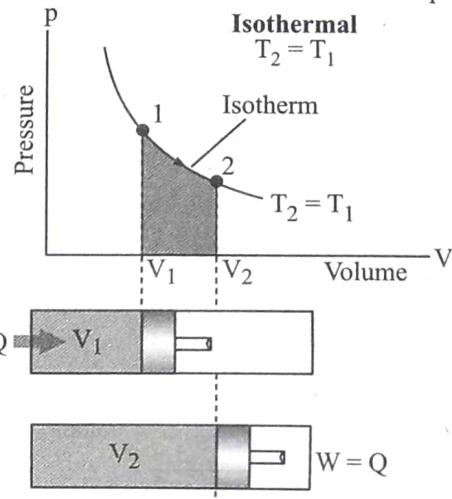
- (a) $W = 0$
- (b) $\Delta E = 0$
- (c) $\Delta H = 0$
- (d) Both (b) and (c)

4. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy?

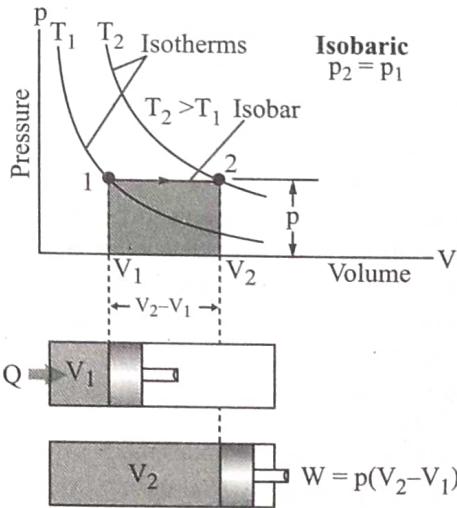
- (a) $< 40 \text{ kJ}$
- (b) Zero
- (c) 40 kJ
- (d) $> 40 \text{ kJ}$

Types of Processes

(i) **Isothermal process:** A process in which temperature of the system remains constant is called isothermal process.

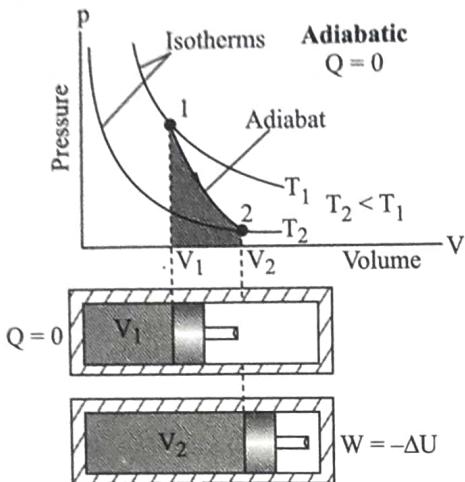


(ii) **Isobaric process:** A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.

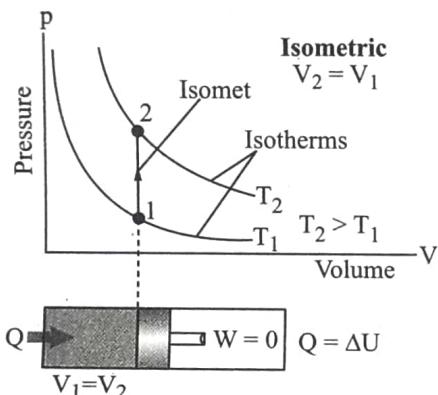


Example: All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

(iii) **Adiabatic process:** A process in which no heat exchange takes place is called adiabatic process. Adiabatic process occurs in systems with insulated walls.



(iv) **Isochoric process:** The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed or rigid vessel.



(v) **Cyclic process:** It is combination of two or more process in which the final state of system, becomes identical to the initial. The net change in all thermodynamic properties of system must be zero. $\Delta T = \Delta P = \Delta V = \Delta H = \Delta S = \Delta G = \dots = 0$

However Q_{net} or W_{net} may or may not be zero.

Types of Thermodynamic Processes on basis of the way the Processes are Carried out

- ❖ **Reversible process:** The process that can be reversed by a very small change is known as reversible process.
- ❖ Reversible process is carried out in such a manner so that the system is always in thermodynamic equilibrium at every stage of the process.
- ❖ Reversible process is carried out such that the difference in driving force and opposing force is infinitesimally small so that process takes place at infinitesimally slow rate.

$$F_{\text{driving}} - F_{\text{opposing}} = dF \text{ and } dF \rightarrow 0$$

- ❖ An ideal reversible process will take infinite time to get completed.
- ❖ Strictly speaking there is no ideal reversible process in universe.

To get an idea of a reversible process we can consider the following system.

An ideal gas is enclosed in a container and a massless piston is put on the gas on which a pile of sand is placed having particles of negligible mass. To carry out a reversible expansion we will slowly decrease the mass of the sand, let's say, by removing the particles one by one, so the expansion of the gas will take place at infinitesimally small rate and we can always assume the system in thermodynamic equilibrium. So, the expansion will be of reversible type.

A process is reversible when the system throughout remain in thermodynamic equilibrium with the surrounding.

A system is said in thermodynamic equilibrium when it simultaneously satisfy the following equilibria.

- (a) **Thermal equilibrium:** Same temperature throughout (No heat transfer within the system)
- (b) **Mechanical equilibrium:** Same pressure or force throughout the system (No work should be performed by one part on the other)
- (c) **Material equilibrium:** No change in the composition of system with time. No mass transfer within the system.
If a system is in thermodynamic equilibrium there is no net energy or mass transfer within the system.
- ❖ **Irreversible process:** The process, which can not be reversed by a small change is known as irreversible process.
- ❖ If a process is carried out in such a manner so that the system is in thermodynamic equilibrium
 - (I) Only at initial & final state of the process but not at the intermediate stages.
 - (II) System may be in thermodynamic equilibrium state at some finite number of intermediate stages only. for example - n step irreversible expansion of a gas
- ❖ If during the process there is a finite difference in driving force and opposing force so that process takes place with a finite rate.
- ❖ Irreversible processes will get completed in finite time.
- ❖ At intermediate stages of the irreversible process, different state function such as Pressure, temperature etc. are not defined.
- ❖ All real process are irreversible.

Work

Thermodynamically, work may be defined as the form of energy which appears only when, there is some change in the boundary of the system. Such work is called mechanical or PV work. Work may also be non-mechanical like electric work.

Presently, we will discuss only mechanical work.

- (i) It is not thermodynamic property of system.
- (ii) It depends on the quantity of system.
- (iii) Sign convention, work on system = (+)ve.

In physics, work is calculate from the force applied by system, but in chemistry due to external force.

$$W = \int_{V_1}^{V_2} P \cdot dV = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$$

| | |
|---------|-----------|
| Physics | Chemistry |
|---------|-----------|

HEAT

Heat is defined as the energy that flows in or out of a system because of a difference in temperature between the system and its surrounding.

According to IUPAC convention:

Heat lost by system is expressed with -ve sign.

Heat given to system is expressed with +ve sign.

❖ $q_v = nC_{v,m}dT$

❖ $q_p = nC_{p,m}dT$

❖ $C_{p,m} - C_{v,m} = R$ (for ideal gas)

❖ C_v & V_p depends on temperature even for an ideal gas.
($C = a + bT + cT^2 \dots$)

Units of heat & work: Heat and work both are forms of energy. Hence, their units of energy, i.e. SI system Joule (J).

1 Nm = 1 J = 10^7 erg = 0.239 cal

1 cal = 4.184 J = 4.2 J

1 L-atm = 101.3 J = 24.206 cal = 101.3×10^7 erg

1 L-atm > cal. > J. > erg

INTERNAL ENERGY (E & U)

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

$U = U_{\text{Kinetics}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{Nuclear}} + \dots$

U is a state function & is an extensive property.

$\Delta U = U_{\text{final}} - U_{\text{initial}}$

For a given closed system

$U = f(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Note: Bomb calorimeter always gives the value of change in internal energy.

Characteristics of I.E.

- (1) Internal energy of a system is an extensive property.
 - (2) Internal energy is a state function.
 - (3) $\Delta U = 0$ (for cyclic process).
- ❖ **Zeroth Law of Thermodynamics:** When a body A is in thermal equilibrium with a body B, and also separately with a body C, then B and C will be in thermal equilibrium with each other.

❖ **First law of thermodynamics:** This law was given by Helmholtz and this law can be expressed as follows:

(i) Energy can neither be created nor be destroyed.

(ii) The total energy of the universe is always a constant, i.e. the sum of energies of a system and its surrounding is always constant.

(iii) Whenever a particular form of energy disappears during a process, an equivalent amount of some other form of energy appears.

$$\Delta U = q + w \text{ (first law equation)}$$

CONCLUSIONS FROM THE FIRST LAW OF THERMODYNAMICS

During Isochoric Process

At constant volume $V_1 = V_2$ i.e. $\Delta V = V_2 - V_1 = 0$

Hence $W = P \Delta V = P \times 0 = 0 \dots \text{no work done at constant volume therefore}$

$$q = \Delta U \text{ (At constant volume)}$$

Thus during isochoric process, heat supplied to the system is equal to change in internal energy.

During an isothermal process: During an isothermal process the temperature of the system remains constant and hence

$$\Delta U = U_2 - U_1 = 0$$

Therefore $q = -W$. Thus during an isothermal process, the total quantity of heat supplied to the system is equal to the work done by the system.

During an adiabatic process: During adiabatic process the system acts an isolated or insulated system and hence $q = 0$ in such cases. Therefore $\Delta U = W$

i.e., work done on the system is equal to change in internal energy.

During Cyclic Process

$$\Delta U = 0 \Rightarrow q = -W$$

i.e., work done by the system is equal to heat absorbed by the system.

During Isobaric process: Let the energy given to system is q and work done by the system is W , then Internal energy $\Delta U = q_p - w$

Here, q_p = energy given to system at constant pressure

$$\text{So } q_p = \Delta U + W \quad \dots(1)$$

$$q_p = (U_2 - U_1) + P(V_2 - V_1)$$

$$q_p = (U_2 + PV_2) - (U_1 + PV_1)$$

$$q_p = H_2 - H_1 \quad \{ \because H = U + PV = \text{enthalpy} \}$$

$$q_p = \Delta H$$

In isobaric process heat behaves as state function,



ENTHALPY

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function Enthalpy (H) as.

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

at constant pressure

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

combining with first law.

$$\Delta H = q_p$$

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

RELATIONSHIP BETWEEN DH AND DU

The difference between ΔH & ΔU becomes significant only when gases are involved (insignificant in solids and liquids).

$$\Delta H = \Delta U + \Delta(PV)$$

If substance is not undergoing chemical reaction or phase change.

$$\Delta H = \Delta U + nR\Delta T$$

In case of chemical reaction

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

Heat capacity/molar heat capacity/specific heat capacity

Heat Capacity [C]: The amount of heat required to raise the temperature of a system by $1^\circ C$ is called heat capacity of system.

$$\text{Heat capacity} = \frac{\text{Heat required}}{\text{rise in temperature}}$$

$$C = \frac{dq}{dT}$$

Units: JK^{-1} , cal K^{-1} , $J^\circ C^{-1}$, cal $^\circ C^{-1}$

+ Heat capacity is extensive property.

Molar heat capacity: Amount of heat required to raise the temperature of 1 mole substance by $1^\circ C$.

Molar heat capacity = heat capacity/mole.

$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{mole of substance}} \Rightarrow C_m = \frac{C}{n}$$

Units: $Jmol^{-1} K^{-1}$, cal $mol^{-1} K^{-1}$, $mol^{-1} ^\circ C^{-1}$, cal $mol^{-1} \circ C^{-1}$

+ Molar heat capacity is an intensive property.

Specific heat capacity: Amount of heat required to raise the temperature of 1 gm. of substance by $1^\circ C$.

Specific heat capacity = heat capacity/1g of substance.

$$c = \frac{C_m}{\text{molecular weight}}$$

Units: $Jg^{-1} K^{-1}$, cal $g^{-1} K^{-1}$, $J g^{-1} \circ C^{-1}$, cal $g^{-1} \circ C^{-1}$

+ Specific heat capacity is an intensive property.

Calorie: Amount of heat required to raise temperature of 1g of water by $1^\circ C$ ($14.5^\circ C$ to $15.5^\circ C$) is called as calorie.

+ If heat is supplied at constant pressure, then

$$C_p = \left(\frac{dq}{dT} \right)_p = \frac{dH}{dT} \quad \dots(i)$$

$$+ \text{ If heat is supplied at constant volume, then } C_v = \left(\frac{dq}{dT} \right)_v = \frac{dE}{dT} \quad \dots(ii)$$

Relation Between C_p and C_v for 1 mole of an ideal gas

$$\therefore H = E + PV$$

for ideal gas,

$$PV = nRT$$

$$PV = RT \text{ for 1 mole}$$

Note: C_p is always $> C_v$

$$\therefore H = E + RT \text{ differentiate w.r.t. temperature}$$

$$\left(\frac{dH}{dT} \right) = \left(\frac{dE}{dT} \right) + R$$

$$C_p = C_v + R$$

$$(i) \boxed{C_p - C_v = R} \text{ Mayer's formula}$$

$$(ii) \boxed{\frac{C_p}{C_v} = \gamma}, \gamma \text{ Poisson's ratio}$$

General values of C_v & C_p for an ideal gas can be taken as follows.

| Gas | Degree of freedom | $C_{v,m} \left(\frac{fR}{2} \right)$ | $C_{p,m} \left(\frac{f+2}{2} \right)R$ | $\gamma = \left(\frac{f+2}{f} \right)$ | Example |
|-----------------------|-------------------|---------------------------------------|---|---|--------------------|
| Monoatomic | 3 | $\frac{3}{2}R$ | $\frac{5}{2}R$ | $\frac{5}{3}$ | He; Ne |
| Diatomeric | 5 | $\frac{5}{2}R$ | $\frac{7}{2}R$ | $\frac{7}{5}$ | $N_2; O_2; H_2$ |
| Linear polyatomic | 5 | $\frac{5}{2}R$ | $\frac{7}{2}R$ | $\frac{7}{5}$ | $CO_2; HCl$ |
| Non Linear polyatomic | 6 | 3R | 4R | $\frac{4}{3}$ | $H_2O; NH_3; CH_4$ |



Train Your Brain

Example 6: 500 joule of heat was supplied to a system at constant volume. It resulted in the increase of temperature of the system from $20^\circ C$ to $25^\circ C$. What is the change in internal energy of the system?

$$\text{Sol. } \Delta E = 500 \text{ J at contant vol. } \Delta E = q$$

Example 7: Calculate the internal energy change in each of the following cases :

- A system absorbs 5 kJ of heat and does 1 kJ of work.
- 5 kJ of work is done on the system and 1 kJ of heat is given out by the system.

Sol. (i) Here $q = +5 \text{ kJ}$ and $w = -1 \text{ kJ}$

$$\therefore \text{According to first law of thermodynamics, } \Delta E = q + w = 5 + (-1) = 4 \text{ kJ}$$

(ii) Here $w = +5 \text{ kJ}$ and $q = -1 \text{ kJ}$

$$\therefore \text{According to first law of thermodynamics } \Delta E = q + w = -1 + (+5) = 4 \text{ kJ}$$

i.e. the internal energy of the system increases by 4 kJ in each case.

Example 8: Represent the following observations in terms of proper IUPAC symbol?

- Heat absorbed by a system is 20 Joule.
- Work done by a system is 40 Joule.
- Work done on a system is 5 Joule.
- Heat given out by system is 50 Joule.

Sol. It is standard practice to represent both types of heat and work (in/out or on/by) by single symbols q and w -

- $q = +20 \text{ Joule}$
- $w = -40 \text{ Joule}$
- $w = +5 \text{ Joule}$
- $q = -50 \text{ Joule}$

Example 9: Predict sign of work done in following reactions at constant pressure.

| Initial state | Final state |
|--------------------------------|---|
| (i) $\text{H}_2\text{O(g)}$ | \rightarrow $\text{H}_2\text{O(l)}$ |
| (ii) $\text{H}_2\text{O(s)}$ | \rightarrow $\text{H}_2\text{O(g)}$ |
| (iii) $\text{H}_2\text{O(l)}$ | \rightarrow $\text{H}_2\text{O(s)}$ |
| (iv) $\text{CaCO}_3(\text{s})$ | \rightarrow $\text{CaO(s)} + \text{CO}_2(\text{g})$ |

Sol. (i) + (ii) - (iii) - (iv) -

Example 10: Explain why variation of enthalpy for a process involving an ideal gas is given by $dH = nC_p dT$, irrespective of process?

Sol. Because

$H_{\text{ideal gas}}$ = independent of pressure or volume.

Example 11: The heat capacity of a molecule depends upon complexity of the molecule. Explain?

Sol. The heat capacity can be defined as energy needed to raise the temperature of a body by 1°C . The molecule which have large number of degree's of freedom requires larger quantity of heat to raise the temperature by 1°C . This is because energy supplied is distributed in each degree of freedom equally.



Concept Application

- If work done by the system is 300 joule when 100 cal heat is supplied to it. The change in internal energy during the process is
 - 200 Joule
 - 400 Joule
 - 720 Joule
 - 120 Joule
- One mole of a gas absorbs 200 J of heat at constant volume. Its temperature rises from 298 K to 308 K. The change in internal energy is :
 - 200 J
 - 200 J
 - $200 \times 308/298 \text{ J}$
 - $200 \times 298/308 \text{ J}$
- A system has internal energy equal to U_1 , 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -
 - $(U_1 + 150 \text{ J})$
 - $(U_1 + 1050 \text{ J})$
 - $(U_1 - 150 \text{ J})$
 - $(U_1 - 1050 \text{ J})$
- The work done by a system is 8 J when 40 J heat is supplied to it. The change in internal energy of the system during the process:
 - 32 J
 - 40 J
 - 48 J
 - 32 J
- The relation between ΔU and ΔH at constant pressure is
 - $\Delta H = \Delta U - P\Delta V$
 - $\Delta H = \Delta U + P\Delta V$
 - $\Delta U = \Delta V + \Delta H$
 - $\Delta U = \Delta H + \Delta P$

CALCULATION OF Q, W, ΔU & ΔH IN VARIOUS PROCESS

Isothermal Expansion or Compression of Ideal Gas

For isothermal process : $\Delta T = 0$

$$\therefore \Delta U = n.C_{p,m}.\Delta T = 0$$

$$\text{and } q = \Delta U - w = -w$$

Now, w depends on path (reversible or irreversible).

Reversible process

$$w_{\text{rev.}} = \int_{V_1}^{V_2} P_{\text{ext}}.dV = - \int_{V_1}^{V_2} (P \pm dP).dV = - \int_{V_1}^{V_2} P.dV = - \int_{V_1}^{V_2} \frac{nRT}{V}.dV$$

$$\therefore w_{\text{rev.}} = nRT \cdot \ln \frac{V_2}{V_1} = -nRT \cdot \ln \frac{P_1}{P_2}$$

Irreversible Process, Against a Constant External Pressure

$$w_{\text{irr.}} = -P_{\text{ext}} \int_{V_1}^{V_2} dV = -P_{\text{ext}}(V_2 - V_1)$$

Free Expansion (or expansion in vacuum)

$P_{\text{ext}} = 0$ but $dV = \text{finite}$, Hence, $w = 0$

Comparison of Magnitude of Work

In expansion, magnitude of work = $-w_{\text{exp}}$

In compression, magnitude of work = w_{comp}

Now, $w_{\text{rev}} - w_{\text{irr.}} (-P_{\text{ext}} dV) - (-P_{\text{ext}} dV) = (P_{\text{ext}} - P) dV$
= -ve, always

In expansion, $P_{\text{ext}} < P$ and $dV = +ve$

In compression, $P_{\text{ext}} > P$ and $dV = -ve$

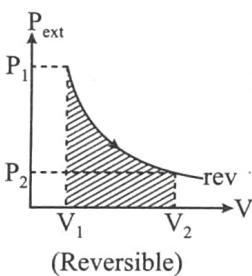
Hence, $w_{\text{rev}} < w_{\text{irr.}}$ (Always, with proper sign).

Now, as magnitude of work in expansion is $-w_{\text{exp}}$, hence,
 $(-w_{\text{rev, exp}}) > (-w_{\text{irr, exp}})$, i.e., magnitude of work is greater
when expansion is reversible.

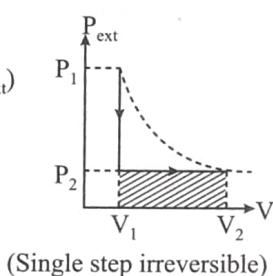
And, as magnitude of work in compression is w_{comp} , hence,
 $(w_{\text{rev, comp}}) < (w_{\text{irr, comp}})$. i.e., magnitude of work is greater
when compression is irreversible.

Graphical Comparison

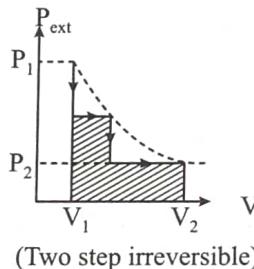
(a) Expansion



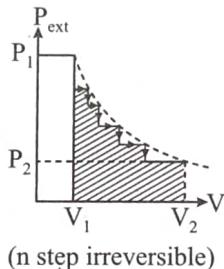
$(P \approx P_{\text{ext}})$



$(\text{Single step irreversible})$

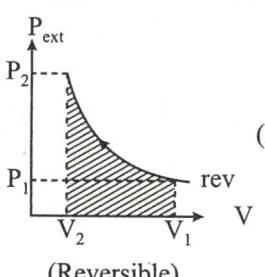


$(\text{Two step irreversible})$

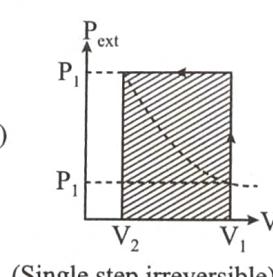


$(-w_{\text{exp}}) : \text{Rev} > n \text{ step} > \dots > 2 \text{ step} > \text{single step}$

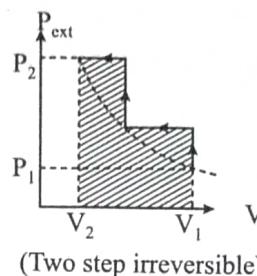
(b) Compression



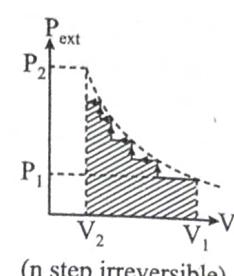
$(P \approx P_{\text{ext}})$



$(\text{Single step irreversible})$



(Two step irreversible)



(n step irreversible)

$(w_{\text{comp}}) : \text{Rev} < n \text{ step} < \dots < 2 \text{ step} < \text{single step}$

ADIABATIC EXPANSION OR COMPRESSION OF IDEAL GAS

$$q = 0$$

$$\therefore \Delta U = w = n.C_{v,m}(T_2 - T_1)$$

$$\text{and } \Delta H = n.C_{p,m}(T_2 - T_1)$$

The change in temperature may be calculated as

$$n \int_{T_1}^{T_2} C_{v,m} dT = - \int_{V_1}^{V_2} P_{\text{ext}} dV$$

(a) If $C_{v,m}$ is temperature independent and the process is reversible, then

$$T \cdot V^{\gamma-1} = \text{constant}$$

$$\text{or, } P \cdot V^\gamma = \text{constant}$$

$$\text{or, } T^\gamma P^{1-\gamma} = \text{constant}$$

(b) If $C_{v,m}$ is temperature independent and the process is irreversible, then

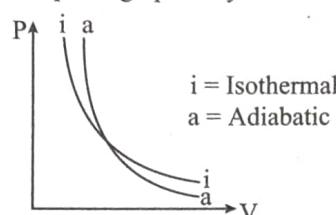
$$n.C_{v,m}(T_2 - T_1) = -P_{\text{ext}}(V_2 - V_1)$$

(i) The temperature of ideal gas decreases in adiabatic expansion (except free expansion, which is isothermal too) and the temperature of ideal gas increases in adiabatic compression.

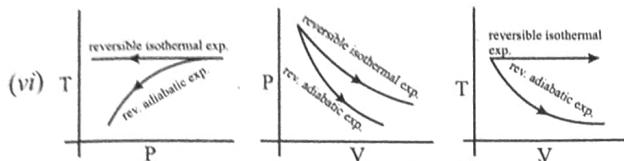
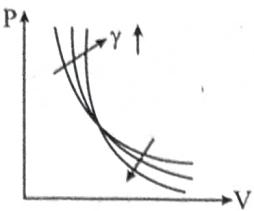
(ii) The final temperature of gas is always higher in irreversible process (expansion or compression) relative to reversible process, for the same change in volume.

(iii) Just like isothermal process, the magnitude of work is maximum when expansion is reversible and compression is irreversible (single step).

(iv) Work in reversible isothermal and adiabatic processes may be compared graphically.



- (v) Work in reversible adiabatic process may be compared graphically.



Comparison of reversible adiabatic expansion and reversible isothermal expansion on TP, PV and TV diagram.

During reversible adiabatic process:

Work of expansion in adiabatic reversible process

$$W = - \int_{V_1}^{V_2} P dV$$

$$\text{For adiabatic process } PV^\gamma = P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$= \text{constant (K)} \quad \text{or} \quad P = \frac{K}{V^\gamma}$$

$$\therefore W = - \int_{V_1}^{V_2} \frac{K dV}{V^\gamma} = -K \int_{V_1}^{V_2} \frac{dV}{V^\gamma}$$

$$= \frac{-1}{1-\gamma} (KV_2^{1-\gamma} - KV_1^{1-\gamma})$$

$$\text{But } P_1 V_1^\gamma = P_2 V_2^\gamma = K$$

$$\therefore W = \frac{-1}{1-\gamma} (P_2 V_2^\gamma \cdot V_2^{1-\gamma} - P_1 V_1^\gamma \cdot V_1^{1-\gamma})$$

$$= \frac{-1}{1-\gamma} (P_2 V_2 - P_1 V_1) = \frac{-1}{1-\gamma} (nRT_2 - nRT_1)$$

$$\boxed{\text{or } W = \frac{-nR(T_2 - T_1)}{1-\gamma}} \quad \dots(1)$$

$$\text{here } \gamma = \frac{C_p}{C_v}$$

C_p and C_v are heat capacities at constant pressure and volume respectively.

from mayer's relation $C_p - C_v = R$

$$\therefore \frac{C_p}{C_v} = \gamma \quad \therefore C_p = C_v \times \gamma$$

$$\therefore C_v \times \gamma - C_v = R \quad \text{or} \quad C_v(\gamma - 1) = R$$

$$\text{or } -C_v(1-\gamma) = R \quad \text{or} \quad C_v = -\frac{R}{1-\gamma}$$

$$\text{so } \boxed{W = nC_v(T_2 - T_1)} \quad \dots(1)$$

for adiabatic process: $\boxed{PV^\gamma = \text{constant}}$

$$\boxed{TV^{\gamma-1} = \text{constant}}$$

$$\boxed{T^\gamma P^{1-\gamma} = \text{constant}}$$

ISOBARIC PROCESS FOR AN IDEAL GAS

$$q = \Delta H = n.C_{v,m} \cdot \Delta T$$

$$\therefore \Delta U = n.C_{v,m} \cdot \Delta T$$

$$w = -P(V_2 - V_1) = -nR \cdot \Delta T$$

ISOCHORIC PROCESS FOR AN IDEAL GAS

$$w = 0$$

$$q = \Delta U = n.C_{v,m} \cdot \Delta T$$

$$\therefore \Delta U = n.C_{v,m} \cdot \Delta T$$

POLYTROPIC PROCESS FOR AN IDEAL GAS

$$\Delta U = n.C_{v,m} \cdot \Delta T$$

$$\therefore \Delta H = n.C_{p,m} \cdot \Delta T$$

For ideal gas is reversible polytropic process and $C_{v,m}$ temperature independent,

$$P \cdot V^\gamma = \text{constant}$$

$$\text{or, } T \cdot V^{\gamma-1} = \text{constant}$$

where γ = polytropic index

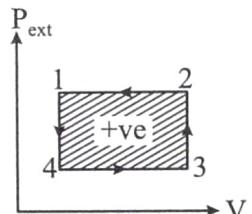
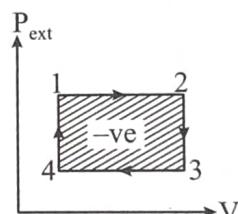
$$w_{\text{rev}} = \frac{P_2 V_2 - P_1 V_1}{1-\gamma} = -\frac{nR(T_2 - T_1)}{1-\gamma} \quad (\gamma \neq 1)$$

$$= -nRT \cdot \ln \frac{V_2}{V_1} \quad (\gamma = 1)$$

$$\text{and } q = n.C_m \cdot \Delta T$$

$$\text{The molar heat capacity, } C_m = C_{v,m} + \frac{P.dV}{n.dT} = C_{v,m} + \frac{R}{1-\gamma}$$

CYLCIC PROCESS



Change in Physical State

$$\text{Solid} \rightleftharpoons \text{liquid}$$

$$\text{Liquid} \rightleftharpoons \text{Gas}$$

$$\text{Solid} \rightleftharpoons \text{Gas}$$

Changes in physical state generally occurs at constant pressure and temperature conditions.

$$\Delta U = q + w$$

$$q = \Delta H$$

$$\text{and } w = -P(V_{\text{final state}} - V_{\text{initial state}})$$



Train Your Brain

Example 12: Ten moles of an ideal gas ($\gamma = 1.2$) is heated from 27°C to 47°C at constant volume. Calculate q , ΔU , w and ΔH .

Sol. $w = 0$

$$q = \Delta U = n \cdot C_{v,m} \Delta T = 2 \times \frac{R}{1.2 - 1} \times 20 = 200R$$

$$\Delta H = \gamma \cdot \Delta U = 240R$$

Example 13: Two moles of an ideal gas undergoes isothermal expansion from 4L to 20L at 27°C . Calculate q , w , ΔU and ΔH , if the process is performed.

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 1 atm .

(iii) As free expansion

Sol. For isothermal process, $\Delta T = 0$. Hence,

$$\Delta U = n \cdot C_{v,m} \cdot \Delta T = 0$$

$$\Delta H = n \cdot C_{p,m} \cdot \Delta T = 0$$

$$(i) w = -nRT \ln \frac{V_2}{V_1} = -2 \times 8.314 \times 300 \times \ln \frac{20}{4} = -8028.52\text{ J}$$

$$\text{and } q = -w = 8028.52\text{ J}$$

$$(ii) w = -P_{\text{ext}} (V_2 - V_1) = -1\text{ atm} (20\text{L} - 4\text{L}) = -16\text{L-atm} = -16 \times 101.3\text{ J} = -1620.8\text{ J}$$

$$q = -w = 1620.8\text{ J}$$

$$(iii) w = 0 \text{ and } q = 0$$

Example 14: Five moles of an ideal monoatomic gas undergoes adiabatic expansion from 12 atm to 1 atm , against a constant external pressure of 1 atm . If the initial temperature of gas is 27°C , calculate the final temperature. Also calculate q , ΔU , w and ΔH .

Sol. $q = 0$

$$\Delta U = w$$

$$\text{or, } n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{\text{ext}} \cdot (V_2 - V_1)$$

$$\text{or, } n \cdot \frac{3}{2} R (T_2 - T_1) = -P_2 \left(\frac{nRT_1}{P_1} - \frac{nRT_2}{P_2} \right)$$

$$\text{or, } \frac{3}{2} (T_2 - 300) = - \left(T_2 - 300 \times \frac{1}{12} \right) \Rightarrow T_2 = 190\text{K}$$

$$\text{or, } \Delta U = w = \frac{3}{2} R \times (190 - 300) = -6859.05\text{J}$$

$$\text{and } \Delta H = \gamma \cdot \Delta U = -11431.75\text{J}$$

Example 15: A gas occupies 2 litre at S.T.P. It is provided 300 joule heat so that its volume becomes 2.5 litre at 1 atm . Calculate change in its internal energy.

Sol. Given $V_1 = 2\text{ litre}$, $V_2 = 2.5\text{ litre}$,

$$q = +300\text{J}, P_{\text{external}} = 1\text{ atm}.$$

$$\therefore \Delta E = q + W$$

$$W = -P_{\text{external}} \Delta V = -P_{\text{external}} (V_2 - V_1)$$

$$= -1\text{ atm} \times$$

$$(2.5 - 2)\text{ litre} = -0.5\text{ litre atm.}$$

$$W = -0.5 \times 101.3\text{ J} = -50.65\text{J}$$

$$\therefore \Delta E = q + W = 300 + (-50.65) = 249.35\text{ J}$$

Example 16: Two litre of N_2 at 0°C and 5 atm are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm . Assuming the gas to be ideal calculate work of expansion?

Sol. Given $P_1 = 5\text{ atm}$, $V_1 = 2\text{ litre}$, $P_2 = 1\text{ atm}$, $V_2 = ?$

We know that - if T is constant then $P_1 V_1 = P_2 V_2$

$$\Rightarrow V_2 = \frac{P_1 V_1}{P_2} = \frac{5 \times 2}{1} = 10\text{ litre}$$

$$W = -P_{\text{ext}} \Delta V = -1(V_2 - V_1) = -1(10 - 2) = -8\text{ litre atm} = -8 \times 101.3 = -810.4\text{ joule}$$



Concept Application

10. Which of the following statement is false?
 - (a) Work is a state function.
 - (b) Temperature is a state function.
 - (c) Change of state is completely defined when initial and final states are specified.
 - (d) Work appears at the boundary of the system.
11. One mole of non-ideal gas undergoes a change of state (2.0 atm , 3.0 L , 95K) to (4.0 atm , 5.0 L , 245 K) with a change in internal energy (ΔU) = 30.0 L-atm . The change in enthalpy (ΔH) of the process in L-atm .

| | |
|----------|--|
| (a) 40.0 | (b) 42.3 |
| (c) 44.0 | (d) Not defined, because pressure is not constant. |
12. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K . The enthalpy change (in kJ) for the process is:

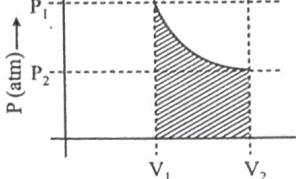
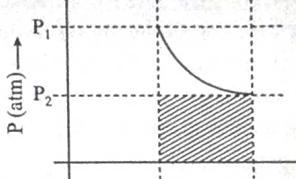
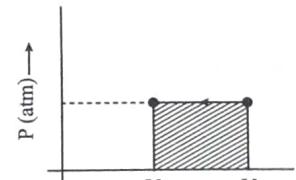
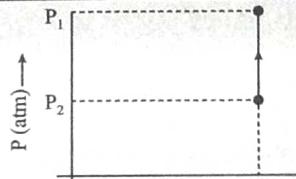
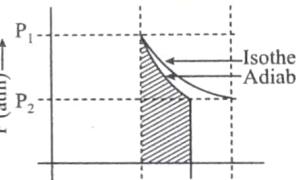
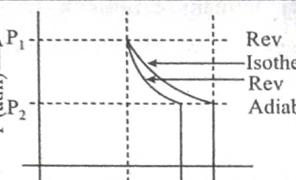
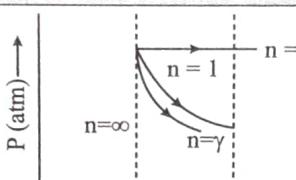
| | |
|----------------------|-----------------------|
| (a) 11.4 kJ | (b) -11.4 kJ |
| (c) 0 kJ | (d) 4.8 kJ |
13. One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temperature.

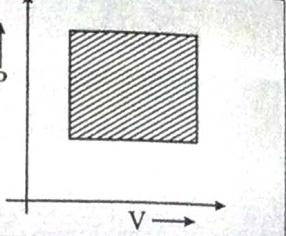
$$(R = 0.0821\text{ litre, atm K}^{-1} \text{ mol}^{-1})$$

| | |
|-------------------------------------|-------------------------------------|
| (a) T | (b) $\frac{T}{\frac{5}{3}-1}$ |
| (c) $T - \frac{2}{3 \times 0.0821}$ | (d) $T + \frac{2}{3 \times 0.0821}$ |
14. Two moles of an ideal gas expand spontaneously into vacuum. The work done is:

| | |
|------------------|------------------|
| (a) Zero | (b) 2 J |
| (c) 4 J | (d) 8 J |

SUMMARY

| Process | Expression for w | Expression for q | ΔU | ΔH | Work on PV-graph |
|--------------------------------|--|--|-------------------------------|-------------------------------|---|
| Reversible isothermal | $w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$ | $q = nRT \ln \left(\frac{V_2}{V_1} \right)$ $q = nRT \ln \left(\frac{P_1}{P_2} \right)$ | 0 | 0 |  |
| Irreversible isothermal | $w = -P_{ext}(V_2 - V_1)$ $= -P_{ext} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$ | $q = P_{ext}(V_2 - V_1)$ | 0 | 0 |  |
| Isobaric process | $w = -P_{ext}(V_2 - V_1)$ $= -nR\Delta T$ | $q = \Delta H = nC_{p,m}\Delta T$ | $\Delta U = nC_{v,m}\Delta T$ | $\Delta H = nC_{p,m}\Delta T$ |  |
| Isochoric process | $w = 0$ | $q = \Delta U = nC_{v,m}\Delta T$ | $\Delta U = nC_{v,m}\Delta T$ | $\Delta H = nC_{p,m}\Delta T$ |  |
| Reversible adiabatic process | $w = nC_{v,m}(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$ | $q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $T^\gamma P^{1-\gamma} = \text{constant}$ | $\Delta U = nC_{v,m}\Delta T$ | $\Delta H = nC_{p,m}\Delta T$ |  |
| Irreversible adiabatic process | $w = nC_{v,m}(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$ | $q = 0$ $nC_{v,m}(T_2 - T_1)$ $= P_{ext} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$ | $\Delta U = nC_{v,m}\Delta T$ | $\Delta H = nC_{p,m}\Delta T$ |  |
| Polytropic | $w = \frac{P_2 V_2 - P_1 V_1}{n-1}$ $w = \frac{R(T_2 - T_1)}{(n-1)}$ | $q = \int_{T_1}^{T_2} C_V dT$ $w = \frac{R(T_2 - T_1)}{(n-1)}$ | $\Delta U = nC_{v,m}\Delta T$ | $\Delta H = nC_{p,m}\Delta T$ |  |

| | | | | | |
|----------------|---|----------|---|---|---|
| Cyclic Process | Area enclosed in PV-diagram For clockwise -ive For anticlockwise +ive | $q = -w$ | 0 | 0 |  |
|----------------|---|----------|---|---|---|

LIMITATION OF FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics can evaluate the value of ΔU and All (i.e. energy difference between two states), but can not predict the feasibility of a process. Many processes can take place on their own and many others require an external force to carry out the process. The first law is clueless about why some processes happens on their own and why some others do not.

Importance of Second Law

What is the driving force for a process which takes system from one state to other on its own? Why such processes (called spontaneous process) take place at all? Answers to these questions are given by second law.

SPONTANEOUS PROCESS

A spontaneous process is the one which takes place on its own & can drive some other process as well. However, in some cases, initiation may be required.

Example:

- (i) Mixing of two gases.
- (ii) Cooling of a hot object by transferring heat to surrounding.
- (iii) Water flowing down the hill.
- (iv) Rusting of iron.
- (v) Burning of coal, coke, hydrocarbons.
- (vi) Volcanic eruptions.

The synonyms of spontaneous processes are **natural processes** and irreversible processes.

It is a common observation that natural processes occur with finite rate. All spontaneous processes take place due to a finite driving force (which can be temperature difference, height difference, potential energy difference, etc.). Also the change brought about by a spontaneous process can not be restored without making some effort (which brings about permanent change in surrounding). Hence it is quite natural to call these processes as irreversible processes.

Example: When water flows from a dam, a part of the potential energy is converted into electrical energy and a part is converted into kinetic energy. The kinetic energy part is lost as heat energy. This loss of extra work is the permanent change in universe, because this heat energy lost cannot be completely converted back into P.E. of water.

DISORDER

The term 'disorder' is related to randomness. Any macroscopic property of a system is an average of large number of microscopic forces which are random in nature. Greater the randomness associated with microscopic forces, greater is the uncertainty about exact microscopic description of a macroscopic state and greater will be the disorder associated with the macroscopic state.

As a rule:

- (i) Greater the number of molecules in which a given energy is distributed, greater is the disorder.
- (ii) Greater the spread of given number of molecules with given energy in space, greater will be the disorder.

SECOND LAW OF THERMODYNAMICS

The entropy of the universe increases in course of every spontaneous process. The entropy of system is a state function. The change in entropy of a system is given by:

$$dS = \frac{dq_{rev}}{T} \text{ where; } dq_{rev} = \text{exchanged by system in a very small step (reversibly).}$$

Entropy

Entropy is a measure of disorder. The entropy is a state function and a basic quantity directly defined by second law. In every spontaneous process, entropy of universe increases.

There are three types of entropy changes:

- (i) ΔS_{system} : Entropy change of system
- (ii) $\Delta S_{\text{Surrounding}}$: Entropy change of surrounding
- (iii) $\Delta S_{\text{Total}} + \Delta S_{\text{surrounding}} = \Delta S_{\text{universe}} = \Delta S_{\text{total}} = \Delta S_{\text{isolated}}$

Normally, ΔS means entropy change of universe

Second Law in Terms of Entropy of Universe

For any spontaneous process (irreversible process):

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

During a reversible process:

$$\Delta S_{\text{universe}} = 0$$

Thus during irreversible process, entropy of universe increases while during reversible process, entropy of universe remains constant.

Physical Significance of Quantity $\frac{dq_{rev}}{T}$

dq_{rev} = heat absorbed by the system. T = absolute temperature at which heat is absorbed. Suppose, similar quantity of heat is absorbed at two different temperatures T_1 and T_2 ($T_2 >> T_1$). When heat is supplied at high temperature, the % age increase in kinetic energy is less compared to heat supplied at low temperature. Hence, disorder will increase by greater value, when heat is supplied at lower temperature.

Determining ' ΔS_{surr} ' for Irreversible Processes

The change in entropy is given by:

$$\frac{\text{heat absorbed by an entity}}{\text{Exact temperature at which heat is absorbed}}$$

The irreversible processes are fast and uncontrolled. The exact temperature of system during exchange of heat cannot be known. Hence, reversible path is needed to evaluate the entropy of system. Along reversible path, the heat exchange and exact temperature both are known.

Surrounding is generally a big entity and heat absorbed by surrounding is comparatively very small as compared to its size. Hence, internal equilibrium of surrounding is not disturbed during exchange of heat.

∴ Actual heat exchange of system is reversible heat exchange of surroundings.

$$\therefore (q_{rev})_{surr} = -q_{irr}$$

[q_{irr} = Actual heat gained by system in a irreversible process].

Hence, exact temperature and heat exchange both are known as far as surrounding is concerned even for an irreversible process.

$$\therefore \text{For irreversible process: } \Delta S_{surr} = \frac{-q_{surr}}{T}$$

| | ΔS_{system} | $\Delta S_{\text{surrounding}}$ |
|-------|---|--|
| (i) | For reversible process: $\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$ | For reversible process: $\Delta S_{\text{surr}} = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = -\Delta S_{\text{system}}$ |
| (ii) | For irreversible process: $\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$ [Where; dq_{rev} = heat gained by system for imaginary reversible path between same states]. | For reversible process: $\Delta S_{\text{surr}} = \frac{q_{irr}}{T}$ |
| (iii) | Always evaluated along reversible path (for both reversible and irreversible process). | For reversible process, ΔS_{surr} is evaluated along reversible path, while for irreversible process, irreversible heat is used to calculate ΔS_{surr} . |

| | | |
|------|---|---|
| (iv) | Since no actual process is reversible. ΔS_{system} is always evaluated by hypothetical path. | For hypothetical process, ΔS_{surr} is evaluated by hypothetical heat, while for real irreversible process, it is evaluated by heat exchanged in irreversible process. |
|------|---|---|

SECOND LAW (IN TERMS OF ENGINE)

- (i) No cyclic engine is possible whose only effect is complete conversion of heat into work without making any change in surrounding on its own.
- (ii) Heat can not flow from cold body to hot body on its own without external intervention.
- (iii) Complete conversion of heat (taken from a single source) into work is not possible in a cyclic process while complete conversion of work into heat is possible in a cyclic process. Thus, heat and work are not equivalent from the view point of II law.

All above statements can be easily justified by realising that heat is a disordered form of energy while work is an ordered form of energy.

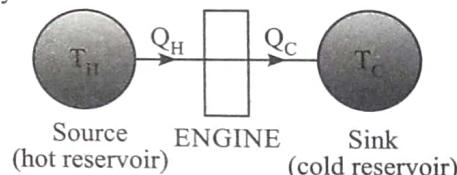
Complete conversion of [Heat → Work] on its own without any external assistance means

[Disorder → Order] on its own - which is impossible.

Heat Engine

A heat engine is a device which can work continuously and cyclically without any external help absorbing heat from a source and rejecting a part of heat into sink. The net heat absorbed by engine (heat absorbed from source - heat given out to sink) is converted into work.

⇒ Heat engine must work in cycles, otherwise it can not work continuously.



$$\text{Efficiency of engine: } \eta = \frac{Q_H - Q_C}{Q_H} = \frac{W_{by}}{Q_H}$$

W_{by} = Work done by engine per cycle.

During operation of heat engine, heat is transferred from source (high temperature reservoir) to sink (low temperature reservoir) thus degrading the quality of energy. Note that net energy of universe remains conserved, but its quality is degraded (i.e. more disordered energy) when heat engine runs spontaneously.

Carnot Engine

A carnot engine (a hypothetical engine) runs in reversible manner. Thus during expansion (work producing process) maximum work is done. However during compression (work requiring process) minimum work need to be done. Thus no engine can be more efficient than carnot engine.

The carnot engine works in following steps. (Assume ideal gas as working material).

- (i) Reversible isothermal expansion ($P_1, V_1, T_2 \rightarrow P_2, V_2, T_2$)
- (ii) Reversible adiabatic expansion ($P_2, V_2, T_2 \rightarrow P_3, V_3, T_1$)
- (iii) Reversible isothermal compression ($P_3, V_3, T_1 \rightarrow P_4, V_4, T_1$)
- (iv) Reversible adiabatic compression ($P_3, V_3, T_1 \rightarrow P_1, V_4, T_2$)

Now:

$$Q_{\text{Net}} = -W_{\text{Net}} \quad \dots(i)$$

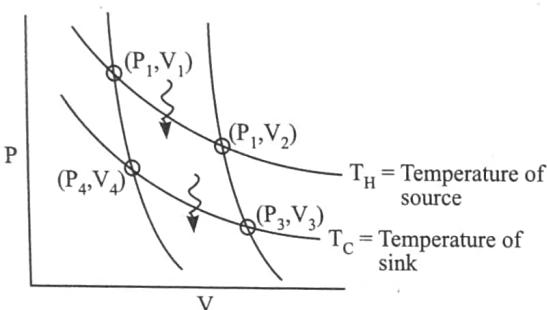
$$W_{\text{Net}} = W_{12} + W_{23} + W_{34} + W_{41} \quad \dots(ii)$$

$$W_{12} = -nRT_H \ln \left(\frac{V_2}{V_1} \right) \quad \dots(iii)$$

$$W_{23} = nC_v (T_C - T_H) \quad \dots(iv)$$

$$W_{34} = nRT_C \ln \left(\frac{V_4}{V_3} \right) \quad \dots(v)$$

$$W_{41} = nC_v (T_H - T_C) \quad \dots(vi)$$



Also since process 2-3 and 4-1 are reversible adiabatic process.

$$T_H V_2^{\gamma-1} = T_C V_3^{\gamma-1} \quad \dots(vii) \text{ for process } 2-3$$

$$T_C V_1^{\gamma-1} = T_H V_4^{\gamma-1} \quad \dots(viii) \text{ for process } 1-4$$

from above equations

$$\left(\frac{V_2}{V_1} \right) = \left(\frac{V_4}{V_3} \right) \quad \dots(ix)$$

Substituting the value $\left(\frac{V_2}{V_1} \right) = \left(\frac{V_4}{V_3} \right)$ in eq, (v) and adding w in individual step.

$$W_{\text{NET}} = -nRT_H \ln \left(\frac{V_2}{V_1} \right) + nC_v(T_C - T_H) - nRT_C \ln \left(\frac{V_4}{V_3} \right) + nC_v(T_C - T_H)$$

$$W_{\text{NET}} = -nRT_H \ln \left(\frac{V_2}{V_1} \right) + nRT_C \ln \left(\frac{V_1}{V_2} \right)$$

$$W_{\text{NET}} = -nR[T_C - T_H] \ln \left(\frac{V_2}{V_1} \right)$$

$$\Rightarrow \text{Efficiency } \eta = -\frac{W_{\text{NET}}}{q_2}$$

$$\eta = \frac{nR \ln \left(\frac{V_1}{V_2} \right) [T_H - T_C]}{nRT_H \ln \left(\frac{V_2}{V_1} \right)}$$

$$\therefore \eta = \frac{T_H - T_C}{T_H}$$

Thus efficiency of carnot engine depends only upon temperature of source and sink.

Note: If working substance is changed (eg. ideal gas by real gas) efficiency of carnot engine remains unaffected.

ENTROPY CHANGE OF AN IDEAL GAS

From definition of entropy of system

$$dS_{\text{system}} = \frac{dq_{\text{rev}}}{T} \quad \dots(i)$$

From first law, $dq_{\text{rev}} = dU + PdV$

For a reversible change involving an ideal gas

$$dq_{\text{rev}} = nC_{V.m} dT + \frac{nRT}{V} dV \quad \dots(ii)$$

$$\Rightarrow \int \frac{dq_{\text{rev}}}{T} = \int \frac{nC_{V.m} dT}{T} + \int_{V_1}^{V_2} nR \frac{dV}{V}$$

$$\begin{aligned} \Delta S_{\text{system}} &= nC_{V.m} \ln \frac{T_2}{T_1} + nR \ln \left(\frac{V_2}{V_1} \right) \\ &= nC_{p.m} \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} \end{aligned}$$

Note: This formula is applicable to all ideal gas process.

Ideal Gas Processes

(i) For isothermal change

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_1^2 dq_{\text{rev}} \quad (\because T = \text{constant})$$

$$\Rightarrow \Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \left(\frac{V_2}{V_1} \right) \quad \left[\because q_{\text{rev}} = nRT \ln \left(\frac{V_2}{V_1} \right) \right]$$

(ii) For isochoric change

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \int_1^2 \frac{nC_{V.m} dT}{T} = nC_{V.m} \int_1^2 \frac{dT}{T} \quad (\because dq_v = nC_{V.m} dT)$$

$$\Rightarrow \Delta S = nC_{V.m} \ell \ln \frac{T_2}{T_1}$$

(iii) For isobaric change

$$\Delta S = \int \frac{dq_p}{T} = \int_1^2 \frac{nC_{p.m} dT}{T} = nC_{p.m} \int_1^2 \frac{dT}{T} \quad (\because dq_p = nC_{p.m} dT)$$

$$\Rightarrow \Delta S = nC_{p.m} \ell \ln \frac{T_2}{T_1}$$

(iv) Reversible adiabatic process

$$\begin{aligned} \Delta S &= \underbrace{nC_v \ln \frac{T_2}{T_1}}_{\text{entropy changed due to change in temperature}} + \underbrace{nR \ln \frac{V_2}{V_1}}_{\text{entropy changed due to change in volume}} \end{aligned}$$

(a) During reversible adiabatic expansion:

$$T_2 < T_1 \text{ and } V_2 > V_1$$

\Rightarrow Sign of two terms are opposite and magnitudes are same because for reversible adiabatic process –

$$nC_{V,m} \ln \frac{T_2}{T_1} = -nR \ln \left(\frac{V_2}{V_1} \right)$$

\Rightarrow +ive and -ive term cancel out each other and hence, $\Delta S = 0$

Thus, decrease in entropy during expansion due to decrease in temperature is exactly cancelled out by increase in entropy due to increase in volume of system in reversible adiabatic expansion.

(b) During reversible adiabatic compression:

$$T_2 > T_1 \text{ and } V_2 < V_1$$

$$\Delta S_{\text{Total}} = \underbrace{nC_V \ln \frac{T_2}{T_1}}_{+\text{ive}} + \underbrace{nR \ln \frac{V_1}{V_2}}_{-\text{ive}}$$

Thus, increase in entropy due to increase in temperature is compensated by decrease in entropy due to decrease in volume of system in reversible adiabatic compression.

Hence, $\Delta S = 0$ for reversible adiabatic compression.

(v) Irreversible adiabatic process

Since process is irreversible, $\Delta S_{\text{Total}} > 0$.

$$\Rightarrow \Delta S_{\text{system}} + \Delta S > 0$$

$$\therefore \Delta S_{\text{surr}} = 0$$

$$\therefore \Delta S_{\text{system}} > 0$$

The physical interpretation is -

(a) During irreversible adiabatic compression, large quantity of heat is produced while decrease in volume is less.

Thus increase in entropy due to rise in temperature exceeds the decrease in entropy due to decrease in volume. Hence net entropy change is positive.

(b) During irreversible adiabatic expansion, due to sudden decrease in external pressure, the system remains less challenged during expansion. Hence system do less work resulting in lesser decrease in temperature.

The increase in volume of system is relatively larger (because system was less challenged)

Thus increase in entropy due to increase in volume exceeds decrease in entropy due to decrease in temperature. The net change in entropy is positive in both processes $\Delta S_{\text{surr}} = 0$ (\because no heat is exchanged with surrounding) and $\Delta S_{\text{total}} > 0$.

(vi) Free expansion of an ideal gas against vacuum

Free expansion of an ideal gas is an example of irreversible adiabatic as well as irreversible isothermal process.

During free expansion, the $P_{\text{ext}} = 0$. Hence, the ideal gas is not challenged at all during expansion. The kinetic energy of ideal gas remains constant. Hence, no temperature difference is created during expansion between system and surrounding.

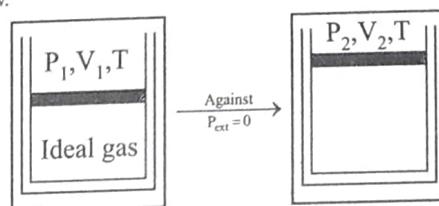
$\therefore \Delta T = 0$, the heat absorbed during the process = 0

Since $V_f > V_i$ and $T = \text{constant}$, $\Delta S_{\text{system}} > 0$

The free expansion is an example where $q_{\text{actual}} = 0$, still $\Delta S_{\text{system}} > 0$.

This is reasonable, because: $\Delta S_{\text{system}} = \int \frac{dq_{\text{rev}}}{T}$.

This example clearly shows that even if q_{actual} between two states is zero, this does not mean that $\int \frac{dq_{\text{rev}}}{T}$ between two states is zero. This outlines the importance of reversible path and q_{rev} in calculation of entropy of system.



$$q_{\text{irr}} = 0; w_{\text{irr}} = 0$$

$$\Delta S_{\text{system}} = \int_1^2 \frac{dq_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total}} = nR \ln \left(\frac{V_2}{V_1} \right) > 0$$

Entropy Calculation

| Process | ΔS_{sys} | ΔS_{surr} |
|-------------------------|---|--|
| Isothermal reversible | ΔS_{sys} | ΔS_{surr} |
| Isothermal irreversible | $\Delta S_{\text{sys}} = nR \ln \left(\frac{V_2}{V_1} \right)$ | $\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T} = \frac{W_{\text{sys}}}{T} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$ |
| Adiabatic reversible | $\Delta S_{\text{sys}} = 0$ | $\Delta S_{\text{surr}} = 0$ |
| Adiabatic irreversible | $\Delta S_{\text{sys}} = nC_{P,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_2}{P_1}$ | $\Delta S_{\text{surr}} = 0$ |

| | | |
|------------------------|---|--|
| Isochoric reversible | $\Delta S_{sys} = nC_{V,m} \ln \frac{T_2}{T_1}$ | $\Delta S_{surr} = \Delta S_{sys}$ |
| Isochoric irreversible | $\Delta S_{sys} = nC_{V,m} \ln \frac{T_2}{T_1}$ | $\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}} = \frac{-nC_{V,m} \Delta T}{T_{final}}$ |

Entropy Change of Solids and liquids Upon Heating

$$\Delta S = \int \frac{dq_{rev}}{T} = \int \frac{mS.dT}{T} = mS \cdot \ln \frac{T_2}{T_1} \quad [S = \text{specific heat of solid/liquid}]$$

For molar change in entropy, $m = M(g/\text{mole})$; where $M = \text{molar mass}$.

Note: For solids and liquids ($MS \approx C_p \approx C_v$).

Reversible phase transitions

Reversible phase transition are always isothermal & isobaric.

$$\Delta S_{\text{system, P.T.}} = \frac{q_{rev}}{T} = \frac{\Delta H_{P.T.}}{T_{\text{transition}}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{P.T.}}{T_{\text{transition}}}$$

$$\Delta S_{\text{total}} = 0$$

$$\text{Thus } \Delta S_{\text{vaporisation}} \text{ at boiling point} = \frac{\Delta H_{\text{vaporisation}}}{T_{\text{vaporisation}}}$$

$$\Delta S_{\text{fusion}} \text{ at melting point} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$$

$$\Delta S_{\text{sublimation}} \text{ at sublimation point} = \frac{\Delta H_{\text{sublimation}}}{T_{\text{sublimation}}}$$

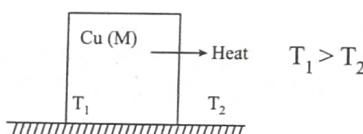
$$\Delta S_{\text{allotropic modification}} = \frac{\Delta H_{\text{allotropic modification}}}{T_{\text{transition}}}$$

❖ Entropy Calculation for solid or liquid systems

(a) 'Cu' block kept in open atmosphere

$$\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{msdT}{T} = ms \ln \frac{T_2}{T_1}$$

$$\therefore \Delta S_{\text{surr}} = \int \frac{dq_{\text{surr}}}{T} = \frac{q_{\text{surr}}}{T_2}$$



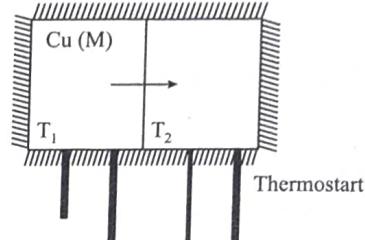
$$\text{but } q_{\text{surr}} = -q_{\text{system}} = -ms(T_2 - T_1) = ms(T_1 - T_2)$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

$$\therefore \Delta S_{\text{universe}} = ms \ln \frac{T_2}{T_1} + \frac{ms(T_1 - T_2)}{T_2} > 0$$

(b) Two copper block kept in contact in thermostat

Two blocks are of same mass



$\Delta S_{\text{surr}} = 0$ (since no heat is lost to surrounding)

$$\Delta S_{\text{system}} = \Delta S_A + \Delta S_B$$

System will reach a common temperature (T_f) and $T_1 > T_f > T_2$

$$\begin{aligned} \Delta S_{\text{system}} &= \int_{T_1}^{T_f} \frac{dq_A}{T} + \int_{T_2}^{T_f} \frac{dq_B}{T} \\ &= \int_{T_1}^{T_f} \frac{msdT}{T} + \int_{T_2}^{T_f} \frac{msdT}{T} = ms \left[\ln \frac{T_f}{T_1} + \ln \frac{T_f}{T_2} \right] \end{aligned}$$

$$\Delta S_{\text{system}} = ms \ln \frac{T_f^2}{T_1 T_2}$$

$$\text{Since } T_f = \frac{T_1 + T_2}{2}$$

$$\therefore \Delta S_{\text{system}} = ms \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}$$

Spontaneity of a process in terms of total entropy change

If, $\Delta S_{\text{total}} = +ve \Rightarrow$ spontaneous process

If, $\Delta S_{\text{total}} = -ve \Rightarrow$ non spontaneous process

If, $\Delta S_{\text{total}} = 0 \Rightarrow$ process is at equilibrium



Train Your Brain

Example 17: What are the signs of ΔS for the system and for the surrounding in each of the following processes?

(a) Water boils in a teakettle on a hot stove.

(b) Ice in an ice cube tray, left on a table melts.

(c) A cup of coffee is reheated in a microwave oven.

Sol. (a) ΔS_{sys} is positive ; ΔS_{surr} is negative.

(b) ΔS_{sys} is positive, ΔS_{surr} is negative.

(c) ΔS_{sys} is positive, ΔS_{surr} is negative.

Example 18: State the thermodynamic condition of spontaneous occurrence of a process?

Sol. $\Delta G = (-) \text{ ve}$ or $\Delta S_{\text{total}} > 0$

- ❖ from 2-3; The temperature remains constant during phase transition

$$\Rightarrow S_3 - S_2 = \Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f} \quad \dots(\text{ii})$$

- ❖ from 3-4; The temperature of liquid increases

$$\Rightarrow S_4 - S_3 = \int_{T_3}^{T_4} \frac{C_{P,\text{liquid}} dT}{T} \quad \dots(\text{iii})$$

- ❖ from 4-5; Reversible vaporisation takes place at constant temperature:

$$\Rightarrow S_5 - S_4 = \Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T_b} \quad \dots(\text{iv})$$

- ❖ from 5-6; The gas is heated

$$\Rightarrow S_6 - S_5 = \int_{T_5}^{T_6} \frac{C_{P,\text{gas}} dT}{T} \quad \dots(\text{v})$$

$$\begin{aligned} \Delta S_{1-6} &= (S_2 - S_1) - (S_3 - S_2) - (S_4 - S_3) - (S_5 - S_4) - (S_6 - S_5) \\ &= (S_6 - S_1) \end{aligned}$$

$$[\because S_1 = 0]$$

- ❖ from 5-6; absolute entropy at 6.

$$\int_{T_1}^{T_6} \frac{C_{P,\text{solid}} dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_1} + \int_{T_1}^{T_3} \frac{C_{P,\text{liquid}} dT}{T} + \frac{\Delta H_{\text{vap.}}}{T_b} + \int_{T_3}^{T_6} \frac{C_{P,\text{gas}} dT}{T}$$

Comment: Absolute entropy of a substance can be calculated using third law by reversible path.

Standard Absolute Molar Entropy

It is the entropy in one mole of substance at standard temperature at 1 bar.

It is calculated assuming that substance is heated isobarically and reversibly at 1 bar from 0 K to standard temperature.

Comparing absolute entropies of substance

(i) The absolute entropies of substance follow the order,

$$S(g) >> S(l) > S(s)$$

- (ii) Entropy increases when solid and liquid is dissolved into solvent, eg;

| | |
|----------------------------|---------------------|
| e.g. CH ₃ OH(l) | S° = 127 J/K-mole |
| CH ₃ OH(aq) | S° = 132.3 J/K-mole |
| NaCl(s) | S° = 72.4 J/K-mole |
| NaCl(aq.) | S° = 115.4 J/K-mole |

- (iii) The entropy of dissolved gas is less than pure gas.

| | |
|-------------|---------------------|
| e.g. HCl(g) | S° = 186.7 J/K-mole |
| HCl(aq) | S° = 55.2 J/K-mole |

- (iv) Entropy rises with increasing mass, (if other factors are similar).

| | |
|-------------------------|-------------------|
| e.g. F ₂ (g) | S° = 203 J/K-mole |
| Cl ₂ (g) | S° = 223 J/K-mole |
| Br ₂ (g) | S° = 245 J/K-mole |

- (v) Entropy is lower in covalently bonded solids, with strong directional bonds, than in solids with partial metallic character.

| | |
|-----------------|--------------------|
| e.g. C(diamond) | S° = 2.44 J/K-mole |
| C(graphite) | S° = 5.69 J/K-mole |
| Sn(gray) | S° = 44.8 J/K-mole |
| Sn(white) | S° = 51.5 J/K-mole |

- (vi) Entropy increases with increasing softness and with weakness of bonds between atoms.

| | | | | |
|-----------------|-------|----------------------|-------|-------|
| e.g. C(diamond) | Be(s) | SiO ₂ (s) | Pb(s) | Hg(l) |
| 2.44 | 9.54 | 41.8 | 64.9 | 77.4 |

diamond hardmetal quartz soft metal liquid

- (vii) Entropy increases with chemical complexity.

| | | |
|-----------|-------------------|-------------------|
| Sub. NaCl | MgCl ₂ | AlCl ₃ |
| 72.4 | 89.5 | 167 |

For CuSO₄.nH₂O

n = 0 n = 1 n = 3 n = 5

S° = 113.150 225 305

Note: Above data is given in SI unit.

Entropy Change (ΔS) of a Chemical Reaction

The change in entropy when reactants turn into products according to a balanced chemical reaction with specified physical state of each reactant and product is called entropy of reaction.

- ❖ Consider a reaction:



where m, n, o, p are physical states at temperature T and pressure P.

$$\Delta S = \sum S(\text{products}) - \sum S(\text{reactants})$$

$$\Delta_r S = cS_c + dS_D - aS_A - bS_B$$

S_A, S_B, S_C and S_D are absolute molar entropies at temperature T and pressure P (from third law)

So, Δ_rS is evaluated from table of data of third law entropies of various substances.

ΔS_{surrounding} for Chemical Reaction

Δ_rH = q_p = heat absorbed by the system during chemical reaction.

-Δ_rH = q_p = q_{surr} = heat absorbed by the surrounding.

Now,

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = -\frac{\Delta_r H}{T}$$

If Δ_rH = -ve (exothermic) heat is lost by the system and gained by the surrounding. Hence, ΔS_{surr} increases.

If Δ_rH = +ve (endothermic process), entropy of surrounding decreases.

$$\therefore \Delta S_{\text{surr}} = \frac{\Delta_r H}{T} = -ve$$

- ❖ We can not comment on entropy change of system from knowledge of Δ_rH. The entropy change of system (Δ_rS) is estimated by third law.

Driving Force of a Spontaneous Chemical Process

The driving force of a spontaneous chemical process is increase in entropy of universe.

In simple terms, negative value of $\Delta_r H$ and positive value of $\Delta_r S$ favours the chemical process.

If $\Delta_r H$ is positive, the enthalpy factor do not support the forward process. Under these conditions, $\Delta_r S$ should be sufficiently positive to drive the reaction in forward direction. If $\Delta_r H$ is +ve and $\Delta_r S$ is -ve, under a given situation, the process become non-spontaneous because both factors tends to decrease the entropy of the universe.

Prediction the Sign of $\Delta_r S$ by Inspecting a Balanced Chemical Reaction

- (i) If more no. of gaseous moles are present on product side. $\Delta_r S$ will be +ve (since gas is more disordered than solid or liquid).
- (ii) If
 - solid \rightarrow liquid
 - solid \rightarrow gas
 - liquid \rightarrow gas
 then, $\Delta_r S$ = +ve.

(iii) If a molecule is undergoing cyclisation, it's rotational modes of motion are replaced by vibrational modes of motion.

Since quantum energy separation of rotational motion is closely spaced compared to vibrational energy state, rotational energy is more disordered. Hence. $\Delta_r S$ = -ve.

Example:

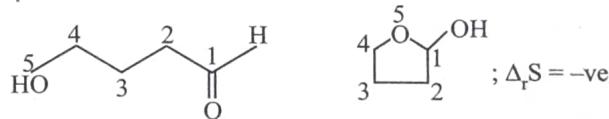
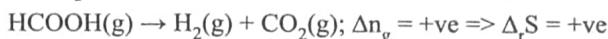


Table for spontaneity or chemical process and sign of $\Delta_r H$, $\Delta_r S$ and dependence on temperature.

| Sign of ΔH | Sign of ΔS | Comment | Example | ΔH°_{298} | ΔS°_{298} |
|--------------------|--------------------|------------------------------------|---|------------------------|------------------------|
| - | + | Spontaneous at all temperature | $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}$ $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ | -185 -394 | 14.1 3 |
| - | - | Spontaneous at low temperature | $\text{H}_2\text{(g)} + 1/2 \text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$ $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{SO}_3\text{(g)}$ | -44 -198 | -119 -187 |
| + | + | Spontaneous at high temperature | $\text{NH}_4\text{Cl(s)} \rightarrow \text{NH}_3\text{(g)} + \text{HCl(g)}$ $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)}$ | 176 180 | 284 25 |
| + | - | Non spontaneous at all temperature | $3\text{O}_2 \rightarrow 2\text{O}_3$, $2\text{H}_2\text{O(l)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)}$ | 286 196 | -137 -126 |

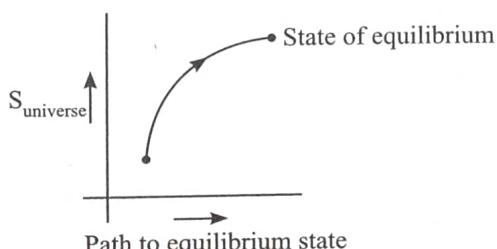
State of Equilibrium

A system at equilibrium is a stable system. Hence, its state variables become constant (do not vary with time) at equilibrium.

If a system is in non-equilibrium state, it moves spontaneously in the direction of equilibrium (because the equilibrium state is stable). During the spontaneous movement towards equilibrium, the entropy of universe increases.

As the system gets closer to equilibrium state, the driving force to attain equilibrium become small and so does the increase in disorder of universe. At equilibrium, the driving force to move ahead finishes and entropy of the universe can not increase further. In nutshell, when a system attains equilibrium, its capacity to increase the disorder of universe is lost.

* At equilibrium, the entropy of universe is maximum.



Train Your Brain

Example 22: The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is 75 J mol^{-1} . The boiling point of the liquid at 1 atm is:

- (a) 250 K (b) 400 K (c) 450 K (d) 600 K

Sol. (b) $T = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = \frac{30 \times 10^3}{75} = 400 \text{ K}$

Example 23: The positive value of ΔS indicates that-

Sol. The system becomes more disordered

Example 24: For a perfectly crystalline solid, $(C_p)_m = aT^3$, where a is a constant. If $(C_p)_m$ at 10K is 0.375 J/K-mol , then find the value of molar entropy at 20K (in J/K-mol).

Sol. $(C_p)_m = aT^3 \therefore 0.375 = a(10)^3 \therefore a = \frac{3}{8} \times 10^{-3}$

$$S_m = \int_0^{20} \frac{(C_p)_m dT}{T} = \int_0^{20} aT^2 dT = \left[\frac{aT^3}{3} \right]_0^{20}$$

$$\frac{8000a}{3} = \frac{8000}{3} \times \frac{3}{8} \times 10^{-3} = 1 \text{ J/K-mol}$$

Example 25: Predict which of the following reaction(s) have a positive entropy change?

- I. $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$
- II. $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- III. $2\text{SO}_3(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$

Sol. (II and III)

ΔS_g value for (I = 0) for (II, III = 1)
 ΔS_g is +ve for II, III



Concept Application

20. Identify the correct statement regarding a spontaneous process:
 - (a) For a spontaneous process in an isolated system, the change in entropy is positive.
 - (b) Endothermic processes are never spontaneous.
 - (c) Exothermic processes are always spontaneous.
 - (d) Lowering of energy in the reaction process is the only criterion for spontaneity.
21. ΔS for the reaction; $\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$ will be:
 - (a) 0
 - (b) -ve
 - (c) +ve
 - (d) ∞
22. Change in entropy is negative for:
 - (a) Bromine (l) \rightarrow Bromine (g)
 - (b) $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$
 - (c) $(\text{C}) \text{N}_2(\text{g}, 10 \text{ atm. } 298 \text{ K}) \rightarrow \text{N}_2(\text{g}, 1 \text{ atm. } 298 \text{ K})$
 - (d) Fe(at 400 K) \rightarrow Fe(at 300 K)
23. For which reaction from the following, ΔS will be maximum?
 - (a) $\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$
 - (b) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 - (c) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
 - (d) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
24. For the process, $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$:
 - (a) Both ΔH and ΔS are +ve.
 - (b) ΔH is -ve and ΔS is +ve.
 - (c) ΔH is +ve and ΔS is -ve.
 - (d) Both ΔH and ΔS are -ve.

GIBB'S FREE ENERGY

Gibb's free energy 'G' is defined as $G = H - TS$.

Since (J is a combination of state variables (a compound state variable), it is a state function. The dimension of Gibb's free energy is the dimension of energy. 'G' is an extensive quantity.

Gibb's free energy provide a very useful criteria for spontaneity of a process taking place at constant temperature and pressure (isobaric, isothermal process).

The entropy of universe is also a very useful criteria of spontaneity, but it is based on properties of system as well as surrounding. The Gibb's free energy provides criteria for spontaneity based only on the properties of system. $\Delta G = \Delta H - \Delta(TS)$

$$\Delta G = \Delta H - T\Delta S \quad (\text{Isothermal Process})$$

Ex. The thermodynamic stability of a substance is dependent upon the value of Gibb's free energy. Explain the stability of solid at low temperature and stability of gas at very high temperature.

Sol. Any stable state tries to minimise its enthalpy while maximising its entropy.

For solids - $G_{\text{solid}} = H_{\text{solid}} - TS_{\text{solid}}$ (at certain T & P)

For liquids - $G_{\text{liquid}} = H_{\text{liquid}} - TS_{\text{liquid}}$ (at certain T & P)

For gas - $G_{\text{gas}} = H_{\text{gas}} - TS_{\text{gas}}$ (at certain T & P)

At any given T and P, $H_{\text{solid}} < H_{\text{liquid}} < H_{\text{gas}}$

and $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$

At very low temperature, TS term contributes very little towards Gibb's free energy. Hence:

$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$ (at very low temperature),

This explains why solids are most stable at low temperature.

At very high temperature, TS term is very important. Since S_{gas} is large, for gas TS term becomes very large at large temperature. Hence:

$\Rightarrow G_{\text{solid}} > G_{\text{liquid}} > G_{\text{gas}}$ (at very high temperature). Thus, gaseous state is most stable at high temperature.

Hence, the low enthalpies of solid are responsible for stability of solid at low temperature, while high entropy of gas is responsible for stability of gas at high temperature.

$\Delta G_{T,p}$ and $\Delta S_{\text{universe}}$

Decrease in Gibb's free energy at constant temperature and pressure is related to ΔS_{total} (total entropy change of system and surrounding).

$$-\Delta G = T(\Delta S_{\text{total}})$$

At constant P, T

if $\Delta G < 0 \Rightarrow$ spontaneous process.

if $\Delta G > 0 \Rightarrow$ non-spontaneous process.

if $\Delta G = 0 \Rightarrow$ reversible process.

At constant P, T, Gibbs energy of a system spontaneously decreases.

Calculate ΔG for Various Processes

(i) Ideal gas subjected to isothermal compression or expansion:

For isothermal change:

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

For ideal gas, $\Delta H = nC_{\text{pm}}\Delta T = 0$

(As $\Delta T = 0$, for isothermal change)

$$\& \Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

(for isothermal change)

$$\Delta G = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Hence, during isothermal expansion Gibb's free energy decreases while during isothermal compression Gibb's function increases.

(ii) Isothermal and isobaric phase transitions:

At transition temperature, the stability (or Gibb's free energy) of two phases are equal. Hence, there is no driving force for conversion of one phase into other. This means phase transitions are examples of reversible processes at transition temperature.

Now, for reversible, isothermal and isobaric change, $\Delta G = 0$
 $\Rightarrow \Delta G = 0$, for phase transitions at transition temperature.
 Thus, $\Delta G = 0$ at boiling point.

Also, $\Delta G_{\text{vap}} = 0$ at melting point:

$$\Delta G_{\text{fusion}} = T_{\text{fusion}} \Delta S_{\text{fusion}}$$

$$T_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{\Delta S_{\text{fusion}}}$$

(iii) $\Delta_r G$ for a chemical reaction.

Consider a reaction : $aA + bB \xrightarrow{T,P} cC + dD$

The change in Gibb's free energy for a chemical reaction is change in ΔG when reactants react according to a given balanced chemical reaction with specified physical state of each reactant and product at given temperature and pressure.

$$\Delta_r G = cG_c + dG_d - aG_A - bG_B \quad \dots(i)$$

Where G_A , G_B , G_C and G_D are molar Gibb's free energy of A, B, C and D respectively at given T and P. also,

$$\left. \begin{array}{l} G_A = H_A - TS_A \\ G_B = H_B - TS_B \\ G_C = H_C - TS_C \\ G_D = H_D - TS_D \end{array} \right\}$$

Substituting (ii) in (i)

$$\begin{aligned} \Delta_r G &= (cH_c + dH_d - aH_A - bH_B) - T(cS_c + dS_d - aS_A - bS_B) \\ &\Rightarrow \Delta_r G = \Delta_r H - T\Delta_r S \end{aligned}$$

| $(\Delta H_r)_{T,P}$ | $(\Delta S_r)_{T,P}$ | (ΔG_r) | Remarks |
|----------------------|----------------------|---|--------------------------------|
| - ve | + ve | Always -ve | Reaction is spontaneous |
| + ve | - ve | Always +ve | Reaction non-spontaneous |
| + ve | + ve | At low temperature, $\Delta G = +ve$ At high temperature, $\Delta G = -ve$ | Non-spontaneous Spontaneous |
| - ve | - ve | At low temperature, -ve | Spontaneous |
| - ve | - ve | At high temperature, +ve | Non spontaneous |

(iv) Gibb's functions of pure substances:

Consider a pure substance having a Gibb's function as follows:

$$G = H - TS = U + PV - TS$$

Let, the pressure and temperature are varied by infinitesimally small value:

$$dG = dU + PdV + VdP - TdS - SdT$$

As, $dU = dq - PdV$ and $TdS = dq$ [Assume only PV-work and reversible process.]

$$dG = VdP - SdT$$

(a) If pressure is varied keeping temperature constant -

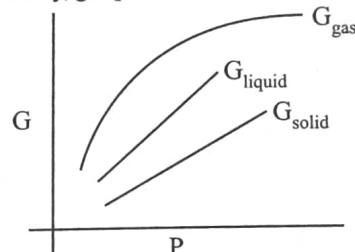
$$dG = VdP \Rightarrow \left(\frac{dG}{dP}\right)_T = V$$

The physical significance of above relation is when pressure over a substance is increased, it's Gibb's function increases & the increase is proportional to molar volume. Since molar volume of gas, liquid and solid are in order, as follows:

$$V_{\text{Gas}} > V_{\text{Liquid}} > V_{\text{Solid}}$$

Hence, Gibb's function of gases increases most rapidly on increasing pressure.

That's why, gas phase becomes unstable at high pressure.



Variation of Gibb's function of pure substance with pressure at constant temperature

(b) If temperature is changed keeping pressure constant

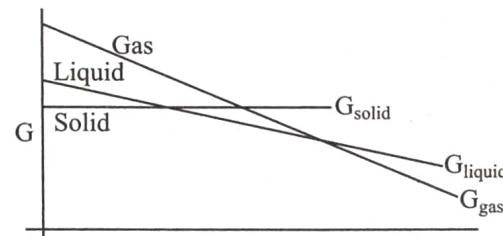
$$dG = -SdT \Rightarrow \left(\frac{dG}{dT}\right)_P = -S$$

Since entropy of pure substances are always positive, the slope of G vs T curve is negative. Also since,

$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

\Rightarrow the slope is more negative for gas.

Thus, on increasing temperature, the Gibb's function of pure substances decreases, but this decrement is maximum for gaseous phase. Thus, gas phase acquire stability on increasing temperature.



Variation of Gibb's function of pure substances with temperature at constant pressure.

Application of Gibb's Energy (as Measure of Non-Pv Work)

For a pure substance

$$dG = d(H - TS) = dH - TdS - SdT$$

also $dH = dU + PdV + VdP$

also $dU = dq - PdV - w_{\text{non-pv}}$

($w_{\text{non-pv}}$ = non-PV work done by system)

Table: Effect of temperature on the spontaneity of a reaction at a given pressure

| Case | ΔH | ΔS° | $\Delta G^\circ = \Delta H - T\Delta S^\circ$ | Remarks |
|------|------------|------------------|---|--|
| I | - | + | Always negative. | Spontaneous at all Temperatures Reverse reaction always non-spontaneous, For example $C(s) + O_2 \rightarrow CO_2(g)$ |
| II | + | - | Always positive. | Non-spontaneous at all temperature For example $N_2(g) + 2O_2(g) \rightarrow NO_2(g)$ |
| III | + | + | + at low temperatures, - at high Temperatures. | Non-spontaneous at low temperatures Spontaneous at higher temperature For example, $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ |
| IV | - | - | - at low temperatures, + at high temperatures. | Spontaneous at low temperatures non-spontaneous at higher temperatures For example $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ |



Train Your Brain

Example 26: 3 moles of $N_2(g)$ originally at 1 atm pressure are mixed isothermally with 5 moles of $H_2(g)$ also at 1 atm pressure to yield a mixture whose total pressure is 1 atm. Assuming ideal behaviour, calculate entropy of mixing.

Sol. Total pressure of mixture = 1 atm

$$\text{Final pressure of } N_2 = \frac{3}{5+3}(1) = 0.375 \text{ atm}$$

$$\text{Final pressure of } H_2 = 1 - 0.375 = 0.625 \text{ atm}$$

For N_2 , entropy change

$$\Delta S_{N_2} = -nR \ln \frac{P_2}{P_1} = -2.303 \times 3 \times 8.314 \times \log \left(\frac{0.325}{1} \right)$$

$$= 28.03 \text{ J/K}$$

For H_2 , entropy change

$$\Delta S_{H_2} = -nR \ln \frac{P_2}{P_1} = -5 \times 8.314 \times 2.303 \log \frac{0.675}{1}$$

$$= 16.34 \text{ J/K.}$$

$$\text{Total entropy change due to mixing} = \Delta S_{N_2} + \Delta S_{H_2}$$

$$= 44.37 \text{ J/K.}$$

Example 27: Calculate free energy change for the esterification reaction,



The equilibrium constant for the reaction at 25°C is 4.

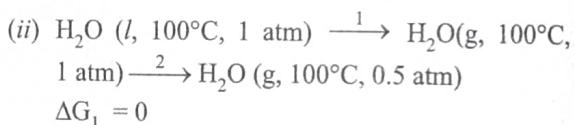
Sol. $\Delta G^\circ = -2.303 RT \log K = -2.303 \times 8.314 \times 298 \log 4$

$$= -(2.303 \times 8.314 \times 298 \times 0.6021) = -3435.49 \text{ J/mol}$$

Example 28: Calculate ΔG_m for the following process:



Sol. (i) $\Delta G = 0$ (Equilibrium condition)



$$\Delta G_2 = nRT \ln$$

$$\frac{P_2}{P_1} = 1 \times R \times 373 \times \ln \frac{0.5}{1} = -2149.5 \text{ J}$$

$$\therefore \Delta G = \Delta G_1 + \Delta G_2 = -2149.5 \text{ J}$$

Example 29: The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_C is:

Sol. $-\Delta G^\circ = RT \ln K_C$



Concept Application

25. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?

- (a) Endothermic and decreasing disorder
- (b) Exothermic and increasing disorder
- (c) Endothermic and increasing disorder
- (d) Exothermic and decreasing disorder

26. For a particular reversible reaction at temperature T , ΔH and ΔS were found to be both +ve. If T_s is the temperature at equilibrium, then reaction would be spontaneous when
 (a) $T < T_s$, (b) $T_s > T$
 (c) $T > T_s$, (d) T_s is 5 times T
27. For a reaction at 25°C , enthalpy change (ΔH) and entropy change (ΔS) are $-11.7 \times 10^3 \text{ J mol}^{-1}$ and $-103 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively. The reaction is
 (a) Spontaneous (b) Non-spontaneous
 (c) At equilibrium (d) Can't say anything
28. Identify the correct statement for change of Gibbs energy for a system at constant temperature and pressure.
 (a) If $\Delta G_{\text{constant}} > 0$, the process is spontaneous.
 (b) If $\Delta G_{\text{constant}} = 0$, the system has attained equilibrium.
 (c) If $\Delta G_{\text{constant}} < 0$, the system is still moving in a particular direction.
 (d) If $\Delta G_{\text{constant}} < 0$, the process is non-spontaneous.
29. In a irreversible process taking place at constant T and P and in which only pressure-volume work is being done the change in Gibbs free energy (dG) and change in entropy (dS) satisfy the criteria:
 (a) $(dS)_{V, P} = 0, (dG)_{T, P} = 0$
 (b) $(dS)_{V, P} = 0, (dG)_{T, P} > 0$
 (c) $(dS)_{V, P} < 0, (dG)_{T, P} < 0$
 (d) $(dS)_{V, P} > 0, (dG)_{T, P} < 0$

THERMOCHEMISTRY

It is a branch of physical chemistry that deals with energy changes accompanying chemical transformations. It is also known as "Chemical Energetics". It is based on the first law of thermodynamics.

Physicochemical changes are classified as endothermic, accompanied by absorption of heat and exothermic, accompanied by the evolution of heat.

For example,



For exothermic reactions ($q < 0$)

At constant pressure, $\Delta H = (H_p - H_R) = -\text{ve}$ ($\because H_p < H_R$)

At constant volume, $\Delta E = (E_p - E_R) = -\text{ve}$ ($\because E_p < E_R$)

For endothermic reaction, ($q > 0$)

At constant pressure, $\Delta H = (H_p - H_R) = +\text{ve}$ ($\because H_p > H_R$)

At constant volume, $\Delta E = (E_p - E_R) = +\text{ve}$ ($\because E_p > E_R$)

Like any other transfer of heat, the heat of a chemical reaction depends upon the conditions that hold during the process by which it is carried out.

Condition I: If the volume of the system is kept constant, no work is done on the system and the first law of thermodynamics reduces to

$$\Delta U = q_v$$

This condition is excellently approximated when the reaction is carried out in a bomb calorimeter, where the volume remains constant.

Condition II: During the course of an experiment under ordinary bench-top conditions, the pressure is kept constant. Many calorimeters operate at this constant atmospheric pressure. Then, we have

$$\Delta H = q_p$$

The heat of reaction measured at constant pressure is exactly equal to the change in enthalpy of the reaction system.

It is often necessary to use data obtained with bomb calorimeter which give ΔE in order to calculate ΔH .

$$\text{We know that, } \Delta H = \Delta U + \Delta(PV)$$

If all the reactants and products are liquids or solids, the PV values change only slightly so $dU = dH$. For reactions in which gases are involved, the values of $\Delta(PV)$ depends on the change in the number of moles of gas as a result of reaction.

$$\therefore \Delta(PV) = \Delta n_g(RT)$$

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

Constant pressure processes are much common in chemistry. Therefore, usually when ever we speak of heat of reaction, it implies enthalpy change at constant pressure.

Enthalpy of a Substance

- ❖ Every substance has a fixed value of enthalpy under any particular state. Though, its exact value cannot be calculated but it has some finite fixed value.
- ❖ The enthalpy of one mole of a substance called molar enthalpy in any particular state can be assigned symbol
- ❖ H_m (substance) : For example molar enthalpy of water vapours at 398 K and 1 atm pressure may be represented as H_m (H_2O , g, 398 K , 1 atm). In very simple words, enthalpy can be considered as heat constant (amount) of substance, and during reaction this heat is being released or absorbed.
- ❖ Molar enthalpy of substance under standard conditions is called standard molar enthalpy of a substance.

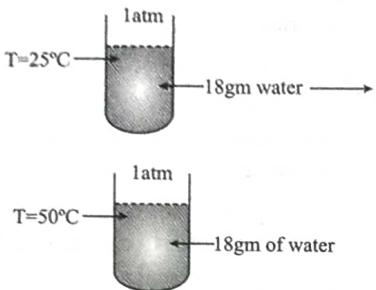
Standard State of any Substance Means

- ❖ For a GAS standard state means ideal gas at 1 bar partial pressure at any given temperature.
- ❖ For a LIQUID – pure liquid at 1 bar pressure at any given temperature.
- ❖ For a PURE CRYSTALLINE SOLID – pure crystalline solid at 1 bar pressure and at any given temperature
- ❖ For any SUBSTANCE or ION IN SOLUTION – the species should be in unit molality, at one bar pressure and at any given temperature.



- Molar standard enthalpy of water vapours at 398 K will be represented as $H^\circ(H_2O, g, 398 K)$ and molar standard enthalpy of liquid water at 398 K will be represented as $H_m^\circ(H_2O, l, 398 K)$
(It is hypothetical but can be calculated).
- We cannot exactly calculate enthalpy content of a substance, only the change in enthalpy can be calculated when substance is taken from one state to other.

For Example:



Let enthalpy content initially be $H_{m,1}^0$ & finally enthalpy content be $H_{m,2}^0$

$$\text{Then, } \Delta H^\circ = H_{m,2}^0 - H_{m,1}^0$$

= heat added at constant pressure to change temperature from 25°C to 50°C .

$$= C_p \Delta T = 18 \text{ Cal/mole } ^\circ\text{C} (25^\circ\text{C}) = 450 \text{ Cal.}$$

ENTHALPY OF REACTION

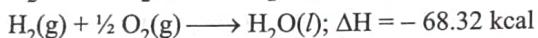
It is defined as the amount of heat evolved or absorbed when the reacting species, as represented by a balanced chemical equation have completely reacted.

Enthalpy or heat of reaction is given by:

$$\Delta H_{\text{reaction}} = \Sigma(\Delta H_f)_{\text{product}} - \Sigma(\Delta H_f)_{\text{reactant}}$$

FACTORS AFFECTING HEAT OF REACTION

- (i) **Physical state of Reactants and Products:** Physical state always affects the heat of reaction as heat energy is involved in changing the physical state of a substance. For example,



Difference in the value of ΔH is observed because heat is evolved when steam condenses.

Allotropic forms of The Elements: The value of ΔH also depends on the allotropic form used in the reaction. For example,



The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is called heat of transition.



- (ii) **Enthalpies of Solution:** Enthalpies of solution differ depending on whether the substances react together in dry state or in solution. For example,



- (iii) **Temperature:** Enthalpy of reaction also depends on temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature.

Relation between ΔH or ΔE and temperature are given by **Kirchoff's equation**.

$$(\Delta H_2 - \Delta H_1) = \Delta C_p (T_2 - T_1)$$

$$(\Delta E_2 - \Delta E_1) = \Delta C_V (T_2 - T_1)$$

The above relations may be derived as follows:

For a reaction at constant pressure, $\Delta H = H_p - H_R$

Differentiating it w.r.t. T at constant P, we get

$$\left(\frac{d\Delta H}{dT} \right)_P = \left(\frac{dH_p}{dT} \right)_P - \left(\frac{dH_R}{dT} \right)_P \\ = (C_p)_P - (C_p)_R = \Delta C_p \quad \text{or} \quad d(\Delta H) = \Delta C_p dT$$

Integrating this equation within appropriate limits, we get

$$\int_{T_1}^{T_2} d(\Delta H) = \Delta C_p \int_{T_1}^{T_2} dT$$

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_p (T_2 - T_1)$$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{(T_2 - T_1)} = \Delta C_p \quad \dots(xvii)$$

This equation is used to find heat of reaction at a temperature when it is known at another temperature.

$$\text{Similarly, } \frac{\Delta E_{T_2} - \Delta E_{T_1}}{(T_2 - T_1)} = \Delta C_V \quad \dots(xviii)$$

In the limit as $(T_2 - T_1) \rightarrow 0$, equation (xvii) yields the differential form $\frac{d(\Delta H)}{dT} = \Delta C_p$

This shows that the rate of change of the enthalpy of a reaction is equal to the difference in heat capacities of products and reactants.

LAWS OF THERMO CHEMISTRY

- (a) **Lavosier and Laplace's law:** Enthalpy of decomposition of a compound is numerically equals to the formation of that compound and only sign changes.

- (b) **Hess's Law:** The total amount of heat evolved or absorbed in a chemical reaction is the same whether the reaction is carried out in one or several steps (by one or more methods). It also does not depend upon the manner in which the chemical reaction is carried out.

Ex. Single step reaction $A \rightarrow B; \Delta H$

Multi step reaction to produce B from A is given



According to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

ENTHALPY OF FORMATION

The amount of heat evolved or absorbed when one mole of a substance is formed from its constituent elements is called heat of formation.



Thus, enthalpy of formation of HCl is -22 kcal.

The formation reaction of a compound has only one mole of the compound and nothing else on the product side. Only elements in their stable states of aggregation appear on the reactant side.

$$H_T^\circ = H_{298}^\circ + \int_{298}^T C_p dT$$

This expression holds good for both elements as well as compounds. For elements, the first term on the right hand side is zero.

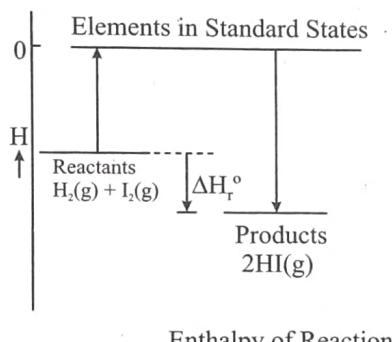
Why do we assign zero value of enthalpy to an element in free state under standard conditions?

Enthalpy of Reaction from Enthalpies of Formation: The enthalpy of reaction can be calculated by

$$\Delta H_r^\circ = \sum v_B \Delta H_f^\circ_{\text{products}} - \sum v_B \Delta H_f^\circ_{\text{reactants}}$$

where v_B is the stoichiometric coefficient

above equation holds good for any reaction as the same reference state is used for reactants and products (shown in figure).



Enthalpy of Reaction

Enthalpy of Formation of Elements

“The standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value.” The specified temperature is usually taken as 25°C.

A few examples are

$$\Delta H_f^\circ(O_2, g) = 0$$

$$\Delta H_f^\circ(C, \text{graphite}) = 0$$

$$\Delta H_f^\circ(\text{Br}_2, \text{liquid}) = 0$$

$$\Delta H_f^\circ(S, \text{rhombic}) = 0$$

$$\Delta H_f^\circ(P, \text{white}) = 0$$

$$\Delta H_f^\circ(S, \text{monoclinic}) \neq 0$$

$$\Delta H_f^\circ(P, \text{black}) \neq 0$$

- “The standard enthalpy of formation of a compound is the change in the standard Enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable state of aggregation.”



Train Your Brain

Example 30: For the reaction : $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$

if $\Delta U^\circ = -1373 \text{ kJ mol}^{-1}$ at 298 K. Calculate ΔH°

$$\text{Sol. } -1368 \text{ kJ mol}^{-1}$$

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

$$\Delta H^\circ = -1373 + \frac{2 \times 8.314 \times 298}{1000}$$

$$\Delta H^\circ = 1368 \text{ kJ mol}^{-1}$$

Example 31: Classify the following processes as exothermic or endothermic:

(a) Burning of a match stick

(b) Melting of ice

(c) Molten metal solidifies

(d) Reaction between Na and H_2O

(e) Rubbing alcohol evaporates.

Sol. Exothermic A, C, D; Endothermic : B, E

Example 32: Calculate heat of the following reaction at constant pressure,



The heats of formation of $F_2O(g)$, $H_2O(g)$ and $HF(g)$ are 5.5 kcal, -57 kcal and -64 kcal respectively.

Sol. Given that

$$\Delta H_{\text{reaction}} = \sum (\Delta H_f)_{\text{product}} - \sum (\Delta H_f)_{\text{reactant}}$$

$$\sum H_{\text{reactions}} = [\Delta H_f(O_2) + 2\Delta H_f(HF)] - [\Delta H_f(F_2O) + \Delta H_f(H_2O)]$$

$$= [0 + (-64) \times 2] - [-5.5 - 57]$$

$$= -65.5 \text{ Kcal.}$$



Concept Application

- 30.** A mixture of 2 mole of CO and 1 mole of O_2 , in a closed vessel is ignited to convert the CO to CO_2 . If ΔH is the enthalpy change and ΔU is the change in internal energy then:

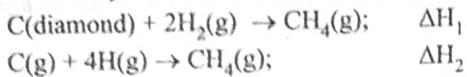
(a) $\Delta H > \Delta U$

(b) $\Delta H = \Delta U$

(c) $\Delta H < \Delta U$

(d) None of these

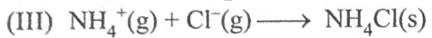
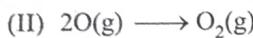
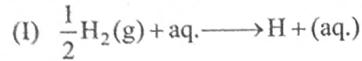
31. For the equations



Predict whether

- (a) $\Delta H_1 = \Delta H_2$
- (b) $\Delta H_1 > \Delta H_2$
- (c) $\Delta H_1 < \Delta H_2$
- (d) $\Delta H_1 = \Delta H_2 + \Delta_{\text{vap}}^{\circ}\text{H}(\text{C}) + \Delta_{\text{diss}}^{\circ}\text{H}(\text{H}_2)$

32. Consider the following changes:

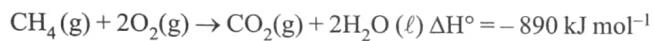


Which of the above does not represent $\Delta H^\circ_{\text{formation}}$ of the product?

- | | |
|----------------|-----------------|
| (a) II, III | (b) I, IV |
| (c) I, II, III | (d) II, III, IV |

ENTHALPY OF COMBUSTION

❖ It is the enthalpy change when one mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.



The standard enthalpy of combustion of methane at 298 K may be written as

$$\Delta H_c^\circ (\text{CH}_4, \text{g}, 298 \text{ K}) = -890 \text{ kJ mol}^{-1}$$

Measurement of Enthalpy of Combustion

Enthalpy of combustion are usually measured by placing a known mass of the compound in a closed steel container (known as bomb calorimeter) which is filled with oxygen at about 30 bar pressure. The calorimeter is surrounded by a known mass of water. The entire apparatus is kept in an insulated jacket to prevent heat entering into or leaving from the container, as shown in figure. The sample is ignited electrically to bring about the combustion reaction. The heat evolved is used in raising the temperature of water and the calorimeter.

If total heat capacity of calorimeter and all of its contents = C, rise in temperature = ΔT

then heat released = $q = C\Delta T$ of this heat is because of mass m of substance then:

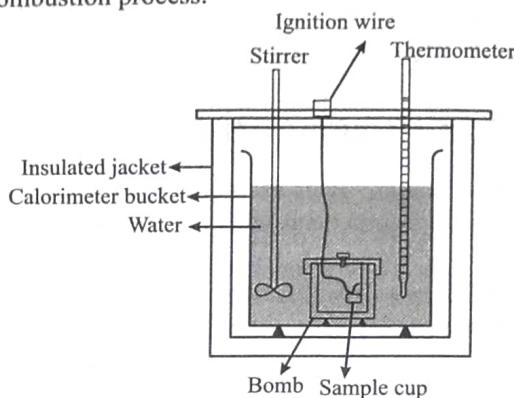
$$\text{due to 1 mole, heat released} = \left(\frac{M}{m} \right) q = \Delta U_c^\circ$$

(Constant volume reaction).

Now, ΔH_c° can be calculated by using,

$$\Delta H_c^\circ = \Delta U_c^\circ + \Delta n_g \text{RT}$$

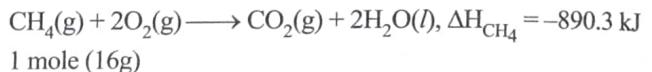
Where Δn_g is the change in stoichiometric number of gaseous species in the balanced chemical equation representing the combustion process.



Bomb calorimeter to determine enthalpy of combustion

Calorific value: The amount of heat produced in calorie or joule when one gram of a substance (food or fuel) is completely burnt or oxidised is called calorific value of food for fuel.

When methane burns, $890.3 \text{ kJ mol}^{-1}$ of energy is released.



$$\text{So, the calorific value of methane} = -\frac{890.3}{16} = -55.6 \text{ kJ/g}$$



Train Your Brain

Example 33: The standard molar heats of formation of ethane, carbon dioxide and liquid water are -21.1 , -94.1 and -68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.

Sol. The required chemical equation for combustion of ethane is:



The equation involves 2 moles of C_2H_6 ; heat of combustion of ethane will be $\frac{\Delta H^\circ}{2}$

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants}) \\ &= [4 \times \Delta H_f^\circ (\text{CO}_2) + 6\Delta H_f^\circ (\text{H}_2\text{O})] - [2\Delta H_f^\circ (\text{C}_2\text{H}_6) + 7\Delta H_f^\circ (\text{O}_2)] \\ &= [4 \times (-94.1) + 6 \times (-68.3)] - [2 \times (-21.1) + 7 \times 0] \\ &= -376.4 - 409.8 + 42.2 \\ &= -744.0 \text{ kcal} \end{aligned}$$

$$\frac{\Delta H^\circ}{2} = \text{Heat of combustion of ethane}$$

$$= -\frac{744.0}{2} = -372.0 \text{ kcal}$$

Example 34: The standard heats of formation of $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -76.2 , -398.8 and $-241.6 \text{ kJ mol}^{-1}$ respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured under normal conditions.

Sol. The required equation for the combustion of methane is:



$$\begin{aligned}\Delta H &= \Delta H_{f(\text{products})} - \Delta H_{f(\text{reactants})} \\ &= \Delta H_{f(\text{CO}_2)} + 2 \times \Delta H_{f(\text{H}_2\text{O})} - \Delta H_{f(\text{CH}_4)} - 2\Delta H_{f(\text{O}_2)} \\ &= -398.8 - 2 \times 241.6 - (-76.2) - 2 \times 0 \\ &= -805.8 \text{ kJ mol}^{-1}\end{aligned}$$

Heat evolved by burning 22.4 litre (1 mole) methane $= -805.8 \text{ kJ}$. So, heat evolved by burning 1000 litre (1m^3) methane.

$$= -\frac{805.8}{22.4} \times 1000 = -35973.2 \text{ kJ}$$

indicates that when 1 mole of hydrogen chloride gas is dissolved in 10 mol of water, there is an evolution of 69.5 kJ of heat. Other values are:



$$\Delta H_2 = -72.3 \text{ kJ mol}^{-1}$$



$$\Delta H_3 = -73.0 \text{ kJ mol}^{-1}$$



$$\Delta H_4 = -74.2 \text{ kJ mol}^{-1}$$



$$\Delta H_5 = -75.0 \text{ kJ mol}^{-1}$$

Note: Whenever amount of solvent is not specified then take its amount to be very large just like in equation no. (iv).

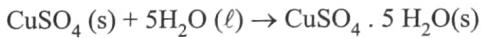
ENTHALPY OF HYDRATION

Enthalpy of hydration is used in following ways.

- ❖ **Enthalpy of hydration of anhydrous or partially hydrated salts:**

Enthalpy of hydration of a given anhydrous or partially hydrated salt is the enthalpy change when it combines with the requisite amount of water to form a new hydrated stable salt.

For example, the hydration of anhydrous cupric sulphate is represented by



There is almost invariably a liberation of heat in such reactions, i.e. the value of ΔH is negative.



$$\Delta H_r^\circ = -68 \text{ kJ mol}^{-1}$$



$$\Delta H_r^\circ = +10 \text{ kJ mol}^{-1}$$

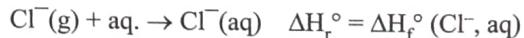
by subtraction, we get $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\ell) \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \Delta H_r^\circ = -78 \text{ kJ mol}^{-1}$

- ❖ **Enthalpy of hydration of gaseous ions.**

Enthalpy of hydration of any gaseous ion is the enthalpy change when 1 mole of the gaseous ion is hydrated in large amount of water to form aqueous ion.

By convention, the standard enthalpy of formation of $\text{H}^+(\text{aq})$ is taken to be zero.

Enthalpy of hydration of Cl^- gaseous ions will be represented by :



ENTHALPY OF NEUTRALIZATION

- ❖ The amount of heat released when one gram equivalent of an acid is neutralised by one gram equivalent of a base.

or

- ❖ The amount of heat released in formation of one mole of water when an acid is neutralised by a base.



Concept Application

33. The heat of combustion of ethyl alcohol is -300 kcal. If the heats of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ are -94.3 and -68.5 kcal respectively, calculate the heat of formation of ethyl alcohol.

34. The standard heat of combustion of solid boron is equal to:

- (a) $\Delta H_r^\circ(\text{B}_2\text{O}_3)$ (b) $1/2 \Delta H_r^\circ(\text{B}_2\text{O}_3)$
 (c) $2\Delta H_r^\circ(\text{B}_2\text{O}_3)$ (d) $1/2 \Delta H_f^\circ(\text{B}_2\text{O}_3)$

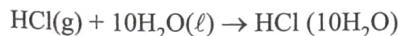
35. Which one of the following expresses Q as the heat of combustion?

- (a) $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O} + Q$
 (b) $\text{C} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO} + Q$
 (c) $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} + Q$
 (d) $2\text{C}_6\text{H}_6 + 15\text{O}_2 \longrightarrow 12\text{CO}_2 + 6\text{H}_2\text{O} + Q$

ENTHALPY OF SOLUTION

The integral enthalpy of solution at the given concentration is the enthalpy change when one mole of the solute is dissolved in a definite quantity of solvent to produce a solution of a desired concentration.

While recording integral enthalpies of solution it is a general practice to state the amount of the solvent in which 1 mole of solute is dissolved; Thus

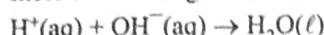


$$\Delta H_1 = -69.5 \text{ kJ mol}^{-1}$$



or

- Enthalpy of neutralization is defined as the enthalpy change when one mole of H^+ in dilute solution combines with one mole of OH^- to give rise to undissociated water, i.e.



$$\Delta H = -57.1 \text{ kJ/mole} = -13.7 \text{ kcal/mol}$$

Remember

- For Strong Acid + Strong Base, heat of neutralisation is always equal to -13.7 kcal/mole or -57.1 kJ/mole.
- For any other combination of acid and base this heat is less than -13.7 kcal/mole or -57.1 kJ/mole.

ENTHALPY OF DILUTION

The amount of heat evolved or absorbed when solution containing one mole of solute is diluted from one concentration to another. For example,



If we subtract first equation from the second in the above set, we get

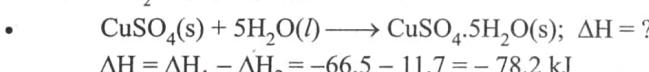
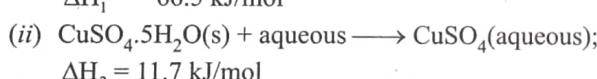
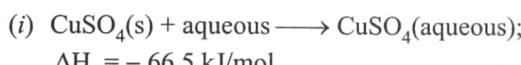


$$\Delta H = (\Delta H_2 - \Delta H_1) = -3.02 \text{ kJ/mol}$$

This value of ΔH is the heat of dilution. The heat of dilution of a solution is dependent on the original concentration of the solution and on the amount of the solvent added.

Example 29: The enthalpies of solution of anhydrous $CuSO_4$ and hydrated $CuSO_4 \cdot 5H_2O$ are -66.5 and 11.7 kJ mol^{-1} respectively. Calculate the enthalpy of hydration of $CuSO_4$ to $CuSO_4 \cdot 5H_2O$.

Sol. Given that



Example 30: 150 ml of 0.5 N nitric acid solution at $25.35^\circ C$ was mixed with 150 ml of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be $28.77^\circ C$. Calculate the heat of neutralisation of nitric acid with sodium hydroxide.

Sol. Total mass of solution = $150 + 150 = 300 \text{ gm}$

$$Q = 300 \times (28.77 - 25.35) = 300 \times 3.42 = 1026 \text{ cal}$$

$$\therefore \text{Heat of neutralisation} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5}$$
$$= \frac{1026}{150} \times 1000 \times \frac{1}{0.5} = 13.68 \text{ kcal.}$$

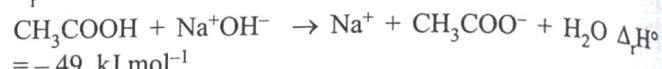
Since, the enthalpy of neutralisation is always $-ve$, so, heat of neutralisation = -13.68 kcal.

ENTHALPY OF IONIZATION OF WEAK ELECTROLYTE

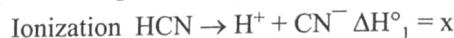
- Whenever a weak acid (or base) reacts with a strong base (or acid), the release of heat is less than 57.1 kJ mol^{-1} .
- It is because of the fact that these acids or bases are not completely ionized in solution. Some of the heat is consumed in ionizing these acids and bases. This heat is known as enthalpy of ionization. Examples are :



$$\Delta_r H^\circ = -12 \text{ kJ mol}^{-1}$$

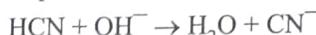


The enthalpy of ionization can be calculated as follows. The neutralization of a weak acid, say HCN, may be represented in two steps, namely,



$$\Delta H^\circ_2 = -57.1 \text{ kJ/mol}$$

The complete reaction is obtained by adding the above two steps. Thus



$$\Delta H^\circ = -12 \text{ kJ/mol}$$

Obviously, $\Delta H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2$

$$\Delta H^\circ_1 = \Delta H^\circ - \Delta H^\circ_2 = [-12 - (-57.1)] = 45.1 \text{ kJ/mol}$$

- Greater the enthalpy of ionization of any weak acid or weak base, weaker will be the acid or base.

ENTHALPY OF TRANSITION

Enthalpy of transition is the enthalpy change when one mole of one allotropic form changes to another.

For example: $C(\text{graphite}) \rightarrow C(\text{diamond})$

$$\Delta H_{trs}^\circ = 1.90 \text{ kJ mol}^{-1}$$



$$\Delta H_C^\circ = -393.51 \text{ kJ mol}^{-1}$$



$$\Delta H_C^\circ = -395.41 \text{ kJ mol}^{-1}$$

Subtracting, we have, $C(\text{graphite}) \rightarrow C(\text{diamond})$

$$\Delta H_{trs}^\circ = 1.90 \text{ kJ mol}^{-1}$$

ENTHALPY OF PRECIPITATION

Enthalpy of precipitation is the enthalpy change when one mole of a precipitate is formed.

For example:



$$\Delta_r H^\circ = -24.27 \text{ kJ mol}^{-1}$$

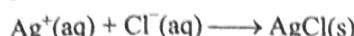


14. Calculate ΔH° for the reaction, $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ at 25°C.

Given $\Delta_f H^\circ(\text{Ag}^+, \text{aq}) = 105 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{AgCl}, \text{s}) = -127 \text{ kJ mol}^{-1}$

Sol. -65 kJ mol^{-1}

For the reaction

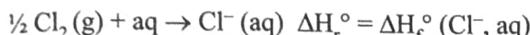


we have

$$\Delta H^\circ = \Delta_f H^\circ(\text{AgCl}, \text{s}) - \Delta_f H^\circ(\text{Ag}^+, \text{aq}) - \Delta_f H^\circ(\text{Cl}^-, \text{aq}) \\ = [-127 - 105 - (-167)] \text{ kJ mol}^{-1} = -65 \text{ kJ mol}^{-1}$$

ENTHALPY OF FORMATION OF IONS

The enthalpy change when one mole of hydrated ions is obtained from element in its standard state as:



By convention, the standard enthalpy of formation of $\text{H}^+(\text{aq})$ is taken to be zero.

We have seen that



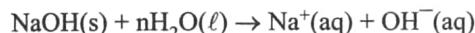
For this reaction, $\Delta H_r^\circ = \Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \{\Delta H_f^\circ(\text{H}^+, \text{aq}) + \Delta H_f^\circ(\text{OH}^-, \text{aq})\}$

Hence, at 25°C, we get $\Delta H_f^\circ(\text{H}^+, \text{aq}) + \Delta H_f^\circ(\text{OH}^-, \text{aq}) = \Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_r^\circ$

$$\text{so } \Delta H_f^\circ(\text{OH}^-, \text{aq}) = \{-286.1 - (-57.1)\} \text{ kJ mol}^{-1} \\ = -229.00 \text{ kJ mol}^{-1}$$

With the enthalpies of formation of these two ions, the enthalpy of formation of any other ion can be found from the enthalpies of formation and solution of its pure compound with H^+ or OH^- . for example, the enthalpy of formation of Na^+ can be calculated from the enthalpy of formation and enthalpy of infinite dilute solution of NaOH. The two values are:

The chemical equation for the formation of infinite dilute solution of $\text{NaOH}(\text{s})$ is



$$\Delta_{\text{aq}} H^\circ(\text{NaOH}, \text{s}) = -44.50 \text{ kJ mol}^{-1}$$

Since there are equal amounts of water on both sides of the above equation, the two enthalpies give no net effect and thus

$$\Delta_{\text{aq}} H^\circ(\text{NaOH}, \text{s}) = \Delta_f H^\circ(\text{Na}^+, \text{aq}) + \Delta_f H^\circ(\text{OH}^-, \text{aq}) \\ - \Delta_f H^\circ(\text{NaOH}, \text{s})$$

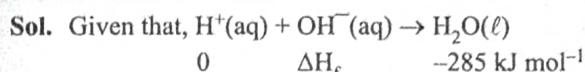
$$\text{or } \Delta_f H^\circ(\text{Na}^+, \text{aq}) = \Delta_{\text{aq}} H^\circ(\text{NaOH}, \text{s}) - \Delta_f H^\circ(\text{OH}^-, \text{aq}) \\ + \Delta_f H^\circ(\text{NaOH}, \text{s}) \\ = [-44.50 - (-229.99) + (-425.61)] \text{ kJ mol}^{-1} \\ = -240.12 \text{ kJ mol}^{-1}$$

Similarly, from $\text{NaCl}(\text{aq})$ or $\text{HCl}(\text{aq})$, the enthalpy of formation of $\text{Cl}^-(\text{aq})$ can be determined, and so on. The changes in enthalpy of any ionic reaction can then be found from these ionic enthalpies of formation and the usual enthalpies of formation of compounds.



Train Your Brain

Example 35: The enthalpy of formation of $\text{H}_2\text{O}(\ell)$ is -285 kJ mol^{-1} and enthalpy of neutralization of a strong acid and a strong base is -55 kJ mol^{-1} . What is the enthalpy of formation of OH^- ions?



$$\Delta_{\text{neut}} H = \Delta_f H(\text{H}_2\text{O}, \ell) - \Delta_f H(\text{OH}^-, \text{aq})$$

$$\text{Hence } \Delta_f H(\text{OH}^-, \text{aq}) = \Delta_f H(\text{H}_2\text{O}, \ell) - \Delta_{\text{neut}} H \\ = [-285 - (-55)] \text{ kJ mol}^{-1} = -230 \text{ kJ mol}^{-1}$$

Example 36: Calculate the enthalpy change when one mole of $\text{HCl}(\text{g})$ is dissolved in a very large amount of water at 25°C. The change in state is:



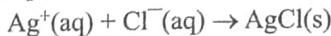
$$\text{Given: } \Delta_f H^\circ(\text{HCl}, \text{g}) = -92 \text{ kJ mol}^{-1} \text{ and} \\ \Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167 \text{ kJ mol}^{-1}$$

Sol. For the reaction,



$$\text{we have } \Delta H^\circ = \Delta H^\circ(\text{Cl}^-, \text{aq}) - \Delta_f H^\circ(\text{HCl}, \text{g}) \\ \Delta H^\circ = [-167 - (-92)] \text{ kJ mol}^{-1} = -75 \text{ kJ mol}^{-1}$$

Example 37: Calculate ΔH° for the reaction,



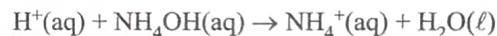
at 25°C. Given $\Delta_f H^\circ(\text{Ag}^+, \text{aq}) = 105 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{AgCl}, \text{s}) = -127 \text{ kJ mol}^{-1}$

Sol. For the reaction $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ we have

$$\Delta H^\circ = \Delta_f H^\circ(\text{AgCl}, \text{s}) - \Delta_f H^\circ(\text{Ag}^+, \text{aq}) - \Delta_f H^\circ(\text{Cl}^-, \text{aq}) \\ = [-127 - 105 - (-167)] \text{ kJ mol}^{-1} \\ = -65 \text{ kJ mol}^{-1}$$

Example 38: Enthalpy of neutralization of HCl by NaOH is -57.1 kJ/mol and by NH_4OH is -51.1 kJ/mol . Calculate the enthalpy of dissociation of NH_4OH .

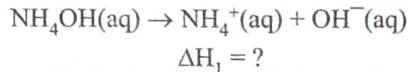
Sol. Given that



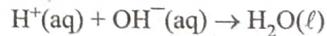
$$\Delta H = -51.1 \text{ kJ/mole}$$

We may consider neutralization in two steps.

(i) Ionization



(ii) Neutralization



$$\Delta H_2 = -57.1 \text{ kJ/mole}$$

$$\text{Thus, } \Delta H = \Delta H_1 + \Delta H_2$$

Therefore,

$$\Delta H_1 = \Delta H - \Delta H_2 = -51.1 \text{ kJ/mol} + 57.1 \text{ kJ mol}^{-1} \\ = 6.0 \text{ kJ/mol}$$



Concept Application

36. 10 mL of each 1 M HCl and 1M H_2SO_4 are neutralized by 1 M NaOH solution that liberate the heat of a & b kJ/mol respectively. What is relation between a and b ?

 - (a) $a = b$
 - (b) $a = 2b$
 - (c) $2a = b$
 - (d) $a = 4b$

37. The standard enthalpy of neutralization of KOH with HCN and HCl in dilute solution is $-2480 \text{ cal.mol}^{-1}$ and $-13.68 \text{ kcal mol}^{-1}$ respectively. Find the enthalpy of dissociation of HCN at the same temperature.

 - (a) 5.2 kcal
 - (b) 11.2 kcal
 - (c) 15 kcal
 - (d) 22.4 kcal

38. The neutralisation of a strong acid by a strong base liberates an amount of energy per mole of H^+ that-

 - (a) Depends upon which acid and base are involved.
 - (b) Depends upon the temperature at which the reaction takes place.
 - (c) Depends upon which catalyst is used.
 - (d) Is always the same

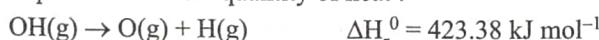
39. If heat of reaction for the given acid-base reaction :
 $\text{HA} + \text{NaOH} \rightarrow \text{NaA} + \text{H}_2\text{O}; \Delta H = -4.7 \text{ kcal}$
The heat of dissociation of HA is _____.
 - (a) 9 kcal
 - (b) -18.4 kcal
 - (c) $+18.4 \text{ kcal}$
 - (d) -9 kcal

BOND ENTHALPIES

The **bond enthalpy** is the average of enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. While **bond dissociation enthalpy** is the enthalpy required to dissociate a given bond of some specific compound. for example the enthalpy of dissociation of the O-H bond depends on the nature of molecular species from which the H atom is being separated. For example, in the water molecule.



However, to break the O-H bond in the hydroxyl radical required a different quantity of heat :



The bond enthalpy, ΔH_{OH} , is defined as the average of these two values, that is:

$$\Delta H_{\text{OH}} = \frac{501.87 \text{ kJ mol}^{-1} + 423.38 \text{ kJ mol}^{-1}}{2} = 462.625 \text{ kJ mol}^{-1}$$

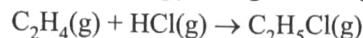
In the case of diatomic molecules, such as H_2 , the bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction.



Thus, the bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthalpies of the bond for a number of molecules in which the pair of atoms appears.

❖ Estimation of Enthalpy of a reaction from bond Enthalpies

Let the enthalpy change for the gaseous reaction



be required from the bond enthalpy data. This may be calculated as follows:

$$\Delta H = \left(\begin{array}{l} \text{Enthalpy required to break reactants} \\ \text{into gasesous atoms} \end{array} \right) - \left(\begin{array}{l} \text{Enthalpy released to form products} \\ \text{from the gasesous atoms} \end{array} \right)$$

$$= [4\Delta H_{C-H} + \Delta H_{C=C} + \Delta H_{H-Cl}] + [-5\Delta H_{C-H} - \Delta H_{C-C} - \Delta H_{C-Cl}]$$

$$= (\Delta H_{C=C} + \Delta H_{H-Cl}) - (\Delta H_{C-H} + \Delta H_{C-C} + \Delta H_{C-Cl})$$

RESONANCE ENERGY

Difference between energy of resonance hybrid and resonating structure in which resonance hybrid have lower energy because stabilised by resonance.

$$\Delta H^\circ_{\text{resonance}} = \Delta H^\circ_{\text{f experimental}} - \Delta H^\circ_{\text{f calculated}}$$

$$= \Delta H^\circ_{\text{combustion, calculated}} - \Delta H^\circ_{\text{combustion, experimental}}$$



Train Your Brain

Example 39: The standard molar enthalpies of formation of cyclohexane (ℓ) and benzene (ℓ) at 25°C are -156 and $+49 \text{ kJ mol}^{-1}$ respectively. The standard enthalpy of hydrogenation of cyclohexene (ℓ) at 25° is -119 kJ mol^{-1} . Use these data to estimate the magnitude of the resonance energy of benzene.

Sol. Enthalpy of formation of 3 carbon-carbon double bonds

$$= \Delta H_f(\text{C}_6\text{H}_6) - \Delta H_f(\text{C}_6\text{H}_5\text{Cl})$$

Given that, $\text{C}_6\text{H}_6 + \text{H}_2 \rightarrow \text{C}_6\text{H}_{12}$ $\Delta H = 119 \text{ kJ}$

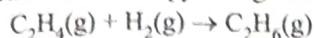
Theoretical enthalpy of formation of 3 double bonds in benzene ring

$$= 3 \times (-119) \text{ kJ} = -357 \text{ kJ.}$$

\therefore resonance energy of benzene

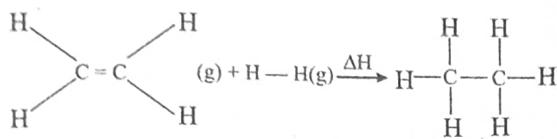
$$= -357 - (-205) \text{ kJ} = -152 \text{ kJ mole}^{-1}$$

Example 40: Using the bond enthalpy data given below, calculate the enthalpy change for the reaction



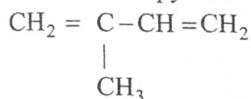
| Data : | Bond | Bond enthalpy |
|--------|-------|--------------------------|
| | C – C | 336 kJ mol ⁻¹ |
| | C = C | 606 kJ mol ⁻¹ |
| | C – H | 410 kJ mol ⁻¹ |
| | H – H | 431 kJ mol ⁻¹ |

Sol. Diagrammatically, we represent the given reaction as follows:



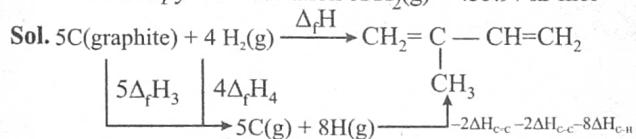
$$\begin{aligned}\Delta H_{\text{reaction}} &= \sum(\text{B.E.})_{\text{reactant}} - \sum(\text{B.E.})_{\text{product}} \\ &= [4 \times \text{B.E.}(\text{C-H})] + \text{B.E.}(\text{C=C}) + \text{B.E.}(\text{H-H}) \\ &\quad - [6 \times \text{B.E.}(\text{C-H}) + \text{B.E.}(\text{C-C})] \\ &= [4 \times 410 + 606 + 431] - [6 \times 410 + 336] \\ &= -119 \text{ kJ/mol.}\end{aligned}$$

Example 41: Using the bond enthalpy data given below, estimate the enthalpy of formation of gaseous isoprene



Data Bond enthalpy of C – H bond = 413.38 kJ mol⁻¹
Bond enthalpy of C – C bond = 347.69 kJ mol⁻¹
Bond enthalpy of C = C bond = 615.05 kJ mol⁻¹
Enthalpy of sublimation of carbon (graphite)
= 718.39 kJ mol⁻¹

Enthalpy of dissociation of H₂(g) = 435.97 kJ mol⁻¹



Applying Hess's law, we get

$$\begin{aligned}\Delta_{\text{f}}\text{H} &= 5\Delta_{\text{f}}\text{H}_3 + 4\Delta_{\text{f}}\text{H}_4 - 2\Delta_{\text{C=C}} - 8\Delta_{\text{C-H}} \\ &= (5 \times 718.39 + 4 \times 435.97 - 2 \times 615.05 - 2 \times 347.69 \\ &\quad - 8 \times 413.38) \text{ kJ mol}^{-1} \\ &= 103.31 \text{ kJ mol}^{-1}\end{aligned}$$

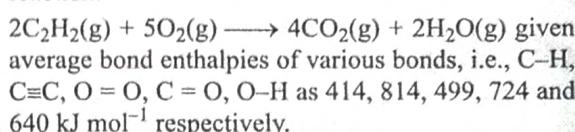


Concept Application

40. Estimate the average S–F bond enthalpy in SF₆. The values of standard enthalpy of formation of SF₆(g), S(g) and F(g) are: -1100, 274 and 80 kJ mol⁻¹ respectively.

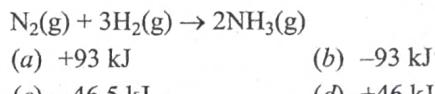
- (a) -746 kJ mol⁻¹ (b) 309 kJ mol⁻¹
(c) 618 kJ mol⁻¹ (d) 154.5 kJ mol⁻¹

41. Calculate the enthalpy change (ΔH) of the following reaction:



- (a) -2573 kJ mol⁻¹ (b) +2573 kJ mol⁻¹
(c) -1286.5 kJ mol⁻¹ (d) 1087 kJ mol⁻¹

42. Bond energies of N ≡ N; H – H and N – H bonds are 945, 463 & 391 kJ mol⁻¹ respectively, the enthalpy of the following reactions is:

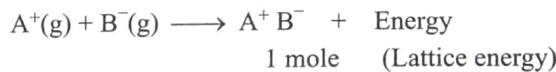


43. Enthalpy change of the reaction 2H(g) → H₂(g) is -104 Kcal. The H – H bond dissociation energy is:

- (a) 104 kcal (b) -104 kcal
(c) -52 kcal (d) +52 kcal

Determination of Lattice Energy (Born-Haber Cycle)

Lattice energy of an ionic compound is defined as the amount of energy released when one mole of the compound is formed by the interaction of constituent gaseous cations and gaseous anions.

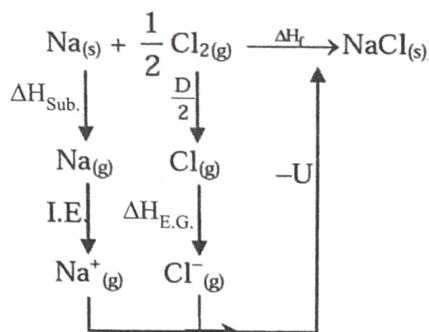


It is represented by the symbol, U. It is given negative sign as the energy is always released. Since, it is difficult to find the lattice energy by direct experiment, it is generally calculated by indirect method known as **Born-Haber cycle** which is based on Hess's law. The cycle can be easily explained by taking the.

Formation of Ionic Compound Born Haber Cycle

A whole series of energy changes are involved when one starts from the elements and finishes with an ionic crystal. These changes are shown in the Born-Haber cycle.

Formation of NaCl(s) involves



$$\text{thus, } \Delta H_{\text{Sub.}} + \text{I.E.} + \frac{D}{2} - \Delta H_{\text{E.G.}} - U = \Delta H_f(\text{NaCl})$$

here, $\Delta H_{\text{Sub.}}$ = heat of sublimation of Na(s)

I.E. = ionisation enthalpy of Na(g)

D = bond dissociation energy of Cl₂(g)

$\Delta H_{E.G.}$ = electron gain enthalpy of Cl(g)

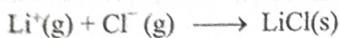
U = lattice energy

ΔH_f = heat of formation of NaCl(s)



Train Your Brain

Example 42: Calculate the lattice energy for the reaction,



from the following data:

$$\Delta H_{sub(Li)} = 160.67 \text{ kJ mol}^{-1}; \frac{1}{2} D(Cl_2) \\ = 122.17 \text{ kJ mol}^{-1}$$

$$IP(Li) = 520.07 \text{ kJ mol}^{-1}; EA(Cl)$$

$$= -365.26 \text{ kJ mol}^{-1}$$

$$\text{and } \Delta H_f^\circ(LiCl) = -401.66 \text{ kJ mol}^{-1}$$

Sol. Applying the equation

$$-Q = \Delta H + \frac{1}{2} D + IP - EA + U$$

and substituting the respective values,

$$-401.66 = 160.67 + 122.17 + 520.07 - 365.26 + U$$

$$U = -839.31 \text{ kJ mol}^{-1}$$

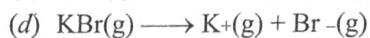
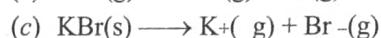
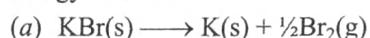


Concept Application

44. Setup of Born-Haber cycle; calculate lattice energy of MgO_(s). The given that - enthalpy of formation of MgO_(s) = -602, sublimation of Mg_(s) = 148 ; 1st & 2nd ionization energy of Mg = 738 & 1450 respectively.

For Oxygen bond dissociation energy = 498; 1st & 2nd electron gain enthalpy = -141 & 844 respectively (all unit in kJ mole⁻¹).

45. For which one of the following reaction does the molar enthalpy change of a reaction corresponds to Lattice energy of KBr?



46. Calculate the electron gain enthalpy of fluorine atom using the following data. (All the values are in kJ mol⁻¹ at 25° C). $\Delta H_{diss}(F_2) = 160$, $\Delta_f H(NaF(s)) = -571$, I.E. [Na(g)] = 494, $\Delta H_{sub}[Na(s)] = 101$, Lattice enthalpy of NaF(s) = 894.

(a) -352 kJ mol⁻¹ (b) +184 kJ mol⁻¹

(c) +352 kJ mol⁻¹ (d) 1078 kJ mol⁻¹



Short Notes

DEFINITION

Deals with interaction of one body with another in terms of energy.

System: Part of universe under investigation.

Surrounding: Rest part of universe except system.

Boundary: Divide system & surrounding.

SYSTEM

- Open system:** Can exchange matter and energy with surrounding.
- Closed system:** Can exchange energy & not matter with surroundings.
- Isolated system:** Can neither exchange energy nor matter with surrounding.

STATE FUNCTION

Properties which depends only on initial & final state of system & not on process or path. e.g. U, H, S, G, etc.

PATH FUNCTION

Depends on path or process. e.g. work, heat.

THERMODYNAMIC PROPERTIES

- Intensive:** Independent of amount of substance, e.g. T.P. viscosity, specific heat capacity density, Boiling point, freezing point, etc.
- Extensive:** Depend upon amount of substances, e.g. mass, volume, energy, entropy, enthalpy, internal energy, etc.

PROCESSES

- Isothermal:** Temperature constant.
- Isobaric:** Pressure constant.
- Isochoric:** volume constant.
- Adiabatic:** Heat change constant.
- Cyclic:** Initial & final state of system are same.

| Reversible process | Irreversible process |
|--|---|
| <ul style="list-style-type: none"> Slow process At any time system and surrounding are in equilibrium. $P_{sys} = P_{surr} \pm dP$ | <ul style="list-style-type: none"> Fast process No equilibrium between system and surrounding $P_{sys} = P_{surr} \pm \Delta P$ |

HEAT (q)

Energy exchange due to temperature difference:

$$q = C\Delta T,$$

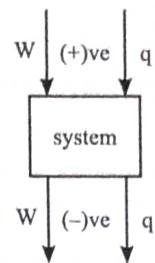
$$q = nC_m\Delta T,$$

$$q = ms\Delta T$$

WORK (W)

| Reversible | Irreversible |
|---|----------------------------------|
| $W_{rev} = - \int_{V_1}^{V_2} P_{ext} \cdot dV$ | $W_{irr} = -P_{ext} (V_2 - V_1)$ |

SIGN CONVENTION



- Heat absorbed by the system = q (+ve)
- Heat evolved by the system = q (-ve)
- Work done on the system = w (+ve)
- Work done by the system = w (-ve)

INTERNAL ENERGY (E & u)

Every system having some quantity of matter is associated with a definite amount of energy called internal energy.

$$U = U_{Kinetics} + U_{Potential} + U_{Electronic} + U_{nuclear} + \dots$$

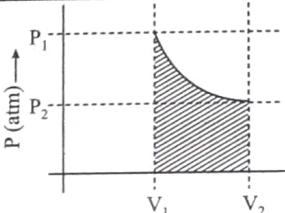
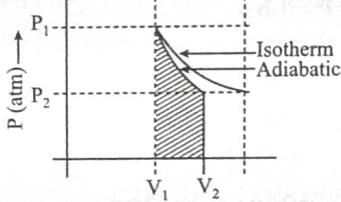
FIRST LAW OF THERMODYNAMICS

Law of conservation of energy

$$\Delta U = q + W$$

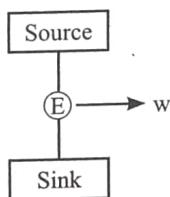
ENTHALPY

$$H = U + PV, \Delta H = \Delta U + (\Delta n_g) RT$$

| Process | Expression for w | Expression for q | Work on PV-graph |
|------------------------------|---|---|---|
| Reversible isothermal | $w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$ | $q = nRT \ln \left(\frac{V_2}{V_1} \right)$ $q = nRT \ln \left(\frac{P_1}{P_2} \right)$ |  |
| Reversible adiabatic process | $w = nC_V(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$ | $q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$ |  |

STATEMENTS OF SECOND LAW OF THERMODYNAMICS

(i) No cyclic engine is possible which take heat from one single source and in a cycle completely convert it into work without producing any change in surrounding.



(ii) In an irreversible process entropy of universe increases but it remains constant in a reversible process.

| | |
|---|--------------------|
| $\Delta S_{syst} + \Delta S_{sur} = 0$ | for rev. process |
| $\Delta S_{syst} + \Delta S_{sur} > 0$ | for irrev. process |
| $\Delta S_{syst} + \Delta S_{sur} \geq 0$ | (In general) |

CALCULATION OF ENTROPY CHANGE FOR AN IDEAL GAS

General Expression

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

Reversible & irreversible isothermal expansion or contraction

$$\text{of an ideal gas } \Delta S = nR \ln \frac{V_2}{V_1}$$

THIRD LAW OF THERMODYNAMICS

"At absolute zero, the entropy of a perfectly crystalline substance is zero". which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

VARIATION OF ΔS_r WITH TEMPERATURE & PRESSURE

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1} = (\Delta C_p)_r \ln \frac{T_2}{T_1}$$

$$(\Delta S_r)_{P_2} - (\Delta S_r)_{P_1} = \Delta n_g R \ln \frac{P_1}{P_2}$$

Similarly

$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1) \quad \{\text{Kirchoff's equation}\}$$

$$(\Delta U_r)_{T_2} - (\Delta U_r)_{T_1} = (\Delta C_V)_r (T_2 - T_1)$$

GIBBS FREE ENERGY (G) AND SPONTANEITY

A new thermodynamic state function G, the Gibbs free energy is defined as:

$$G = H - TS$$

at constant temperature and pressure

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

- If $(\Delta G)_{T,P} < 0$ Process is irreversible (spontaneous)
 $(\Delta G)_{T,P} = 0$ Process is reversible
 $(\Delta G)_{T,P} > 0$ Process is impossible (non spontaneous)

SOME FACTS TO BE REMEMBERED

(a) Standard condition

- ❖ For gases/solid/liquid
 $P = 1 \text{ bar}$
- ❖ For ion/substance in solution
Concentration = 1M

$$(b) \Delta G_r = (\Delta G_f)_{\text{product}} - (\Delta G_f)_{\text{reactant}}$$

$$\Delta H_r = (\Delta H_f)_{\text{product}} - (\Delta H_f)_{\text{reactant}}$$

$$\Delta S_r = (\Delta S_f)_{\text{product}} - (\Delta S_f)_{\text{reactant}}$$

(All above equation will be derived in thermochemistry)

THERMOCHEMISTRY

Bond Enthalpy

Average amount of enthalpy required to dissociate one mole gaseous bond into separate gaseous atoms.

$\Delta_r H = (\text{Sum of bond enthalpy of gaseous reactant}) - (\text{Sum of bond enthalpy of gaseous product})$

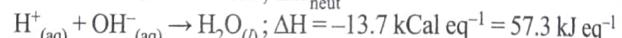
Resonance Energy

$$\begin{aligned} \Delta H_{\text{resonance}} &= D_f H^\circ (\text{experimental}) - D_f H^\circ (\text{calculated}) \\ &= D_C H^\circ (\text{calculated}) - D_C H^\circ (\text{experimental}) \end{aligned}$$

Enthalpy Change

$$\Delta H^\circ = \sum H^\circ (\text{products}) - \sum H^\circ (\text{reactants})$$

1. **Enthalpy of reaction:** The enthalpy change accompanying a chemical reaction when the number of moles of reactants reacts to give the products as given by the balanced chemical equation.
2. **Enthalpy of Combustion ($D_c H^\circ$):** The amount of heat change when 1 mole of substance is completely burnt in excess of oxygen or air. $\Delta_c H^\circ$ is always negative.
3. **Enthalpy of solution:** The enthalpy change when one mole of a substance is dissolved in large excess of solvent so that further dilution does not give any further enthalpy change.
4. **Enthalpy of hydration:** The enthalpy change during the hydration of 1 mole of anhydrous salt to a specific hydrate.
5. **Enthalpy of neutralization (dH_{neut})** Always exothermic: Change in enthalpy when one gram equivalent of an acid is completely neutralized by one g-equivalent of a base in dilute solution.



In case of weak acid/base or both $|\Delta H_N| < 13.7 \text{ Kcal}/\text{eq}^{-1}$ and the difference is enthalpy of ionisation of ionisation of weak species except in case of HF when $|\Delta H_N| > 13.7 \text{ Kcal}/\text{eq}^{-1}$ due to hydration of F^- .

- ❖ If in a reaction heat of reactant & products are given then heat of that reaction can be measured as follows:

(a) For heat of combustion & for bond enthalpy

$$\Delta_r H = \sum (\Delta H_C)_{\text{reactant}} - \sum (\Delta H_C)_{\text{product}}$$

(b) For heat of formation

$$\Delta_r H = \sum (\Delta H_f)_{\text{product}} - \sum (\Delta H_f)_{\text{reactant}}$$

Hess's Law: The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.



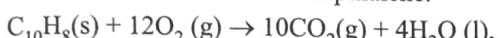
Solved Examples

1. The enthalpy change (ΔH) for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is -92.38 kJ at 298 K . What is ΔU at 298 K ?

$$\text{Sol. } \Delta U = \Delta H - \Delta n_g RT = -92.38 - (-2) \times \frac{8.314}{1000} \times 298 \\ = -87.42\text{ kJ}$$

2. The heat of combustion of naphthalene $\{C_{10}H_8(s)\}$ at constant volume was measured to be -5133 kJ mol^{-1} at 298 K . Calculate the value of enthalpy change (Given $R = 8.314\text{ JK}^{-1}\text{ mol}^{-1}$).

Sol. The combustion reaction of naphthalene.



$$\Delta E = -5133\text{ kJ}$$

$$\Delta n_g = 10 - 12 = -2\text{ mol.}$$

Now applying the relation. ΔH

$$= \Delta E + \Delta n_g RT = -5133 \times 10^3 + (-2)(8.314)(298) \\ = -5133000\text{ J} - 4955.14\text{ J} = -5137955.14\text{ joule}$$

3. For certain processes the heat and work exchanged between system and surrounding is given in standard format. Describe the physical interpretation of each observation.

$$(a) q = +10\text{ kJ}$$

$$(b) w = -20\text{ kJ}$$

Sol. (a) $q = +10\text{ kJ}$

Since numerical value of q is positive, this shows heat is absorbed by the system from surrounding resulting in gain of energy by system.

(b) $w = -20\text{ kJ}$:

Since numerical value of work is negative, this shows work is done by the system on surrounding resulting in loss of energy of system.

4. Two moles of an ideal monoatomic gas undergoes adiabatic expansion from 5 L , 127°C to 40 L . Calculate q , ΔU , w and ΔH , if the process is performed.

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 0.1 atm .

(iii) As free expansion

Sol. For adiabatic process, $q = 0$

$$(i) TV^{\gamma-1} = \text{constant} \Rightarrow T_1 \cdot V_1^{\gamma-1} = T_2 \cdot V_2^{\gamma-1}$$

$$\therefore T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 400 \times \left(\frac{5}{40} \right)^{\frac{5}{3}} = 100\text{ K}$$

$$\text{Now, } w = \Delta U = nC_v \Delta T = -7482.6\text{ J}$$

$$\Delta H = \gamma DU = -12471\text{ J}$$

$$(ii) \Delta U = w = -P_{\text{ext}}(V_2 - V_1) = 0.1 \times (40 - 5) \times 101.3 \\ = -354.55\text{ J}$$

$$\text{and } \Delta H = \frac{5}{3} \cdot \Delta U = -590.92\text{ J}$$

$$(iii) \Delta U = w = 0$$

$$\text{and } \Delta H = 0$$

5. 90 gm water is completely converted into steam at 100°C and 1 atm . Calculate q , ΔU , w and ΔH . Latent heat of vaporisation of water at 100°C is 540 cal/gm .

$$\text{Sol. } DH = m \cdot L = 90 \times 540 = 48600\text{ cal}$$

$$w = -P(V_{\text{vap}} - V_{\text{water}}) = -P \cdot V_{\text{vap}}$$

$$= -nRT = -\frac{90}{18} \times 2 \times 373 = -3730\text{ cal}$$

$$\Delta U = q + w = 48600 + (-3430) = 44870\text{ cal}$$

6. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3 . Calculate the enthalpy change in this process. $C_{v,m}$ for argon is $12.48\text{ JK}^{-1}\text{ mol}^{-1}$

$$\text{Sol. } \Delta H = -115\text{ J}$$

$$T_1 V_1^{\gamma-1} - T_2 V_2^{\gamma-1}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$T_2 = 300 (1/2)^{8.3/12.48} \left[\gamma^{-1} \frac{R}{C_{\gamma,m}} \right]$$

$$T_2 = 189.2\text{ Kelvin}$$

$$n = \frac{P_1 V_1}{R T_1} = \frac{(1)(1.25)}{(0.0821)(300)} = 0.507$$

$$\Delta H = n C_{p,m} (T_2 - T_1)$$

$$= 0.0507 (20.78) (189.2 - 300)$$

$$= -116.732\text{ Jule.}$$

7. One mole of a liquid (1 bar , 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar . Then at a constant pressure of 100 bar , volume decrease by 1 ml . Find ΔU and ΔH .

$$\text{Sol. } \Delta U = 10\text{ J}, \Delta H = 990\text{ J}$$

$$0 + w = \Delta U$$

$$\Delta U = -P_{\text{ext}} (Y_2 - V_1)$$

$$= -100 \left(\frac{-1}{1000} \right)$$

$$= 0.1\text{ bar litre}$$

$$\Delta H = \Delta U + P_2 Y_2 - P_1 Y_1$$

$$\Delta H = 0.1 + \left[\frac{100(99) - (1)(100)}{1000} \right]$$

$$\Delta H = 0.1 + 9.8$$

$$\Delta H = 9.9 \text{ bar. litre}$$

$$\Delta H = 990 \text{ Joules}$$

8. One mole of an ideal diatomic undergoes isobaric expansion from 27°C to 87°C. Calculate q, ΔU , w and ΔH .

$$\text{Sol. } q = \Delta H = n.C_{v,m}.\Delta T = 1 \times \frac{7}{2} R \times 60 = 1745.94 \text{ J}$$

$$\Delta U = \frac{\Delta H}{\gamma} = 1247.1 \text{ J}$$

$$\text{and } w = -nR.\Delta T = -1 \times 8.314 \times 60 = -498.84 \text{ J}$$

9. Three moles of an ideal gas at 200 K and 2.0 atm pressure undergoes reversible adiabatic compression until the temperature becomes 250 K. For the gas C_v is $27.5 \text{ JK}^{-1} \text{ mol}^{-1}$ in this temperature range. Calculate q, w, ΔU , ΔH and final V and final P.

$$[R = 8.3 \text{ Joul/mol. K or } R = 0.0821 \text{ atm litre/mol.K}]$$

$$\text{Sol. } q = 0, \quad V_f = 11.8 \text{ dm}^3$$

$$w = \Delta U = 4.125 \text{ kJ, } P = 5.22 \text{ atm}$$

$$\Delta H = 5.372$$

10. One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps:

(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from T_1 to T_2 . (BC) Cooling at constant volume to bring the gas to the original pressure and temperature. The steps are shown schematically in the figure shown.

(a) Calculate T_1 jmd T_2

(b) Calculate ΔU , q and w (in calories) for the cycle

(Given : $\ln 10 = 2.3$, $R = 0.0821 \text{ atm.litre/mol-K}$ or $R = 2 \text{ cal/mol. K}$)

$$\text{Sol. } T_1 = 243.60$$

$$T_2 = 2436 \text{ K}$$

$$\Delta U = 0, q = -w = 3264$$

11. Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a constant external pressure of 1 atm. Calculate q, w, ΔU & ΔH . Calculate the corresponding value of all if the above process is carried out reversibly. ($\ln 2 = 0.7$)

$$\text{Sol. } w_{\text{irr}} = -1125 \text{ R, } w_{\text{rev}} = -2100 \text{ R. } \Delta U = \Delta H = 0, q = -w$$

12. One mole of an ideal monoatomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

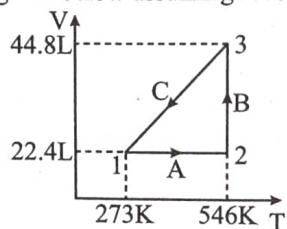


Table-1

| State | P | V | T |
|-------|---|---|---|
| 1 | | | |
| 2 | | | |
| 3 | | | |

| State | Name of process | q | w | ΔU | ΔH |
|---------|-----------------|---|---|------------|------------|
| A | | | | | |
| B | | | | | |
| C | | | | | |
| overall | | | | | |

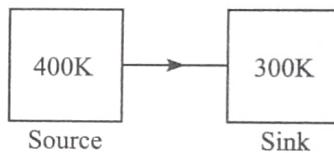
Sol.

Table-1

| State | P | V | T |
|-------|-------|------|-----|
| 1 | 1 atm | 22.4 | 273 |
| 2 | 2 atm | 22.4 | 546 |
| 3 | 1 atm | 44.8 | 546 |

| State | Name of process | q | w | ΔU | ΔH |
|-------|-----------------|-------------------|-------------------|-------------------|-------------------|
| A | Isochoric | $3/2 R$ (273) | 0 | $3/2 R$ (273) | $5/2 R$ (273) |
| B | Isothermal | $546 R \ln 2$ | $-546 R \ln 2$ | 0 | 0 |
| C | Isobaric | $-5/2 R$ (273) | $-2/2 R$ (273) | $-3/2 R$ (273) | $-5/2 R$ (273) |

13. 100 kJ heat is transferred from a larger heat reservoir at 400 K to another large heat reservoir at 300 K. Suppose there is no change in temperature due to exchange of heat :



Find ΔS_{source} , ΔS_{sink} and ΔS_{total} Comment on spontaneity of process.

$$\text{Sol. (i) } \Delta S_{\text{source}} = \frac{\text{heat absorbed by source}}{\text{Temperature of source}}$$

$$\Delta S_{\text{source}} = \frac{-100 \text{ kJ}}{400} = 250 \text{ J/K}$$

$$\text{(ii) } \Delta S_{\text{sink}} = \frac{\text{heat absorbed by sink}}{\text{Temperature of sink}}$$

$$= \frac{+100000 \text{ J}}{300} = 333.33 \text{ J/K}$$

$$\text{(iii) } \Delta S_{\text{total}} = \Delta S_{\text{source}} + \Delta S_{\text{sink}} = +83.33 \text{ J/K}$$

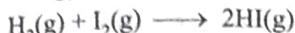
14. At what minimum temperature would a given reaction become spontaneous if $\Delta H = +119 \text{ kJ}$ and $\Delta S = +263 \text{ J/K}$?

$$(a) 452 \text{ K} \quad (b) 2210 \text{ K}$$

$$(c) 382 \text{ K} \quad (d) 2.21 \text{ K}$$

Sol. (a) $T = \frac{\Delta H}{\Delta S} = \frac{119 \times 10^3}{263} = 452.47 \text{ K}$

15. Using $G_f^\circ(\text{HI}) = 1.3 \text{ kJ/mole}$, calculate the standard free energy change for the following reaction,



Sol. $\Delta G^\circ = \Sigma G_f^\circ(\text{products}) - \Sigma G_f^\circ(\text{reactants})$

$$= 2 \times (1.3) - (0 + 0)$$

$$= 2.6 - 0 = 2.6 \text{ kJ/mol}$$

16. Calculate the value of K_p at 25°C for an equilibrium reaction, if $\Delta G^\circ = -20 \text{ kJ/mol}$.

Sol. $\Delta G_p^\circ = -2.303 \text{ RT} \log K_p$

$$-20 \times 1000 = -2.303 \times 8.314 \times 298 \log K_p$$

$$\log K_p = \frac{20 \times 1000}{2.303 \times 8.314 \times 298} = 3.464$$

$$K_p = \text{antilog}(3.464) = 2.91 \times 10^3$$

17. Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.1 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is $4.2 \text{ J g}^{-1} \text{ K}^{-1}$, what is the final temperature of water?

Sol. $W = -2.1 [6 - 4]$

$$= -2.1 \times 2$$

$$= -4.2 \text{ atm} \times \text{lit.} = -4.2 \times 101.325 \text{ J}$$

This work is used to heat up the water

$$\text{Specific heat of H}_2\text{O} = 4.2 \frac{\text{J}}{\text{gram} \cdot \text{K}}$$

Heat required for increasing temperature by 1°C of 1 mole
 $= 4.2 \times 18 = 75.6 \text{ J}$

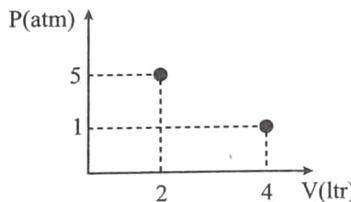
$$4.2 \times 101.325 = 75.6 [T - 293]$$

$$5.63 = T - 293$$

$$T = 298.63 \text{ K}$$

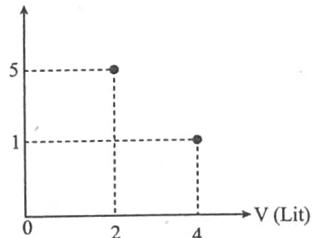
$$298.63 \text{ K}$$

18. Following graph shows a single stage expansion process, then workdone by the system is



- (a) -9104 J (b) -202.6 J (c) -506 J (d) -101.3 J

Sol. (b) $W = -P_{\text{ext}}(V_2 - V_1) = -1 \times 2 \times 101.325 \text{ J} = -202.6 \text{ J}$



19. One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is:

$$[R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}]$$

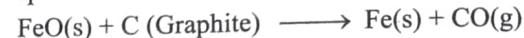
- (a) 0 (b) $R \ln(24.6)$
(c) $R \ln(2490)$ (d) $3/2 R \ln(24.6)$

Sol. (b) $\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) = R \ln \left(\frac{P_i}{P_f} \right)$
 $= R \ln \left(\frac{300 \text{ K}}{1 \text{ L} \times 1 \text{ atm}} \right) = R \ln(24.6)$

20. Given the following data :

| Substance | $\Delta H^\circ (\text{kJ/mol})$ | $S^\circ (\text{J/mol K})$ | $\Delta G^\circ (\text{kJ/mol})$ |
|--------------|----------------------------------|----------------------------|----------------------------------|
| FeO(s) | -266.3 | 57.49 | -245.12 |
| C (Graphite) | 0 | 5.74 | 0 |
| Fe(s) | 0 | 27.28 | 0 |
| CO(g) | -110.5 | 197.6 | -137.15 |

Determine at what temperature the following reaction is spontaneous ?



(a) 298 K

(b) 668 K

(c) 966 K

(d) ΔG° is +ve, hence the reaction will never be spontaneous

Sol. (c) $\text{FeO(s)} + \text{C (graphite)} \longrightarrow \text{Fe(s)} + \text{CO(g)}$

$$\Delta H = 0 + [-110.5] - (-266.3)$$

$$= -110.5 + 266.3$$

$$= +155.8 \text{ kJ/mol}$$

$$\Delta S = 27.28 + 197.6 - 57.49 - 5.74 = 161.65 \text{ J/mol}$$

$$\Delta G = \Delta H - T\Delta S = 0 = 155.8 - T \times 161.65 \times 10^{-3}$$

$$T \times 161.65 \times 10^{-3} = 155.8 \Rightarrow T = 963.8 \text{ K}$$

21. What is the work done against the atmosphere when 25 grams of water vaporizes at 373 K against a constant external pressure of 1 atm? Assume that steam obeys perfect gas laws. Given that the molar enthalpy of vaporization is 9.72 kcal/mole, what is the change of internal energy in the above process?

(a) 1294.0 cal, 11247 cal (b) 921.4 cal, 11074 cal

(c) 1024.8 cal, 12470.6 cal (d) 1129.3 cal, 10207 cal

Sol. (c) Mole of $\text{H}_2\text{O} = 1.39$

$$Pv = nRT$$

$$1 \times v = 1.39 \times 0.082 \times 373$$

$$v = 42.80$$

$$w = P_{\text{ext}} \cdot dv = 1 \times [42.80] \text{ atm} \times \text{lit.}$$

$$= -42.80 \times 101.325 \text{ J} = -\frac{42.80 \times 101.325}{4.2}$$

= 1024.8 cal.

$\Delta H = \Delta E + [P\Delta V]$, = 12470.6 cal.

22. If ΔH_f° for Ag^+ (infinitely diluted), NO_3^- (infinitely diluted), Cl^- (infinitely diluted) and AgCl(s) are 105.579, -207.36, -167.159 and -127.068 respectively. Calculate the enthalpy change for the reaction



- (a) 21.471 KJ/mol (b) 145.688 KJ/mol
 (c) -65.488 KJ/mol (d) None of these

Sol. (c) $\Delta H_{\text{reaction}}^\circ = [\Delta H_f^\circ(\text{AgCl}) + \Delta H_f^\circ(\text{H}^+) + \Delta H_f^\circ(\text{NO}_3^-)] - [\Delta H_f^\circ(\text{Ag}^+) + \Delta H_f^\circ(\text{NO}_3^-) + \Delta H_f^\circ(\text{Cl}^-) + \Delta H_f^\circ(\text{H}^+)]$
 $= -127.068 - [105.579 - 167.159] = -65.488 \text{ kJ/mol.}$

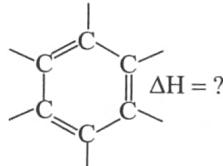
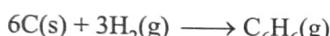
23. Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies:

$\text{C-C} = 83 \text{ kcal}$, $\text{C=C} = 140 \text{ kcal}$, $\text{C-H} = 99 \text{ kcal}$

Heat of atomisation of C = 170.9 kcal

Heat of atomisation of H = 52.1 kcal

- Sol. We have to calculate ΔH for the reaction



For reactants:

Heat of atomisation of 6 moles of C = $6 \times 170.9 \text{ kcal}$

heat of atomisation of 6 moles of H = $6 \times 52.1 \text{ kcal}$

For products:

Heat of formation of 6 moles of C-H bonds = -6×99

Heat of formation of 3 moles of C-C = -3×83

Heat of formation of 3 moles of C=C bonds = -3×140 on adding, we get heat of formation of C_6H_6 , i.e.,

$$\Delta_f^\circ \text{H} = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140 = -75 \text{ kcal}$$

24. Two blocks of equal masses and heat capacity but at different temperatures are taken in an adiabatic vessel. Show that total change in entropy when both attain thermal equilibrium is always positive.

Sol. Let the temperature of hot body be T_H , temperature of cold body be T_C & the final temperature be T_F . Now, net heat exchanged by two bodies must be zero.

$$\Rightarrow mS(T_F - T_H) + mS(T_F - T_C) = 0$$

$$\Rightarrow T_F = \frac{T_H + T_C}{2}$$

Since both bodies are of finite mass, entropy of both bodies are evaluated by reversible paths.

$$\Delta S_{\text{Hot}} = \int_{T_H}^{T_F} mS \cdot \frac{dT}{T} = mS \cdot \ell n \frac{T_F}{T_H}$$

$$\Delta S_{\text{Cold}} = \int_{T_C}^{T_F} mS \cdot \frac{dT}{T} = mS \cdot \ell n \frac{T_F}{T_C}$$

$$\Rightarrow \Delta S_{\text{total}} = (mS) \cdot \ell n \left(\frac{T_F^2}{T_H T_C} \right)$$

$$\Rightarrow T_H^2 + T_C^2 + 2T_H T_C - 4T_H T_C = (T_H - T_C)^2 > 0$$

$$\Rightarrow (T_H - T_C)^2 > 4T_H T_C$$

$$\Rightarrow \Delta S_{\text{total}} > 0$$

Exercise-1 (Topicwise)

THERMODYNAMICS FIRST LAW

Basic Definitions

1. Warming ammonium chloride with sodium hydroxide in a test tube is an example of :

- (a) Closed system (b) Isolated system
- (c) Open system (d) None of these

2. Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV), intensive properties are :

- (a) I, II (b) I, II, III
- (c) I, III, IV (d) All of the above

3. In which case, bodies become hot due to mechanical energy losses:

- (i) Rub our hands for sometime
- (ii) Two vehicles collide with each other
- (iii) Aeroplane crash
- (iv) Sliding of legs on roof surface
- (v) Transfer of energy from hot body to cold body
- (a) 5 (b) 4
- (c) 3 (d) 2

4. Predict the total number of intensive properties :

- (i) Free energy (ii) Critical density
- (iii) Viscosity (iv) Specific heat capacity
- (v) molar heat capacity (vi) Kinetic energy
- (vii) Specific gravity (viii) Dielectric constant
- (ix) pH
- (a) 9 (b) 8
- (c) 7 (d) 6

5. An ideal gas filled at pressure of 2 atm and temperature of 300 K, in a balloon is kept in vacuum within a large insulated container. If wall of balloon is punctured, then container's temperature will:

- (a) Decrease (b) Increase
- (c) Remain constant (d) Unpredictable

6. Internal pressure of a perfect gas (ideal gas) is:

- (a) Zero
- (b) Infinite
- (c) Calculated by $PV = nRT$
- (d) Can not say directly

Thermodynamics Processes & Graph

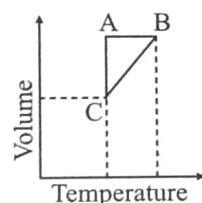
7. A gaseous system changes from state A (P_1, V_1, T_1) to B (P_2, V_2, T_2), B to C (P_3, V_3, T_3) and finally from C to A. The whole process may be called :

- (a) Reversible process (b) Cyclic process
- (c) Isobaric process (d) Spontaneous process

8. A well stoppered thermoflask contains some ice cubes. This is an example of an

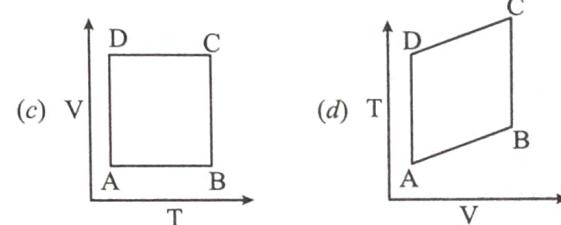
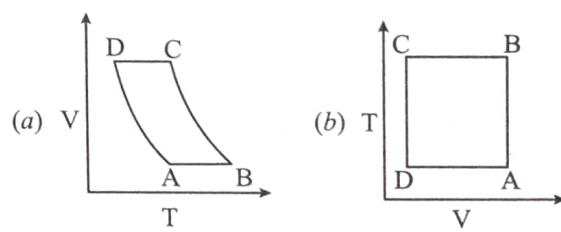
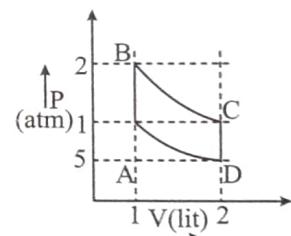
- (a) Closed system
- (b) Open system
- (c) Isolated system
- (d) Non-thermodynamic system

9. Five moles of a gas is put through a series of changes as shown graphically in a cyclic process A \rightarrow B, B \rightarrow C and C \rightarrow A respectively are

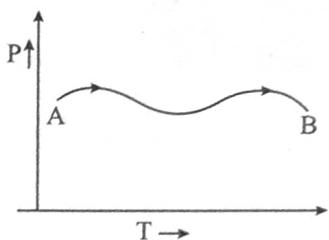


- (a) Isochoric, Isobaric, Isothermal
- (b) Isobaric, Isochoric, Isothermal
- (c) Isothermal, Isobaric, Isochoric
- (d) Isochoric, Isothermal, Isobaric

10. A cyclic process ABCD is shown in P-V diagram for an ideal gas, which of the diagram represent the same process?



11. The P-T graph as given below was observed for a process on an ideal gas, which of the following statement is true?



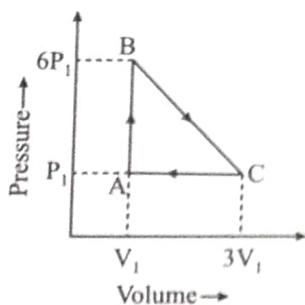
- (a) $w = +ve, \Delta H = +ve$ (b) $w = -ve, \Delta H = -ve$
 (c) $w = -ve, \Delta H = +ve$ (d) $w = +ve, \Delta H = -ve$

12. In a laboratory, liquid in a thermally insulated container is stirred for one hr, by a mechanical linkage to a stirrer. For this process:
 (a) $W < 0; q = 0$ (b) $W < 0; q > 0$
 (c) $W < 0; q > 0$ (d) $W > 0; q = 0$

Work Calculation

13. A thermodynamic system goes from states (i) P_1, V to $2P_1, V$ (ii) P, V_1 to $P, 2V_1$. Then work done in the two cases is:
 (a) Zero, Zero (b) Zero, $-PV_1$
 (c) $-PV_1$, Zero (d) $-PV_1, -P_1V_1$
14. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at $25^\circ C$, is:
 (a) $-2.303 \times 298 \times 0.082 \log 2$
 (b) $-298 \times 10^7 \times 8.31 \times 2.3031 \log 2$
 (c) $-2.303 \times 298 \times 0.082 \log 0.5$
 (d) $-8.31 \times 10^7 \times 298 \times 2.303 \log 0.5$

15. An ideal gas is taken around the cycle ABCA as shown in P-V diagram. The net work done by the gas during the cycle is equal to :



- (a) $12P_1V_1$ (b) $6P_1V_1$
 (c) $5P_1V_1$ (d) P_1V_1

Heat & Internal Energy

16. If a liquid is freezed in a system then :
 (a) $q = 0$
 (b) $q > 0$
 (c) $q < 0$
 (d) $q > 0$ or $q < 0$ (depending on the nature of liquid)

17. For 2 mole of an ideal gas; the relation between C_p & C_v (non-molar) are :
 (a) $C_p - C_v = 2R$ (b) $C_v - C_p = 2R$
 (c) $C_p - C_v = R$ (d) $C_v - C_p = R$

First Law of Thermodynamics

18. A system absorb 600 J of heat and work equivalent to 300 J on its surroundings. The change in its internal energy is :
 (a) 300 J (b) 400 J
 (c) 500 J (d) 600 J
19. In an isochoric process, the increase in internal energy is:
 (a) Equal to the heat absorbed.
 (b) Equal to the heat evolved.
 (c) Equal to the work done.
 (d) Equal to the sum of the heat absorbed and work done.
20. In an isothermal expansion of an ideal gas, select wrong statement :
 (a) There is no change in the temperature of the gas.
 (b) There is no change in the internal energy of the gas.
 (c) The work done by the gas is equal to the heat supplied to the gas.
 (d) The work done by the gas is equal to the change in its internal energy.

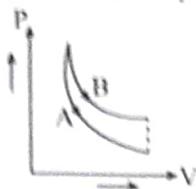
21. A system undergoes a process which absorbed 0.5 kJ of heat and undergoing an expansion against external pressure of 1 atm, during the process change in its internal energy is 300 J. Then, predict the change in volume (lit.) :
 (a) 1 (b) 2
 (c) 3 (d) 4

22. When two moles of hydrogen atoms join together to form a mole of hydrogen molecules in a rigid vessel
 $H(g) + H(g) \longrightarrow H_2(g)$
 then:
 (a) $w < 0$ (b) $\Delta U = \text{negative}$
 (c) $q_{\text{system}} = \text{positive}$ (d) $q_{\text{surroundings}} = \text{negative}$

Adiabatic, Isothermal, Polytropic & Free Expansion Processes

23. The temperature of the system decreases in all:
 (a) Adiabatic compression (b) Isothermal compression
 (c) Isothermal expansion (d) Adiabatic expansion
24. 1 mole of NH_3 gas at $27^\circ C$ is expanded in reversible adiabatic condition to make volume 8 times ($\gamma = 1.33$). Final temperature and work done respectively are :
 (a) 150 K, 900 cal (b) 150 K, 400 cal
 (c) 250 K, 1000 cal (d) 200 K, 800 cal

25. In figure, A and B are two adiabatic curves for two different gases. Then gases A and B corresponds to :

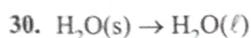


- (a) Ar and He respectively
 (b) He and H₂ respectively
 (c) O₂ and H₂ respectively
 (d) H₂ and He respectively
26. If W₁, W₂ & W₃ are magnitude of work done of an ideal gas in an isothermal, adiabatic & isobaric reversible expansion process from same initial stage to same final volume (only). Then, correct order will be:
 (a) W₃ > W₁ > W₂ (b) W₃ > W₂ > W₁
 (c) W₂ > W₁ > W₃ (d) W₁ > W₂ > W₃

Enthalpy

27. One mole of a non-ideal gas undergoes a change of state (1.0 atm, 3.0 L, 200 K) to (4.0 atm, 5.0 L, 250 K) with a change in internal energy (ΔU) = 40 L-atm. The change in enthalpy of the process in L-atm:
 (a) 43 (b) 57
 (c) 42 (d) None of these
28. For the isothermal expansion of an ideal gas:
 (a) U and H increases.
 (b) U increases but H decreases.
 (c) H increases but U decreases.
 (d) U and H are unaltered.
29. A vessel contains 100 litres of a liquid X. Heat is supplied to the liquid in such a fashion that, Heat given = change in enthalpy, the volume of the liquid increases by 2 litres. If the external pressure is one atm, and 202.6 Joules of heat were supplied then, [U - total internal energy]
 (a) $\Delta U = 0$, $\Delta H = 0$
 (b) $\Delta U = + 202.6 \text{ J}$, $\Delta H = + 202.6 \text{ J}$
 (c) $\Delta U = - 202.6 \text{ J}$, $\Delta H = - 202.6 \text{ J}$
 (d) $\Delta U = 0$, $\Delta H = + 202.6 \text{ J}$

Phase Transition



This phase transition is carried out at constant temperature and pressure, then work done during the process:

- (a) $W < 0$ (b) $W > 0$
 (c) $W = 0$ (d) Can't be determined
31. At 1 atm pressure freezing of 'n' moles of water liquid (0°C) to ice(0°C), then heat transfer:
 (a) $n\Delta H_{\text{fusion}}$ (b) $-n\Delta H_{\text{fusion}}$
 (c) $nC_{v,m}\Delta T$ (d) ΔH_{fusion}

THERMODYNAMICS SECOND AND THIRD LAW

Introduction About Entropy

32. In which state, the matter have highest entropy?
 (a) Solid (b) Liquid
 (c) Gas (d) Equal in all
33. Predict which of the following reaction(s) has a positive entropy change?
 I. $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
 II. $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$
 III. $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
 (a) I and II (b) III
 (c) II and III (d) II
34. Mixing of non-reacting ideal gases is generally accompanied by:
 (a) Decrease in entropy.
 (b) Increase in entropy.
 (c) Change in enthalpy.
 (d) Increase in free energy.
35. Which of the following reactions is associated with the most negative change in entropy?
 (a) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
 (b) $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
 (c) C(s, graphite) + O₂ → CO₂(g)
 (d) $3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{g})$
36. For the gas - phase decomposition,
 $\text{PCl}_5(\text{g}) \xrightleftharpoons{\Delta} \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$:
 (a) $\Delta H < 0$, $\Delta S < 0$ (b) $\Delta H > 0$, $\Delta S > 0$
 (c) $\Delta H > 0$, $\Delta S < 0$ (d) $\Delta H < 0$, $\Delta S > 0$
37. Which one of the following has ΔS° greater than zero?
 (a) $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{CaCO}_3(\text{s})$
 (b) $\text{NaCl}(\text{aq}) \rightleftharpoons \text{NaCl}(\text{s})$
 (c) $\text{NaNO}_3(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
 (d) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
38. For which reaction from the following, will have maximum entropy change?
 (a) $\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$
 (b) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 (c) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
 (d) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
39. Which of the following statement is true? The entropy of the universe:
 (a) Increases and tends towards maximum value.
 (b) Decreases and tends to be zero.
 (c) Remains constant.
 (d) Decreases and increases with a periodic rate.

Entropy Calculation

40. An isolated system comprises the liquid in equilibrium with vapours. At this stage, the molar entropy of the vapour is:
- Less than that of liquid
 - More than that of liquid
 - Equal to zero
 - Equal to that of liquid
41. When two mole of an ideal gas ($C_{p,m} = \frac{5}{2}R$) is heated from 300 K to 600 K at constant pressure, the change in entropy of gas (ΔS) is :
- $\frac{3}{2}R \ln 2$
 - $-\frac{3}{2}R \ln 2$
 - $5R \ln 2$
 - $\frac{5}{2}R \ln 2$
42. In previous problem calculate ΔS_{gas} , if process is carried out at constant volume :
- $5R \ln 2$
 - $\frac{3}{2}R \ln 2$
 - $3R \ln 2$
 - $-3R \ln 2$
43. The entropy change when two moles of an ideal monoatomic gas is heated from 200 to 300°C reversibly and isochorically?
- $\frac{3}{2}R \ln\left(\frac{300}{200}\right)$
 - $\frac{5}{2}R \ln\left(\frac{573}{273}\right)$
 - $3R \ln\left(\frac{573}{473}\right)$
 - $\frac{3}{2}R \ln\left(\frac{573}{473}\right)$
44. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state and $\Delta H = -401.7 \text{ J mol}^{-1}$ for the transition. Assume the surroundings to be an ice-water bath at 0°C :
- -1.09 J K^{-1}
 - 1.47 J K^{-1}
 - 0.38 J K^{-1}
 - None of these
45. Given $\Delta_r S^\circ = -266$ and the listed $[S_m^\circ]$ values in JK^{-1} . Calculate S° for $\text{Fe}_3\text{O}_4(s)$:
- $$4\text{Fe}_3\text{O}_4(s) [.....] + \text{O}_2(g) [205] \rightarrow 6\text{Fe}_2\text{O}_3(s) [87]$$
- +111.1
 - +122.4
 - 145.75
 - 248.25

Free Energy

46. Which of the following is incorrect regarding gibbs free energy?
- It is a state function.
 - It is an extensive property.
 - It is macroscopic property.
 - It is an intensive property.
47. Which of the following conditions regarding a chemical process ensures its spontaneity at all temperature ?
- $\Delta H > 0, \Delta S < 0$
 - $\Delta H < 0, \Delta S > 0$
 - $\Delta H < 0, \Delta S < 0$
 - $\Delta H > 0, \Delta S < 0$

48. When reaction is in standard state at equilibrium, then:
- $\Delta H^\circ = 0$
 - $\Delta S^\circ = 0$
 - Equilibrium constant, $K = 0$
 - Equilibrium constant, $K = 1$
49. Which of the natural process is spontaneous?
- Formation of curd from milk after doing initiation.
 - Conversion of C (graphite) \rightarrow C (diamond) at 25°C and latex.
 - Formation of $\text{H}_2(g)$ and $\text{O}_2(g)$ from $\text{H}_2\text{O}(\ell)$.
 - Formation of CrO_5 from H_2O_2 and $\text{K}_2\text{Cr}_2\text{O}_7$ in basic medium.
50. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure?
- 80 cal
 - 540 cal
 - 620 cal
 - Zero
51. The enthalpy change for a given reaction at 298 K is $-x \text{ J mol}^{-1}$ (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature:
- Can be negative but numerically larger than $x/298$.
 - Can be negative but numerically smaller than $x/298$.
 - Cannot be negative.
 - Cannot be positive.
52. A reaction has $\Delta H = -33 \text{ kJ}$ and $\Delta S = -58 \text{ J/K}$. This reaction would be:
- Spontaneous at all temperatures.
 - Non-spontaneous at all temperatures.
 - Spontaneous above a certain temperature.
 - Spontaneous below a certain temperature.
53. For a reaction $\text{A}(g) \rightleftharpoons \text{B}(g)$, at equilibrium, the partial pressure of B is found to be one fourth of the partial pressure of A. The value of ΔG° of the reaction $\text{A}(g) \rightleftharpoons \text{B}(g)$ is:
- $RT \ln 4$
 - $-RT \ln 4$
 - $RT \log 4$
 - $-RT \log 4$
54. If $\Delta G^\circ = -177 \text{ kcal}$ for
- $$(I) 2 \text{Fe}(s) + \frac{3}{2} \text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$$
- and $\Delta G = -19 \text{ kcal}$
- $$(II) 4 \text{Fe}_2\text{O}_3(s) + \text{Fe}(s) \longrightarrow 3\text{Fe}_3\text{O}_4(s)$$
- What is the Gibbs free energy of formation of $\text{Fe}_3\text{O}_4(s)$?
- + 229.6 kcal/mol
 - 242.3 kcal/mol
 - 727 kcal/mol
 - 229.6 kcal/mol
55. For a particular reaction $\Delta H^\circ = -76.6 \text{ kJ}$ and $\Delta S^\circ = 226 \text{ JK}^{-1}$. This reaction is:
- Spontaneous at all temperatures.
 - Non spontaneous at all temperatures.
 - Spontaneous at temperature below 66°C.
 - Spontaneous at temperature above 66°C.

THERMOCHEMISTRY

Calculation ΔU , ΔH & W

56. The free energy change for a reversible reaction at equilibrium is:

 - (a) Positive
 - (b) Negative
 - (c) Zero
 - (d) Cannot say

57. ΔH° for the reaction $X_{(g)} + Y_{(g)} \rightleftharpoons Z_{(g)}$ is -4.6 kcal, the value of ΔU° of the reaction at 227°C is : ($R = 2 \text{ cal.mol}^{-1} \text{ K}^{-1}$):

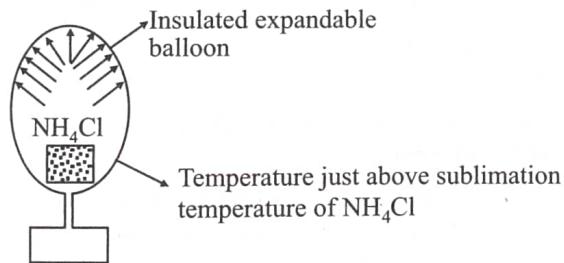
 - (a) -3.6 kcal
 - (b) -5.6 kcal
 - (c) -4.6 kcal
 - (d) -2.6 kcal

58. Determine which of the following reactions at constant pressure represent surrounding that do work on the system?

 - I. $4\text{NH}_3(\text{g}) + 7\text{O}_2(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
 - II. $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\ell)$
 - III. $\text{C(s, graphite)} + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$
 - IV. $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\ell)$
 - (a) III, IV
 - (b) II and III
 - (c) II, IV
 - (d) I and II, IV

59. Consider the reaction at 300 K
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g}); \quad \Delta H^\circ = -185 \text{ kJ}$
 If 2 mole of H_2 completely react with 2 mole of Cl_2 to form HCl . What is ΔU° for this reaction?

 - (a) 0
 - (b) -185 kJ
 - (c) 370 kJ
 - (d) -370 kJ



Basics & Kirchoff's law

61. For which of the following change, $\Delta H \neq \Delta E$?

 - (a) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$
 - (b) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$
 - (c) $C(s) + O_2(g) \longrightarrow CO_2(g)$
 - (d) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Enthalpy of Formation & Combustion

65. In the reaction, $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$; $\Delta H = 2.8 \text{ kJ}$, ΔH represents:

 - Heat of reaction
 - Heat of combustion
 - Heat of formation
 - Heat of solution

66. Given, $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow 2\text{HBr}(\text{g})$, ΔH_1^0 and standard enthalpy of condensation of bromine is ΔH_2^0 . Standard enthalpy of formation of HBr at 25°C is:

 - $\Delta H_1^0 / 2$
 - $\Delta H_1^0 / 2 + \Delta H_2^0$
 - $\Delta H_1^0 / 2 - \Delta H_2^0$
 - $(\Delta H_1^0 - \Delta H_2^0) / 2$

67. For the following reaction,

$$\text{C (diamond)} + \text{O}_2 \longrightarrow \text{CO}_2(\text{g}); \Delta H = -94.3 \text{ kcal/mol}$$

$$\text{C (graphite)} + \text{O}_2 \longrightarrow \text{CO}_2(\text{g}); \Delta H = -97.6 \text{ kcal/mol}$$

The heat required to change 1 g of C (diamond) \longrightarrow C (graphite) is:

 - 1.59 kcal
 - 0.1375 kcal
 - 0.55 kcal
 - 0.275 kcal

68. The heat of combustion of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is 1350 kcal/mol. How much of heat will be liberated when 17.1 g of sucrose is burnt?

 - 67.5 kcal
 - 13.5 kcal
 - 40.5 kcal
 - 25.5 kcal

69. If $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$, $\Delta H = -298.2 \text{ kJ mole}^{-1}$
 $\text{SO}_2 + 1/2 \text{ O}_2 \longrightarrow \text{SO}_3$, $\Delta H = -98.7 \text{ kJ mole}^{-1}$
 $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$, $\Delta H = -130.2 \text{ kJ mole}^{-1}$



then the enthalpy of formation of H_2SO_4 at 298 K will be -

- (a) $-814.4 \text{ kJ mol}^{-1}$ (b) $+814.4 \text{ kJ mol}^{-1}$
 (c) $-650.3 \text{ kJ mol}^{-1}$ (d) $-433.7 \text{ kJ mol}^{-1}$

70. When a certain amount of ethylene was combusted, 5644 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ, the volume of O_2 (at NTP) that entered into the reaction is:

- (a) 268.8 ml (b) 268.8 L
 (c) $6226 \times 22.4 \text{ L}$ (d) 22.4 L

71. The values of heat of combustion of ethane (C_2H_6) and ethyne (C_2H_2) are -341 and -310 kcal, respectively. Then, which of the following is better fuel on mass basis?

- (a) C_2H_2 (b) C_2H_6
 (c) Both (a) & (b) (d) None of these

Bond Enthalpy Method & Resonance Energy

72. If enthalpy of dissociation of CH_4 and C_2H_6 are 320 and 600 calories respectively, then bond energy of C-C bond is :

- (a) 80 cal (b) 40 cal
 (c) 60 cal (d) 120 cal

73. The bond dissociation energy of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. The enthalpy of formation for HCl gas will be:

- (a) -44.0 kcal (b) -22.0 kcal
 (c) 22.0 kcal (d) 44.0 kcal

74. AB , A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2 , AB & B_2 are in the ratio $1 : 1 : 0.5$ and enthalpy of formation of AB from A_2 and B_2 is -100 kJ/mol^{-1} . What is the bond enthalpy of A_2 ?

- (a) 400 kJ/mol (b) 200 kJ/mol
 (c) 100 kJ/mol (d) 300 kJ/mol

Enthalpy of Solution & Born Haber's Cycle

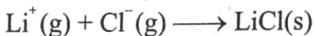
75. One mole of anhydrous $MgCl_2$ dissolves in water and liberates 25 cal/mol of heat. $\Delta H_{\text{hydration}}$ of $MgCl_2 = -30 \text{ cal/mol}$. Heat of dissolution of $MgCl_2 \cdot H_2O$ is:

- (a) $+5 \text{ cal/mol}$
 (b) -5 cal/mol
 (c) 55 cal/mol
 (d) -55 cal/mol

76. The enthalpy of solution of $NaOH(s)$ in water is -41.6 kJ/mol when $NaOH$ is dissolved in water then, the temperature of water :
 (a) Increases
 (b) Decreases
 (c) Does not change
 (d) Fluctuates

77. The enthalpy change for the reaction of 5 litre of ethylene with 5 litre of H_2 gas at 1.5 atm pressure is $\Delta H = -0.5 \text{ kJ}$. The value of ΔU will be : (1 atm L = 100 J)
 (a) -1.25 kJ
 (b) $+1.25 \text{ kJ}$
 (c) 0.25 kJ
 (d) -0.25 kJ

78. Calculate the lattice energy for the reaction



given that

$$\begin{aligned}\Delta H_{\text{sub}}(Li) &= 160; \Delta H_{\text{diss}}(Cl_2) = 244; IP(Li) = 520; \\ E_A(Cl) &= -365 \text{ and } \Delta H_f(LiCl) = -400 \text{ (all in kJ mole}^{-1}) \\ (a) -837 & (b) -959 \\ (c) -1567 & (d) -37\end{aligned}$$

Enthalpy of Neutralization

79. The enthalpy of neutralization of which of the following acid & base is nearly -13.6 kcal ?

- (a) HCN and $NaOH$
 (b) CH_3COOH and NH_4OH
 (c) HCl and KOH
 (d) HCl and NH_4OH

80. Equal volume of $HCOOH$ and $NaOH$ are mixed. If x is the heat of formation of water, then heat evolved of neutralization is:

- (a) More than x
 (b) Equal to x
 (c) Twice of x
 (d) Less than x

81. If heat of dissociation of $CHCl_2COOH$ is 0.7 kcal/mole , then ΔH for the reaction :



- (a) -13 kcal (b) $+13 \text{ kcal}$
 (c) -14.4 kcal (d) -13.7 kcal

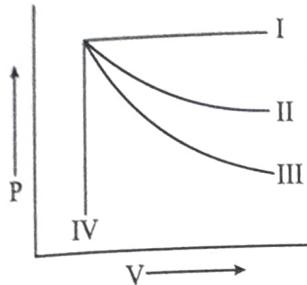


Exercise-2 (Learning Plus)

1. In which one of the following sets, all the properties belong to same category (all extensive or all intensive)?

- (a) Mass, volume, pressure
- (b) Temperature, pressure, volume
- (c) Heat capacity, density, entropy
- (d) Enthalpy, internal energy, volume.

2.



The plots between P and V which represent isochoric and isobaric process respectively:

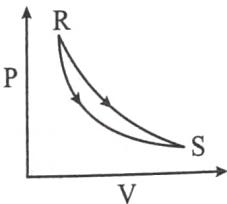
- | | |
|-----------|-------------|
| (a) I, II | (b) IV, I |
| (c) I, IV | (d) II, III |

3. Match the entries of column I with appropriate entries of column II and choose the correct option out of the four options (A), (B), (C) and (D).

| Column-I | | Column-II | |
|----------|------------|-----------|----------------|
| A. | Isothermal | (p) | $\Delta T = 0$ |
| B. | Isobaric | (q) | $\Delta V = 0$ |
| C. | Adiabatic | (r) | $\Delta P = 0$ |
| D. | Isochoric | (s) | $q = 0$ |

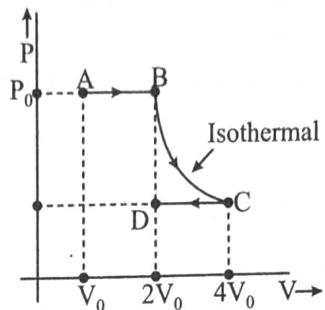
- (a) A-p, B-q, C-r, D-s (b) A-p, B-r, C-s, D-q
- (c) A-s, B-p, C-r, D-q (d) A-s, B-p, C-q, D-r

4. Consider the cyclic process R → S → R as shown in the Fig. You are told that one of the path is adiabatic and the other one isothermal. Which one of the following is(are) true?



- (a) Process R → S is isothermal
- (b) Process S → R is adiabatic
- (c) Process R → S is adiabatic
- (d) Such a graph is not possible

5. Work for the following process ABCD on a monoatomic gas is:



- (a) $w = -2 P_0 V_0 \ln 2$
- (b) $w = -2 P_0 V_0 \ln 2$
- (c) $w = -P_0 V_0 (1 + \ln 2)$
- (d) $w = -P_0 V_0 \ln 2$

6. 50 L of a certain liquid is confined in a piston system at the external pressure 100 atm. This pressure is suddenly released and liquid is expanded against the constant atmospheric pressure, volume of the liquid increases by 1 L and the final pressure on the liquid is 10 atm. Find the workdone.

- | | |
|---------------|--------------|
| (a) 1 L.atm | (b) 5 L.atm |
| (c) 500 L.atm | (d) 50 L.atm |

7. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process in an ideal gas?

- (a) Isothermal process : $q = -w$
- (b) Cyclic process : $q = -w$
- (c) Adiabatic process : $\Delta E = q$
- (d) Expansion of a gas into vacuum : $\Delta E = q$

8. One mole of an ideal gas ($C_{v,m} = \frac{5}{2}R$) at 300 K and 5 atm is expanded adiabatically to a final pressure of 2 atm against a constant pressure of 2 atm. Final temperature of the gas is:

- | | |
|-------------|-----------|
| (a) 270 K | (b) 273 K |
| (c) 248.5 K | (d) 200 K |

9. The magnitudes of enthalpy changes for irreversible adiabatic expansion of a gas from 1 L to 2 L is ΔH_1 and for reversible adiabatic expansion for the same expansion is ΔH_2 . Then:

- (a) $\Delta H_1 > \Delta H_2$
- (b) $\Delta H_1 < \Delta H_2$
- (c) $\Delta H_1 = \Delta H_2$, enthalpy being a state function ($\Delta H_1 = \Delta H_2$)
- (d) $\Delta H_1 = \Delta E_1$ & $\Delta H_2 = \Delta E_2$ where ΔE_1 & ΔE_2 are magnitudes of change in internal energy of gas in these expansions respectively.

10. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is 50 J/ $^{\circ}$ C. Then, the enthalpy change during the process is: (1 L atm \approx 100 J)

- (a) $\Delta H = 15 \text{ kJ}$ (b) $\Delta H = 15.7 \text{ kJ}$
 (c) $\Delta H = 14.4 \text{ kJ}$ (d) $\Delta H = 14.7 \text{ kJ}$

11. In which of the following option the first compound has less entropy than second?

- (a) (i) Aqueous solution of 1 M of MgCl₂.
 (ii) Aqueous solution of 1 M of NaCl.
 (b) (i) Br₂ liquid at 25°C
 (ii) Br₂ liquid at 20°C
 (c) (i) HgO solid
 (ii) HgS solid
 (d) (i) Br₂ liquid
 (ii) I₂ solid

12. Select the correct statement(s):

S₁: AlCl₃ when dissolve in H₂O its entropy decreases therefore, it is a non-spontaneous process.

S₂: When H₂ gas is adsorbed on the surface of Pd, some amount of heat is released.

S₃: Entropy of D₂ gas is greater than that of H₂ gas.

- (a) S₁, S₂ & S₃
 (b) S₁ & S₃
 (c) S₂ & S₃
 (d) S₁ & S₂

13. Isoentropic process is:

- (a) Adiabatic and irreversible process.
 (b) Isothermal and reversible process.
 (c) Adiabatic and reversible process.
 (d) Isothermal and reversible for which q = 0.

14. According to third law of thermodynamics:

- (a) The entropy of a substance at 0 K is zero.
 (b) Entropy of hydrogen ion is zero at 0 K.
 (c) Net change in entropy in conversion H_{2(g)} (130 K) \rightarrow H_{2(g)} (200 K) is zero.
 (d) Entropy generally decrease in combustion reactions.

15. Select the correct statements:

S₁: For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

S₂: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

S₃: Spontaneity is related to change in entropy of universe.

- (a) S₁ S₂ S₃ (b) only S₁
 (c) S₂, S₃ (d) S₁, S₃

16. Combustion of sucrose is used by aerobic organisms for providing energy for the life sustaining processes. If all the capturing of energy from the reaction is done through electrical process (non P-V work), then calculate maximum available energy which can be captured by combustion of 34.2 g of sucrose.

Given : $\Delta H_{\text{combustion}}(\text{sucrose}) = -6000 \text{ kJ mol}^{-1}$

$\Delta S_{\text{combustion}} = 180 \text{ J/K mol}$ and body temperature is 300 K

- (a) 600 kJ (b) 594.6 kJ
 (c) 5.4 kJ (d) 605.4 kJ

17. Given the following data :

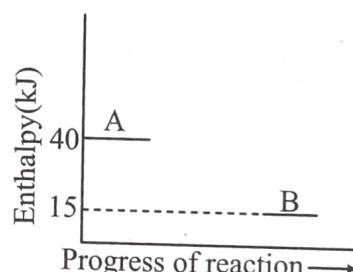
| Substance | ΔH° (kJ/mol) | S° (J/mol K) | ΔG° (kJ/mol) |
|--------------|------------------------------|------------------------|------------------------------|
| FeO(s) | -266.3 | 57.49 | -245.12 |
| C (Graphite) | 0 | 5.74 | 0 |
| Fe(s) | 0 | 27.28 | 0 |
| CO(g) | -110.5 | 197.6 | -137.15 |

Determine at what temperature the following reaction is spontaneous?



- (a) 298 K
 (b) 668 K
 (c) 964 K
 (d) ΔG° is +ve, hence the reaction will never be spontaneous

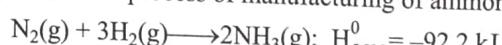
18. Look at the following diagram :



The enthalpy change for the reaction A \rightarrow B will be :

- (a) -25 kJ (b) -40 kJ
 (c) +25 kJ (d) -65 kJ

19. In Haber's process of manufacturing of ammonia :



| Molecule | N ₂ (g) | H ₂ (g) | NH ₃ (g) |
|--|--------------------|--------------------|---------------------|
| C _P (JK ⁻¹ mol ⁻¹) | 29.1 | 28.8 | 35.1 |

If C_P is independent of temperature, then reaction at 100°C as compared to that of 25°C will be :

- (a) More endothermic
 (b) Less endothermic
 (c) More exothermic
 (d) Less exothermic

20. In the reaction $\text{AB}_2(\ell) + 3\text{X}_2(\text{g}) \rightleftharpoons \text{AX}_2(\text{g}) + 2\text{BX}_2(\text{g})$, $\Delta H = -270$ kcal per mol of $\text{AB}_2(\ell)$, the enthalpies of formation of $\text{AX}_2(\text{g})$ & $\text{BX}_2(\text{g})$ are in the ratio of 4 : 3 and have opposite sign. If the value of ΔH_f° ($\text{AB}_2(\ell)$) = + 30 kcal/mol, then
 (a) $\Delta H_f^\circ (\text{AX}_2) = -96$ kcal /mol
 (b) $\Delta H_f^\circ (\text{BX}_2) = +480$ kcal /mol
 (c) $K_p = K_c$ & $\Delta H_f^\circ (\text{AX}_2) = +480$ kcal /mol
 (d) $K_p = K_c RT$ & $\Delta H_f^\circ (\text{AX}_2) + \Delta H_f^\circ (\text{BX}_2) = -240$ kcal /mol

21. The heat of formation of $\text{C}_2\text{H}_5\text{OH}(\ell)$ is - 66 kcal/mole. The heat of combustion of $\text{CH}_3\text{OCH}_3(\text{g})$ is - 348 kcal/mole. ΔH_f for H_2O and CO_2 are -68 kcal/mole and -94 kcal/mole respectively. Then, the ΔH for the isomerisation reaction $\text{C}_2\text{H}_5\text{OH}(\ell) \rightarrow \text{CH}_3\text{OCH}_3(\text{g})$, and ΔE for the same are at $T = 25^\circ\text{C}$
 (a) $\Delta H = 18$ kcal/mole, $\Delta E = 17.301$ kcal/mole
 (b) $\Delta H = 22$ kcal/mole, $\Delta E = 21.408$ kcal/mole
 (c) $\Delta H = 26$ kcal/mole, $\Delta E = 25.709$ kcal/mole
 (d) $\Delta H = 30$ kcal/mole, $\Delta E = 28.522$ kcal/mole

22. Caesium chloride is formed according to the following equation $\text{Cs}(\text{s}) + 0.5 \text{Cl}_2(\text{g}) \rightarrow \text{CsCl}(\text{s})$. The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs and electron affinity of chlorine are 81.2, 243.0, 375.7 and -348.3 kJ mol^{-1} . The energy change involved in the formation of CsCl is -388.6 kJ mol^{-1} . Calculate the lattice energy of CsCl .
 (a) 618.7 kJ mol^{-1}
 (b) 1237.4 kJ mol^{-1}
 (c) -1237.4 kJ mol^{-1}
 (d) -618.7 kJ mol^{-1}

23. The enthalpies of neutralization of a weak base AOH and a strong base BOH by HCl are -12250 cal/ mol and -13000 cal/ mol respectively. When one mole of HCl is added to a solution containing 1 mole of AOH and 1 mole of BOH, the enthalpy change was -12500 cal/ mol. In what ratio the acid is distributed between AOH and BOH?
 (a) 2 : 1
 (b) 2 : 3
 (c) 1 : 2
 (d) None of these

24. The enthalpy of neutralization of 40.0 g of NaOH by 60.0 g of CH_3COOH will be :
 (a) 57.1 kJ equiv^{-1}
 (b) Less than 57.1 kJ equiv^{-1}
 (c) More than 57.1 kJ equiv^{-1}
 (d) 13.7 kJ equiv^{-1}

25. Given $\Delta_{\text{ionic}} H^\circ (\text{HCN}) = 45.2$ kJ mol^{-1} and $\Delta_{\text{ionic}} H^\circ (\text{CH}_3\text{COOH}) = 2.1$ kJ mol^{-1} . Which one of the following facts is true?
 (a) $pK_a (\text{HCN}) = pK_a (\text{CH}_3\text{COOH})$
 (b) $pK_a (\text{HCN}) > pK_a (\text{CH}_3\text{COOH})$
 (c) $pK_a (\text{HCN}) < pK_a (\text{CH}_3\text{COOH})$
 (d) $pK_a (\text{HCN}) = (45.17/2.07) pK_a (\text{CH}_3\text{COOH})$

26. The average O-H bond energy in H_2O with the help of following data.
 (I) $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{g}) ; \Delta H = +40.6$ kJ mol^{-1}
 (II) $2\text{H}(\text{g}) \rightarrow \text{H}_2(\text{g}) ; \Delta H = -435.0$ kJ mol^{-1}
 (III) $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g}) ; \Delta H = +489.6$ kJ mol^{-1}
 (IV) $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\ell) ; \Delta H = -571.6$ kJ mol^{-1}
 (a) 584.9 kJ mol^{-1}
 (b) 279.8 kJ mol^{-1}
 (c) 462.5 kJ mol^{-1}
 (d) 925 kJ mol^{-1}

27. Enthalpy of polymerisation of ethylene, as represented by the reaction, $n\text{CH}_2=\text{CH}_2 \rightarrow (-\text{CH}_2-\text{CH}_2-)_n$ is -100 kJ per mole of ethylene. Given bond enthalpy of C=C bond is 600 kJ mol^{-1} , enthalpy of C-C bond (in kJ mol) will be:
 (a) 116.7
 (b) 350
 (c) 700
 (d) Indeterminate

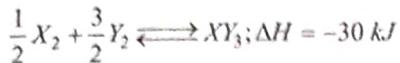
28. The average energy required to break a P-P bond in $\text{P}_4(\text{s})$ into gaseous atoms is 53.2 kcal mol^{-1} . The bond dissociation energy of $\text{H}_2(\text{g})$ is 104.2 kcal mol^{-1} ; ΔH_f° of $\text{PH}_3(\text{g})$ from $\text{P}_4(\text{s})$ is 5.5 kcal mol^{-1} . The P-H bond energy in kcal mol^{-1} is [Neglect presence of Van der Waals forces in $\text{P}_4(\text{s})$]
 (a) 85.2
 (b) 57.6
 (c) 76.9
 (d) 63.3

29. The enthalpy of formation of water from hydrogen and oxygen is . The enthalpy of decomposition of water into hydrogen and oxygen is.
 (a) -286.0
 (b) -143.0
 (c) 286.0
 (d) 143.0

30. The heat of combustion of yellow phosphorus and red phosphorus are and respectively. The heat of transition of yellow phosphorus to red phosphorus is
 (a) -18.69 kJ
 (b) +1.13 kJ
 (c) +18.69 kJ
 (d) -1.13 kJ

31. The bond dissociation energies for Cl_2 , I_2 and ICl are 242.3, 151 and 211.3 kJ/mol respectively. The enthalpy of sublimation of iodine is 62.8 kJ/mol . What is the standard enthalpy of formation of $\text{ICl}(\text{g})$?
 (a) -211.3 kJ/mol
 (b) -14.6 kJ/mol
 (c) 16.8 kJ/mol
 (d) 33.5 kJ/mol

32. Standard entropies of X_2 , Y_2 and XY_3 are 60, 40 and $50\text{ J K}^{-1}\text{ mol}^{-1}$ respectively. For the reaction:



to be at equilibrium, the temperature should be:

- (a) 750 K (b) 1000 K
(c) 1250 K (d) 500 K

33. ΔH and ΔS for a reaction are $+30.558\text{ kJ mol}^{-1}$ and $0.066\text{ kJ K}^{-1}\text{ mol}^{-1}$ at 1 atm pressure. The temperature at which free energy change is zero and the nature of the reaction below this temperature is

- (a) 483 K, spontaneous
(b) 443 K, non-spontaneous
(c) 443 K, spontaneous
(d) 463 K, non-spontaneous

34. The ΔG in the process of melting of ice at 15°C would be

- (a) ΔG is ve (b) ΔG is +ve
(c) $\Delta G = 0$ (d) All of these

35. $\Delta_{\text{C}}H^\circ_{\text{C}_2\text{H}_6}$ and $\Delta_{\text{C}}H^\circ_{\text{C}_2\text{H}_2}$ are 341.1 kcal mole⁻¹ and 310.0 kcal mole⁻¹ respectively then

- (a) ethane is better welding gas having more magnitude of $\Delta_{\text{C}}H^\circ$.
(b) ethyne is better welding gas having more value of $\Delta_{\text{C}}H^\circ$.
(c) ethyne is better welding gas having more magnitude of $\Delta_{\text{C}}H^\circ/\text{unit weight}$.
(d) ethane is better welding gas as here oxidation state of C is 3.

36. On adding 0.5 L each of NaOH and HCl rise in temperature has found as 4°C , on adding

1. L of each rise in temperature must be
(a) 1°C (b) 2°C
(c) 3°C (d) 4°C

37. $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO(g)}; \Delta_rH^\circ = 110\text{ kJ}$
 $\text{C(s)} + \text{H}_2\text{O(g)} \longrightarrow \text{CO(g)} + \text{H}_2\text{(g)}; \Delta_rH^\circ = 132\text{ kJ}$

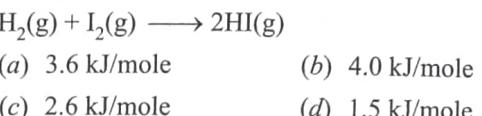
Composition of steam and O_2 when it passed over coke keeping temperature 1273 K will be

- (a) 1 : 2 (b) 5 : 3
(c) 4 : 5 (d) 1 : 1

38. How many ml of 1M KOH and 0.5 M H_2SO_4 solutions, respectively when mixed for a total volume of 100 ml produce the highest rise in temperature?

- (a) 67 : 33 (b) 33 : 67
(c) 40 : 60 (d) 50 : 50

39. Using $G_f^\circ(\text{HI}) = 1.3\text{ kJ/mole}$, calculate the standard free energy change for the following reaction



40. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process in ideal gas?

- (a) Isothermal process: $q = -w$
(b) Cyclic process: $q = -w$
(c) Adiabatic process: $\Delta E = q$
(d) Expansion of a gas into vacuum: $\Delta E = q$

Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

1. Which of the following properties of a system are intensive?

- (a) Color
(b) Kinetic energy per mole
(c) X (where $X = U + H$)
(d) Specific volume (volume per unit mass)

2. Choose the correct statement :

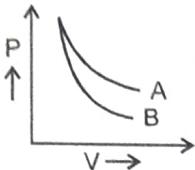
- (a) System and surrounding are always separated by a real or imaginary boundary.
(b) Perfectly isolated system can never be created.

- (c) In reversible process, energy change in each step can be reversed.
(d) Irreversible process is also called quasi-equilibrium state.

3. In an isothermal expansion of a gaseous sample, the correct relation is : (consider w (work) with sign according to new IUPAC convention)

[The reversible and irreversible processes are carried out between same initial and final states.]

- (a) $w_{\text{rev}} > w_{\text{irrev}}$ (b) $w_{\text{irrev}} > w_{\text{rev}}$
(c) $q_{\text{rev}} < q_{\text{irrev}}$ (d) $\Delta E_{\text{rev}} = \Delta E_{\text{irrev}}$



12. The normal boiling point of a liquid 'X' is 400 K. Which of the following statement is true about the process $X(l) \rightarrow X(g)$?

 - At 400 K and 1 atm pressure $\Delta G = 0$.
 - At 400 K and 2 atm pressure $\Delta G = +$ ve.
 - At 400 K and 0.1 atm pressure $\Delta G = -$ ve.
 - At 410 K and 1 atm pressure $\Delta G = +$ ve.

13. For isothermal expansion in case of an ideal gas :

 - $\Delta H = 0$
 - $\Delta E = 0$
 - $\Delta G = -T \cdot \Delta S$
 - $T_{\text{final}} = T_{\text{initial}}$

14. Which of the following is(are) endothermic reaction?

 - Combustion of methane.
 - Decomposition of water.
 - Dehydrogenation of ethane to ethylene.
 - Conversion of graphite to diamond.

15. Heat of reaction depend upon:

 - Physical state of reactants and products.
 - Whether the reaction is carried out at constant pressure or at constant volume.
 - Method by which the final products are obtained from the reactants.
 - Temperature of the reaction.

16. Which of the following reaction cannot be used to define the heat of formation of $\text{CO}_2(g)$?

 - $\text{CO}(g) + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2(g)$
 - $\text{C}_6\text{H}_6(\ell) + \frac{7}{2}\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 3\text{H}_2\text{O}(\ell)$
 - $\text{C}(\text{diamond}) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g)$
 - $\text{C}(\text{graphite}) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$

17. Heat of formation of CH_4 are:

If given heat:

$$\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) ; \Delta H = -394 \text{ kJ}$$

$$2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(\ell) ; \Delta H = -284 \text{ kJ}$$

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(\ell) ; \Delta H = -892 \text{ kJ}$$
 - 70 kJ
 - 16.7 kcal
 - 244 kJ
 - 50 kcal

18. Heat of neutralization of the acid-base reaction is 57.32 kJ for:

 - $\text{HCOOH} + \text{KOH}$
 - $\text{CH}_3\text{COOH} + \text{NaOH}$
 - $\text{HNO}_3 + \text{LiOH}$
 - $\text{HCl} + \text{NaOH}$

19. For which of the following reaction, $\Delta H_{\text{reaction}}^{\circ}$ is not equal to ΔH_f° of product?

 - $2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$
 - $\text{N}_2(g) + \text{O}_3(g) \rightarrow \text{N}_2\text{O}_3(g)$
 - $\text{CH}_4(g) + 2\text{Cl}_2(g) \rightarrow \text{CH}_2\text{Cl}_2(\ell) + 2\text{HCl}(g)$
 - $\text{Xe}(g) + 2\text{F}_2(g) \rightarrow \text{XeF}_4(g)$

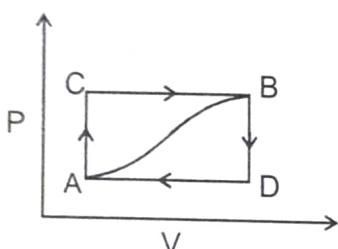
20. Which of the reaction defines molar ΔH_f° ?
- $\text{CaO(s)} + \text{CO}_2(\text{g}) \longrightarrow \text{CaCO}_3(\text{s})$
 - $\frac{1}{2} \text{Br}_2(\ell) + \frac{1}{2} \text{H}_2(\text{g}) \longrightarrow \text{HBr(g)}$
 - $\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{NH}_4 \text{NO}_3(\text{s})$
 - $\frac{1}{2} \text{I}_2(\text{s}) + \frac{1}{2} \text{H}_2(\text{g}) \longrightarrow \text{HI(g)}$

21. If $\Delta H_{f(C_2H_6)}^\circ (\text{g}) = -85 \text{ kJ mol}^{-1}$, $\Delta H_{f(C_3H_8)}^\circ (\text{g}) = -104 \text{ kJ mol}^{-1}$, ΔH° for $\text{C(s)} \rightarrow \text{C(g)}$ is 718 kJ mol^{-1} and heat of formation of H-atom is 218 kJ mol^{-1} , then:

- $\Delta H_{\text{C-C}} = 345 \text{ kJ}$
- $\Delta H_{\text{C-H}} = 414 \text{ kJ}$
- $\Delta H_{\text{H-H}} = 436 \text{ kJ}$
- $\Delta H_{\text{H-H}} = 218 \text{ kJ}$

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 22 to 24): When a system is taken from state A to state B along path ACB as shown in figure below, 80 J of heat flows into the system and the system does 30 J of work.



22. How much heat flows into the system along path ADB if the work done by the system is 10 J?
- 40 J
 - 60 J
 - 80 J
 - 100 J
23. When the system is returned from state B to A along the curved path, the work done on the system is 20 J. Does the system absorb or liberate heat and by how much?
- 70 J; heat is liberated
 - 60 J; heat is liberated
 - +70 J; heat is absorbed
 - +60 J; heat is absorbed.
24. If $E_D - E_A = -40 \text{ J}$, the heat absorbed in the processes AD and DB are respectively:
- $q_{AD} = 30 \text{ J}$ and $q_{DB} = -90 \text{ J}$
 - $q_{AD} = -60 \text{ J}$ and $q_{DB} = 30 \text{ J}$
 - $q_{AD} = 30 \text{ J}$ and $q_{DB} = 90 \text{ J}$
 - $q_{AD} = -30 \text{ J}$ and $q_{DB} = 90 \text{ J}$

Comprehension (Q. 25 to 27): Entropy is a state function and its value depends on two or three variables temperature (T), pressure (P) and volume (V). Entropy change for an ideal gas having number of moles (n) can be determined by the following equation.

$$\Delta S = 2.303 nC_V \log \left(\frac{T_2}{T_1} \right) + 2.303 nR \log \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = 2.303 nC_p \log \left(\frac{T_2}{T_1} \right) + 2.303 nR \log \left(\frac{P_1}{P_2} \right)$$

Since free energy change for a process or a chemical equation is a deciding factor for spontaneity, which can be obtained by using entropy change (ΔS) according to the expression, $\Delta G = \Delta H - T\Delta S$ at a temperature T.

25. What would be the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5 L to a volume of 50 L at 25°C ? [Given $R = 8.3 \text{ J/mole K}$]
- 38.23 J/K
 - 26.76 J/K
 - 20 J/K
 - 28.23 J/K
26. An isobaric process having one mole of an ideal gas has entropy change 23.03 J/K for the temperature range 27°C to 327°C . What would be the molar specific heat capacity (C_V)?
- $\frac{10}{\log 2} \text{ J/K mol}$
 - $\frac{10}{\log 2} - 8.3 \text{ J/K mol}$
 - $10 \times \log 2 \text{ J/K mol}$
 - $10 \log 2 + 8.3 \text{ J/K mol}$
27. For a reaction $\text{M}_2\text{O(s)} \longrightarrow 2\text{M(s)} + \frac{1}{2} \text{O}_2(\text{g})$; $\Delta H = 30 \text{ kJ/mol}$ and $\Delta S = 0.07 \text{ kJ/K-mol}$ at 1 atm. Calculate upto which temperature the reaction would not be spontaneous?
- $T > 428.6 \text{ K}$
 - $T > 300.8 \text{ K}$
 - $T < 300.8 \text{ K}$
 - $T < 428.6 \text{ K}$

Comprehension (Q. 28 to 32): Dependence of spontaneity on temperature :

For a process to be spontaneous, at constant temperature and pressure, there must be decrease in free energy of the system in the direction of the process, i.e. $(\Delta G)_{P,T} < 0$. $(\Delta G)_{P,T} = 0$ implies the equilibrium condition and $(\Delta G)_{P,T} > 0$ corresponds to non-spontaneity.

Gibbs-Helmholtz equation relates the free energy change to the enthalpy and entropy change of the process as :

$$(\Delta G)_{P,T} = \Delta H - T\Delta S \quad \dots(1)$$

The magnitude of ΔH does not change much with the change in temperature but the entropy factor $T\Delta S$ changes appreciably. Thus, spontaneity of a process depends very much on temperature. For endothermic process, both ΔH and ΔS are positive. The energy factor, the first factor of equation, opposes the spontaneity whereas entropy factor favours it. At low temperature, the favourable factor $T\Delta S$ will be small and may be less than ΔH , ΔG will have positive value indicating the non-spontaneity of the process. On raising temperature, the factor $T\Delta S$ increases appreciably and when it exceeds ΔH , ΔG would become negative and the process would be spontaneous.

For an exothermic process, both ΔH and ΔS would be negative. In this case, the first factor of eq. 1 favours the spontaneity whereas the second factor opposes it. At high temperature, when $T\Delta S > \Delta H$,

ΔG will have positive value, showing thereby the non-spontaneity of the process. However, on decreasing temperature, the factor $T\Delta S$ decreases rapidly and when $T\Delta S < \Delta H$, ΔG becomes negative and the process occurs spontaneously. Thus, an exothermic process may be spontaneous at low temperature and non-spontaneous at high temperature.

28. When CaCO_3 is heated to a high temperature, it undergoes decomposition into CaO and CO_2 whereas it is quite stable at room temperature. The most likely explanation of it is:
- The enthalpy of reaction (ΔH) outweighs the term $T\Delta S$ at high temperature.
 - The term $T\Delta S$ outweighs the enthalpy of reaction at high temperature.
 - At high temperature, both enthalpy of reaction and entropy change becomes negative.
 - None of these.

29. For the reaction at 25°C , $\text{X}_2\text{O}_4(\ell) \rightarrow 2\text{XO}_2(\text{g})$
 $\Delta H = 2.1 \text{ kcal}$ and $\Delta S = 20 \text{ cal K}^{-1}$. The reaction would be:

- Spontaneous
- Non-spontaneous
- At equilibrium
- Unpredictable

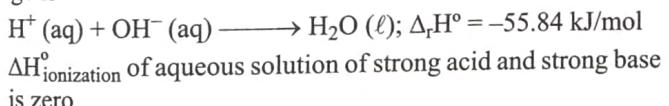
30. For the reaction at 298 K , $2\text{A} + \text{B} \rightarrow \text{C}$
 $\Delta H = 100 \text{ kcal}$ and $\Delta S = 0.050 \text{ kcal K}^{-1}$. If ΔH and ΔS are assumed to be constant over the temperature range, above what temperature will the reaction become spontaneous?
- 1000 K
 - 1500 K
 - 2000 K
 - 2500 K

31. A reaction has a value of $\Delta H = -40 \text{ kcal}$ at 400 K . Above 400 K , the reaction is spontaneous, below this temperature, it is not. The values of ΔG and ΔS at 400 K are respectively.
- $0, -0.1 \text{ cal K}^{-1}$
 - $0, 100 \text{ cal K}^{-1}$
 - $-10 \text{ kcal}, -100 \text{ cal K}^{-1}$
 - $0, -100 \text{ cal K}^{-1}$

32. The enthalpy change for a certain reaction at 300 K is $-15.0 \text{ kcal mol}^{-1}$. The entropy change under these conditions is $-7.2 \text{ cal K}^{-1} \text{ mol}^{-1}$. The free energy change for the reaction and its spontaneous/non-spontaneous character will be
- $-12.84 \text{ kcal mol}^{-1}$, spontaneous
 - $12.84 \text{ kcal mol}^{-1}$, non-spontaneous
 - $-17.16 \text{ kcal rnol}^{-1}$, spontaneous
 - None of these

Comprehension (Q. 33 to 35): Enthalpy of neutralization is defined as the enthalpy change when 1 mole of an acid/a base is completely neutralized by a base/an acid in dilute solution.

For strong acid and strong base, neutralizations net chemical change is



When a dilute solution of a weak acid or base is neutralized, the enthalpy of neutralization is some what less because of the absorption of heat in the ionization of the weak acid or weak base, for a weak acid/weak base

$$\Delta H_{\text{neutralization}}^\circ = \Delta H_{\text{ionization}}^\circ + \Delta_f H^\circ (\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O})$$

33. If enthalpy of neutralization of CH_3COOH by NaOH is -49.86 kJ/mol , then enthalpy of ionization of CH_3COOH is:
- 5.98 kJ/mol
 - 5.98 kJ/mol
 - 105.7 kJ/mol
 - None of these
34. What is ΔH° for complete neutralization of strong diacidic base $\text{A}(\text{OH})_2$ by HNO_3 ?
- 55.84 kJ
 - 111.68 kJ
 - 55.84 kJ/mol
 - None of these
35. Under the same condition, how many mL of 0.1 M NaOH and 0.05 M H_2A (strong diprotic acid) solution should be mixed for a total volume of 100 mL to produce the highest rise in temperature :
- 25 : 75
 - 50 : 50
 - 75 : 25
 - 66.66 : 33.33

MATCH THE COLUMN TYPE QUESTIONS

36. Match Column-I with Column-II.

| | Column-I | | Column-II |
|----|--|----|--|
| A. | Reversible isothermal expansion of an ideal gas. | p. | $w = -2.303 nRT \log \left(\frac{V_2}{V_1} \right)$ |
| B. | Reversible adiabatic compression of an ideal gas. | q. | $PV^\gamma = \text{constant}$ |
| C. | Irreversible adiabatic expansion of an ideal gas. | r. | $w = \frac{nR}{(\gamma-1)} (T_2 - T_1)$ |
| D. | Irreversible isothermal compression of an ideal gas. | s. | $\Delta H = 0$ |

- A-(p, s); B-(q, r); C-(r); D-(s)
- A-(p); B-(r); C-(p, r); D-(s, q)
- A-(p, q); B-(p, s); C-(r); D-(s)
- A-(s); B-(p, r); C-(p, r); D-(q, p)

37. Match Column-I with Column-II.

| | Column-I | | Column-II |
|----|---|----|------------------------------|
| A. | A process carried out infinitesimally slowly. | p. | Adiabatic |
| B. | A process in which no heat enters or leaves the system. | q. | $\Delta E = 0, \Delta H = 0$ |
| C. | A process carried out at constant temperature. | r. | Reversible |
| D. | Cyclic process. | s. | Isothermal |

- A-(p); B-(s); C-(r); D-(q)
- A-(r); B-(p); C-(s); D-(q)
- A-(s); B-(r); C-(q); D-(s)
- A-(p); B-(q); C-(r); D-(s)

38. Match Column-I with Column-II

| Column-I | | Column-II | |
|----------|--|-----------|------------------------------------|
| A. | $(\Delta G_{\text{system}})_{T,P} = 0$ | p. | Process is in equilibrium |
| B. | $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ | q. | Process is > 0 , non-spontaneous |
| C. | $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ | r. | Process is < 0 , spontaneous |
| D. | $(\Delta G_{\text{system}})_{T,P} > 0$ | s. | System is unable to do useful work |

- (a) A-(q, s); B-(r); C-(p, s); D-(q, s)
- (b) A-(q, s); B-(r); C-(q, s); D-(p, s)
- (c) A-(p, s); B-(r); C-(q, s); D-(q, s)
- (d) A-(p, s); B-(s); C-(r); D-(q, s)

39. Match Column-I with Column-II.

| Column-I | | Column-II | |
|----------|---|-----------|---|
| A. | Reversible adiabatic | p. | $\Delta S_{\text{system}} > 0$ compression |
| B. | Reversible vaporisation of liquid | q. | $\Delta S_{\text{system}} < 0$ |
| C. | $2N(g) \longrightarrow N_2(g)$ | r. | $\Delta S_{\text{surrounding}} < 0$ |
| D. | $MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$ | s. | $\Delta S_{\text{surrounding}} = 0$ |

- (a) A-(s); B-(p, r); C-(q); D-(p, r)
- (b) A-(q); B-(p, r); C-(s); D-(p, r)
- (c) A-(s); B-(q, r); C-(q); D-(p)
- (d) A-(s); B-(p, r); C-(q); D-(p, s)

40. Match Column-I with Column-II.

| Column-I | | Column-II | |
|----------|--|-----------|---------------------------------------|
| A. | $C(s, \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$ | p. | $\Delta H^\circ_{\text{combustion}}$ |
| B. | $C(s, \text{graphite}) \longrightarrow C(g)$ | q. | $\Delta H^\circ_{\text{formation}}$ |
| C. | $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ | r. | $\Delta H^\circ_{\text{atomization}}$ |
| D. | $CH_4(g) \longrightarrow C(g) + 4H(g)$ | s. | $\Delta H^\circ_{\text{sublimation}}$ |

- (a) A-(q, r, s); B-(p, r, s); C-(p, q); D-(r)
- (b) A-(r, s); B-(q, r, s); C-(p); D-(p, s)
- (c) A-(p); B-(q, s); C-(p, q, r); D-(r)
- (d) A-(p, q); B-(q, r, s); C-(p); D-(r)

NUMERICAL TYPE QUESTIONS

41. How many statements are false?

- (i) Thermodynamics is concerned with total energy of the system.

- (ii) 1st law of thermodynamics can be applied on the individual particle enclosed in vessel.
- (iii) Many thermodynamic properties can not be measured absolutely, so change in thermodynamic property is required for calculation.
- (iv) Feasibility of any chemical reaction can not be explained by thermodynamics.
- (v) When surrounding is always in equilibrium with the system, the process called reversible.
- (vi) Thermodynamics predict the time to attain the equilibrium.

42. How many of the following physical properties are extensive?

- | | |
|-------------------------------|-------------------------------|
| (i) Free energy | (ii) Vapour pressure |
| (iii) Mole | (iv) Kinetic energy |
| (v) Entropy | (vi) Internal energy |
| (vii) Enthalpy | (viii) Specific heat capacity |
| (ix) Coefficient of viscosity | (x) Total heat capacity |

43. How many of the following are state function?

- | | |
|-----------------------------|-------------------------|
| (i) Internal energy | (ii) Heat |
| (iii) Enthalpy | (iv) Entropy |
| (v) Pressure | (vi) Temperature |
| (vii) Volume | (viii) Work |
| (ix) Specific heat capacity | (x) Molar heat capacity |

44. Two molar of He gas ($\gamma = 5/3$) is initially at temp 27°C and occupy a volume of 20 litres. The gas is first expanded at constant pressure until its volume is doubled, then it undergoes a reversible adiabatic change, until the volume become 110 lit, then predict the value of $T/100$ (where T is the final temperature, $\left(\frac{4}{11}\right)^{2/3} = \frac{1}{2}$)

45. A sample of an ideal gas is expanded from 1dm^3 to 3 dm^3 in a reversible process for which $P = KV^3$, with $K = 1/5$ (atm/dm^3), what is work done by gas (in L atm)?

46. The valve on a cylinder containing initially 1 liter of an ideal gas at 7 atm and 25°C is opened to the atmosphere, whose pressure is 760 torr and the temperature is 25°C . Assuming that the process is isothermal, how much work (in L atm) is done on the atmosphere by the action of expansion?

47. A system is provided 50 joule of heat and the change in internal energy during the process is 60 J. Magnitude of work done on the system is _____.

48. A system works in a cyclic process. It absorbs 20 calories of heat and rejects 60 J of heat during the process. The magnitude of work done (J) is [1 calorie = 4.2 J].

49. The work done in an adiabatic compression of 2 mole of an ideal monoatomic gas by constant external pressure of 2 atm starting from intial pressure of 1 atm and initial temperature of 30 K ($R = 2 \text{ cal/mol-degree}$), is _____.

50. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) \rightarrow (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta U = 30.0 \text{ L. atm}$. Calculate change in enthalpy of the process in L. atm.

51. For the reaction at 298 K

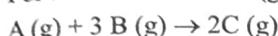


If $\Delta H^\circ = -29.8 \text{ Kcal}$ and $\Delta S^\circ = -0.1 \text{ Kcal K}^{-1}$ then calculate equilibrium constant (K):

52. One mole of an ideal gas is expanded isothermally at 300 K until its volume is tripled. Find the values of ΔS_{total} under the condition.

Expansion is carried out irreversibly where 900 J of heat is less absorbed than expansion is carried out reversibly. (Approximate integer value, Used $e^{1.09} = 3$ & $8.314 \times 1.09 = 9$)

53. For the formation of C (g) at 300 K.



Calculate the magnitude of ΔG° (kcal) if given data:

| | A | B | C |
|---|----|----|-----|
| $\Delta H_f^\circ (\text{kcal mol}^{-1})$ | 0 | 0 | -10 |
| $\Delta S_f^\circ (\text{cal K}^{-1} \text{ mol}^{-1})$ | 40 | 30 | 45 |

54. The entropies of $H_2(g)$ and $H(g)$ are 60 and $50 \text{ J mole}^{-1} \text{ K}^{-1}$ respectively at 300 K. Using the data given below calculate the bond enthalpy of $H_2(g)$ in kcal mole $^{-1}$.



55. Calculate the magnitude of standard entropy change for reaction $X \rightleftharpoons{} Y$, if $\Delta H^\circ = 25 \text{ kJ}$ and $K_{\text{eq}} = 10^{-7}$ at 300 K.

56. For the reaction $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightarrow NH_3(g)$; $\Delta H = -30 \text{ kJ}$ to be at equilibrium at 477°C. If standard entropy of $N_2(g)$ and $NH_3(g)$ are 60 and $50 \text{ J mole}^{-1} \text{ K}^{-1}$ respectively, then calculate the standard entropy of $H_2(g)$ in $\text{J mole}^{-1} \text{ K}^{-1}$.

57. The enthalpy of combustion at 25°C of $H_2(g)$, cyclohexane and cyclohexene are -241 , -3920 and $-3717 \text{ kJ mole}^{-1}$ respectively. The heat of hydrogenation of cyclohexene is (Kcal/mole) approximate integer:

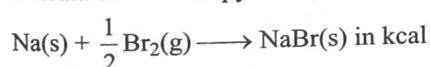
58. When 0.36 g of glucose was burned in a bomb calorimeter (Heat capacity 600 J K^{-1}) the temperature rise by 10 K. Calculate the standard molar enthalpy of combustion (MJ/mole).

59. For reduction of ferric oxide by hydrogen, $Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$;

$\Delta H_{300}^\circ = -26.72 \text{ kJ}$. The reaction was found to be too exothermic. To be convenient, it is desirable that ΔH° should be at the most -26 kJ . At what temperature difference it is possible?

$C_P[Fe_2O_3] = 105$, $C_P[Fe(s)] = 25$, $C_P[H_2O(l)] = 75$, $C_P[H_2(g)] = 30$ (all are in J/mol)

60. Calculate the enthalpy change of 1 mole of reaction:



Given: $\Delta H_{\text{sub}}(Na) = 137 \text{ kJ mole}^{-1}$;

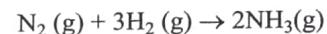
$$\begin{aligned}\Delta H_{\text{bond dissociation}}(Br_2(g)) &= 144 \text{ kJ mole}^{-1} \\ \Delta H_{\text{1st ionisation}}(Na(g)) &= 496 \text{ kJ mole}^{-1}; \\ \Delta H_{\text{1st electron affinity}}(Br(g)) &= -325 \text{ kJ mole}^{-1} \\ \Delta H_{\text{lattice energy}}(NaBr) &= +742\end{aligned}$$

61. How many of the following have standard heat of formation is zero?

- | | |
|--------------------------------|--------------------------|
| (i) $Br_2(l)$ | (ii) $CO_2(g)$ |
| (iii) $C_{(\text{graphite})}$ | (iv) $Cl_2(l)$ |
| (v) $Cl_2(g)$ | (vi) $F_2(g)$ |
| (vii) $F(g)$ | (viii) $I_2(g)$ |
| (ix) $S_{(\text{monoclinic})}$ | (x) $N_2(g)$ |
| (xi) $P_{(\text{Black})}$ | (xii) $P_{(\text{red})}$ |
| (xiii) CH_4 | |

62. Standard enthalpy of combustion of cyclopropane is -2091 kJ/mole at 25°C , then calculate the enthalpy of formation of cyclopropane. If $\Delta H_f^\circ(CO_2) = -393.5 \text{ kJ/mole}$ and $\Delta H_f^\circ(H_2O) = -285.8 \text{ kJ/mole}$.

63. The reaction of nitrogen with hydrogen to make ammonia has $\Delta H = -92 \text{ kJ}$.



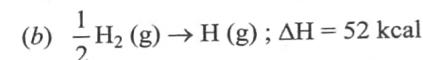
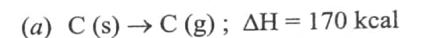
What is the value of ΔU (in kJ) if the reaction is correct out at a constant pressure of 40 bar and the volume change is -1.25 litre ?

64. Calculate ΔU of reaction for the hydrogenation of acetylene at constant volume and at 77°C .

Given that $-\Delta H_f^\circ(H_2O) = -678 \text{ kcal mole}$; $\Delta H_{\text{comb}}(C_2H_2) = -310.1 \text{ kcal/mole}$

$$\Delta H_{\text{comb}}(C_2H_4) = -337.2 \text{ kcal/mole}$$

65. Calculate the C-C bond enthalpy from the following data:



(c) Heat of formation of ethane = -20 kcal

(d) C-H bond enthalpy = 99 kcal .

66. Pressure over 1000 mL of a liquid is gradually increased from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate ΔU and ΔH of the process, assuming linear variation of volume with pressure.

67. At 500 kilobar pressure, density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature 'T'. Find the value $|\Delta H - \Delta U|$ (kJ/mole) for the conversion of 1 mole of graphite to 1 mole of diamond at temperature 'T':

68. 2 mole of ideal monoatomic gas was subjected to reversible adiabatic compression from initial state of $P = 1 \text{ atm}$ and $T = 300 \text{ K}$ till the pressure is $4\sqrt{2} \text{ atm}$ and temperature is $T \text{ K}$. The gas is then subjected to reversible isothermal expansion at $T \text{ K}$ till the internal pressure is one atm. The gas is now isobarically cooled to attain initial state. Find W_{Net} (in calorie) for whole process.
[Use $In 2 = 0.7$, $R = 2 \text{ cal/K-mol}$]

69. One mole of an ideal gas at 300 K is heated at constant volume (V_1) until its temperature is doubled, then it is subjected to isothermal reversible expansion till it reaches the original pressure. Finally the gas is cooled at constant pressure till system reached to the half of original volume ($V_1/2$). Determine total work done ($|w|$) in cal.

[Use : $\ln 2 = 0.70$; $R = 2 \text{ Cal/K. mol.}$]

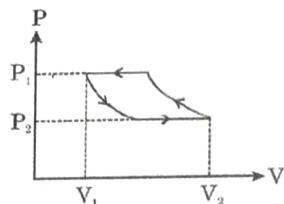
70. How many times volume of diatomic gas should be expanded reversibly & adiabatically in order to reduce its r.m.s velocity to half.

71. 0.5 mole each of two ideal gases A ($C_v = \frac{3}{2} R$) and B ($C_v = \frac{5}{2} R$) are taken in a container and expanded reversing and adiabatically from $V=1 \text{ L}$ to $V=4 \text{ L}$ starting from initial temperature $T = 300 \text{ K}$. Find $|\Delta H|$ for the process (in cal/mol).

72. An ideal gas is carried through a thermodynamic cycle.

$$P_1 = 2 \text{ bar}, V_1 = \frac{1}{\ln 10} \text{ litre}$$

$$P_2 = 2 \text{ bar}, V_2 = \frac{8}{\ln 10} \text{ litre}$$



Consisting of two isobaric and two isothermal processes. Calculate the net work in the entire cycle in litre bar. ($\log_{10} 2 = 0.3$).

73. The K_p for reaction $A + B \rightleftharpoons C + D$ is 2.0 at 27°C and 8.0 at 127°C . Determine the standard free energy change of this reaction at each temperature and ΔH° for the reaction over this range of temperature ($\ln 2 = 0.7$)?

74. Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure (1 atm) always remains constant, then calculate total entropy change ($\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$) for given process.

75. $2\text{A(s)} \rightleftharpoons \text{B(g)} + 2\text{C(g)} + 3\text{D(g)}$

Total pressure developed in a closed container by decomposition of A at equilibrium is 12 bar at 727°C . Calculate $|\Delta G^\circ|$ (in kcal) of the reaction at 727°C ($R = 2 \text{ cal/mole-K}$, $\ln 2 = 0.7$, $\ln 3 = 1.1$).

76. Oxygen is heated from 300 to 600 K at a constant pressure of 1 bar. What is the increase in molar entropy? The molar

heat capacity (in $\text{J K}^{-1} \text{ mol}^{-1}$) for the O_2 is $C_{\text{p,m}} = 10 + 10^{-2}T$
(Given : $\ln 2 = 0.7$)

77. For a reaction : $2\text{A(s)} + \text{B(g)} \longrightarrow 3\text{C(l)}$, standard entropy change of reaction is -2 kJ/mol-K and standard enthalpy of combustion of A(s), B(g) and C(l) are -100 , -60 , -285 kJ/mol respectively, then find the maximum useful work that can be obtained at 27°C and 1 bar pressure from the reaction (in kJ/mol).

78. The enthalpy of formation of $\text{C}_2\text{H}_5\text{OH(l)}$ is -66 kcal/mol . The enthalpy of combustion of $\text{CH}_3-\text{O}-\text{CH}_3$ is -348 kcal/mol . Given that the enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O(l)}$ are -94 kcal/mol & -68 kcal/mol respectively, calculate ΔH for the isomerisation of ethanol to methoxy methane. All data are at 25°C .

79. Calculate the bond enthalpy of the O-H bond in water at 298K using the data/information given below:

$$(a) \Delta_f H^\circ[\text{H(g)}] = 218 \text{ kJ/mol}$$

$$(b) \Delta_f H^\circ[\text{Og}] = 249.2 \text{ kJ/mol}$$

$$(c) \Delta_f H^\circ[\text{H}_2\text{O(g)}] = -241.8 \text{ kJ/mol}$$

The bond enthalpy of the O-H bond in water is defined as one-half of the enthalpy change for the reaction $\text{H}_2\text{O(g)} \rightarrow 2\text{H(g)} + \text{O(g)}$.

Also, determine the ΔU of the O-H bond in water at 298 K. Assume ideal gas behaviour. Given: $(8.314 \times 0.298 = 2.5)$

80. (i) From the following data:

Enthalpy of formation of $\text{C}_2\text{H}_6 = -83 \text{ kJ/mol}$

Enthalpy of sublimation of graphite = 719 kJ/mol

Enthalpy of bond dissociation of $\text{H}_2 = 435 \text{ kJ/mol}$

C-H bond enthalpy = 414 kJ/mol

Calculate the bond enthalpy of C-C bond.

- (ii) By using data of above question calculate bond enthalpy of $\text{C}\equiv\text{N}$ if enthalpy of formation of $\text{CH}_3\text{CN} = 87 \text{ kJ/mol}$ and enthalpy of bond dissociation of nitrogen = 945 kJ/mol .

81. The enthalpy of formation of ethane(g), ethylene(g) and benzene(g) from the gaseous atoms are -2840 , -2275 and $-5530 \text{ kJ mol}^{-1}$ respectively. Calculate the magnitude of resonance energy of benzene. The bond enthalpy of C-H bond is given as equal to $+ 410 \text{ kJ/mol}$.

82. Calculate the enthalpy of combustion of methyl alcohol (l) at 298 K from the following data:

| | | | | | |
|------|-----|-----|-----|-----|-----|
| Bond | C-H | C-O | O-H | O=O | C=O |
|------|-----|-----|-----|-----|-----|

| | | | | | |
|---------------|-----|-------|-------|-----|-----|
| Bond Enthalpy | 414 | 351.5 | 464.5 | 494 | 711 |
|---------------|-----|-------|-------|-----|-----|

(kJ mol $^{-1}$)

Resonance energy of $\text{CO}_2 = -143 \text{ kJ mol}^{-1}$

Latent heat of vaporisation of methyl alcohol = 35.5 kJ mol^{-1} .

Latent heat of vaporisation of water = 40.6 kJ mol^{-1} .

Exercise-4 (Past Year Questions)

1. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be: ($R = 8.314 \text{ J/mol K}$) ($\ln 7.5 = 2.01$) (2013)

- (a) $q = +208 \text{ J}, w = -208 \text{ J}$
- (b) $q = -208 \text{ J}, w = -208 \text{ J}$
- (c) $q = -208 \text{ J}, w = +208 \text{ J}$
- (d) $q = +208 \text{ J}, w = +208 \text{ J}$

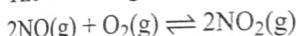
2. For complete combustion of ethanol, $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$, the amount of heat produced as measured in bomb calorimeter, is $1364.47 \text{ kJ mol}^{-1}$ at 25°C . Assuming ideality the enthalpy of combustion, $\Delta_{\text{C}}\text{H}$, for the reaction will be: ($R = 8.314 \text{ kJ mol}^{-1}$) (2014)

- (a) $-1366.95 \text{ kJ mol}^{-1}$
- (b) $-1361.95 \text{ kJ mol}^{-1}$
- (c) $-1460.50 \text{ kJ mol}^{-1}$
- (d) $-1350.50 \text{ kJ mol}^{-1}$

3. The heat of atomisation of methane and ethane are 360 kJ/mol and 620 kJ/mol , respectively. The longest wavelength of light capable of breaking the C–C bond is: (Avogadro number = 6.02×10^{23} , $h = 6.62 \times 10^{-34} \text{ J s}$) (2015)

- (a) $2.48 \times 10^3 \text{ nm}$
- (b) $1.49 \times 10^3 \text{ nm}$
- (c) $2.49 \times 10^4 \text{ nm}$
- (d) $2.48 \times 10^4 \text{ nm}$

4. The following reaction is performed at 298 K



The standard free energy of formation of $\text{NO}(g)$ is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $\text{NO}_2(g)$ at 298 K? ($K_p = 1.6 \times 10^{12}$) (2015)

- (a) $R(298) \ln (1.6 \times 10^{12}) - 86600$
- (b) $86600 + R(298) \ln (1.6 \times 10^{12})$
- (c) $86600 - \frac{\ln (1.6 \times 10^{12})}{R(298)}$
- (d) $0.5 [2 \times 86,600 - R(298) \ln (1.6 \times 10^{12})]$

5. The heats of combustion of carbon and carbon monoxide are -393.5 and $-283.5 \text{ kJ mol}^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is: (2016)

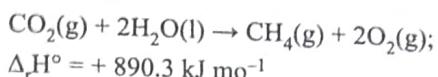
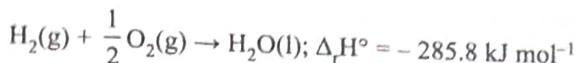
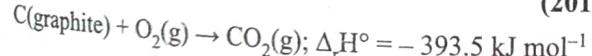
- (a) 676.5
- (b) -676.5
- (c) -110.5
- (d) 110.5

6. The heats of combustion of carbon and carbon monoxide are -393.5 and $-283.5 \text{ kJ mol}^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is: (2016)

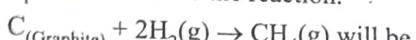
- (a) 676.5
- (b) -676.5
- (c) -110.5
- (d) 110.5

7. Given

(2017)



Based on the above thermochemical equations, the value of $\Delta_f\text{H}^\circ$ at 298 K for the reaction.



- (a) $+74.8 \text{ kJ mol}^{-1}$
- (b) $+144.0 \text{ kJ mol}^{-1}$
- (c) $-74.8 \text{ kJ mol}^{-1}$
- (d) $-144.0 \text{ kJ mol}^{-1}$

8. ΔU is equal to:

(2017)

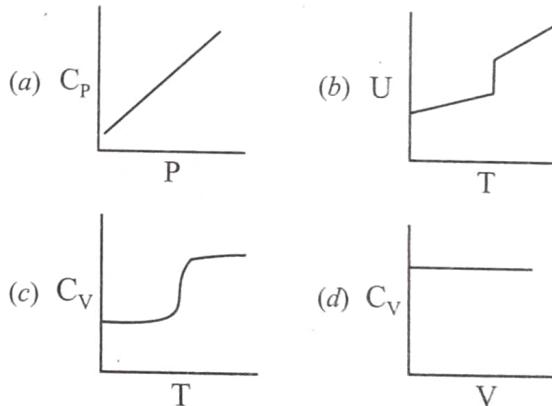
- (a) Isochoric work
- (b) Isobaric work
- (c) Adiabatic work
- (d) Isothermal work

9. The combustion of benzene (*l*) gives $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$. Given that heat of combustion of benzene at constant volume is $-3263.9 \text{ kJ mol}^{-1}$ at 25°C ; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be: ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) (2018)

- (a) -452.46
- (b) 3260
- (c) -3267.6
- (d) 4152.6

10. For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?

(2019)



11. Among the following, the set of parameters that represents path function is:

- (I) $q + w$
- (II) q
- (III) w
- (IV) $H - TS$

(2019)

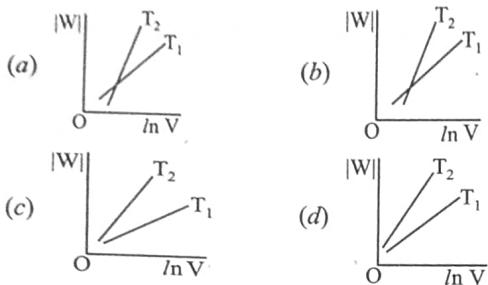
- (a) I and IV
- (b) I, II and III
- (c) II and III
- (d) II, III and IV

12. An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 Nm^{-2} . Heat

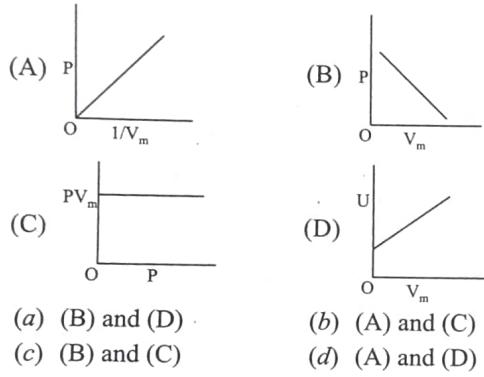
released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is $24 \text{ J mol}^{-1} \text{ K}^{-1}$, the temperature of Al is increased by: (2019)

- (a) $\frac{3}{2} \text{ K}$ (b) 2 K
 (c) $\frac{2}{3} \text{ K}$ (d) 1 K

13. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures. The correct plot is: (2019)



14. The combination of plots which do not represent isothermal expansion of an ideal gas is: (2019)



- (a) (B) and (D)
 (b) (A) and (C)
 (c) (B) and (C)
 (d) (A) and (D)

15. The reaction

$\text{MgO(s)} + \text{C(s)} \rightarrow \text{Mg(s)} + \text{CO(g)}$, for which $\Delta_r H^\circ = +491.1 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 198.0 \text{ JK}^{-1}$ is not feasible at 298 K. Temperature above which reaction will be feasible is: (2019)

- (a) 2040.5 K (b) 1890.0 K
 (c) 2480 K (d) 2380 K

16. Two blocks of the same metal having same mass and at temperature T_1 and T_2 respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS , for this process is: (2019)

- (a) $C_p \ln \left[\frac{(T_1 + T_2)^2}{4T_1 T_2} \right]$ (b) $2C_p \ln \left[\frac{(T_1 + T_2)^{1/2}}{T_1 T_2} \right]$
 (c) $2C_p \ln \left[\frac{(T_1 + T_2)}{4T_1 T_2} \right]$ (d) $2C_p \ln \left[\frac{(T_1 + T_2)}{2T_1 T_2} \right]$

17. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by:

$$\Delta r G^\circ = A - BT$$

Where A and B are non-zero constant. Which of the following is TRUE about this reaction? (2019)

- (a) Endothermic if $A > 0$
 (b) Exothermic if $A > 0$ and $B < 0$
 (c) Endothermic if $A < 0$ and $B > 0$
 (d) Exothermic if $B < 0$

18. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is: (Specific heat of water liquid and water vapours are $4.2 \text{ kJ K}^{-1} \text{ kg}^{-1}$ and $2.0 \text{ kJ K}^{-1} \text{ kg}^{-1}$, heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491 kJ kg^{-1} , respectively) ($\log 273 = 2.436$, $\log 373 = 2.572$, $\log 383 = 2.583$) (2019)

- (a) $7.90 \text{ kJ K}^{-1} \text{ kg}^{-1}$ (b) $2.64 \text{ kJ K}^{-1} \text{ kg}^{-1}$
 (c) $8.49 \text{ kJ K}^{-1} \text{ kg}^{-1}$ (d) $9.26 \text{ kJ K}^{-1} \text{ kg}^{-1}$

19. A process that has $\Delta H = 200 \text{ J mol}^{-1}$ and $\Delta S = 40 \text{ J K}^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous: (2019)

- (a) 20 K (b) 12 K
 (c) 5 K (d) 4 K

20. The process with negative entropy change is: (2019)

- (a) Dissociation of $\text{CaSO}_4(\text{s})$ to $\text{CaO}(\text{s})$ and $\text{SO}_3(\text{g})$.
 (b) Sublimation of dry ice.
 (c) Dissolution of iodine in water.
 (d) Synthesis of ammonia from N_2 and H_2 .

21. For the equilibrium

$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$, the value of ΔG° at 298 K is approximately (2019)

- (a) 100 kJ mol^{-1} (b) -80 kJ mol^{-1}
 (c) 80 kJ mol^{-1} (d) -100 kJ mol^{-1}

22. A process will be spontaneous at all temperatures if: (2019)

- (a) $\Delta H > 0$ and $\Delta S < 0$
 (b) $\Delta H < 0$ and $\Delta S > 0$
 (c) $\Delta H > 0$ and $\Delta S > 0$
 (d) $\Delta H < 0$ and $\Delta S < 0$

23. Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas? (Assume non-expansion work is zero) (2019)

- (a) Cyclic process : $q = -w$
 (b) Isothermal process : $q = -w$
 (c) Adiabatic process : $\Delta U = -w$
 (d) Isochoric process : $\Delta U = -q$

24. For silver, $C_p(\text{JK}^{-1}\text{mol}^{-1}) = 23 + 0.01 T$. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of ΔH will be close to: (2019)

- (a) 21 kJ (b) 16 kJ
 (c) 13 kJ (d) 62 kJ

25. 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_V = 28 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔU and ΔpV for this process. ($R = 8.0 \text{ J K}^{-1} \text{ mol}^{-1}$) (2019)

- (A) $\Delta U = 14 \text{ kJ}$; $\Delta(pV) = 4 \text{ kJ}$
 (B) $\Delta U = 14 \text{ kJ}$; $\Delta(pV) = 18 \text{ kJ}$
 (C) $\Delta U = 2.8 \text{ kJ}$; $\Delta(pV) = 0.8 \text{ kJ}$
 (D) $\Delta U = 14 \text{ kJ}$; $\Delta(pV) = 0.8 \text{ kJ}$

26. During compression of a spring, the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. The change in internal energy, ΔU (in kJ) is: (2019)

- (a) 8 (b) 12
 (c) -12 (d) -8

27. An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is (2019)

- (a) -9.0 (b) +10.0
 (c) -0.9 (d) -2.0

28. For the chemical reaction $X \rightleftharpoons{} Y$, the standard reaction Gibbs energy depends on temperature T (in K) as $\Delta_f G^\circ$ (in kJ mol^{-1}) = $120 - \frac{3}{8}T$. The major component of the reaction mixture at T is: (2019)

- (a) Y if $T = 280 \text{ K}$ (b) Y if $T = 300 \text{ K}$
 (c) X if $T = 315 \text{ K}$ (d) X if $T = 350 \text{ K}$

29. Given:

- (i) $\text{C(graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_f H^\circ = x \text{ kJ mol}^{-1}$
 (ii) $\text{C(graphite)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}; \Delta_f H^\circ = y \text{ kJ mol}^{-1}$
 (iii) $\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_f H^\circ = z \text{ kJ mol}^{-1}$

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct? (2019)

- (a) $x = y + z$ (b) $z = x + y$
 (c) $y = 2z - x$ (d) $x = y - z$

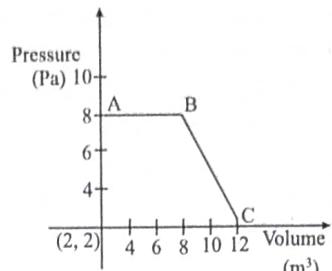
30. Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C . If specific heat of $\text{I}_2(\text{s})$ and $\text{I}_2(\text{vap})$ are 0.055 and $0.031 \text{ cal g}^{-1} \text{ K}^{-1}$ respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is: (2019)

- (a) 2.85 (b) 11.4
 (c) 5.7 (d) 22.8

31. The difference between ΔH and ΔU ($\Delta H - \Delta U$), when the combustion of one mole of heptane (I) is carried out at a temperature T, is equal to (2019)

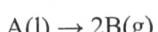
- (a) $3RT$ (b) $-3RT$
 (c) $-4RT$ (d) $4RT$

32. The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is _____. (2020)



33. At constant volume, 4 mol of an ideal gas when heated from 300 K to 500 K changes its internal energy by 5000 J . The molar heat capacity at constant volume is _____. (2020)

34. For the reaction: (2020)



$$\Delta U = 2.1 \text{ kcal}, \Delta S = 20 \text{ cal K}^{-1} \text{ at } 300 \text{ K.}$$

Hence, ΔG in kcal is _____

35. The true statement amongst the following is: (2020)

- (a) Both S and ΔS are not functions of temperature.
 (b) S is not a function of temperature but ΔS is a function of temperature.
 (c) Both ΔS and S are functions of temperature.
 (d) S is a function of temperature but ΔS is not a function of temperature.

36. The standard heat of formation ($\Delta_f H_{298}^\circ$) of ethane (in kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are -1560 , -393.5 and -286 kJ/mol , respectively is _____. (2020)

37. If enthalpy of atomisation for $\text{Br}_2(\text{l})$ is $x \text{ kJ/mol}$ and bond enthalpy for Br_2 is $y \text{ kJ/mol}$, the relation between them is: (2020)

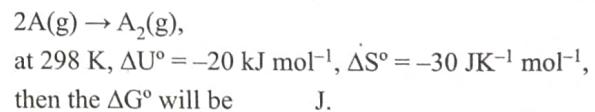
- (a) Is $x = y$ (b) Is $x < y$
 (c) Does not exist (d) Is $x > y$

38. The heat of combustion of ethanol into carbon dioxide and water is -327 kcal at constant pressure. The heat evolved (in cal) at constant volume and 27°C (if all gases behave ideally) is ($R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$) (2020)

39. Lattice enthalpy and enthalpy of solution of NaCl are 788 kJ mol^{-1} and 4 kJ mol^{-1} , respectively. The hydration enthalpy of NaCl is (2020)

- (a) 784 kJ mol^{-1} (b) -780 kJ mol^{-1}
 (c) 780 kJ mol^{-1} (d) -784 kJ mol^{-1}

40. For a dimerization reaction, (2020)



41. The variation of equilibrium constant with temperature is given below: (2020)

| Temperature | Equilibrium Constant |
|----------------------------|----------------------|
| $T_1 = 25^\circ \text{C}$ | $K_1 = 10$ |
| $T_2 = 100^\circ \text{C}$ | $K_2 = 100$ |

- The values of ΔH° , ΔG° at T_1 and ΔG° at T_2 (in kJ mol^{-1}) respectively, are close to [Use $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]
 (a) 28.4, -5.71 and -14.29 (b) 0.64, -7.14 and -5.71
 (c) 28.4, -7.14 and -5.71 (d) 0.64, -5.71 and -14.29
42. The internal energy change (in J) when 90 g of water undergoes complete evaporation at 100°C is _____.
 [To the nearest integer]
 (Given: ΔH_{vap} for water at $373 \text{ K} = 41 \text{ kJ/mol}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) (2020)
43. Five moles of an ideal gas at 1 bar and 298 K is expanded into vacuum to double the volume. The work done is: (2020)
 (a) Zero (b) $-RT \ln V_2/V_1$
 (c) $C_V(T_2 - T_1)$ (d) $-RT(T_2 - T_1)$
44. For one mole of an ideal gas, which of these statements must be true? (2020)
 (A) U and H each depends only on temperature
 (B) Compressibility factor Z is not equal to 1
 (C) $C_{P,m} - C_{V,m} = R$
 (D) $dU = C_V dT$ for any process
 (a) (A) and (C) (b) (A), (C) and (D)
 (c) (B), (C) and (D) (d) (C) and (D)
45. Five moles of an ideal gas at 293 K is expanded isothermally from an initial pressure of 2.1 MPa to 1.3 MPa against a constant external pressure 4.3 MPa . The heat transferred in this process is ____ kJ mol^{-1} . (Use $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) (2021)
46. A system does 200 J of work and at the same time absorbs 150 J of heat. The magnitude of the change in internal energy is ____ J . (2021)
47. For water at 100°C and 1 bar (2021)
 $\Delta_{\text{vap}} H - \Delta_{\text{vap}} U = \text{_____} \times 10^2 \text{ J mol}^{-1}$.
 [Use: $R : 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$]
 [Assume volume of $\text{H}_2\text{O}(l)$ is much smaller than volume $\text{H}_2\text{O}(g)$. Assume $\text{H}_2\text{O}(g)$ can be treated as an ideal gas]
48. The reaction of cyanamide, $\text{NH}_2\text{CN}_{(s)}$ with oxygen was run in a bomb calorimeter and ΔU was found to be $-742.24 \text{ kJ mol}^{-1}$ at 298 K . The magnitude of ΔH_{298} for the reaction:

$$\text{NH}_2\text{CN}_{(s)} + \frac{3}{2} \text{O}_2(g) \rightarrow \text{N}_2(g) + \text{O}_2(g) + \text{H}_2\text{O}(l)$$
 is ____ kJ . (Rounded off to the nearest integer)
 [Assume ideal gases and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$] (2021)
49. At 25°C , 50 g of iron reacts with HCl to form FeCl_2 . The evolved hydrogen gas expands against a constant pressure of 1 bar. The work done by the gas during this expansion is ____ J .
 (Round off to the nearest integer)
 [Given : $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. Assume, hydrogen is an ideal gas]
 [Atomic mass of Fe is 55.85 u] (2021)
50. At 298 K , the enthalpy of fusion of a solid (X) is 2.8 kJ mol^{-1} and the enthalpy of vaporisation of the liquid (X) is 98.2 kJ mol^{-1} . The enthalpy of sublimation of the substance (X) in kJ mol^{-1} is _____. (2021)
51. For a chemical reaction $A + B \rightleftharpoons C + D$ ($\Delta H^\circ = 80 \text{ kJ mol}^{-1}$) the entropy change $\Delta_r S^\circ$ depends on the temperature T (in K) as $\Delta_r S^\circ = 2T(\text{J K}^{-1} \text{ mol}^{-1})$. Minimum temperature at which it will become spontaneous is ____ K . (2021)
52. The incorrect match in the following is:
 (a) $\Delta G^\circ > 0, K < 1$ (b) $\Delta G^\circ < 0, K < 1$
 (c) $\Delta G^\circ = 0, K = 1$ (d) $\Delta G^\circ < 0, K > 1$
53. For the reactions $A_{(g)} \rightarrow B_{(g)}$, the value of the equilibrium constant at 300 K and 1 atm is equal to 100.0. The value of $\Delta_f G$ for the reaction at 300 K and 1 atm in J mol^{-1} is $-xR$ where x is: (2021)
54. For a given chemical reaction $A \rightarrow B$ at 300 K , the free energy change is $-49.4 \text{ kJ mol}^{-1}$ and the enthalpy of reaction is 51.4 kJ mol^{-1} . The entropy change of the reaction is ____ $\text{J K}^{-1} \text{ mol}^{-1}$. (2021)
55. For the reaction, $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$, when $\Delta H = -57.8 \text{ kJ mol}^{-1}$, $\Delta S = -176.0 \text{ J K}^{-1}$, the magnitude of ΔG at 298 K for the reaction is kJ mol^{-1} . (Nearest integer) (2021)
56. Data given for the following reaction is as follows:

$$\text{FeO}_{(s)} + \text{C}_{(\text{graphite})} \rightarrow \text{Fe}_{(s)} + \text{CO}_{(g)}$$

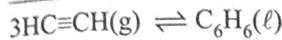
 The minimum temperature in K at which the reaction becomes spontaneous is (Integer answer) _____. (2021)
57. The incorrect expression among the following is: (2021)
 (a) For isothermal process $w_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$
 (b) $\frac{\Delta G_{\text{system}}}{\Delta G_{\text{total}}} = -T_{(\text{at constant P})}$
 (c) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$
 (d) $K = e^{-\Delta G^\circ/RT}$
58. During which of the following processes, does entropy decrease? (2021)
 (I) Freezing of water to ice at 0°C
 (II) Freezing of water to ice at -10°C
 (III) $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$
 (IV) Adsorption of $\text{CO}(g)$ on lead surface
 (V) Dissolution of NaCl in water
 (a) (I), (II), (III) and (IV) only
 (b) (II) and (III) only
 (c) (I) and (III) only
 (d) (I), (III) and (V) only
59. Data given for the following reaction is as follows: (2021)

$$\text{FeO}_{(s)} + \text{C}_{(\text{graphite})} \longrightarrow \text{Fe}_{(s)} + \text{CO}_{(g)}$$

| Substance | $\Delta_f H^\circ \text{ (kJ mol}^{-1}\text{)}$ | $\Delta S^\circ \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$ |
|-------------------------|---|---|
| $\text{FeO}_{(s)}$ | - 266.3 | 57.49 |
| $C_{(\text{graphite})}$ | 0 | 5.74 |
| $\text{Fe}_{(s)}$ | 0 | 27.28 |
| $\text{CO}_{(g)}$ | - 110.5 | 197.6 |

The minimum temperature in K at which the reaction becomes spontaneous is _____. (Integer answer)

60. Assuming ideal behaviour, the magnitude of $\log K$ for the following reaction at 25°C is $x \times 10^{-1}$. The value of x is _____. (2021)



[Given: $\Delta_f G^\circ(\text{HC}\equiv\text{CH}) = -2.04 \times 10^5 \text{ J mol}^{-1}$; $\Delta_f G^\circ(\text{C}_6\text{H}_6) = -1.24 \times 10^5 \text{ J mol}^{-1}$; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]

61. The average S–F bond energy in kJ mol^{-1} of SF_6 is _____. (Rounded off to the nearest integer)

[Given : The values of standard enthalpy of formation of $\text{SF}_6(\text{g})$, $\text{S}(\text{g})$ and $\text{F}(\text{g})$ are - 1100, 275 and 80 kJ mol^{-1} respectively.] (2021)

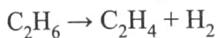
62. For a given chemical reaction $A \rightarrow B$ at 300 K, the free energy change is $-49.4 \text{ kJ mol}^{-1}$ and the enthalpy of reaction is 51.4 kJ mol^{-1} . The entropy change of the reaction is _____. $\text{J K}^{-1} \text{ mol}^{-1}$. (2021)

63. The standard enthalpies of formation of Al_2O_3 and CaO are $-1675 \text{ kJ mol}^{-1}$ and -635 kJ mol^{-1} respectively.

For the reaction $3\text{CaO} + 2\text{Al} \rightarrow 3\text{Ca} + \text{Al}_2\text{O}_3$, the standard reaction enthalpy $\Delta rH^\circ =$ _____. kJ. (2021)

64. If the standard molar enthalpy change for combustion of graphite powder is $-2.48 \times 10^2 \text{ kJ mol}^{-1}$, the amount of heat generated on combustion of 1 g of graphite powder is _____. kJ. (2021)

65. For the reaction



the reaction enthalpy $\Delta rH =$ _____. kJ mol^{-1} .

[Given: Bond enthalpies in kJ mol^{-1} : C–C : 347, C=C : 611; C–H : 414, H–H : 436] (2021)

66. For the reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$, when $\Delta S = -176.0 \text{ J K}^{-1}$ and $\Delta H = -57.8 \text{ kJ mol}^{-1}$, the magnitude of ΔG at 298 K for the reaction is _____. kJ mol^{-1} . (2021)

67. 200 mL of 0.2 M HCl is mixed with 300 mL of 0.1 M NaOH . The molar heat of neutralization of this reaction is -57.1 kJ . The increase in temperature in $^\circ\text{C}$ of the system on mixing is $x \times 10^{-2}$. The value of x is _____. (Assume no volume change on mixing) (2021)

[Given: Specific heat of water = $4.18 \text{ J g}^{-1} \text{ K}^{-1}$, Density of water = 1.00 g cm^{-3}] (2021)

68. For water $\Delta_{\text{vap}} H = 41 \text{ kJ mol}^{-1}$ at 373 K and 1 bar pressure. Assuming that water vapour is an ideal gas that occupies a much larger volume than liquid water, the internal energy change during evaporation of water is _____. kJ mol^{-1} [Use : $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$]

69. The ionization enthalpy Na^+ formation from $\text{Na}_{(g)}$ is $495.8 \text{ kJ mol}^{-1}$, while the electron gain enthalpy of Br is $-325.0 \text{ kJ mol}^{-1}$. Given the lattice enthalpy of NaBr is $-728.4 \text{ kJ mol}^{-1}$. The energy for the formation of NaBr ionic solid is $(-)$ _____. $\times 10^{-1} \text{ kJ mol}^{-1}$. (2021)

70. For the reaction $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ the reaction enthalpy $\Delta_f H^\circ =$ _____. kJ mol^{-1} .

[Given: Bond enthalpies in kJ mol^{-1} : C–C : 347, C=C : 611; C–H : 414, H–H : 436] (2021)

71. When 400 mL of 0.2 M H_2SO_4 solution is mixed with 600 mL of 0.1 M NaOH solution, the increase in temperature of the final solution is $\times 10^{-2} \text{ K}$. (2021)

[Use : $\text{H}^+(\text{aq}) + \text{OH}^- \rightarrow \text{H}_2\text{O}; \Delta H = -57.1 \text{ kJ mol}^{-1}$

Specific heat of $\text{H}_2\text{O} = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$

Density of $\text{H}_2\text{O} = 1.0 \text{ g cm}^{-3}$

Assume no. change in volume of solution on mixing.

72. The Born-Haber cycle for KCl is evaluated with the following data: (2021)

$\Delta_f H^\circ$ For $\text{KCl} = -436.7 \text{ kJ mol}^{-1}$; $\Delta_{\text{sub}} H^\circ$ for $\text{K} = 89.2 \text{ kJ mol}^{-1}$

$\Delta_{\text{ionization}} H^\circ$ for $\text{K} = 419 \text{ kJ mol}^{-1}$; $\Delta_{\text{electron gain}} H^\circ$ for $\text{Cl}(\text{g}) = -348.6 \text{ kJ mol}^{-1}$

$\Delta_{\text{bond}} H^\circ$ for $\text{Cl}_2 = 243.0 \text{ kJ mol}^{-1}$

The magnitude of lattice enthalpy of KCl in kJ mol^{-1} is _____. (2021)

73. For water $\Delta_{\text{vap}} H = 41 \text{ kJ mol}^{-1}$ at 373 K and 1 bar pressure vapour that occupies a much larger volume than liquid water, the internal energy changing during evaporation of water is _____. kJ mol^{-1} [Use : $R = 8.3 \text{ mol}^{-1} \text{ K}^{-1}$] (2021)

74. An average person needs about 10000 kJ energy per day. The amount of glucose (molar mass = 180.0 g mol^{-1}) needed to meet this energy requirement is _____. g. (Use : $\Delta_c H(\text{glucose}) = -2700 \text{ kJ mol}^{-1}$) (2021)

75. Match List-I with List-II.

| List-I | | List-II | |
|--------|--|---------|--|
| A. | Spontaneous process | p. | $\Delta H < 0$ |
| B. | Process with $\Delta P = 0$, $\Delta T = 0$ | q. | $\Delta G_{T,P} < 0$ |
| C. | $\Delta H_{\text{reaction}}$ | r. | Isothermal and isobaric process |
| D. | Exothermic process | s. | [Bond energies of molecules in reactants] - [Bond energies of product molecules] |

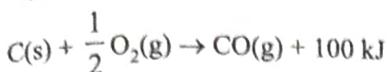
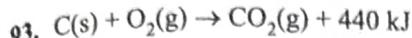
(2022)

Choose the correct answer from the options given below:

- (a) A-(r), B-(q), C-(s), D-(p)
 (b) A-(q), B-(r), C-(s), D-(p)
 (c) A-(q), B-(r), C-(p), D-(s)
 (d) A-(q), B-(p), C-(r), D-(s)

76. The standard entropy change for the reaction $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$ is -550 J K^{-1} at 298 K. [Given: The standard enthalpy change for the reaction is -165 kJ mol^{-1} . The temperature in K at which the reaction attains equilibrium is _____.] (2022)
77. Which of the following relation is not correct? (2022)
- $\Delta H = \Delta U - P\Delta V$
 - $\Delta U = q + W$
 - $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$
 - $\Delta G = \Delta H - T\Delta S$
78. 2.2 g of nitrous oxide (N_2O) gas is cooled at a constant pressure of 1 atm from 310 K to 270 K causing the compression of the gas from 217.1 mL to 167.75 mL. The change in internal energy of the process, ΔU is ' x ' J. The value of ' x ' is _____.
(Given: atomic mass of N = 14 g mol⁻¹ and of O = 16 g mol⁻¹. Molar heat capacity of N_2O is 100 J K⁻¹ mol⁻¹) (2022)
79. 4.0 L of an ideal gas is allowed to expand isothermally into vacuum until the total volume is 20 L. The amount of heat absorbed in this expansion is _____ L atm. (2022)
80. When 5 moles of He gas expand isothermally and reversibly at 300 K from 10 litre to 20 litre, the magnitude of the maximum work obtained is _____. J.
(Given: R = 8.3 J K⁻¹ mol⁻¹ and log 2 = 0.3010) (2022)
81. A fish swimming in water body when taken out from the water body is covered with a film of water of weight 36 g. When it is subjected to cooking at 100°C, then the internal energy for vaporization in kJ mol⁻¹ is _____.
[Assume steam to be an ideal gas. Given $A_{\text{vap}}H^\ominus$ for water at 373 K and 1 bar is 41.1 kJ mol⁻¹; R = 8.31 J K⁻¹ mol⁻¹] (2022)
82. The molar heat capacity for an ideal gas at constant pressure is $20.785 \text{ J K}^{-1} \text{ mol}^{-1}$. The change in internal energy is 5000 J upon heating it from 300 K to 500 K. The number of moles of the gas at constant volume is _____.
(Given: R = 8.314 J K⁻¹ mol⁻¹) (2022)
83. Among the following the number of state variable is _____.
Internal energy (U)
Volume (V)
Heat (q)
Enthalpy (H)
84. For the reaction $\text{H}_2\text{F}_2\text{(g)} \rightarrow \text{H}_2\text{(g)} + \text{F}_2\text{(g)}$ $\Delta U = -59.6 \text{ kJ mol}^{-1}$ at 27°C
The enthalpy change for the above reaction is (-)____ kJ mol⁻¹ [nearest integer] Given : R = 8.314 J K⁻¹ mol⁻¹.

85. At 25°C and 1 atm pressure, the enthalpy of combustion of benzene (*l*) and acetylene (*g*) are $-3268 \text{ kJ mol}^{-1}$ and $-1300 \text{ kJ mol}^{-1}$, respectively. The change in enthalpy for the reaction $3\text{C}_2\text{H}_2\text{(g)} \rightarrow \text{C}_6\text{H}_6\text{(l)}$, is: (2022)
- + 324 kJ mol⁻¹
 - + 632 kJ mol⁻¹
 - 632 kJ mol⁻¹
 - 732 kJ mol⁻¹
86. At 25°C and 1 atm pressure, the enthalpies of combustion are as given below:
- | Substance | H_2 | C(graphite) | $\text{C}_2\text{H}_6\text{(g)}$ |
|--|--------------|-------------|----------------------------------|
| $\Delta_cH^\ominus (\text{kJ mol}^{-1})$ | -286.0 | -394.0 | -1560.0 |
- The enthalpy of formation of ethane is: (2022)
- + 54.0 kJ mol⁻¹
 - 68.0 kJ mol⁻¹
 - 86.0 kJ mol⁻¹
 - + 97.0 kJ mol⁻¹
87. The enthalpy of combustion of propane, graphite and dihydrogen at 298 K are: $-2220.0 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ respectively. The magnitude of enthalpy of formation of propane (C_3H_8) is ____ kJ mol⁻¹. (2022)
88. 17.0 g of NH_3 completely vapourises at -33.42°C and 1 bar pressure and the enthalpy change in the process is 23.4 kJ mol⁻¹. The enthalpy change for the vapourisation of 85 g of NH_3 under the same conditions is ____ kJ. (2022)
89. For combustion of one mole of magnesium in an open container at 300 K and 1 bar pressure, $\Delta_cH^\ominus = -601.70 \text{ kJ mol}^{-1}$, the magnitude of change in internal energy for the reaction is ____ kJ.
(Given: R = 8.3 J K⁻¹ mol⁻¹) (2022)
90. For complete combustion of methanol
- $$\text{CH}_3\text{OH}(l) + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O}(l)$$
- the amount of heat produced as measured by bomb calorimeter is 726 kJ mol⁻¹ at 27°C. The enthalpy of combustion for the reaction is $-x \text{ kJ mol}^{-1}$, where x is _____.
(Given : R = 8.3 J K⁻¹ mol⁻¹) (2022)
91. While performing a thermodynamics experiment, a student made the following observations,
 $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$, $\Delta H = -57.3 \text{ kJ mol}^{-1}$
 $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$
 $\Delta H = -55.3 \text{ kJ mol}^{-1}$.
The enthalpy of ionization of CH_3COOH as calculated by the student is ____ kJ mol⁻¹. (2022)
92. A gas (Molar mass = 280 g mol⁻¹) was burnt in excess O_2 in a constant volume calorimeter and during combustion the temperature of calorimeter increased from 298.0 K to 298.45 K. If the heat capacity of calorimeter is 2.5 kJ K^{-1} and enthalpy of combustion of gas is 9 kJ mol⁻¹, then amount of gas burnt is ____ g. (2022)



When coal of purity 60% is allowed to burn in presence of insufficient oxygen, 60% of carbon is converted into 'CO' and the remaining is converted into 'CO₂'.

The heat generated when 0.6 kg of coal is burnt is _____. (2022)

- (a) 1600 kJ (b) 3200 kJ
 (c) 4400 kJ (d) 6600 kJ

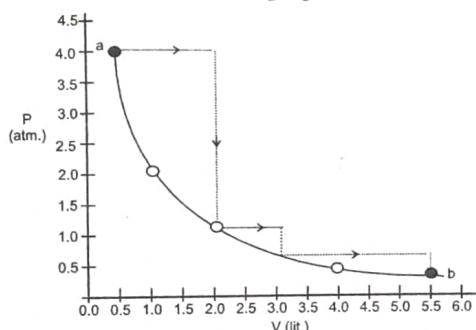
94. When 600 mL of 0.2 M HNO₃ is mixed with 400 mL of 0.1 M NaOH solution in a flask, the rise in temperature of the flask is $x \times 10^{-2} \text{ }^{\circ}\text{C}$. The value of x is _____. (Enthalpy of neutralisation = 57 kJ mol⁻¹ and Specific heat of water = 4.2 J K⁻¹ g⁻¹) (Neglect heat capacity of flask) (2022)

95. 2.4 g coal is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atm pressure.

The temperature of the calorimeter rises from 298 K to 300 K. The enthalpy change during the combustion of coal is $-x \text{ kJ mol}^{-1}$. The value of x is _____. (Given : Heat capacity of bomb calorimeter 20.0 kJ K⁻¹. Assume coal to be pure carbon) (2022)

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96. One mole of an ideal gas is taken from a and b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d , then the integer closest to the ratio w_d/w_s is: (2010)



97. Match the transformation in column-I with appropriate options in column-II. (2011)

| Column-I | | Column-II | |
|----------|---|-----------|------------------------|
| A. | $CO_2(s) \rightarrow CO_2(g)$ | p. | phase transition |
| B. | $CaCO_3(s) \rightarrow CaO(s) (q) + CO_2(g)$ | q. | allotropic change |
| C. | $2H \rightarrow H_2$ | r. | ΔH is positive |
| D. | $P_{(white, solid)} \rightarrow P_{(red, solid)}$ | s. | ΔS is positive |
| | | t. | ΔS is negative |

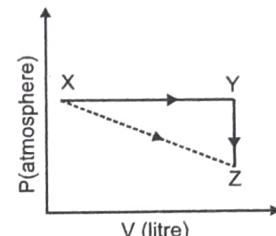
(a) A (p, r, s); B-(r, s); C-(t); D-(p, q, t)

(b) A (r, s); B-(p, r, s); C-(p, q, t); D-(t)

(c) A (t); B-(r, s); C-(p, r, s); D-(p, q, t)

(d) A (p, r); B-(r, s, t); C-(t); D-(p, q, t)

98. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [take ΔS as change in entropy and w as work done]. (2012)



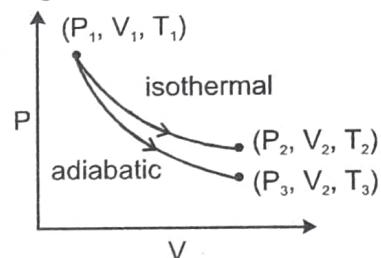
(a) $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$

(b) $w_{x \rightarrow z} = w_{x \rightarrow y} + w_{y \rightarrow z}$

(c) $w_{x \rightarrow y \rightarrow z} = w_{x \rightarrow y}$

(d) $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$

99. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct? (2012)



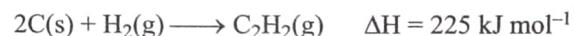
(a) $T_1 = T_2$

(b) $T_3 > T_1$

(c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$

(d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

100. Using the data provided, calculate the multiple bond energy (kJ mol⁻¹) of a C≡C bond C₂H₂. That energy is (take the bond energy of a C-H bond as 350 kJ mol⁻¹) (2012)



(a) 1165

(b) 837

(c) 865

(d) 815

101. The standard enthalpies of formation of CO₂(g), H₂O(l) and glucose(s) at 25°C are -400 kJ/mol, -300 kJ/mol and -1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is: (2013)

(a) +2900 kJ

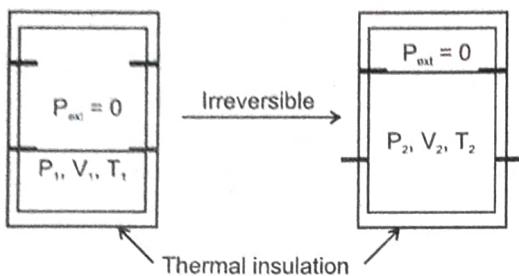
(b) -2900 kJ

(c) -16.11 kJ

(d) +16.11 kJ

102. An ideal gas in a thermally insulated vessel at internal pressure = P₁, volume = V₁ and absolute temperature = T₁

expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2 , V_2 and T_2 , respectively. For this expansion, (2014)



- (a) $q = 0$ (b) $T_2 = T_1$
 (c) $P_2 V_2 = P_1 V_1$ (d) $P_2 V_2^\gamma = P_1 V_1^\gamma$

103. For the process, $H_2O(\ell) \rightarrow H_2O(g)$

at $T = 100^\circ\text{C}$ and 1 atmosphere pressure, the correct choice is: (2014)

- (a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$
 (b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$
 (c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$
 (d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$

Comprehension (Q. 104 to 105): When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant ($-57.0 \text{ kJ mol}^{-1}$), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

(Consider heat capacity of all solutions as $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ and density of all solutions as 1.0 g mL^{-1})

104. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is: (2015)

- (a) 1.0 (b) 10.0
 (c) 24.5 (d) 51.4

105. The pH of the solution after Expt. 2 is: (2015)

- (a) 2.8 (b) 4.7
 (c) 5.0 (d) 7.0

106. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. (2015)

| | Column-I | Column-II |
|----|---|------------|
| A. | Freezing of water at 273 K and 1 atm. | p. $q = 0$ |
| B. | Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions. | q. $w = 0$ |

| | | |
|----|---|--|
| C. | Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container. | r. $\Delta S_{\text{sys}} < 0$ |
| D. | Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K , followed by reversible cooling to 300 K at 1 atm. | s. $\Delta U = 0$ t. $\Delta G = 0$ |

- (a) A-(p, r); B-(p, q, s); C-(p, q); D-(q, s, t)
 (b) A-(r, t); B-(p, q); C-(q, s); D-(s, t)
 (c) A-(r, t); B-(p, q, s); C-(p, q, s); D-(p, q, s, t)
 (d) A-(p, t); B-(p, q, r); C-(p, q, s); D-(p, q, r)

107. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm . In this process, the change in entropy of surroundings (ΔS_{surv}) in J K^{-1} is: (2016)

- (a) 5.763 (b) 1.013
 (c) -1.013 (d) -5.763

108. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by: (2017)

- (a) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases.
 (b) With increase in temperature, the value of K for endothermic reaction increases because favourable change in entropy of the surroundings decreases.
 (c) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative.
 (d) With increase in temperature, the value of K for endothermic reaction decreases because the entropy change of the system is positive.

109. An ideal gas is expanded from (P_1, V_1, T_1) to (P_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are): (2017)

- (a) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.
 (b) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$ and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$.
 (c) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.
 (d) The work done on the gas is maximum when it is compressed irreversibly from (P_2, V_2) to (P_1, V_1) against constant pressure P_1 .

110. The standard state Gibbs free energies of formation of C (graphite) and C (diamond) at T = 298 K are:

$$\Delta_f G^\circ [\text{C(graphite)}] = 0 \text{ kJ mol}^{-1}$$

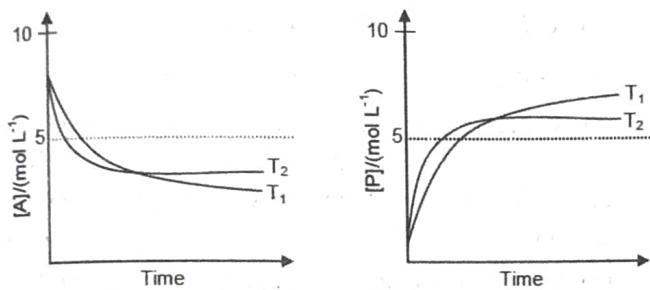
$$\Delta_f G^\circ [\text{C(diamond)}] = 2.9 \text{ kJ mol}^{-1}$$

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. If C(graphite) is converted to C (diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is _____. (2017)

[Useful information: 1 J = 1 kg m² s⁻², 1 Pa = 1 kg m⁻¹ s⁻²; 1 bar = 10^5 Pa]

- (a) 58001 bar (b) 1450 bar
(c) 14501 bar (d) 29001 bar

111. For a reaction, A ⇌ P, the plots of [A] and [P] with time at temperature T₁ and T₂ are given below. (2018)



If T₂ > T₁, the correct statement(s) is (are)

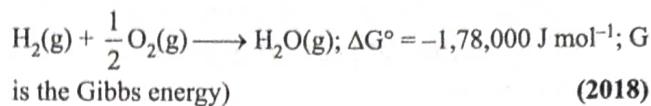
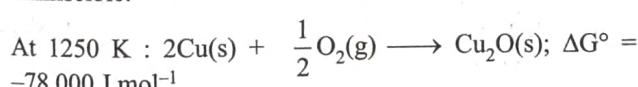
(Assume ΔH° and ΔS° are independent of temperature and ratio of ln K at T₁ to ln K at T₂ is greater than $\frac{T_2}{T_1}$. Here H, S, G and K are enthalpy, entropy, Gibb's energy and equilibrium constant, respectively.)

- (a) ΔH° < 0, ΔS° < 0 (b) ΔG° < 0, ΔH° > 0
(c) ΔG° < 0, ΔS° < 0 (d) ΔG° < 0, ΔS° > 0

112. The surface of copper gets tarnished by the formation of copper oxide. N₂ gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N₂ gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below :

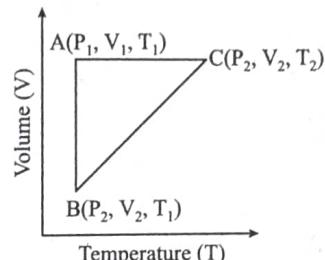


pH₂ is the minimum partial pressure of H₂ (in bar) needed to prevent the oxidation at 1250 K. The value of ln pH₂ is _____. (Given: total pressure = 1 bar, R (universal gas constant) = 8 J K⁻¹ mol⁻¹, ln(10) = 2.3, Cu(s) and Cu₂O(s) are mutually immiscible.



(2018)

113. A reversible cyclic process for an ideal gas is shown below. Here, P, V and T are pressure, volume and temperature, respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively.



The correct option(s) is (are):

- (a) q_{AC} = ΔU_{BC} and w_{AB} = P₂(V₂ - V₁)
(b) w_{BC} = P₂(V₂ - V₁) and q_{BC} = ΔH_{AC}
(c) ΔH_{CA} < ΔU_{CA} and q_{AC} = ΔU_{BC}
(d) q_{BC} = ΔH_{AC} and ΔH_{CA} > ΔU_{CA}

114. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. (2019)

- (a) $\frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{O}_3\text{(g)}$
(b) $\frac{1}{8}\text{S}_8\text{(s)} + \text{O}_2\text{(g)} \rightarrow \text{SO}_2\text{(g)}$
(c) $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)}$
(d) $2\text{C(g)} + 3\text{H}_2\text{(g)} \rightarrow \text{C}_2\text{H}_6\text{(g)}$

115. In thermodynamics the P-V work done is given by

$$w = - \int dV P_{ext}$$

For a system undergoing a particular process, the work done is,

$$w = - \int dV \left(\frac{RT}{V-b} - \frac{a}{V^2} \right) \quad (2020)$$

This equation is applicable to a:

- (a) System that satisfies the van der Waals equation of state.
(b) Process that is reversible and isothermal.
(c) Process that is reversible and adiabatic.
(d) Process that is irreversible and at constant isothermal.

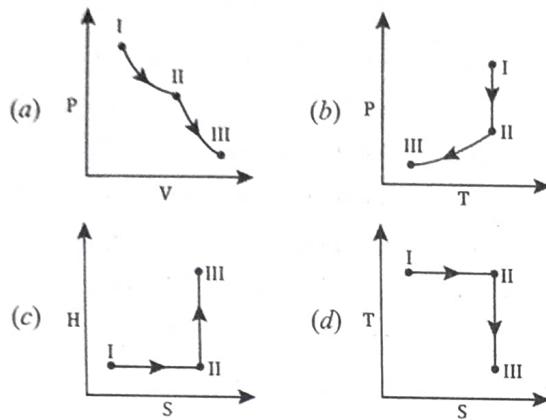
116. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place.

At 298 K: $\Delta_f H^\circ(\text{SnO}_2\text{(s)}) = -581.0 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(\text{CO}_2\text{(g)}) = -394.0 \text{ kJ mol}^{-1}$

$S^\circ(\text{SnO}_2\text{(s)}) = 56.0 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^\circ(\text{Sn(s)}) = 52.0 \text{ J K}^{-1} \text{ mol}^{-1}$,

$S^\circ(C(s)) = 0.6 \text{ J K}^{-1}\text{mol}^{-1}$, $S^\circ(\text{CO}_2(g)) = 210.0 \text{ J K}^{-1}\text{mol}^{-1}$.
Assume that the enthalpies and the entropies are temperature independent. (2020)

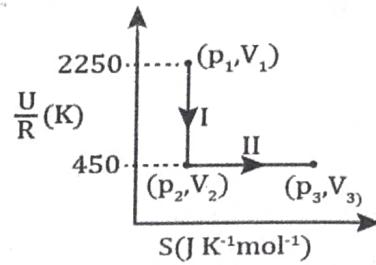
117. An ideal gas undergoes a reversible isothermal expansion from state I to state II followed by a reversible adiabatic expansion from state II to state III. The correct plot(s) representing the changes from state I to state III is (are) (p:pressure, V:volume, T:temperature, H:enthalpy, S:entropy) (2021)



118. One mole of an ideal gas at 900 K, undergoes two reversible processes, I followed by II, as shown below. If the work done by the gas in the two process are same, the value of $\frac{V_3}{V_2}$ is:

(U: internal energy, S: entropy, P: pressure, V: volume, R: gas constant)

(Given: molar heat capacity at constant volume, $C_{v,m}$ of the gas is $\frac{5}{2}R$)



(2021)

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|----------------|---------|--------------------------------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (d) | 3. (d) | 4. (b) | 5. (d) | 6. (a) | 7. (a) | 8. (a) | 9. (b) | 10. (a) |
| 11. (c) | 12. (c) | 13. (c) | 14. (a) | 15. (d) | 16. (c) | 17. (b) | 18. (a) | 19. (d) | 20. (a) |
| 21. (c) | 22. (d) | 23. (b) | 24. (a) | 25. (b) | 26. (c) | 27. (b) | 28. (b) | 29. (d) | 30. (c) |
| 31. (b) | 32. (d) | 33. -94.1 kcal | | 34. (b) | 35. (c) | 36. (c) | 37. (b) | 38. (d) | 39. (a) |
| 40. (b) | 41. (a) | 42. (a) | 43. (a) | 44. 3890 kJ mole ⁻¹ | 45. (c) | 46. (a) | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (c) | 3. (b) | 4. (c) | 5. (c) | 6. (a) | 7. (b) | 8. (c) | 9. (a) | 10. (c) |
| 11. (c) | 12. (d) | 13. (b) | 14. (b) | 15. (c) | 16. (c) | 17. (a) | 18. (a) | 19. (a) | 20. (d) |
| 21. (b) | 22. (b) | 23. (d) | 24. (a) | 25. (b) | 26. (a) | 27. (b) | 28. (d) | 29. (d) | 30. (b) |
| 31. (b) | 32. (c) | 33. (c) | 34. (b) | 35. (d) | 36. (b) | 37. (c) | 38. (b) | 39. (a) | 40. (b) |
| 41. (c) | 42. (c) | 43. (c) | 44. (c) | 45. (c) | 46. (d) | 47. (b) | 48. (d) | 49. (a) | 50. (d) |
| 51. (b) | 52. (d) | 53. (a) | 54. (b) | 55. (a) | 56. (c) | 57. (a) | 58. (d) | 59. (d) | 60. (b) |
| 61. (d) | 62. (a) | 63. (b) | 64. (d) | 65. (a) | 66. (d) | 67. (d) | 68. (a) | 69. (a) | 70. (b) |
| 71. (a) | 72. (d) | 73. (b) | 74. (a) | 75. (a) | 76. (a) | 77. (c) | 78. (a) | 79. (c) | 80. (d) |
| 81. (a) | | | | | | | | | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (b) | 3. (b) | 4. (d) | 5. (a) | 6. (a) | 7. (c) | 8. (c) | 9. (b) | 10. (b) |
| 11. (c) | 12. (c) | 13. (c) | 14. (b) | 15. (c) | 16. (d) | 17. (c) | 18. (a) | 19. (c) | 20. (c) |
| 21. (b) | 22. (a) | 23. (a) | 24. (b) | 25. (b) | 26. (c) | 27. (b) | 28. (c) | 29. (c) | 30. (d) |
| 31. (c) | 32. (a) | 33. (d) | 34. (b) | 35. (c) | 36. (c) | 37. (d) | 38. (b) | 39. (d) | 40. (c) |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|-----------------------------|-------------------------------|-----------------------------------|-------------|----------------------------------|-------------|-----------------------------------|--|-------------|-------------|
| 1. (a,b,d) | 2. (a,b,c) | 3. (b,d) | 4. (a,b,c) | 5. (b,c,d) | 6. (b,d) | 7. (a,b,c,d) | 8. (b,d) | 9. (a,b) | 10. (a,b,d) |
| 11. (a,b,d) | 12. (a,b,c) | 13. (a,b,c,d) | 14. (b,c,d) | 15. (a,b,d) | 16. (a,b,c) | 17. (a,b) | 18. (c,d) | 19. (a,b,c) | 20. (b,c,d) |
| 21. (a,b,c) | 22. (b) | 23. (a) | 24. (d) | 25. (a) | 26. (b) | 27. (d) | 28. (b) | 29. (a) | 30. (c) |
| 31. (d) | 32. (a) | 33. (a) | 34. (b) | 35. (b) | 36. (a) | 37. (b) | 38. (c) | 39. (a) | 40. (d) |
| 41. [7] | 42. [6] | 43. [3] | 44. [4] | 45. [6] | 46. [10] | 47. [24] | 48. [72] | 49. [44] | 50. [1] |
| 51. $[3 \text{ JK}^{-1}]$ | 52. $[7 \text{ kJ mol}^{-1}]$ | 53. [8] | 54. [8] | 55. [51] | 56. [40] | 57. [9 Kcal/mole] | 58. [3] | | |
| 59. [9] | 60. [7] | 61. [5] | 62. [53] | 63. [87] | 64. [40] | 65. [78 Kcal] | 66. $[\Delta U = 501 \text{ J}, \Delta H = 99 \text{ kJ}]$ | | |
| 67. [100] | 68. $[-1200 \text{ cal}]$ | 69. [1014] | 70. [32] | 71. [6000 cal] | | 72. [0] | 73. [3360 cal] | | |
| 74. [16] | 75. $[-17.8 \text{ kcal}]$ | 76. [10] | 77. [5kJ] | 78. [22 kcal] | | 79. $[\Delta U = 461 \text{ kJ}]$ | | | |
| 80. [(i) 342kJ, (ii) 891kJ] | | 81. $[23.68 \text{ kJ mol}^{-1}]$ | | 82. $[-137 \text{ kJ mol}^{-1}]$ | | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|---------------|-------------|--------------------|-----------------|----------------------|------------|-------------------------|-----------|------------|-----------|
| 1. (a) | 2. (a) | 3. (b) | 4. (d) | 5. (c) | 6. (c) | 7. (c) | 8. (c) | 9. (c) | 10. (a) |
| 11. [3] | 12. (c) | 13. (a) | 14. (a) | 15. (c) | 16. (a) | 17. (a) | 18. (d) | 19. (c) | 20. (d) |
| 21. (c) | 22. (b) | 23. (c,d) | 24. (d) | 25. (a) | 26. (a) | 27. (c) | 28. (c) | 29. (a) | 30. (d) |
| 31. (c) | 32. [48.00] | 33. [6.25 to 6.25] | | 34. [-2.70 to -2.70] | 35. (c) | 36. [-192.50 or -85.00] | 37. (d) | | |
| 38. [-326400] | | 39. (d) | 40. [-13537.57] | | 41. (a) | 42. [189494] | | 43. (a) | 44. (b) |
| 45. [3] | 46. (50) | 47. (31) | 48. [741] | 49. (2218) | 50. [101] | 51. [200] | 52. (b) | 53. [1380] | 54. [336] |
| 55. [5] | 56. [964] | 57. (c) | 58. (a) | 59. [964] | 60. [855] | 61. [309] | 62. [360] | 63. [230] | 64. [21] |
| 65. [128] | 66. [5] | 67. [82] | 68. (38) | 69. [5576] | 70. [128] | 71. [82] | 72. [718] | 73. [38] | 74. [667] |
| 75. (b) | 76. [300] | 77. (a) | 78. [195] | 79. [0] | 80. [8630] | 81. [38] | 82. [2] | 83. [3] | 84. [57] |
| 85. (c) | 86. (c) | 87. [104] | 88. [117] | 89. [600] | 90. [727] | 91. [2] | 92. [35] | 93. (d) | 94. [54] |
| 95. [200] | | | | | | | | | |

JEE Advanced

- | | | | | | | | | | |
|---------------|----------|--------------|--------------|----------|------------|--------------|------------|------------|--------------|
| 96. [2] | 97. (a) | 98. (a,c) | 99. (a,d) | 100. (d) | 101. (c) | 102. (a,b,c) | 103. (b) | 104. (a) | 105. (b) |
| 106. (c) | 107. (c) | 108. (a,b) | 109. (a,c,d) | 110. (c) | 111. (a,c) | 112. [-14.6] | 113. (b,c) | 114. (a,b) | 115. (a,b,c) |
| 116. [935.00] | | 117. (a,b,d) | 118. [10] | | | | | | |

CHAPTER

5

Equilibrium

INTRODUCTION

The term “equilibrium” in physical sense is defined as the “no change of state of the body”. The state of the body can be either the state of rest or the state of uniform motion. Such static equilibrium can be further categorized into stable and unstable equilibriums. You all must be acquainted with another well known equilibrium, equilibrium between liquid water and its vapour, $H_2O(l) \rightleftharpoons H_2O(g)$. When $H_2O(l)$ is taken in a closed container, some water molecules go into the vapour phase (vaporization process) and simultaneously, water molecules return to the liquid phase (condensation process). Initially, the rate of vaporization is greater than the rate of condensation but after some time the rate of evaporation and the rate of condensation becomes equal. Thus, the number of water molecules leaving and the number of water molecules returning to the liquid phase are equal.

At this stage, both the processes takes place but it seems that the changes are not occurring, as the composition of the system does not change. Such processes in which forward and backward changes are occurring at the same rate are referred as **dynamic equilibrium**. This $H_2O(l) \rightleftharpoons H_2O(g)$ equilibrium involving two phases of the same substance is called **physical equilibrium** because the changes that occur are physical changes.

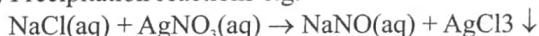
In this lesson, we will be more concerned with the state of equilibrium attained in chemical reactions. Most of the chemical reactions are reversible in nature (i.e., occurs in both the directions). At the start of a reversible process containing only reactants, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, theoretically the reverse process also begins to take place and reactant molecules are formed from product molecules.

Types of Chemical Reactions

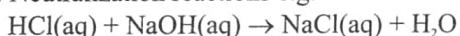
Irreversible Reactions

The reaction which proceed in one direction only

(a) Precipitation reactions e.g.



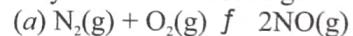
(b) Neutralization reactions e.g.



(c) Reactions in open vessels with one of the gaseous product

Reversible Reactions

Reactions which proceed in both the direction. These are possible only in closed vessel e.g.



Difference between Irreversible and Reversible Reactions

| Irreversible Reactions | | Reversible Reactions | |
|--|--|---|--|
| 1. The reaction which proceeds in one direction (forward direction) only | | 1. The reaction which proceed in both the direction under the same set of experimental conditions | |
| 2. Reactants are almost completely converted into products. Products do not react to form reactants again. | | 2. Reactants form products and products also form reactants in backward direction simultaneously. These are possible in closed vessels. | |

| | | | |
|----|---|----|--|
| 3. | Do not attain equilibrium state. | 3. | Attain the equilibrium state and never go to completion. |
| 4. | Such reactions are represented by single arrow (\rightarrow) | 4. | Represented by double arrow (\rightleftharpoons) or ($\longleftarrow\rightleftharpoons$) |
| 5. | <p>Examples:</p> <p>(a) Precipitation reactions e.g. $\text{NaCl(s)} + \text{AgNO}_3(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{AgCl} \downarrow$</p> <p>(b) Neutralization reactions e.g. $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}$</p> <p>(c) $2\text{KClO}_3(\text{s}) \xrightarrow{\Delta} 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$</p> <p>(d) Reactions in open vessels Even a reversible reaction will become irreversible if it is carried out in open vessel. Example-</p> <p>$\text{CaCO}_3(\text{s}) \xrightarrow{\Delta} \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$</p> <p>$\text{NH}_4\text{HS}(\text{s}) \xrightarrow{\Delta} \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$</p> | 5. | <p>Examples:</p> <p>(a) Homogeneous reactions-only one phase is present</p> <p>(i) Gaseous phase $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI(g)}$ $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO(g)}$ [<small>Birkland eyde process (HNO_3)</small>]</p> <p>$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ (<small>Haber's process</small>)</p> <p>(ii) Liquid phase $\text{CH}_3\text{COOH(l)} + \text{C}_2\text{H}_5\text{OH(l)} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O(l)}$</p> <p>Heterogeneous reactions: More than one phases are present $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$</p> |

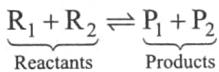
STATE OF CHEMICAL EQUILIBRIUM

State of equilibrium means the balance of driving forces i.e. the factors taking the reaction in forward direction and the backward direction are balancing each other.

The equilibrium state represents a compromise between two opposing tendencies.

- ❖ Tendency to minimise energy.
- ❖ Molecules try to maximise entropy.

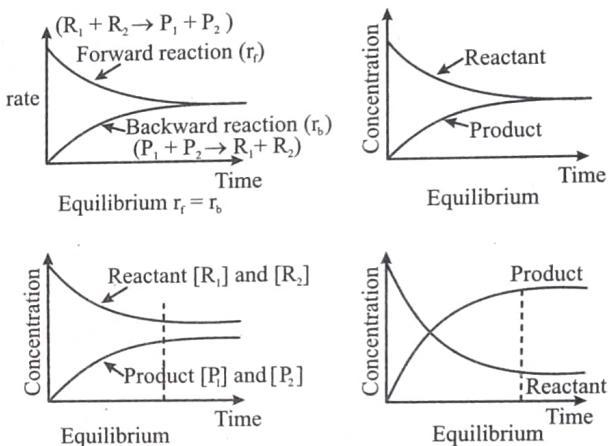
In a reversible reaction like-



Initially only reactants are present. R_1 and R_2 combine to form P_1 and P_2 . As soon as P_1 and P_2 are formed, they start the backward reaction. As concentrations of R_1 and R_2 decrease rate of forward reaction decreases and rate of backward reaction increases. Ultimately a stage is reached when both the rates become equal. Such a state is known as "Chemical Equilibrium" or "state of Equilibrium".

At Equilibrium:

- (i) Rate of forward reaction (r_f) = rate of backward reaction (r_b) (dynamic nature)
- (ii) All measurable parameters become constant with respect to time.

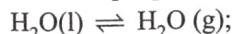


Types of Equilibrium on the Basis of Process

Physical Equilibrium

Equilibrium in physical process is called physical equilibrium.

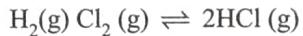
For example phase changes like



Chemical Equilibrium

Equilibrium in chemical process is called chemical equilibrium.

For example



Types of Equilibria on the Basis of Physical State

Homogeneous equilibrium
When all reactants and products are in same phase
 $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
 $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

Heterogeneous equilibrium
when more than one phase are present
 $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
 $2Na_2O_2(s) + 2H_2O(l) \rightleftharpoons 4NaOH + O_2(g)$

CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

- ❖ The nature and the properties of the equilibrium state are the same regardless of the direction from which it is achieved. It can be achieved from both directions.
- ❖ Equilibrium is dynamic in nature.
- ❖ It means that at microscopic level reaction has not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So there is no net change. Thus equilibrium is not static in nature.
- ❖ A catalyst can alter the rate of approach of equilibrium but does not change the state of equilibrium. By using catalyst, the equilibrium can be achieved in different (more/less) time, but the relative concentrations of reactants and products are same irrespective of the presence or absence of a catalyst.
- ❖ Equilibrium can be observed by constancy of some observable properties like colour, pressure, concentration, density, temperature, refractive index etc. which may be suitable in a given reaction.
- ❖ At equilibrium, free energy change $\Delta G = 0$
- ❖ Equilibrium state can be affected by altering factors like pressure, volume, concentration and temperature etc. (Le Chateliers Principle).
- ❖ System moves toward an equilibrium state spontaneously even if it is disturbed. It will return to original state.

Law of mass action: [By Guldberg and Waage]

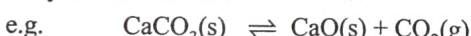
- ❖ Rate at which a substance reacts \propto [Active Mass of the substance]^x

Active Mass = Molar concentration i.e. Moles/Litres

$$= \frac{\text{Wt of substance (gram)}}{\text{Molar wt.} \times \text{Vol. (Litre)}}$$

It is represented in square brackets i.e. [] e.g. $[A]$, $[N_2]$ etc.

- ❖ For pure solids and pure liquids, although they have their own active masses but their concentration remain constant during a chemical change (reaction). Therefore, these are taken to be unity for the sake of convenience.



$$K_C = [CO_2(g)], K_p = P(CO_2(g))$$

The rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers of their stoichiometric coefficients.

Ex. $aA(g) + bB(g) \rightarrow \text{products}$
Rate of reaction $\propto [A]^a [B]^b$
Rate = $k [A]^a [B]^b$,
where k is the rate constant of the reaction.

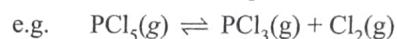
EQUILIBRIUM CONSTANT (K)

For a general reaction : $aA + bB \rightleftharpoons cC + dD$,
Forward reaction rate $r_f = k_f [A]^a [B]^b$,
Backward reaction rate $r_b = k_b [C]^c [D]^d$,
At equilibrium $r_f = r_b$

$$k_f [A]^a_{eq} [B]^b_{eq} = k_b [C]^c_{eq} [D]^d_{eq}$$

The concentrations of reactants & products at equilibrium are related by $\frac{k_f}{k_b} = K_C = \frac{[C]^c_{eq} [D]^d_{eq}}{[A]^a_{eq} [B]^b_{eq}}$

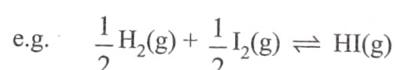
- ❖ K_C is a constant and is called the equilibrium constant in terms of concentration. Where all the concentrations are at equilibrium and are expressed in moles/litre.



$$\Rightarrow K_C = \frac{[PCl_3]_{eq} [Cl_2]_{eq}}{[PCl_5]_{eq}}$$

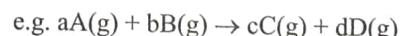


$$\Rightarrow K_C = \frac{[NH_3]_{eq}^2}{[N_2]_{eq} [H_2]_{eq}^3}$$



$$\Rightarrow K_C = \frac{[HI]_{eq}}{[H_2]_{eq}^{1/2} [I_2]_{eq}^{1/2}}$$

- ❖ $K_p \rightarrow$ Equilibrium constant in terms of partial pressure. It is defined for the equilibrium reaction which contains gaseous component. If component other than gas is present its active mass must be one.



$$K_p = \frac{[P_C]_{eq}^c [P_D]_{eq}^d}{[P_A]_{eq}^a [P_B]_{eq}^b}$$

where various pressures are the partial pressures of various gases substances.



Train Your Brain

Example 1: Four vessel each of volume $V = 10 \text{ Litres}$ contains

- (a) 16 g $\text{CH}_4(\text{g})$ (b) 18 g $\text{H}_2\text{O}(\text{g})$
 (c) 35.5 g $\text{Cl}_2(\text{g})$ (d) 44 g $\text{CO}_2(\text{g})$

Find the active masses in all the containers.

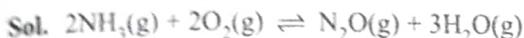
$$\text{Sol. (a)} \Rightarrow [\text{CH}_4] = \frac{16}{16 \times 10} = 0.1 \text{ M}$$

$$\text{(b)} \Rightarrow [\text{H}_2\text{O}] = \frac{18}{18 \times 10} = 0.1 \text{ M}$$

$$\text{(c)} \Rightarrow [\text{Cl}_2] = \frac{35.5}{71 \times 10} = 0.05 \text{ M}$$

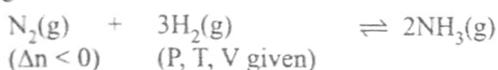
$$\text{(d)} \Rightarrow [\text{CO}_2] = \frac{44}{44 \times 10} = 0.1 \text{ M}$$

Example 2: The equilibrium constant expression for the equilibrium



$$K_c = \frac{[\text{N}_2\text{O}] \times [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 \times [\text{O}_2]^2}$$

Example 3: Calculate the expression for K_c and K_p if initially a moles of N_2 and b moles of H_2 is taken for the following reaction.



$$\text{At } t=0 \quad \begin{matrix} a \\ \text{N}_2(\text{g}) \end{matrix} \quad \begin{matrix} b \\ \text{H}_2(\text{g}) \end{matrix} \quad \begin{matrix} 0 \\ \text{NH}_3(\text{g}) \end{matrix}$$

$$[N_2] = \frac{a-x}{V}, [H_2] = \frac{b-3x}{V}, [NH_3] = \frac{2x}{V}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$

Total no. of moles at equilibrium = $a + b - 2x$

$$[P_{N_2}] = \frac{(a-x)}{a+b-2x} \cdot P, \quad [P_{H_2}] = \frac{(b-3x)}{a+b-2x} \cdot P,$$

$$[P_{NH_3}] = \frac{(2x) \cdot P}{a+b-2x}$$

$$\therefore K_p = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{\left(\frac{2x}{a+b-2x} \cdot P\right)^2}{\left(\frac{a-x}{a+b-2x} \cdot P\right) \left[\left(\frac{b-3x}{a+b-2x} \cdot P\right)^3\right]}$$

$$K_p = \frac{\frac{4x^2 \cdot P^2}{(a+b-2x)^2}}{P^4 \cdot \frac{(a-x)(b-3x)^3}{(a+b-2x)^4}} = \frac{(a+b-2x)^2 \cdot 4x^2}{P^2(a-x)(b-3x)^3}$$



Concept Application

1. The decomposition of N_2O_4 to NO_2 was carried out in chloroform at 280°C . At equilibrium, 0.2 mol of N_2O_4 and 2×10^{-3} mole of NO_2 were present in 2L of solution. The equilibrium constant for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is

- (a) 0.01×10^{-3} (b) 2.0×10^{-3}
 (c) 2.0×10^{-5} (d) 0.01×10^{-5}

2. In a reaction $\text{A(g)} + \text{B(g)} \rightleftharpoons \text{C(g)} + \text{D(g)}$, A and B are mixed in a vessel at temperature T. The initial concentration of A was twice the initial concentration of B. After the equilibrium is reached, concentration of C was thrice the concentration of B. Calculate K_c .

- (a) 1.2 (b) 1.4
 (c) 1.6 (d) 1.8

3. An example of a reversible reaction is:

- (a) $\text{Pb(NO}_3)_2(\text{aq}) + 2\text{NaI}(\text{aq}) \rightleftharpoons \text{PbI}_2(\text{s}) + 2\text{NaNO}_3(\text{aq})$
 (b) $\text{AgNO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightleftharpoons \text{AgCl}(\text{s}) + \text{HNO}_3(\text{aq})$
 (c) $2\text{Na}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$
 (d) $\text{KNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightleftharpoons \text{KCl}(\text{aq}) + \text{NaNO}_3(\text{aq})$

4. For the reaction, $\text{A} + \text{B} \rightleftharpoons 3\text{C}$, if 'a' mol/litre of each 'A' & 'B' are taken initially then at equilibrium the incorrect relation is:

- (a) $[\text{A}] - [\text{B}] = 0$ (b) $3[\text{B}] + [\text{C}] = 3\text{a}$
 (c) $3[\text{A}] + [\text{C}] = 3\text{a}$ (d) $[\text{A}] + [\text{B}] = 3[\text{C}]$

♦ Relation between K_p & K_c

$$PV = nRT \quad \text{or} \quad P = \frac{n}{V} RT$$

$$P = CRT \text{ where } C = \frac{n}{V} = (\text{moles per litre})$$

$$P_C = [C] RT; P_D = [D] RT; P_A = [A] RT; P_B = [B] RT$$

$$\Rightarrow K_p = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

$$K_p = K_c (RT)^{\Delta n_g}$$

Where $\Delta n_g = (c+d)-(a+b)$, calculation of Δn involves only gaseous components.

$\Rightarrow \Delta n_g$ = sum of the number of moles of gaseous products – sum of the number of moles of gaseous reactants. Δn_g can be positive, negative, zero or even fraction.



$\Delta n_g = 1$ (because there is only one gas component in the products and no gas component in the reactant)

$$\Rightarrow K_p = K_c \cdot (RT)$$

UNIT OF EQUILIBRIUM CONSTANTS

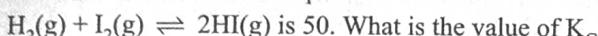
- Unit of K_p is $(\text{atm})^{\Delta n}$
 - Unit of K_c is $(\text{mole/Lit})^{\Delta n} = (\text{conc.})^{\Delta n}$

Note: In fact, equilibrium constant does not carry any unit because it is based upon the activities of reactants and products and activities are unitless quantities. Under ordinary circumstances, where activities are not known, above types of equilibrium constant and their units are employed.



Train Your Brain

Example 4: The value of K_p for the reaction



Sol. (c) As $\Delta n_a = 0$

$$\text{So, } K_c = K_o (RT)^{\Delta n_g}$$

Put $\Delta n_c = 0$

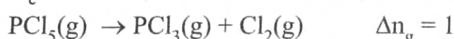
$$\Rightarrow \boxed{K_p = K_c}$$

$$\text{So } K_p = 50$$

Example 5: The equilibrium constant K_C for the decomposition of PCl_5 is 0.625 mole/lit at 300°C . Then the value of K_p is

- (a) 29.36 atm
 - (b) 0.0625 atm
 - (c) 6.25 atm
 - (d) 0.00625 atm

Sol. (a) $K_c = 0.625$ mole/litre

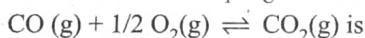


$$K_p = K_c(RT)$$

$$K_c = 0.625 \times 0.0821 \times 573$$

$$= 29.36 \text{ atm}$$

Example 6: The ratio of K_p/K_C for the reaction :



- (a) 1.0
 - (b) RT
 - (c) $1/\sqrt{RT}$
 - (d) $(RT)^{1/2}$

$$\text{Sol. (c)} \quad \Delta n_g = 1 - \frac{1}{2} - 1 = -\frac{1}{2}$$

$$\frac{K_p}{K_c} = (RT)^{-1/2} = \frac{1}{\sqrt{RT}}$$

$$\text{So, } \frac{K_p}{K_c} = \frac{1}{\sqrt{RT}}$$

70



Concept Application

5. For which of the following K_p is less than K_c ?

 - $N_2O_4 \rightleftharpoons 2NO_2$
 - $N_2 + 3H_2 \rightleftharpoons 2NH_3$
 - $H_2 + I_2 \rightleftharpoons 2HI$
 - $CO + H_2O \rightleftharpoons CO_2 + H_2$

6. For homogeneous gas reaction $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$. The equilibrium constant K_c has the unit of-

 - (concentration)¹
 - (concentration)⁻¹
 - (concentration)⁹
 - (concentration)¹⁰

7. The value of K_p for the reaction.
 $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$ is 0.03 atm at 427°C, when the partial pressure are expressed in atmosphere, then the value of K_C for the same reaction is

 - 5.23×10^{-4}
 - 7.34×10^{-4}
 - 3.2×10^{-3}
 - 5.43×10^{-5}

CHARACTERISTICS OF EQUILIBRIUM CONSTANT & FACTORS AFFECTING IT

- ❖ Equilibrium constant does not depend upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached.
 - ❖ The equilibrium constant does not give any idea about time taken to attain equilibrium.
 - ❖ **Equilibrium constant depends only on the temperature.**
It means K_p and K_c will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.
 - ❖ However if temperature is changed,
$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]; \Delta H = \text{Enthalpy of reaction}$$

If $T_2 > T_1$ then $K_2 > K_1$ provided $\Delta H = +ve$
(endothermic reaction)

$K_2 < K_1$ if $\Delta H = -ve$ (exothermic reaction)

In the above equation, the unit of R and $\Delta H/T$ should be same.

 - ❖ If two chemical reactions at equilibrium having equilibrium constants K_1 and K_2 are added then the resulting equation has equilibrium constant $K = K_1 \cdot K_2$

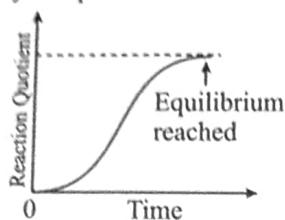
$A(g) \rightleftharpoons B(g) K_1$
 $B(g) \rightleftharpoons C(g) K_2$

On adding $A(g) \rightleftharpoons C(g) K = K_1 \cdot K_2$

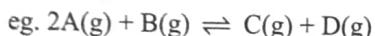
 - ❖ If the reaction having eq. constant K_1 is reversed then resulting equation has eq. constant $\frac{1}{K_1}$

It helps in predicting the direction of a reaction.

The expression $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ at any time during reaction is called reaction quotient. The concentrations [C], [D], [A], [B] are not necessarily at equilibrium.



- ❖ The reaction quotient is a variable quantity with time.
- ❖ It helps in predicting the direction of a reaction.
- ❖ If $Q > K_c$ reaction will proceed in backward direction until equilibrium is reached.
- ❖ If $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.
- ❖ If $Q = K_c$ Reaction is at equilibrium.



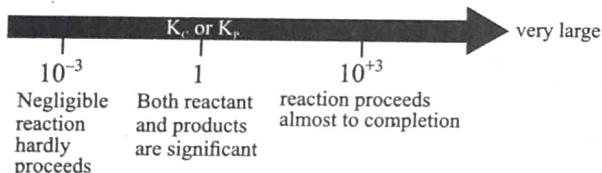
Q_c = Reaction quotient in terms of concentration

$$Q_c = \frac{[C][D]}{[A]^2[B]}$$

$$K_c = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}^2[B]_{eq}} \quad [\text{Here all the conc. are at equilibrium}]$$

❖ Predicting the extent of the reaction

$$K = \frac{[\text{Product}]_{eq}}{[\text{Reactant}]_{eq}}$$



Case-I: If K is large ($K > 10^3$) then product concentration is very very larger than the reactant ($[\text{Product}] \gg [\text{Reactant}]$). Hence concentration of reactant can be neglected with respect to the product. In this case, the reaction is product favourable and equilibrium will be more in forward direction than in backward direction.

Case-II: If K is very small ($K < 10^{-3}$)

$$[\text{Product}] \ll [\text{Reactant}]$$

Hence concentration of Product can be neglected as compared to the reactant.

In this case, the reaction is reactant favourable.

Ex. The K_p values for three reactions are 10^{-5} , 20 and 300 then what will be the correct order of the percentage composition of the products.

Sol. Since K_p order is $10^{-5} < 20 < 300$ so the percentage composition of products will be greatest for $K_p = 300$.

- ❖ **Calculating equilibrium concentrations:** The concentration of various reactants and products can be calculated using the equilibrium constant and the initial concentrations.



Train Your Brain

Example 10: For the reaction $\text{NOBr}(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2} \text{Br}_2(g)$

$K_p = 0.15$ atm at 90°C . If NOBr , NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 0.2 atm respectively, will Br_2 be consumed or formed?

$$\text{Sol. } Q_p = \frac{[\text{P}_{\text{Br}_2}]^{1/2} [\text{P}_{\text{NO}}]}{[\text{P}_{\text{NOBr}}]} = \frac{[0.2]^{1/2} [0.4]}{[0.50]} = 0.36$$

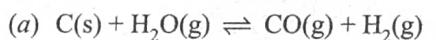
$$K_p = 0.15$$

$$\therefore Q_p > K_p$$

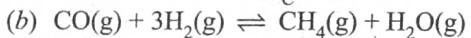
Hence, reaction will shift in backward direction

$\therefore \text{Br}_2$ will be consumed

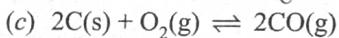
Example 11: Assuming that the system is at equilibrium, which of the following reactions goes most nearly to 100% completion-



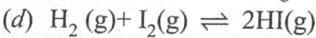
$$K_c = 6.5 \times 10^{-23}$$



$$K_c = 0.176$$



$$K_c = 1 \times 10^{16}$$



$$K_c = 54.5$$

Sol. Fast rate for completion.

K_c must be greater value.

$$K_c = \frac{\text{Product concentration}}{\text{Reactant concentration}}$$

More product concentration, more value of K_c , so, reaction goes to fast completion.

Example 12: Assertion: For a reaction concentration quotient Q is equal to K when the reaction is in equilibrium.

Reason: If a catalyst is added to the reaction at equilibrium, the value of Q remains no longer equal to K .

(a) Both assertion & reason are correct and reason is the correct explanation for assertion

(b) Both assertion & reason are correct but reason is not the correct explanation for assertion

(c) Assertion is correct but reason is incorrect

(d) Both assertion & reason are incorrect

Sol. (c) Assertion is correct & reason is incorrect.

Catalyst will effect of rate of forward and rate of backward reaction equally.

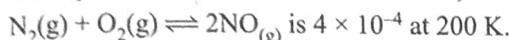


Concept Application

12. Q_p represent the reaction quotient of a gas phase reaction and K_p represent the equilibrium constant of the same gas phase reaction. For the non-spontaneous reaction-

- (a) $\frac{Q_p}{K_p} > 1$ (b) $\frac{Q_p}{K_p} < 1$
 (c) $\frac{Q_p}{K_p} = 1$ (d) $Q_p K_p = 1$

13. The equilibrium constant for the reaction;



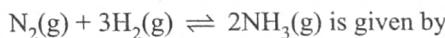
is 4×10^{-4} at 200 K.
In the presence of a catalyst the equilibrium is attained 10 times faster. Therefore the equilibrium constant in presence of catalyst at 200 K is

- (a) 4×10^{-3}
 (b) 4×10^{-4}
 (c) 4×10^{-5}
 (d) None of these

14. Which of the following statements is/are true about reaction quotient Q?

- (I) $Q \geq K_c$
 (II) $Q = K_c$ at equilibrium
 (III) If $Q > K_c$ then reaction will proceed in forward direction
 (IV) If $Q < K_c$ then reaction will proceed in backward direction
 (a) I, IV
 (b) III, IV
 (c) I, II
 (d) I, II, III

15. The reaction quotient Q for:



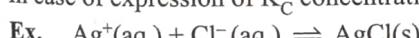
$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

is given by
The reaction will proceed in backward direction, when:

- (a) $Q = K_c$ (b) $Q < K_c$
 (c) $Q > K_c$ (d) $Q = 0$

EQUATION INVOLVING IONS

Equilibrium involving ions always take place in aqueous medium.
In case of expression of K_C concentration of ion is taken.



$$K_c = \frac{1}{[Ag^+][Cl^-]}$$

Homogeneous liquid system: Formation of ethyl acetate: The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.



$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Heterogeneous Equilibrium: For pure solid and pure liquid, active mass is taken to be unity i.e. 1 as their concentration remain constant throughout the reaction



$$K_p = (P_{CO_2})_{eq}, K_C = [CO_2(g)]_{eq}$$

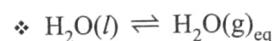
$$[CaCO_3(s)] = \frac{\text{moles}}{\text{volume}} = \frac{W_{CaCO_3}}{M_{CaCO_3} \cdot V}$$

$$= \frac{\text{density } CaCO_3}{M_{CaCO_3}} = \text{constant}$$

$$K = \frac{[CaO(s)]_{eq} [CO_2(g)]_{eq}}{[CaCO_3(s)]_{eq}}$$

$$\frac{K \cdot [CaCO_3(s)]_{eq}}{[CaO(s)]_{eq}} = [CO_2(g)]_{eq}$$

$$K_C = [CO_2(g)]_{eq}$$



$$K_p = (P_{H_2O(g)})_{eq}, K_C = [H_2O(g)]_{eq}$$

[For pure solid and pure liquid active mass is taken as unity i.e. = 1]

DEGREE OF DISSOCIATION (α)

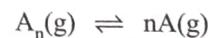
It is the fraction of one mole dissociated into the products. (Defined for one mole of substance)

So, $\alpha = \text{no. of moles dissociated} / \text{initial no. of moles taken}$
 = fraction of moles dissociated out of 1 mole.

Note: % dissociation = $\alpha \times 100$

Suppose 5 moles of PCl_5 is taken and if 2 moles of PCl_5 dissociated then $\alpha = \frac{2}{5} = 0.4$

Let 1 mole of gas A_n dissociates to give n moles of A as follows-



$$t = 0 \quad a \quad 0$$

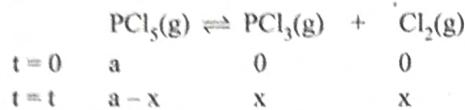
$$t = t_{eq} \quad a - x \quad n.x \quad \alpha = \frac{x}{a} \Rightarrow x = a\alpha.$$

$$\begin{aligned} \text{Total number of moles} &= a - a\alpha + n.a\alpha \\ &= [1 + (n - 1)\alpha]a \end{aligned}$$



Train Your Brain

Example 13: Calculate the degree of dissociation and K_p for the following reaction.



Since for a mole, x moles are dissociated

Sol. ∵ For 1 mole, $\frac{x}{a}$ moles = α are dissociated

$$\therefore x = a\alpha$$



$$\therefore \text{At } t = t_{\text{eq}} \quad a - a\alpha \quad a\alpha \quad a\alpha$$

$$\text{Total no. of moles at equilibrium} = a + a\alpha = a(1 + \alpha)$$

$$P_{\text{PCl}_5} = \frac{a(1-\alpha)P}{a(1+\alpha)}, P_{\text{PCl}_3} = \frac{a\alpha.P}{a(1+\alpha)},$$

$$P_{\text{Cl}_2} = \frac{a\alpha}{a(1+\alpha)}.P$$

$$K_p = \frac{\left(\frac{a\alpha}{1+\alpha}\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P}$$

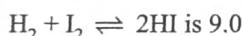
$$K_p = \frac{\alpha^2.P}{1-\alpha^2} \text{ (Remember)}$$

Example 14: For the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$

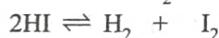
The value of equilibrium constant is 9.0. The degree of dissociation of HI will be

- (a) 2
- (b) 2/5
- (c) 5/2
- (d) 1/2

Sol. Equilibrium constant of the reaction



So the equilibrium constant for the dissociation of HI i.e. $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ will be 1/9.



| | | |
|-------|---------------|---------------|
| 1 | 0 | 0 |
| 1 - x | $\frac{x}{2}$ | $\frac{x}{2}$ |

$$K_c = \frac{x \times \frac{x}{2}}{2(1-x)} \times \frac{1}{(1-x)}$$

$$\frac{1}{9} = \frac{x^2}{2 \times 2(1-x)^2} \times \frac{1}{3} = \frac{x}{2(1-x)}$$

$$\text{or } 2 - 2x = 3x \quad 5x = 2 \quad x = 2/5$$

Example 15: The equilibrium constant for the decomposition of water $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ is given by: (α = degree of dissociation of H_2O (g); p = Total equilibrium pressure)

$$(a) K = \frac{\alpha^2 p^{1/2}}{(1+\alpha)(2-\alpha)^{1/2}} \quad (b) K = \frac{\alpha^{3/2} p^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$$

$$(c) K = \frac{\alpha^3 p^{1/2}}{\sqrt{2}} \quad (d) K = \frac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$



| | | |
|--------------|----------|------------|
| 1 | 0 | 0 |
| 1 - α | α | $\alpha/2$ |

$$\text{Total moles at equilibrium} = 1 - \alpha + \alpha + \alpha/2 = 1 + \alpha/2$$

Let the total pressure at equilibrium be = p

$$\text{So, } p_{\text{H}_2\text{O}} = \frac{1-\alpha}{1+\alpha/2} \times p$$

$$p_{\text{H}_2} = \frac{\alpha}{1+\alpha/2} \times p$$

$$p_{\text{O}_2} = \frac{\alpha/2}{1+\alpha/2} \times p$$

$$\text{So, } K_p = \frac{(p_{\text{O}_2})^{1/2} (p_{\text{H}_2})}{(p_{\text{H}_2\text{O}})}$$

$$= \frac{\left(\frac{\alpha/2}{1+\alpha/2} \times p\right)^{1/2} \left(\frac{\alpha}{1+\alpha/2} \times p\right)}{\left(\frac{1-\alpha}{1+\alpha/2}\right)p}$$

$$K_p = \frac{\alpha^{3/2} p^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$$



Concept Application

16. For the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, N_2 & H_2 were taken in the molar ratio of 1:3. Up to the point of equilibrium 50% each reactant has been reacted. If total pressure at equilibrium is P. The partial pressure of ammonia would be

- (a) P/3
- (b) P/6
- (c) P/4
- (d) P/8

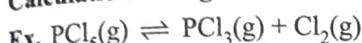
17. For reaction; $\text{A}_{(\text{g})} + \text{B}_{(\text{g})} \rightleftharpoons \text{AB}_{(\text{g})}$, we start with 2 moles of A and B each. At equilibrium 0.8 moles of AB is formed. Then how much of A changes to AB.

- (a) 20%
- (b) 40%
- (c) 60%
- (d) 4%

18. At 444°C, the equilibrium constant K for the reaction $2AB_{(g)} \rightleftharpoons A_{2(g)} + B_{2(g)}$ is $\frac{1}{64}$. The degree of dissociation of AB will be
 (a) 10% (b) 20% (c) 30% (d) 50%
19. For the reaction: $N_2O_{3(g)} \rightleftharpoons NO_{(g)} + NO_{2(g)}$; total pressure = P, degree of dissociation = 50%. Then K_p would be -
 (a) 3P (b) 2P
 (c) $\frac{P}{3}$ (d) $\frac{P}{2}$

Degree of Dissociation In Terms of Vapour Density or Molar Mass

Calculation of Degree of dissociation from vapour density:



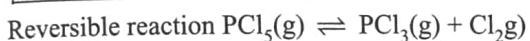
$$\alpha = \frac{D_T - D_0}{D_0} \text{ or } \frac{D - d}{d}$$

Where: D_T or D = Principle or theoretical vapour density

D_0 or d = Observed or practical vapour density

α = Degree of dissociation

| | |
|------------------|------------------|
| Vapour density = | Molecular weight |
| | 2 |



| | Total moles | Volume at NTP | Vapour density |
|----------------------|----------------|--------------------------|-----------------------------|
| Let initial moles | 1 | 0 | 0 |
| | 1 | $V_T = 22.4$ | $D_T \propto \frac{1}{V_T}$ |
| Moles at equilibrium | $(1 - \alpha)$ | α | α |
| | $1 + \alpha$ | $V_0 = 22.4(1 + \alpha)$ | $D_0 \propto \frac{1}{V_0}$ |

If α is the degree of dissociation

$$\frac{D_T}{D_0} = \frac{V_0}{V_T} = \frac{22.4(1 + \alpha)}{22.4}$$

$$\frac{D_T}{D_0} = 1 + \alpha \text{ or } \alpha = \frac{D_T - D_0}{D_0} - 1 \text{ or } \alpha = \frac{D_T - D_0}{D_0}$$

So for a general reversible reaction $n_1A \rightleftharpoons n_2B + n_3C$

$$\alpha = \frac{n_1}{\Delta n} \left(\frac{D_T - D_0}{D_0} \right)$$

When

- (i) $\Delta n > 0$ then $D_T > D_0$
- (ii) $\Delta n = 0$ then $D_T = D_0$
- (iii) $\Delta n < 0$ then $D_T < D_0$



Train Your Brain

Example 16: If PCl_5 is 80% dissociated at 250°C then its vapour density at room temperature will be

- (a) 56.5
- (b) 104.25
- (c) 101.2
- (d) 52.7

$$\text{Sol. } D_T = \frac{\text{Molecular weight}}{2} = \frac{208.5}{2} = 104.25$$

Vapour density at room temperature (D_T) is 104.25, which is fixed.

Example 17: Vapour density of the equilibrium mixture of thereaction

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is 50. The extent of dissociation of $SO_2Cl_2(g)$ is

- (a) 33.33 %
- (b) 35.0 %
- (c) 30.0 %
- (d) 66.67 %

$$\text{Sol. (b) } \alpha = \frac{D_T - D_0}{D_0(n-1)}$$

$$\text{or } \alpha = \frac{67.5 - 50}{50(2-1)} = 0.35$$

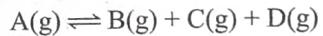


Concept Application

20. The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2 . The percentage dissociation of N_2O_4 at the final temperature is;

- (a) 87
- (b) 60
- (c) 40
- (d) 70

21. An unknown compound A dissociates at 500°C to give products as follows:



Vapour density of the equilibrium mixture is 50 when it dissociates to the extent to 10%. What will be the molecular weight of Compound A -

- (a) 120
- (b) 130
- (c) 134
- (d) 140

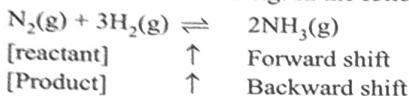
22. N_2O_4 dissociates as $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 273 K and 2 atm pressure. The equilibrium mixture has a density of 41. What will be the degree of dissociation

- (a) 14.2%
- (b) 16.2%
- (c) 12.2%
- (d) None of the above

EXTERNAL FACTORS AFFECTING EQUILIBRIUM (LE CHATELIER'S PRINCIPLE)

If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change applied and the equilibrium is established again under new conditions.

- ❖ **Effect of concentration:** If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration. e.g. In the following example.



- ❖ If concentration of reactant is increased at equilibrium then reaction shifts in the forward direction.
- ❖ If concentration of product is increased then reaction shifts in the backward direction.

Note: The addition of any solid component does not affect the equilibrium.

- ❖ **Effect of pressure:** On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e. no. of moles in the reaction decreases and vice versa.

$P \propto \text{no. of moles}$

(i) For $\Delta n_g = 0 \rightarrow$ No. effects

(ii) For $\Delta n_g > 0$, $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

$$Q_p = \frac{(X_{\text{PCl}_3} P) \cdot (X_{\text{Cl}_2} P)}{(X_{\text{PCl}_5} \cdot P)}$$

$\Rightarrow Q_p \propto P$ [X = mole fraction]

$P \downarrow; Q_p \downarrow$; (Forward shift)

$P \uparrow; Q_p \uparrow$; (Backward shift)

(iii) For $\Delta n < 0$, eg. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$$Q_p = \frac{[(X_{\text{NH}_3} P)]^2}{[(X_{\text{N}_2} \cdot P)][(X_{\text{H}_2} \cdot P)]^3} \Rightarrow Q_p \propto \frac{1}{P^2}$$

$P \uparrow; Q_p \downarrow$; (Forward shift); $P \downarrow; Q_p \uparrow$; (Backward shift)

EFFECT OF VOLUME

- ❖ If volume is increased, pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
- ❖ If volume is increased then,
 - $\Delta n_g > 0$ reaction will shift in the forward direction
 - $\Delta n_g < 0$ reaction will shift in the backward direction
 - $\Delta n_g = 0$ reaction will not shift.
eg. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ (No effect)

Explanation

- (i) $\Delta n_g > 0$, eg. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

$$Q_C = \frac{\frac{(n_{\text{Cl}_2})}{V} \times \frac{(n_{\text{PCl}_3})}{V}}{\frac{(n_{\text{PCl}_5})}{V}} \Rightarrow Q_C \propto \frac{1}{V} \text{ for } \Delta n_g > 0$$

On increasing V, Q_C , decreases.

Now, for $Q_C < K_C$ reaction will shift in forward direction.
Thus, if, Volume \uparrow $Q_C \downarrow$ (Forward shift)

Volume \downarrow $Q_C \uparrow$ (Backward shift)

- (ii) $\Delta n_g < 0$, eg. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$$Q_C = \frac{\left\{ \frac{(n_{\text{NH}_3})}{V} \right\}^2}{\left\{ \frac{(n_{\text{N}_2})}{V} \right\} \left\{ \frac{(n_{\text{H}_2})}{V} \right\}^3}$$

$$\Rightarrow Q_C \propto V^2 \quad \text{for } \Delta n_g < 0$$

V \uparrow $Q_C \uparrow$ (Backward shift); V \downarrow $Q_C \downarrow$ (Forward shift)

- ❖ **Effect of catalyst:** Due to catalyst, the state of equilibrium is not affected i.e. no shift will occur as catalyst lowers the activation energy of both the forward & reverse reaction by same amount, thus altering the forward & reverse rate equally and hence, the equilibrium will be attained faster i.e time taken to reach the equilibrium is less.

- ❖ **Effect of inert gas addition**

- (i) **At constant volume:** Inert gas addition has no effect at constant volume

- (ii) **At constant pressure:** If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

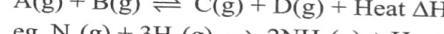
(i) $\Delta n_g > 0$, reaction will shift in the forward direction

(ii) $\Delta n_g < 0$, reaction will shift in the backward direction

(iii) $\Delta n_g = 0$, no effect

- ❖ **Effect of temperature**

- (i) **Exothermic reaction:** The reaction in which heat is evolved



T $\uparrow \Rightarrow K' \text{ will decrease}$

$$\log \frac{K_1}{K_2} = \frac{\Delta H^\circ}{2.303} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (\text{from vant' hoff equation})$$

$$\log \frac{K_1}{K_2} < 0$$

$\Rightarrow \log K_1 - \log K_2 > 0$

$\Rightarrow \log K_1 > \log K_2$

$\Rightarrow K_1 > K_2$

$$\text{So, } \left(K \propto \frac{1}{T} \right)$$

Reaction will shift in backward direction.

$T \downarrow \Rightarrow K$ will increases.

Reaction will shift in forward direction.

(ii) **Endothermic reaction:** energy consumed.



$$\therefore \Delta H = + \text{ve}$$

$T \uparrow \Rightarrow K \uparrow \Rightarrow$ Forward; $T \downarrow \Rightarrow K \downarrow \Rightarrow$ Backward

So, ($K \propto T$)



Train Your Brain

Example 18: In a vessel containing SO_3 , SO_2 and O_2 at equilibrium, some helium gas is introduced so that the total pressure increases while temperature and volume remains constant. According to Le-chatelier principle, the dissociation of SO_3 :

- (a) increase (b) decrease
- (c) remain unaltered (d) changes unpredictable



$\Delta H = + \text{ve}$ endothermic reaction

Inert gas doesn't show reaction with the reacting mixture it show effect only due to its volume.

At constant volume doesn't effect of inert gas. Thus dissociation of SO_3 unchanged.

$$V = \text{constant} = \Delta n = 0$$

No effect of inert gas.

Example 19: Consider the reaction, $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$; in closed container at equilibrium. What would be the effect of addition of CaCO_3 on the equilibrium concentration of CO_2 ?

- (a) Increases
- (b) Decreases
- (c) Remains unaffected
- (d) Data is not sufficient to predict it

Sol. (c) Remains unaffected a CaCO_3 is solid and there is no effect of adding solid or liquid on equilibrium.

Example 20: In the reaction, $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) + X \text{ cals}$, most favourable condition of temperature and pressure for greater yield of SO_3 are-

- (a) Low temperature and low pressure
- (b) High temperature and low pressure
- (c) High temperature and high pressure
- (d) Low temperature and high pressure

Sol. (d) As reaction is exothermic so it is favoured at low temperature condition.

As $\Delta n_g < 0$ so SO_3 formation is favourable at high pressure condition.



Concept Application

23. For the gas phase reaction

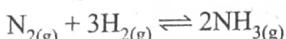
$\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$, $\Delta H = -32.7 \text{ kcal}$ carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by -

- (a) Increasing the temperature
- (b) Increasing concentration of H_2
- (c) Decreasing temperature
- (d) Increasing pressure

24. On adding inert gas to the equilibrium $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$ at constant pressure. The degree of dissociation will remain -

- (a) Unchanged
- (b) Decreased
- (c) Increased
- (d) None of these

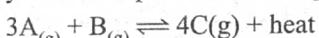
25. Adding inert gas to system



at equilibrium at constant volume will be -

- (a) N_2 and H_2 are formed in abundance
- (b) N_2 , H_2 and NH_3 will have the same molar concentration
- (c) The production of ammonia increases
- (d) No change in the equilibrium

26. Which among the following conditions, increase the yield of the product in the equilibrium,



- (a) Increase in pressure
- (b) Increase in volume
- (c) Increase in temperature
- (d) Decrease in temperature

THERMODYNAMICS OF EQUILIBRIUM

For a general reaction, $m\text{A} + n\text{B} \rightleftharpoons p\text{C} + q\text{D}$,

ΔG is given by-

$$\Delta G = \Delta G^\circ + 2.303 RT \log_{10} Q$$

where ΔG = Gibb's Free energy change

ΔG° = Standard Gibb's Free energy change

Q = reaction quotient

Since, at equilibrium, $Q = K$

Here K is thermodynamic equilibrium constant replacing K_c or K_p

$$K = \frac{(a_C)^p (a_D)^q}{(a_A)^m (a_B)^n}; \text{ Here } a_X \text{ denotes the activity of } X.$$

In fact, ' a_x ' is the ratio of the activity of substance at equilibrium and its activity in standard condition. That is why it is unitless and K is also unitless.

Note:

- (i) Thermodynamic equilibrium constant is unitless since activity is unitless.
- (ii) For pure solids & pure liquids, activity is unity.
- (iii) For gases (ideal behaviour), the activity is its partial pressure (in atm).
- (iv) For components in solution, activity is molar concentration.

At equilibrium, $\Delta G = 0$

$$\Rightarrow \Delta G^\circ = -2.303 RT \log_{10} K$$

Now since,

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

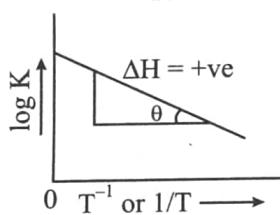
where ΔH° = Standard enthalpy change of the reaction

ΔS° = Standard entropy change

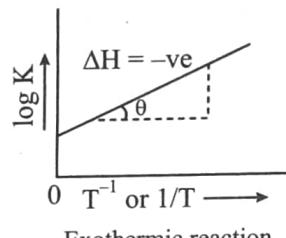
$$\Rightarrow -2.303 RT \log_{10} K = \Delta H^\circ - T\Delta S^\circ$$

$$\Rightarrow \log_{10} K = -\frac{\Delta H^\circ}{2.303R} \cdot \frac{1}{T} + \frac{\Delta S^\circ}{2.303R}$$

If plot of $\ln k$ vs $\frac{1}{T}$ is plotted then it is a straight line with slope $= -\frac{\Delta H^\circ}{R}$, and intercept $= \frac{\Delta S^\circ}{R}$



Endothermic reaction



Exothermic reaction

$$\text{Slope} = \frac{-\Delta H^\circ}{2.303R} = \tan \theta, \text{ y intercept} = \frac{\Delta S^\circ}{2.303R}$$

If at temperature T_1 , equilibrium constant is K_1 and at T_2 , it is K_2 then;

$$\log_{10} K_1 = \frac{-\Delta H^\circ}{2.303R} \cdot \frac{1}{T_1} + \frac{\Delta S^\circ}{2.303R} \quad \dots(i)$$

$$\log_{10} K_2 = \frac{-\Delta H^\circ}{2.303R} \cdot \frac{1}{T_2} + \frac{\Delta S^\circ}{2.303R} \quad \dots(ii)$$

[Assuming ΔH° and ΔS° remains constant in this temperature range.] Subtract eq. (ii) from (i) we get

$$\text{Van't Hoff equation : } \log \left(\frac{K_1}{K_2} \right) = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Note:

- ❖ ΔH should be substituted with sign.
- ❖ Unit of $\Delta H/T$ and gas constant R should be same.
- ❖ For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature
- ❖ For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature

Condition for Spontaneity: $\Delta G < 0$ for spontaneous process or reaction.

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

$$\Rightarrow \Delta H - T\Delta S < 0 \Rightarrow T > \Delta H/\Delta S$$

❖ $\Delta G > 0$ for non-spontaneous process or reaction

❖ $\Delta G = 0$ for equilibrium

Ex. From the following data:



State whether the reaction (iii) is exothermic or endothermic?

Sol. Equation (iii) = $-[2 \times (i) + (ii)]$

$$\therefore K_{2000(iii)} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$\because T \uparrow K \downarrow \Rightarrow$ reaction is exothermic.



Train Your Brain

Example 21: For the reaction,

$A(g) + B(g) \rightleftharpoons C(g) + D(g)$ at 298K, the values of ΔH° and ΔS° are -29.8 kcal and -0.1 kcal K^{-1} respectively. The values of ΔG° and equilibrium constant K_c are -

- (a) 1, 2 respectively (b) 0, 2 respectively
(c) 0, 1 respectively (d) 0, 0 respectively

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

$$\Delta H^\circ = -29.8 \times 10^3 \text{ Cal}$$

$$\Delta S^\circ = -0.1 \times 10^3 \text{ Cal}$$

$$\Delta G^\circ = -29.8 \times 10^3 - [-0.1 \times 10^3 \times 298]$$

$$\Delta G^\circ = -29800 + 29800$$

$$\Delta G^\circ = 0$$

$$\Delta G = \Delta G^\circ + 2.303 RT \log_{10} K_c$$

$$\Delta G = \text{zero at equilibrium}$$

$$\Delta G^\circ = -2.303 n RT \log_{10} K_c$$

$$K_c = 1$$

$$\log_{10} K_c = \frac{-\Delta G^\circ}{2.303 \times RT} = \frac{0}{2.303 \times 8.314 \times 298}$$

$$\log_{10} K_c = 0 \quad K_c = 1$$

Example 22: For the reaction,

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, the values of ΔH° and ΔS° at 298K are 77.2 kJ mol^{-1} and $122 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. The standard equilibrium constant at the same temperature is -

- (a) 0.695×10^{-8}
(b) 6.95×10^{-8}
(c) 69.5×10^{-8}
(d) 695×10^{-8}

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

$$= 77.2 \times 10^3 - 298 \times 122$$

$$= 77.2 \times 10^3 - 36356$$

$$= 40844$$

$$\begin{aligned}
 \text{at equ. } \Delta G^\circ &= -2.303 RT \log_{10} K_c \\
 40844 &= -2.303 \times 2477.58 \log_{10} K_c \\
 &= -5634.4737 \log_{10} K_c \\
 &= -\frac{40844}{5634.4737} = \log_{10} K_c \\
 \text{Antilog } &= 7.2489468 = \log K_c \\
 0.76 \times 10^{-8} &= K_c \\
 K_c &= 6.95 \times 10^{-8}
 \end{aligned}$$

PHYSICAL EQUILIBRIUM

Physical reaction: Those reaction in which change in only and only state of substance takes place without any chemical change is called physical reaction.

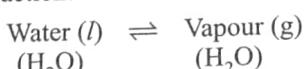
(a) **Ice-water system (melting of ice):** Melting of ice is accompanied by absorption of heat (endothermic) and decrease in volume



Hence both increase of temperature and pressure will favour the melting of ice into water.

(b) **Water-water vapour system (Vapourisation of water):**

Vapourisation of water is an endothermic and condensation of vapour into water is an exothermic reaction:

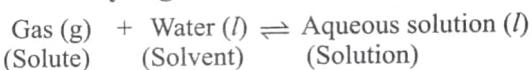


• The equilibrium shifts towards right side when the temperature is increased so rise in temperature will increase the vapour.

• The equilibrium shifts towards left side when the pressure is increased (i.e. volume is decreased) so increase in pressure will favour the rate of condensation of vapour into water.

• Thus favourable conditions for conversion of water into vapour are high temperature and low pressure.

(c) **Solubility of gases:**



• Effect of pressure → Solubility of gases which dissolve in a solvents increases with a decrease in volume, and with increasing pressure.

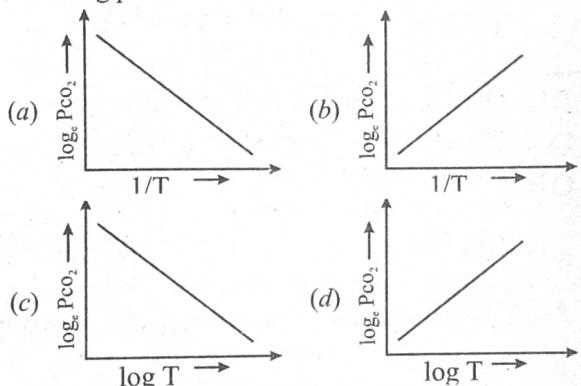
Concept Application

27. Van't Hoff's equation giving the effect of temperature on chemical equilibrium may be represented as -

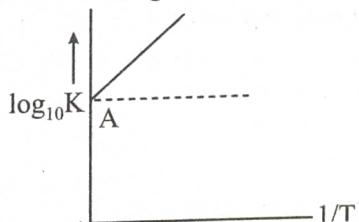
- (a) $\frac{d}{dT} \ln K_p = \frac{\Delta H^\circ}{RT^2}$ (b) $\frac{d}{dT} \ln K_c = \frac{\Delta H^\circ T^2}{R}$
 (c) $\frac{d}{dT} \ln K_p = \frac{\Delta H^\circ T^2}{R}$ (d) $\frac{d}{dT} \ln K_p = \frac{RT^2}{\Delta H^\circ}$

28. For the chemical equilibrium, $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

ΔH_f° can be determined from which one of the following plots?



29. Variation of $\log_{10} K$ with $\frac{1}{T}$ is shown by the following graph in which straight line is at 45° , hence ΔH° is:



- (a) + 4.606 cal
 (b) - 4.606 cal
 (c) 2 cal
 (d) - 2 cal

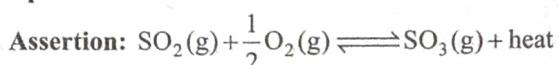


Train Your Brain

Example 23: On applying pressure to the equilibrium $\text{ice} \rightleftharpoons \text{water}$, which phenomenon will happen:

Sol. More water will be formed.

Example 24:



Forward reaction is favoured at low temperature and low pressure.

Reason:- Reaction is exothermic.

Sol. Assertion is incorrect & reason is correct



Concept Application

30. The solubility of CO_2 in water increases with :

- increase in temperature
- reduction of gas pressure
- increase in gas pressure
- increase in volume

31. In the melting of ice, which one of the conditions will be more favourable -

- High temperature and high pressure
- Low temperature and low pressure
- Low temperature and high pressure
- High temperature and Low pressure

IONIC EQUILIBRIUM

Introduction

Ionic Equilibrium: Weak electrolytes are partially ionised in aqueous solution and an equilibrium is situated between the ionised and unionised electrolyte. This type of equilibrium is known as ionic equilibrium.

Let us consider an acid HA which dissolved in water, an equilibrium will setup between ionised and unionised acid molecule as below -



All the substances can be classified into

Non electrolytic substances

- ❖ Does not dissociate into ions on dissolving in solvent like water.
- ❖ Solution will not conduct electricity eg. C_6H_6 , diethyl ether

Electrolytic Substances

- ❖ Will dissociate on dissolving in water into ions.
- ❖ Solution will conduct electricity eg. all acids, bases, all salts Hg_2Cl dissolve but dissociate negligible.

Electrolytic Substances

Strong electrolyte

- ❖ $\alpha = \text{unity (100% ionisation)}$
- Eg. Strong acids (generally HClO_4 , HI , HBr , HCl , H_2SO_4 , HNO_3), strong bases (generally NaOH , KOH , RbOH , CsOH and Ba(OH)_2), all type of soluble salts (SASB, SAWB, WASB, or WAWB).

Weak electrolyte

- ❖ $\alpha \ll 10\%$ or $\alpha < 0.1$ (generally valid if $K_{eq} < 10^{-3}$) electrolytes not 100% dissociated
- Eg. weak acids (CH_3COOH , HCN), weak bases (NH_3 , Zn(OH)_2) All sparingly soluble salts AgCl , BaSO_4 etc.

DEGREE OF DISSOCIATION

- ❖ When an electrolyte is dissolved in a solvent (H_2O), it spontaneously dissociates into ions.
- ❖ It may dissociate partially ($\alpha \ll 1$) or sometimes completely ($\alpha \approx 1$)



- ❖ The degree of dissociation of an electrolyte (α) is the fraction of one mole of the electrolyte that has dissociated under the given conditions.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

The value of α depends

- Nature of electrolyte:** Strong electrolyte dissociate completely where as weak electrolytes dissociate partially.
- Nature of solvent:** A solvent having high value of dielectric constant will favour dissociation.
- Dilution:** For weak electrolytes degree of dissociation will increases on dilution (Ostwald's dilution law)
- Temperature:** On increasing temperature generally degree of dissociation increases.
- Presence of other solute:** When a substance is present, it may effect the solubility of the another solute. Generally presence of common ion suppresses degree of dissociation of weak electrolyte.

ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION OR IONIZATION

- When an electrolyte dissociates into water, it gives two types of charged particles called ions.
- Ions which carry (+) ve charge and move towards cathode are called as 'Cations' while ions carrying (-) ve charge and moving towards anode called as 'anion'.
- Every electrolytic solution is always neutral in nature.
- Quantity or part of electrolyte which is ionized or decomposed or dissociate called as "Degree of Ionisation".
- Electrolyte which gives H^+ ions after dissociation in the aqueous solution is called as acid while that which gives OH^- after dissociation in the aqueous solution is called as base.

OSTWALD'S DILUTION LAW

This law deals with the application of the law of mass action to the equilibrium between the ions and unionized molecules in aqueous solutions of weak binary electrolytes such as acetic acid, propanoic acid, HCN, NH_4OH , etc.

Consider a dilute solution of a weak binary electrolyte AB containing c moles in 1 litre. At any given temperature, there will be equilibrium between the unionized molecules of AB and the ions A⁺ and B⁻. Let 'α' be the degree of dissociation of AB at equilibrium.



| | | | |
|-----------------------|----------|----|----|
| Initial conc. | c | 0 | 0 |
| Conc. at. equilibrium | c(1 - α) | cα | cα |

Then according to the law of mass action, the equilibrium constant K_{eq} will be given by

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha}$$

This expression "K_{eq} = $\frac{\alpha^2 c}{1-\alpha}$ " is called *Ostwald's dilution law*.

K_{eq} is called the dissociation (or ionization) constant of the weak electrolyte. α has a very small value for a weak electrolyte and is therefore negligible in comparison with unity.

$$\therefore 1 - \alpha \approx 1. \quad \therefore K_{eq} = \alpha^2 c$$

$$\alpha = \sqrt{\frac{K_{eq}}{c}} \quad \alpha \propto \sqrt{V}$$

This law is valid only for weak electrolytes that too in dilute solutions. It is not applicable for strong electrolytes.

ACIDS BASES AND SALTS

Arrhenius Concept:

Arrhenius Acid: Substance which gives H⁺ ion on dissolving in water (H⁺ donor)

e.g. HNO₃, HClO₄, HCl, HI, HBr, H₂SO₄, H₃PO₄ etc.

Types of Acids

| Mono basic acid | Di basic acid | Tri basic acid |
|---|---|---|
| ❖ Gives single H ⁺ per molecule e.g HA HNO ₃ , HClO ₄ , HCl | ❖ Gives two H ⁺ per molecule e.g H ₂ A H ₂ SO ₄ , H ₃ PO ₃ | ❖ Gives three H ⁺ per molecule e.g H ₃ A H ₃ PO ₄ |

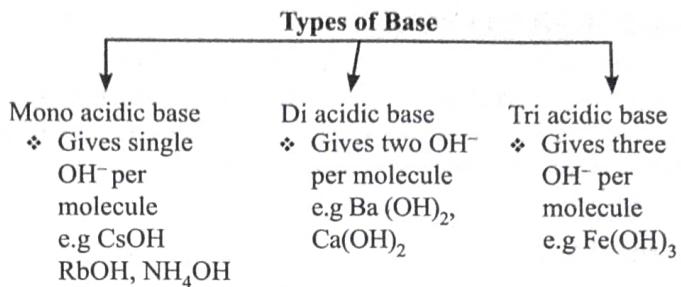
❖ H₃BO₃ is not Arrhenius acid.

❖ H⁺ ion in water is extremely hydrated (in form of H₃O⁺, H₅O₂⁺, H₇O₃⁺) and high charge density.

❖ The structure of solid HClO₄ is studied by X-ray, It is found to be consisting of H₃O⁺ and ClO₄⁻.



Arrhenius base: Any substance which releases OH⁻ (hydroxyl) ion in water (OH⁻ ion donor)



- ❖ OH⁻ ion also in hydrated form of H₃O₂⁻, H₇O₄⁻, H₅O₃⁻
- ❖ First group elements (except Li.) form strong bases.

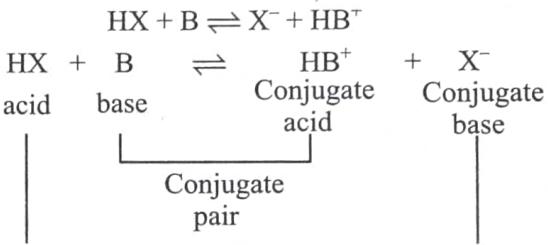
Bronsted - Lowery concept: (Conjugate acid - base concept) (Protonic concept)

Acid: Substances which donate H⁺ are Bronsted Lowery acids (H⁺ donor)

Base: Substances which accept H⁺ are Bronsted Lowery bases (H⁺ acceptor)

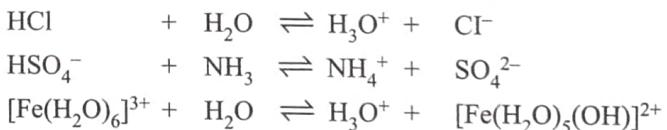
Conjugate acid - base pairs

In a typical acid base reaction



- ❖ Forward reaction – Here HX, being a proton donor, is an acid B, being a proton acceptor, is a base.
- ❖ Backward reaction – Here HB⁺, being a proton donor, is an acid X⁻, being a proton acceptor, is a base.

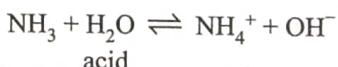
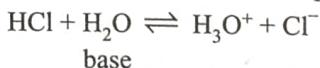
| Acid | Base | Conjugate Acid | Conjugate Base |
|------|------|----------------|----------------|
|------|------|----------------|----------------|



- ❖ Conjugate acid - base pair differ only by one proton
- ❖ Strong acid will have weak conjugate base and vice versa
- ❖ Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

| e.g. Acid | Conjugate base | Base | Conjugate acid |
|--------------------------------|-------------------------------|------------------|-------------------------------|
| HCl | Cl ⁻ | NH ₃ | NH ₄ ⁺ |
| H ₂ SO ₄ | HSO ₄ ⁻ | H ₂ O | H ₃ O ⁺ |
| HSO ₄ ⁻ | SO ₄ ²⁻ | RNH ₂ | RNH ₃ ⁺ |
| H ₂ O | OH ⁻ | | |

Amphoteric (amphiprotic): substances which can act as acid as well as base are known as amphoteric



Lewis Acids and Bases

According to Lewis concept of acids and bases, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor. An acid base reaction is the sharing of an electron pair with an acid by a base. This process is simply defined as coordination or neutralisation.

Lewis Acids

- Generally cations act as Lewis acids i.e., H^+ , Ag^+ , Fe^{2+} etc.
- Electron deficient molecules in which octet of central atom is not complete.
e.g. $AlCl_3$, BF_3 , BCl_3 , $BeCl_2$ etc.
- Molecules whose central atom can show expansion of octet due to availability of empty d-orbital.
e.g., SiX_4 , GeX_4 , SnX_4 , PX_3 , PF_5 , SF_4 , $TeCl_4$, SeF_4 etc.

Lewis Bases

- Neutral species having at least one or more lone pair of electrons available at central atom
e.g. $:PH_3$, $:NH_3$, $R\ddot{O}H$, $R-\ddot{N}H_2$ etc.
- Negatively charged species or anions e.g., Cl^- , CN^- , OH^- , X^- , NH_2^- , SH^- etc.
- Molecules having a multiple bond between atoms of dissimilar electronegativities
e.g., CO_2 , SO_2 etc.

Note: All bronsted bases are also Lewis bases but all bronsted acids are not Lewis acids.

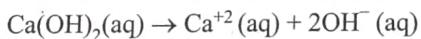
Strong and Weak Acids and Bases

Acids and Bases are classified as strong or weak.

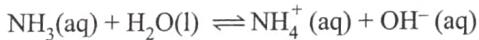
A **strong acid** is an acid that ionizes completely in water
e.g., $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
 $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

A **weak acid** is an acid that is only partially ionized in water
 $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
 $HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$

A **strong base** is a base that ionizes completely in water



A **weak base** is a base which is partially ionized in water

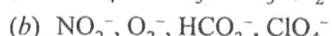
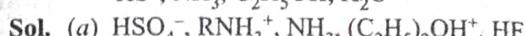


Train Your Brain

Example 25:

- Write conjugate acids of
 SO_4^{2-} , RNH_2 , NH_2^- , $C_2H_5O^-$, $C_2H_5^-$, F^-
- Write conjugate base of
 HNO_2 , OH^- , H_2CO_3 , $HClO_4$.

(c) Write conjugate acids and conjugate base of amphoteric species.



(c) Conjugate acids: H_2S , NH_4^+ , $C_2H_5OH_2^+$, H_3O^+
Conjugate base: S^{2-} , NH_2^- , $C_2H_5O^-$, OH^-

Example 26: The conjugate acid of HPO_4^{2-} is



Example 27: In the reaction $SnCl_2 + 2Cl^- \rightarrow SnCl_4$ is regarded as

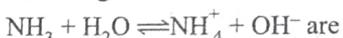
- Lewis acid
- Lewis base
- Neutral salt
- Basic salt

Sol. (a) $SnCl_2$ is a lewis acid because $SnCl_2$ is a electron acceptor.



Concept Application

32. According to Bronsted concept, the acids in the following reaction



- NH_3 and H_4^+
- H_2O and OH^-
- H_2O and NH_4^+
- NH_3 and OH^-

33. According to the Lewis acid-base concept-

- species in which the central atom has completed octet cannot act as an acid
- negatively charged ions are acids
- molecule in which a central atom has vacant d-orbitals available acts as an acid
- all positively charged ions are bases

34. Which equilibrium can be described as an acid-base reaction using the Lewis acid-base definition but not using Bronsted and Lowry concept?

- $NH_3 + CH_3COOH \rightleftharpoons CH_3COO^- + NH_4^+$
- $H_2O + CH_3COOH \rightleftharpoons CH_3COO^- + H_3O^+$
- $4NH_3 + Cu^{2+} \rightleftharpoons [Cu(NH_3)_4]^{2+}$
- $HCl + CH_3COOH \rightleftharpoons CH_3COO^+H_2 + Cl^-$

Properties of Water

❖ **Amphoteric (amphiprotic) Acid/base nature:** Water acts as an acid as well as base according to Arhenius and Bronsted-Lowry theory but according to Lewis concept it can be generally taken as base.

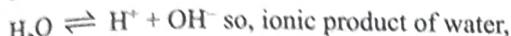
In pure water $[H^+] = [OH^-]$ so it is Neutral.



❖ **Molar concentration/Molarity of water:**

$$\text{Molarity} = \frac{\text{No. of moles/litre}}{18\text{gm / mole}} = \frac{1000\text{gm / litre}}{18\text{gm / mole}} = 55.55 \text{ mole/litre} = 55.55 \text{ M} (\text{density} = 1 \text{ gm/cc})$$

❖ **Ionic product of water :** According to Arrhenius concept



$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ at } 25^\circ \text{ (experimental)}$$

❖ Dissociation of water, is endothermic, so on increasing temperature K_{eq} increases.

The value of K_w increases with the increase in temperature i.e. the ionisation of water increases with increase in temperature and finally the concentration of H^+ and OH^- ion increases.

(a) Values of K_w at various temperature:

| Temperature ($^\circ\text{C}$) | Value of K_w |
|----------------------------------|----------------------------------|
| (1) 20 – 35 or 25° | 1×10^{-14} (Room temp.) |
| (2) 90 | 1×10^{-12} |

K_w increases with increase in temperature.

Now $\text{pH} = -\log[\text{H}^+] = 7$ and $\text{pOH} = \log[\text{OH}^-] = 7$ for water at 25° (experimental)

$$\begin{aligned} \text{pH} = 7 &= \text{pOH} \Rightarrow \text{neutral} \\ \text{pH} < 7 \text{ or } \text{pOH} > 7 &\Rightarrow \text{acidic} \\ \text{pH} > 7 \text{ or } \text{pOH} < &\Rightarrow \text{Basic} \end{aligned} \quad \left. \right\} \text{at } 25^\circ\text{C}$$

❖ Ionic product of water is always a constant value whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.

❖ **Degree of dissociation of water:**

$$\begin{aligned} \text{H}_2\text{O} &\rightleftharpoons \text{H}^+ + \text{OH}^- \\ \Rightarrow \alpha &= \frac{\text{no. of moles dissociated}}{\text{total no. of moles initially taken}} \\ &= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7}\% \end{aligned}$$

ACIDITY AND PH SCALE

❖ Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.

So greater the tendency to give H^+ , more will be the acidic strength of the substance.

❖ Basic strength means the tendency of a base to give OH^- ions in water.

So greater the tendency to give OH^- ions, more will be basic strength of the substance.

❖ The concentration of H^+ ions is written in a simplified form introduced by Sorenson known as pH scale.

pH of solution may be defined as negative logarithm of hydronium ion concentration.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]; [\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$\text{pH} = \log \frac{1}{[\text{H}_3\text{O}^+]}$$

Similarly, we can define pOH as $\text{pOH} = -\log[\text{OH}^-]$, $[\text{OH}^-] = 10^{-\text{pOH}}$. The pH range at 25°C is taken as 0 to 14.

pH = 7 Neutral

pH > 7 Basic

pH < 7 Acidic

Relation between pH & pOH

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 10^{-14} \text{ at } 25^\circ\text{C}$$

$$\log[\text{H}_3\text{O}^+] + \log[\text{OH}^-] = \log K_w = \log 10^{-14} = -14$$

$$\boxed{\text{pH} + \text{pOH} = \text{p}K_w = 14 \text{ at } 298 \text{ K.}}$$

Common ion effect

For pure water $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$.

If acid is added to pure water, then

$$[\text{H}_3\text{O}^+] > 10^{-7}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]}$$

If base is added to pure water

$$[\text{OH}^-] > 10^{-7}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

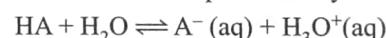
According to common ion effect, the ionization of weak electrolyte is suppressed in presence of some electrolyte, (if the strong electrolyte gives an ion which is common to the ion of weak electrolyte).

Ionization Constants of Weak Acids and Weak Bases

The dissociation of weak acids or weak bases in water can be represented as an equilibrium process eg.



In general, If a weak acid is represented by HA, its dissociation in water can be represented by the equilibrium.



Applying the law of chemical equilibrium, the expression for equilibrium constant will be

$$K = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}][\text{H}_2\text{O}]}$$

As H_2O is solvent, its concentration is large and remains almost constant. So, we can multiply both constant $K(\text{H}_2\text{O}) = K_a$ called dissociation constant of the acid Thus,

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

Knowing the value of the dissociation constant of the acid (K_a) and the concentration (c) of the weak acid HA. The concentration of H_3O^+ or $\text{H}^+(\text{aq})$ in the solution can be calculated as follows



Initial concentration c 0 0

Conc. at eqm. $(c - c\alpha)$ $c\alpha$ $c\alpha$

(Here α is degree of ionisation)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{\alpha c \times \alpha c}{c(1-\alpha)} = \frac{\alpha^2 c^2}{c(1-\alpha)}$$

Hence, for $\alpha \ll 1$

$$K_a = \alpha^2 c$$

$$\alpha = \left(\frac{K_a}{C}\right)^{1/2}$$

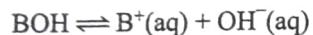
$$\alpha = (K_a \times V)^{1/2}$$

Here, V is the volume of the solution in litres containing 1 mole of the electrolyte, $c = \frac{1}{V}$.

In case of a weak electrolyte, at a given temperature, the degree of ionisation is inversely proportional to the square root of the molar concentration or directly proportional to square root of the volume of the solution which contains one mole electrolyte.

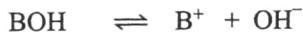
This is called **Ostwald's dilution law**.

Similarly the dissociation of a weak base in water can be represented by the equilibrium



The dissociation constant of the weak base, represented by K_b , will be given by

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$$



| | | | |
|------------------------------|---------------|------------|------------|
| Initial concentration | c | 0 | 0 |
| Concentration at equilibrium | $c(1-\alpha)$ | αc | αc |

$$\text{Now, } K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} = \frac{\alpha c \times \alpha c}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha}$$

For a weak electrolyte, if α is very small, it can be neglected

$$\therefore K_b = \alpha^2 c$$

Knowing the ionization constant, K_a of an acid and K_b of a base and its initial concentration c , it is possible to calculate the equilibrium concentration of all species and also the degree of ionisation of the acid and base and the pH of the solution

Degree of ionisation for acid (α)

$$= \sqrt{\frac{K_a}{c}} \text{ or } \left(\frac{K_a}{c}\right)^{1/2} \text{ and } c\alpha = [\text{H}_3\text{O}^+]$$

Degree of ionisation for base (α)

$$= \sqrt{\frac{K_b}{c}} \text{ or } \left(\frac{K_b}{c}\right)^{1/2} \text{ and } c\alpha = [\text{OH}^-]$$

Factors Affecting Acidic Strength

Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid mainly depends upon two factors i.e. strength and polarity of the H-A bond

Weaker the H-A bond, more easily it gets dissociated to give H^+ ion and hence, stronger is the acid. Similarly, greater the polarity of the H-A bond i.e., larger the electronegativity difference between the atoms H and A, more easily the bond breaks and hence, greater is the acidic strength.

For elements in the same group of periodic table, the bond strength dominates over the polar nature. Thus, down the group, as size of the atoms increases, bond strength decreases and hence, acidic strength increases. For example, for the element of group-17.

HF < HCl < HBr < HI
↓
Acidic strength increases
Similarly, for the elements of group-16, acidic strength increases as:



For the elements along the same period, however the polarity of the H-A bond decides the acidic strength. With increase in the electronegativity of A the polarity of the bond increases and hence the acidic strength also increases. For example

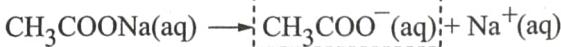
$\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$
↓
Acidic strength increases electronegativity
increases polarity increases

Common Ion Effect in the Ionization of Acids and Bases

We know that a weak electrolyte is dissociated to small extent in solution and there is an equilibrium between the undissociated electrolyte and the ions formed in solution. If we add a strong electrolyte, having an ion common with the weak electrolyte, then the dissociation of the weak electrolyte gets further suppressed or decreased.

“The suppression in the dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion is called common ion effect.”

For example: Ionization of acetic acid (CH_3COOH) and effect of addition of a small amount of acetate on



Common ion

Due to the presence of common CH_3COO^- (aq) ions, the equilibrium will be shifted to the left according to Le Chatelier's principle.

In order to evaluate the pH of the solution resulting on addition of 0.05 M acetate ion to 0.05 M acetic acid solution we shall consider the acetic acid dissociation equilibrium once again.

| | | | | |
|---------------------------|-------------------------------------|----------------------|---|---|
| | $\text{CH}_3\text{COOH}(\text{aq})$ | \rightleftharpoons | $\text{CH}_3\text{COO}^- + \text{H}^+(\text{aq})$ | |
| Initial concentration | 0.05M | | 0.05M | 0 |
| Equilibrium Concentration | 0.05-x | | (0.05+x) | x |

Here α is the extent of ionization of acetic acid

$$\text{Now, } K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

The dissociation of acid is now decided by the non-common ion, therefore

$$[\text{H}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

Here, concentration of $(\text{CH}_3\text{COO}^-)$ ion after adding acetate ion becomes $(0.05 + x)$

For a weak electrolyte, $x \ll 0.05$

$$\text{Hence. } (0.05 + x) = (0.05 - x) - 0.05$$

$$\text{Thus, } [\text{H}^+] = \frac{K_a \times 0.05}{0.05}$$

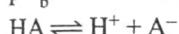
$$[\text{H}^+] = K_a = 1.8 \times 10^{-5} \text{ M}$$

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

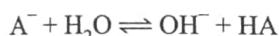
Relationship between pK_a and pK_b

pK_a = Ionization constant of weak acid

pK_b = Ionization constant of conjugate base



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \dots(i)$$



$$K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} \quad \dots(ii)$$

Multiplying equation (i) & (ii)

$$K_a \times K_b = [\text{H}^+][\text{OH}^-] = K_w$$

$$\text{i.e., } K_a \times K_b = K_w$$

$$\therefore \log K_a + \log K_b = \log K_w$$

$$pK_a + pK_b = pK_w$$

PH CALCULATIONS OF DIFFERENT TYPES OF SOLUTIONS

(a) Strong acid Solution:

(i) If concentration is greater than 10^{-6} M

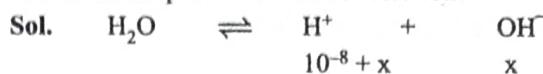
In this case H^+ ions coming from water can be neglected, so $[\text{H}^+]$ = normality of strong acid solution.

(ii) If concentration is less than 10^{-6} M

In this case H^+ ions coming from water cannot be neglected,

So $[\text{H}^+]$ = normality of strong acid + H^+ ions coming from water in presence of this strong acid

Ex: Calculate pH of 10^{-8} M HCl solution.



$$K_w = [\text{H}^+][\text{OH}^-]$$

$$10^{-14} = x(x \times 10^{-8})$$

$$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2}$$

$$= \frac{-10^{-8} + 10^{-7} \sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401} - 1)10^{-8}}{2}$$

$$= 0.95 \times 10^{-7}$$

$$[\text{H}^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7} \text{ M}$$

$$\text{pH} = 7 - \log 1.05 \approx 6.98$$

$$\text{for } 10^{-9} \text{ M HCl pH} \approx 7$$

$$\text{for } 10^{-12} \text{ M HCl pH} \approx 7$$

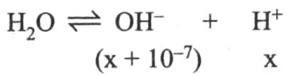
(b) Strong base Solution: Calculate the $[\text{OH}^-]$ which will be equal to normality of the strong base solution and then use $K_w = [\text{H}^+] \times [\text{OH}^-] = 10^{-14}$, to calculate $[\text{H}^+]$.

Ex: Calculate pH of 10^{-7} M NaOH solution.

Sol. $[\text{OH}^-]$ from NaOH = 10^{-7} M

$[\text{OH}^-]$ from water = $x < 10^{-7} \text{ M}$

(due to common ion effect)



$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} = x(x + 10^{-7})$$

$$x^2 + 10^{-7}x - 10^{-14} = 0$$

$$\Rightarrow x = \frac{\sqrt{5} - 1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \text{ M} = [\text{H}^+]$$

$$\text{pH} = 7.21 \quad (\sqrt{5} = 2.236)$$

(c) pH of mixture of two strong acids: If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of another strong acid solution of normality N_2 , then

equi. of H^+ ions from I - solution = $N_1 V_1$

equi. of H^+ ions from II - solution = $N_2 V_2$

If final normality is N and final volume is V , then

$$NV = N_1 V_1 + N_2 V_2$$

$$[\text{H}^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

(d) pH of mixture of two strong bases: similar to above calculation

$$[\text{OH}^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \quad \& \quad [\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]}$$

(e) pH of mixture of a strong acid and a strong base:

• Acid Base neutralisation reaction will take place.

• The solution will be acidic or basic depending on which component has been taken in excess.

• If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of a strong base solution of normality N_2 , then

- Number of eq. H^+ ions from I-solution = $N_1 V_1$
- Number of eq. OH^- ions from II-solution = $N_2 V_2$

↓

If $N_1 V_1 > N_2 V_2$

$$[H^+] = N = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

solution will be acidic in nature

↓

If $N_2 V_2 > N_1 V_1$

$$[OH^-] = N = \frac{N_2 V_2 - N_1 V_1}{V_1 + V_2}$$

solution will be basic in nature

$$[H^+] = \frac{10^{-14}}{[OH^-]}$$



Train Your Brain

Example 28: Calculate pH of a KOH solution having:

- 5.6 g of KOH mixed in 50 ml water.
- if it is further diluted to make 100 ml.

Sol. (a) Mole of KOH = $\frac{5.6}{56} = 0.1$

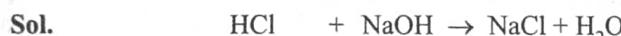
$$[OH^-] = 2M$$

$$pOH = -0.3 \Rightarrow pH = 14.3$$

(b) $[OH^-] = 1M$

$$pOH = 0 \Rightarrow pH = 14$$

Example 29: Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.



| | | | | |
|-------------|------------------|----------------|-----|-----|
| Meq. before | 100×0.1 | 9.9×1 | 0 | 0 |
| reaction | = 10 | = 9.9 | | |
| Meq. after | 0.1 | 0 | 9.9 | 9.9 |

reaction

$$\therefore [H^+] \text{ left from HCl} = \frac{0.1}{109.9} = 9.099 \times 10^{-4} M$$

$$\therefore pH = -\log H^+ = -\log 9.099 \times 10^{-4}$$

$$pH = 3.04$$

Example 30: The pH of a solution obtained by mixing 50 ml of 0.4 N HCl and 50 ml of 0.2 N NaOH is

- $-\log 2$
- $-\log 0.2$
- 1.0
- 2.0

Sol. (c) $[H^+] = \frac{(50 \times 0.4) - (50 \times 0.2)}{100} = \frac{10}{100} = 0.1$

$$pH = -\log[H^+] = 1$$

Example 31: Calculate pH of mixture of (400ml, $\frac{1}{200}$ M $Ba(OH)_2$) + (400ml, $\frac{1}{50}$ M HCl) + (200ml of Water)

$$\text{Sol. } [H^+] = \frac{\left(400 \times \frac{1}{50}\right) - \left(400 \times \frac{1}{200} \times 2\right)}{1000} = 4 \times 10^{-3} M,$$

$$\text{so } pH = 3 - 2 \log 2 = 2.4$$



Concept Application

35. When 100 ml $Ca(OH)_2$ solution of 0.01 M is diluted with water, the pH of the resulting solution changes to 12. Volume of water added is-

- 10 ml
- 50 ml
- 100 ml
- 200 ml

36. Which of the following have largest pH?

- | | |
|-------------------------|--------------------------|
| (a) $\frac{M}{10} HCl$ | (b) $\frac{M}{100} HCl$ |
| (c) $\frac{M}{10} NaOH$ | (d) $\frac{M}{100} NaOH$ |

37. Solution X has pH = 2 and solution Y has pH = 5 which one of the following is correct ?

- Solution X is twice as acidic as Y
- Solution Y is twice as acidic as X
- Solution X is 1000 times more acidic than Y
- Solution Y is 1000 times more acidic than X

38. 20 ml of 0.5 N HCl and 35 ml of 0.1 N NaOH are mixed. The resulting solution will

- be basic
- be neutral
- turn methyl orange red
- turn phenolphthalein solution pink

(f) pH of a weak acid (monoprotic) Solution:

- Weak acid does not dissociate 100% therefore we have to calculate the percentage dissociation using K_a dissociation constant of the acid.
- We have to use Ostwald's Dilution law (as we have been derived earlier)



$$t=0 \quad C \quad 0 \quad 0$$

$$t=t_{eq} \quad C(1-\alpha) \quad C\alpha \quad C\alpha$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha^2}{1-\alpha}$$

$$\text{If } \alpha \ll 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2$$

$$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \quad (\text{is valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$[H^+] = C\alpha = C \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$$

$$\Rightarrow \text{So } pH = \frac{1}{2}(pK_a - \log C)$$

on increasing dilution

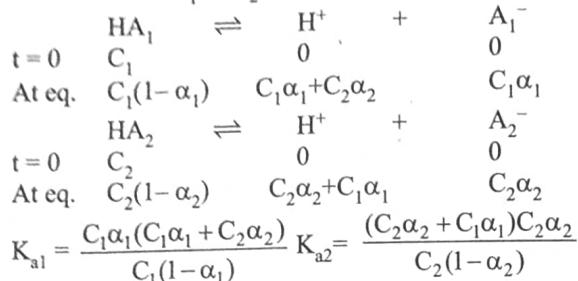
$\Rightarrow C \downarrow \Rightarrow \alpha \uparrow \text{ and } [H^+] \downarrow \Rightarrow pH \uparrow$



- If the total $[H^+]$ from the acid is greater than $10^{-6} M$, then contribution from the water can be neglected at $25^\circ C$. If not then we have to take $[H^+]$ from the water also.

(h) **pH of a mixture of two weak acid (both monoprotic) solutions:**

- Both acids will dissociate partially.
- Let the acid are HA_1 & HA_2 and their concentrations in the mixture are C_1 & C_2 respectively, then



(Since α_1, α_2 both are small in comparison to unity)

$$K_{a1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1; K_{a2} = (C_1\alpha_1 + C_2\alpha_2)\alpha_2$$

$$\Rightarrow \frac{K_{a1}}{K_{a2}} = \frac{\alpha_1}{\alpha_2}$$

$$\begin{aligned} [H^+] &= C_1\alpha_1 + C_2\alpha_2 \\ &= \frac{C_1K_{a1}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} + \frac{C_2K_{a2}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} \end{aligned}$$

$$\Rightarrow [H^+] = \sqrt{C_1K_{a1} + C_2K_{a2}}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected. So, $[H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$



Train Your Brain

Example 35: Calculate pH of solution obtained by mixing equal volume of $0.02 M$ $HOCl$ & $0.2 M$ CH_3COOH solutions. Given that K_{a1} ($HOCl$) = 2×10^{-4} , K_{a2} (CH_3COOH) = 2×10^{-5} also calculate $[OH^-]$, $[OCl^-]$, $[CH_3COO^-]$ at equilibrium.

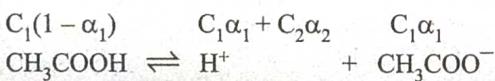
Sol. Volume of final solution become double.

So concentration become half

$$C_1 = 0.01 M, \quad C_2 = 0.1 M$$

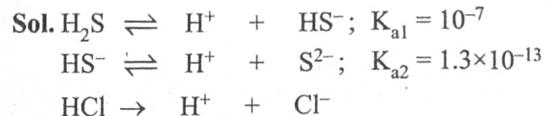
$$\begin{aligned} [H^+] &= \sqrt{K_{a1}C_1 + K_{a2}C_2} \\ &= \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1} \\ &= \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3} M \end{aligned}$$

$$pH = 3 - \log 2 = 2.7$$



$$\begin{array}{l} C_2(1-\alpha_2) \quad C_1\alpha_1 + C_2\alpha_2 \quad C_2\alpha_2 \\ \alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 0.1 \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 0.01 \\ [OCl^-] = C_1\alpha_1 = 0.01 \times 10^{-1} = 1 \times 10^{-3} M \\ [CH_3COO^-] = C_2\alpha_2 = 0.1 \times 10^{-2} = 1 \times 10^{-3} M \\ [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12} M \end{array}$$

Example 36: A solution contains $0.1 M$ H_2S and $0.3 M$ HCl . Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a1} and K_{a2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.



Due to common ion effect the dissociation of H_2S is suppressed and the $[H^+]$ in solution is due to HCl .

$$\therefore K_{a1} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$\Rightarrow 10^{-7} = \frac{[0.3][HS^-]}{[0.1]} \quad [\because [H^+] \text{ from } HCl = 0.3]$$

$$\therefore [HS^-] = \frac{10^{-7} \times 0.1}{0.3} = 3.3 \times 10^{-8} M$$

$$\text{Further } K_{a2} = \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$\Rightarrow 1.3 \times 10^{-13} = \frac{[0.3][S^{2-}]}{3.3 \times 10^{-8}}$$

$$\therefore [S^{2-}] = \frac{1.3 \times 10^{-13} \times 3.3 \times 10^{-8}}{0.3} = 1.43 \times 10^{-20} M$$

Concept Application

42. For $10^{-2}(M)$ H_3PO_3 solution which of the following relations is correct?

- $[H_3PO_3] + [H_2PO_3^-] + [HPO_3^{2-}] + [PO_3^{2-}] = 10^{-2}$
- $[H_3PO_3] + [H_2PO_3^-] + [HPO_3^{2-}] = 10^{-2}$
- $[H_2PO_3^-] + [HPO_3^{2-}] + [PO_3^{2-}] = 10^{-2}$
- $[H_3PO_3] + [H_2PO_3^-] + 2[HPO_3^{2-}] = 10^{-2}$

43. The ratio of acid strength of $HOCl$ and HCN is about Given K_a of $HOCl = 1.2 \times 10^{-4}$ and K_a of $HCN = 4.2 \times 10^{-10}$

- 534 : 1
- 1 : 548
- $2.86 \times 10^5 : 1$
- $2.86 \times 10^4 : 1$

44. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} & 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be
 (a) 5.0×10^{-5} (b) 5.0×10^{15}
 (c) 5.0×10^{-15} (d) $0.2 \times 10_5$

- All these steps can be followed for the calculation of pOH for weak base and their mixtures (we just have to replace K_a with K_b).

pH of a mixture of a weak acid/ weak base with weak/strong base/acid respectively.

For this type of mixtures there can be two cases in general.

- (i) if the acids and bases are mixed in equal amounts (equivalents)
 - (ii) if the acids and bases are mixed in different amounts (equivalents)

First case will lead to phenomenon of **Salt Hydrolysis** and second case will lead to formation of **Buffer Solutions**.

SALTS

- (a) Species formed by the reaction of neutralization of acid and base is called as salt.
 - (b) salt formation is the exothermic process and released energy by this reaction is called as the heat of neutralization for 1 eq. monoacidic base and 1 eq. monobasic acid.
 - (c) The value of heat of neutralization is equal to 13.6 kcal.
 - (d) Salts are generally crystalline solid.
 - (e) Salts are classified into following four types.

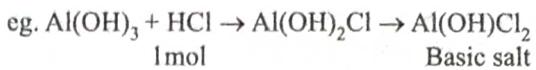
SIMPLE SALTS

These salts formed by the neutralisation process, which are of three types.

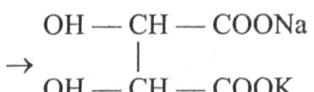
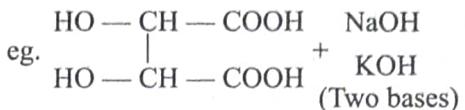
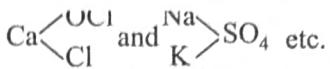
- (a) **Normal Salt:** These salts are formed by the neutralization reaction of simple acid and simple base, like - NaCl, NH₄Cl, CH₃COONa, KNO₃ etc.

(b) **Acidic Salt:** It is formed by the incomplete neutralization reaction of acid with the base is called the acidic salt and gives proton in aqueous solution. Like - NaHCO₃, NaHSO₄, Na₂HPO₄
 eg. $\text{H}_2\text{SO}_4 + \text{NaOH} \rightarrow \text{NaHSO}_4$

(c) **Basic salt:** Salt which is formed by the incomplete neutralization reaction of base with acid called the basic salt and gives OH⁻ ion in aqueous solution. Like- Zn(OH)Cl, Mg(OH)Cl, Fe(OH)₂Cl etc.
 eg. $\text{Ca}(\text{OH})_2 + \text{HCl} \rightarrow \text{Ca}(\text{OH})\text{Cl}$
 1mol Basic salt
 eg. $\text{Mg}(\text{OH})_2 + \text{HNO}_3 \rightarrow \text{Mg}(\text{OH})\text{NO}_3$
 1mol Basic salt



Mixed Salts: Salt which are formed by the neutralisation reaction of more than two different acids and bases are called mixed salt. Or Salts which furnish more than one cation or more than one anion when dissolved in water are also as mixed salt. Like Rochelle Salt,



Double salts: Salts which are formed by the addition of two or more simple salts are called as double salt.



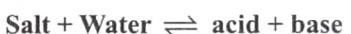
Complex Salts:

- (a) Salt which are formed by the donation of electron pair by the ligand molecule with the metal ion are called as complex salts. Or salts which are formed by the combination of simple salts or molecular compounds.

(b) Complex salts are stable in solid state.

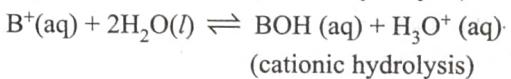
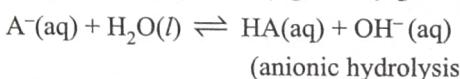
(c) On dissolving in the water, complex salts gives minimum one complex ion -
 eg. $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4] SO_4$
 or all coordination compound
 $K_4 [Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

SALT HYDROLYSIS (REVERSE OF NEUTRALISATION)



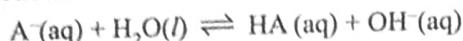
When acids and bases are mixed in equal amounts(equivalents), then we will be having salt solutions only in the water and we have to calculate pH of salt solutions.

When a salt is added to water, the solid salt first dissolves and breaks into ions completely(unless otherwise specified). The ions of the salt may or may not react with water, the cations when react with water will produce H_3O^+ ions and the anions on reaction with water will produce OH^- ions. Depending on the extent of hydrolysis and on the amounts of H_3O^+ and OH^- ions the solution can be acidic, basic or neutral. If salt is BA, then



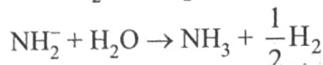
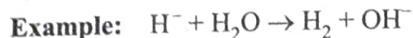
ANIONIC HYDROLYSIS

Anions can function as a base on reaction with water and hydrolyse as follows :



The extent of hydrolysis of a given anion depends on its basic strength

(a) **Complete hydrolysis:** The anions, which are stronger base than OH^- and the conjugate acids of the anions are weaker acid than H_2O , they will show complete hydrolysis in aqueous medium.



(b) **Hydrolysis to a limited extent:** The anions, which are weaker base than OH^- and the conjugate acids are stronger acid than H_2O but weaker acid than H_3O^+ will hydrolyse to a limited extent in aqueous medium



Other Examples are CH_3COO^- , NO_2^- , S^{2-} etc.

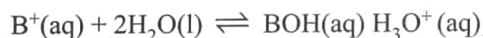
(c) **No hydrolysis:** The anions that are weaker base than OH^- and the conjugate acids are stronger than both H_2O and H_3O^+ do not hydrolyse at all.



Other Examples include SO_4^{2-} , NO_3^- , ClO_4^- etc.

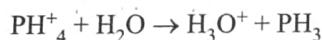
CATIONIC HYDROLYSIS

Cations can function as acid on reaction with water and hydrolysis as follows.

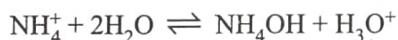


The extent of hydrolysis of a given cation depends on its acidic strength.

(a) **Complete hydrolysis:** The cations, which are stronger acid than H_3O^+ and their conjugate bases are very much weaker than H_2O will show complete hydrolysis. Example is PH_4^+ ion.



(b) **Hydrolysis to a limited extent:** The cations, which are weaker acid than H_3O^+ ion and their conjugate bases are stronger than H_2O but weaker than OH^- , show hydrolysis to a limited extent. For Example



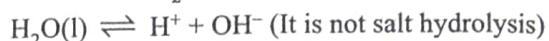
Other ions showing hydrolysis to limited extent are $C_6H_5NH_3^+$, $CH_3NH_3^+$ etc.

(c) **No hydrolysis:** The cations, which are weaker acid than H_3O^+ and their conjugate bases are stronger than both H_2O and OH^- do not hydrolyze at all. Example is alkali and alkaline earth metal ions.



(A) Hydrolysis of strong acid and strong base [SA – SB] types of salt –

Ex. $NaCl$, $BaCl_2$, Na_2SO_4 , $KClO_4$, $BaSO_4$, $NaNO_3$, KBr , KCl etc.



(i) Hydrolysis of salt of [SA – SB] is not possible.

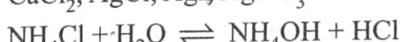
(ii) Aqueous solution of these type of salt is neutral in nature. ($pH = pOH = 7$)

(iii) pH of the solution is 7.

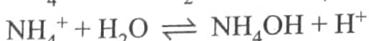
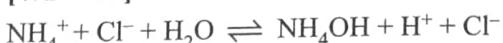
(iv) No effect on litmus paper.

(B) Hydrolysis of strong acid and weak base [SA - WB] types of salt –

Ex. $CaSO_4$, NH_4Cl , $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$, $AgCl$, AgI , $AgNO_3$ etc



[WB - SA]



(i) In this type of salt hydrolysis, cation reacts with H_2O therefore called as cationic hydrolysis.

(ii) Solution is acidic in nature as $[H^+]$ is increased.

(iii) pH of the solution is less than 7.

(iv) Solution turns blue litmus paper red.

K_h = Hydrolysis constant

K_w = Ionic product of water

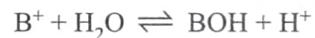
K_a = Ionisation constant of acid

K_b = Ionisation constant of base

h = Degree of hydrolysis

C = Concentration of salt (concentration of ions)

(a) Relation between K_h , K_w and K_b



Hydrolysis constant $[K_h]$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad \dots(1)$$

For weak Base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \dots(2)$$

For water $H_2O \longrightarrow H^+ + OH^-$

$$K_w = [H^+] [OH^-] \quad \dots(3)$$

Now multiplying Eq. (1) and (2) = Eq. (3)

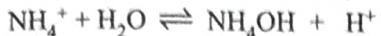
$$\frac{[NH_4OH][H^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} = [H^+] [OH^-]$$

$$\text{i.e. } K_h \times K_b = K_w$$

$$K_h = \frac{K_w}{K_b}$$

...(4)

(b) Degree of hydrolysis – Represented by h



Initial concentration of salt

$$\begin{array}{ccc} C & 0 & 0 \\ C - Ch & Ch & Ch \end{array}$$

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{Ch \times Ch}{C - Ch}$$

$$= \frac{C^2 h^2}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

Since $h \ll \ll \ll 1$ then $(1-h) \approx 1$

$$\therefore K_h = Ch^2 \quad \dots(5)$$

$$h^2 = \frac{K_h}{C} \Rightarrow h = \sqrt{\frac{K_h}{C}} \quad \dots(6)$$

$$\therefore K_h = \frac{K_w}{K_b} \Rightarrow h = \sqrt{\frac{K_w}{K_b}}$$

$$h = \sqrt{\frac{K_w}{K_b \times C}} \quad \dots(7)$$

(c) pH of the solution: $\text{pH} = -\log [\text{H}^+]$

$$[\text{H}^+] = Ch = C \sqrt{\frac{K_w}{K_b \times C}} \Rightarrow [\text{H}^+] = \sqrt{\frac{K_w \times C}{K_b}} \quad \dots(8)$$

taking $-\log$ on both sides

$$-\log [\text{H}^+] = -\log \sqrt{\frac{K_w \times C}{K_b}}$$

$$\Rightarrow \text{pH} = -\log \left(\frac{K_w \times C}{K_b} \right)^{1/2}$$

$$\text{pH} = -\frac{1}{2} [\log K_w + \log C - \log K_b]$$

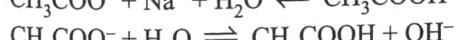
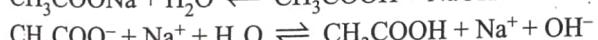
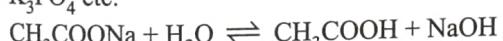
$$\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log C - \frac{1}{2} (-\log K_b)$$

$$\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \log C - \frac{1}{2} \text{p}K_b$$

$$\boxed{\text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C} \quad \dots(9)$$

(C) Hydrolysis of weak acid and strong base [WA – SB] types of salt –

Ex. CH_3COONa , HCOONa , KCN , NaCN , K_2CO_3 , BaCO_3 , K_3PO_4 etc.



• In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis.

• Solution is basic in nature as $[\text{OH}^-]$ increases.

• pH of the solution is greater than 7.

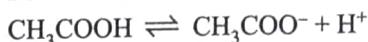
• Solution turns red litmus paper blue.

(i) Relation between K_h , K_w and K_a



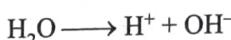
$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \dots(1)$$

For weak acid



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \dots(2)$$

For water



$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots(3)$$

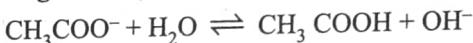
Now multiply eq. (1) \times eq. (2) = eq. (3)

$$\frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \\ = [\text{H}^+][\text{OH}^-]$$

$$K_h \times K_a = K_w$$

$$\boxed{K_h = \frac{K_w}{K_a}} \quad \dots(4)$$

(ii) Degree of hydrolysis (h):



$$\begin{array}{ccc} C & 0 & 0 \\ C - Ch & Ch & Ch \end{array}$$

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2 h^2}{C(1-h)}$$

$$K_h = \frac{Ch^2}{(1-h)}$$

Since $h \ll \ll \ll 1$ then $(1-h) \approx 1$

$$\therefore \boxed{K_h = Ch^2} \quad \dots(5)$$

$$h^2 = \frac{K_h}{C} \text{ or } h = \sqrt{\frac{K_h}{C}} \quad \dots(6)$$

$$\boxed{h = \sqrt{\frac{K_w}{K_a \times C}}} \quad \dots(7)$$

(iii) pH of the solution

$$[\text{OH}^-] = Ch$$

$$[\text{OH}^-] = C \times \sqrt{\frac{K_w}{K_a \times C}} \text{ or } [\text{OH}^-] = \sqrt{\frac{K_w \times C}{K_a}}$$

$$\therefore K_w = [\text{OH}^-][\text{H}^+]$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}} \\ [H^+] = \sqrt{\frac{K_w \times K_a}{C}} \quad \dots(8)$$

taking - log on both sides

$$-\log [H^+] = -\log \sqrt{\frac{K_w \times K_a}{C}}$$

$$pH = -\log \left(\frac{K_w \times K_a}{C} \right)^{1/2}$$

$$pH = -\frac{1}{2} [\log K_w + \log K_a - \log C]$$

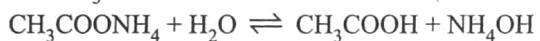
$$pH = -\frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log C$$

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C \quad \dots(9)$$

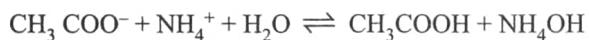
(D) Hydrolysis of weak acid and weak base (WA - WB) type of salt:

Ex. $\text{CH}_3\text{COONH}_4$, AgCN , NH_4CN , CaCO_3 , $[\text{NH}_4]_2\text{CO}_3$, ZnHPO_3 etc.



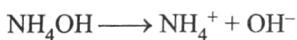
+ Solution is almost neutral but it may be acidic or basic depending upon the nature of acid and base and pH of the solution is near to 7.

(a) Relation between K_h , K_w , K_a and K_b



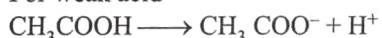
$$K_h = \frac{[CH_3\text{COOH}][NH_4\text{OH}]}{[CH_3\text{COO}^-][NH_4^+]} \quad \dots(1)$$

For weak base



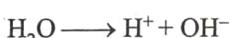
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4\text{OH}]} \quad \dots(2)$$

For weak acid



$$K_a = \frac{[CH_3\text{COO}^-][H^+]}{[CH_3\text{COOH}]} \quad \dots(3)$$

For water



$$K_w = [H^+][OH^-] \quad \dots(4)$$

Multiply Eq. (1) \times Eq. (2) \times Eq. (3) = Eq. (4)

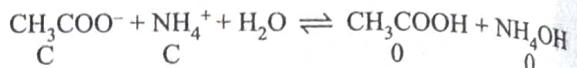
$$\frac{[CH_3\text{COOH}][NH_4\text{OH}]}{[CH_3\text{COO}^-][NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4\text{OH}]} \times$$

$$\frac{[CH_3\text{COO}^-][H^+]}{[CH_3\text{COOH}]} = [H^+][OH^-]$$

$$K_h \times K_b \times K_a = K_w$$

$$K_h = \frac{K_w}{K_a \times K_b}$$

(b) Degree of hydrolysis (h) -



$$K_h = \frac{[CH_3\text{COOH}][NH_4\text{OH}]}{[CH_3\text{COO}^-][NH_4^+]} = \frac{Ch \times Ch}{(C-Ch)(C-Ch)}$$

$$= \frac{C^2 h^2}{C(1-h) \times C(1-h)}$$

Since $h \llll 1$ then $(1-h) \approx 1$

$$\therefore K_h = h^2$$

... (6)

$$\text{or } h^2 = \frac{K_w}{K_a \times K_b} \text{ or } h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

... (7)

(c) pH of the solution

from equation (3)

$$K_a = \frac{[CH_3\text{COO}^-][H^+]}{[CH_3\text{COOH}]}$$

$$[H^+] = \frac{K_a \times [CH_3\text{COOH}]}{[CH_3\text{COO}^-]} = \frac{K_a \times Ch}{C-Ch} = \frac{K_a \times h}{1-h}$$

Since $h \llll 1$ then $(1-h) \approx 1$

$[H^+] = K_a \times h$ [Now put the value of h from eq. (7)]

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$[H^+] = \sqrt{\frac{K_w \times K_a}{K_b}}$$

... (8)

taking - log on both sides -log $[H^+]$

$$= -\log \left(\frac{K_w \times K_a}{K_b} \right)^{1/2}$$

$$pH = -\frac{1}{2} [\log (K_w \times K_a) - \log K_b]$$

$$pH = -\frac{1}{2} [\log K_w + \log K_a - \log K_b]$$

$$pH = -\frac{1}{2} [\log K_w] - [\log K_a] - [-\log K_b]$$

$$pH = + \frac{1}{2} pK_w + pK_a - \frac{1}{2} pK_b$$

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

... (9)

47. A salt of strong acid and weak base is dissolved in water. Its hydrolysis in solution is-
- unaffected on heating
 - increased by adding strong acid
 - suppressed by diluting
 - suppressed by adding strong acid
48. The dissociation constant of CH_3COOH is 1.8×10^{-5} . The hydrolysis constant for 0.1 M sodium acetate is -
- 5.56×10^4
 - 5.56×10^{-10}
 - 1.8×10^{-5}
 - 1.8×10^9
49. The degree of hydrolysis of which of the following salt is independent of the concentration of salt solution?
- CH_3COONa
 - NH_4Cl
 - $\text{CH}_3\text{COONH}_4$
 - NaCl

BUFFER SOLUTIONS

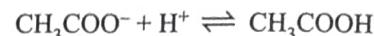
Buffer Solutions are those, which resist to change in pH upon addition of small amount of acid or base. This does not mean that the pH will not change, and all it means is that the pH change would be less than the change that would have occurred had it not been a buffer.

- In certain applications of chemistry and biochemistry we require solutions of constant pH. Such solutions are called buffer solution.
- A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called buffer solution.
- Buffer solutions are also called solutions of reverse acidity or alkalinity.
- Following are the characteristics of buffer solutions
 - It must have approx. constant pH.
 - Its pH should not be changed on long standing
 - Its pH should not be changed on dilution.
 - Its pH should not be changed to any great extent on addition of small quantity of acid or base.
- Buffer solutions can be classified as follows.
 - Simple buffer
 - Mixed buffer

SIMPLE BUFFER

- It is a solution of one compound i.e. salts of $\text{WA} + \text{WB}$ (Refer salt hydrolysis.)
 - Buffer action of such solution can be explained as follows,
In the salt solution of $\text{CH}_3\text{COONH}_4$ following equilibria will be there,
- $$(a) \text{CH}_3\text{COO}^-(\text{aq.}) + \text{NH}_4^+(\text{aq.}) + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq.}) + \text{NH}_4\text{OH}(\text{aq.})$$
- (Salt hydrolysis)

- $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ (weak base)
 - $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ (weak acid)
 - $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ (feebly ionised)
- on addition of small amount of acid the $[\text{H}^+]$ in solution will increase.



equilibria will shift in forward direction. Similarly on addition of small amount of base, the $[\text{OH}^-]$ in solution will increase



equilibria will shift in forward direction. Hence one can conclude that there will be no change (almost) in the pH of the solution.

- (iii) Simple buffer solutions have very little significance since

$$\text{pH} = 7 + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b \text{ so solution of desired pH can not be prepared.}$$

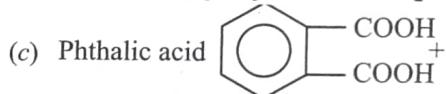
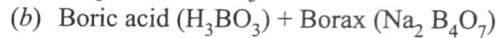
Mixed buffer: Mixed buffers are solutions of more than one compounds. They can be further classified as

- Acidic buffer
- Basic buffer

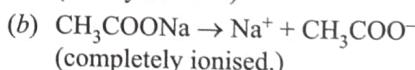
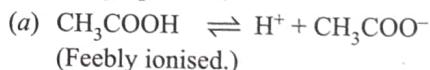
ACIDIC BUFFER

- (i) These are the mixture of a weak acid and its salt with strong base.

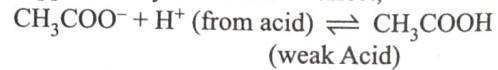
e.g.



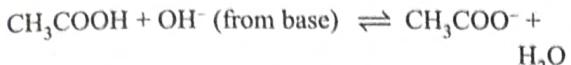
- (ii) Buffer action of acidic buffer can be explained with following equilibria,



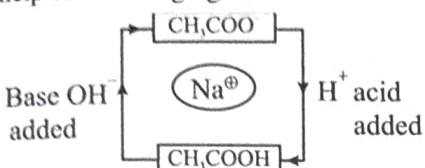
When a strong acid is added in the solution $[\text{H}^+]$ increases, which will combine with CH_3COO^- to form feebly ionised CH_3COOH , which is also suppressed by common ion effect,



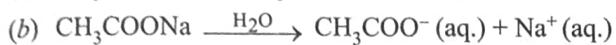
Again when strong base is added in the solution it will attack on unionised acid CH_3COOH to form feebly ionised H_2O molecules



- (iii) One can remember the buffer action of acidic buffer with the help of following figure -



- (iv) pH of such acidic buffer can be calculated as follows.



CH_3COOH is feebly ionised and its ionisation is also suppressed by presence of common ion (CH_3COO^-). So one can fairly assume $[\text{CH}_3\text{COO}^-] = [\text{salt}]$ and $[\text{CH}_3\text{COOH}] = [\text{Acid}]$ taken initially in buffer solution.

$$\text{so } K_a = \frac{[\text{H}^+] [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\text{or } [\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$\log[\text{H}^+] = \log K_a + \log[\text{CH}_3\text{COOH}] - \log[\text{CH}_3\text{COO}^-]$$

$$-\log[\text{H}^+] = -\log K_a - \log[\text{CH}_3\text{COOH}] + \log[\text{CH}_3\text{COO}^-]$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

$$\text{or } \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Above equation called Henderson's equation.

- ❖ If we increase the concentration of given salt in acidic buffer, pH will also increases.
- ❖ If we increase the concentration of acid in acidic buffer, pH will decreases.
- ❖ If conc. and volume are given for salt and acid then the pH is given by the following formula-

$$\text{pH} = \text{p}K_a + \log \frac{[\text{N}_2\text{V}_2]}{[\text{N}_1\text{V}_1]}$$

Where N_2V_2 = normality & volume of salt

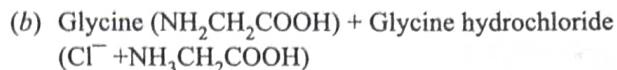
N_1V_1 = normality & volume of acid

Note: Mixture of weak acid and strong base solution can also act as an acidic buffer, if value of N_1V_1 of weak acid is greater than the value of N_2V_2 of strong base.

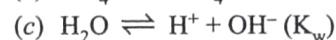
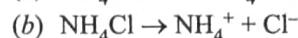
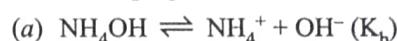
BASIC BUFFER

- (i) These are the mixture of a weak base and its salt with strong acid.

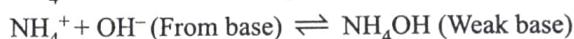
e.g.



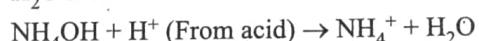
- (ii) Buffer action of basic buffer can be explained with the help of following equilibria



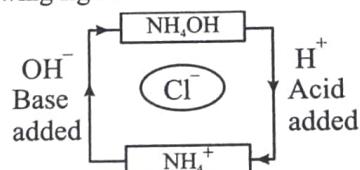
When a strong base is added in the solution $[\text{OH}^-]$ increases, which will combine with NH_4^+ to form feebly ionised NH_4OH , which is also suppressed by common ion effect.



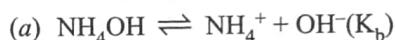
Again when strong acid is added in the solution it will attack on unionised base NH_4OH to form feebly ionised H_2O molecules.



- (iii) One can remember the buffer action of basic buffer with the help of following figure -



- (iv) pH of such basic buffer can be calculated from Henderson - Hasselbalch equation as follows.



NH_4OH is feebly ionised and its ionisation is also suppressed by presence of common ion (NH_4^+). So one can fairly assume $[\text{NH}_4^+] = [\text{Salt}]$ and $[\text{NH}_4\text{OH}] = [\text{Base}]$ taken initially in buffer solution.

$$\text{so } K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$\text{or } [\text{OH}^-] = \frac{K_b[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = \frac{K_b[\text{Base}]}{[\text{Salt}]}$$

$$\text{or } \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

This is known as the Henderson's equation of a buffer. or $\text{pH} = 14 - \text{pOH}$

BUFFER CAPACITY

- (i) The property of a buffer solution to resist alteration in its pH value is known as buffer capacity.

- (ii) Buffer capacity is number of moles of acid or base added in one litre of solution as to change the pH by unity, i.e.

$$\text{Buffer capacity} = \frac{\text{Number of moles acid or base added to 1 lit. sol.}}{\text{Change in pH}}$$

Maximum buffer capacity: It can be proved that the maximum buffer is achieved when the salt and acid or base concentration is equal.



Train Your Brain

Example 40: The pH of a blood stream is maintained by a proper balance of H_2CO_3 and NaHCO_3 . What volume of 5M NaHCO_3 Solution should be mixed with 10 ml of a sample of Solution which is 2.5 M in H_2CO_3 (assume no NaHCO_3), in order to maintain a pH = 7.4. (pK_a for H_2CO_3 = 6.7, $\log 2 = 0.3$)

$$\text{Sol. } \text{pH} = \text{pK}_a + \log \frac{\text{salt}}{\text{base}}$$

$$\Rightarrow 7.4 = 6.7 + \log \frac{\text{salt}}{\text{base}} \Rightarrow \frac{\text{salt}}{\text{base}} = 5$$

$$\Rightarrow 5 \times 2.5 \times 10 \times 10^{-3} = 5 \times V$$

$$\therefore \text{required volume} = 25 \text{ ml}$$

Example 41: 20 mL of 0.2 M NaOH are added to 50 mL of 0.2 M acetic acid ($\text{K}_a = 1.8 \times 10^{-5}$).

(a) What is pH of solution?

(b) Calculate volume of 0.2 M NaOH required to make the pH of solution 4.74.



| | | | | |
|-----------------|-----------------|-----------------|---|---|
| Millimole added | 20×0.2 | 50×0.2 | 0 | 0 |
| | = 4 | = 10 | 0 | 0 |
| Millimole | 0 | 6 | 4 | 4 |

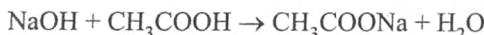
after reaction

$$\therefore [\text{Molarity}] = \frac{\text{millimole}}{\text{Total volume}}$$

$$\therefore [\text{CH}_3\text{COOH}] = \frac{6}{70}; [\text{CH}_3\text{COONa}] = \frac{4}{70}$$

$$\therefore \text{pH} = -\log 1.8 \times 10^{-5} + \log \frac{4/70}{6/70} = 4.57$$

(b) Let V mL of 0.2 M NaOH is required to make pH 4.74 then



| | | | | |
|-----------------|----------------|-----------------|--------|--------|
| Millimole added | $0.2 \times V$ | 50×0.2 | 0 | 0 |
| Millimole | 0 | $(10 - 0.2V)$ | $0.2V$ | $0.2V$ |

after reaction

$$\therefore [\text{Acid}] = \frac{10 - 0.2V}{50 + V};$$

$$[\text{Salt}] = \frac{0.2V}{50 + V}$$

$$\therefore 4.74 = -\log 1.8 \times 10^{-5} + \log \frac{(0.2V)/(50 + V)}{(10 - 0.2V)/(50 + V)}$$

$$\therefore V = 25 \text{ mL}$$

Example 42: Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer Solution of pH = 9, when total concentration of buffering reagents is 0.6 mol litre⁻¹. pK_b for $\text{NH}_3 = 4.7$, $\log 2 = 0.30$

$$\text{Sol. } \text{pOH} = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$5 = 4.7 + \log \frac{a}{b}$$

$$\frac{a}{b} = 2$$

$$\therefore a = 2b$$

$$\text{Given } a + b = 0.6$$

$$2b + b = 0.6$$

$$\therefore 3b = 0.6$$

$$\text{or } b = 0.2 \text{ mole and } a = 0.4 \text{ mole}$$

$$\text{Thus, } [\text{Salt}] = 0.4 \text{ M and } [\text{Base}] = 0.2 \text{ M}$$

Example 43: Calculate the buffer capacity of 1 litre of

(i) 0.1M CH_3COOH and 0.1 M CH_3COONa

(ii) 0.2M CH_3COOH and 0.2 M CH_3COONa

$\text{pK}_a \text{ CH}_3\text{COOH} = 4.74$

which will be a better buffer

$$\text{Sol. } \frac{\delta x}{\text{dpH}} = \frac{2.303(a+x)(b-x)}{a+b}$$

$$\frac{2.303 ab}{a+b} \quad x \ll a, b$$

$$(i) \text{ Buffer capacity} = \frac{0.1 \times 0.1 \times 2.303}{0.1 + 0.1} = 0.11515$$

$$(ii) \text{ Buffer capacity} = \frac{0.2 \times 0.2 \times 2.303}{0.2 + 0.2} = 0.2303$$

Second buffer Solution can be said better buffer



Concept Application

50. What is $[\text{H}^+]$ of a solution that is 0.1M HCN and 0.2 M NaCN? (K_a for HCN = 6.2×10^{-10})

- (a) 3.1×10^{10} (b) 6.2×10^5
 (c) 6.2×10^{-10} (d) 3.1×10^{-10}

51. The pH of a buffer is 4.745. When 0.01 mole of NaOH is added to 1 litre of it, the pH changes to 4.832. Calculate its buffer capacity

- (a) 0.01 (b) 0.115
 (c) 0.126 (d) 0.02

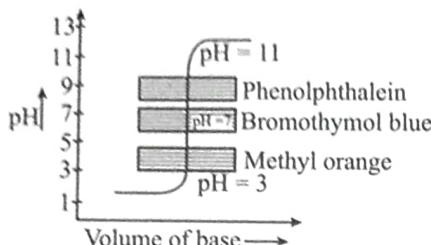
52. A solution is prepared by mixing equal volumes of 0.4 M CH_3COOH and 0.2 M CH_3COONa . K_a for $\text{CH}_3\text{COOH} = 10^{-6}$. The pH of the resulting solution would be -

- (a) 6 (b) 5.69
 (c) 6.69 (d) 6.5

Note: Phenolphthalein cannot be used as indicator in the titration of strong acid and weak base

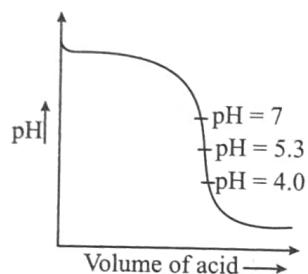
Plots of pH values by using different indicators

- (i) Titration of strong acid by strong base, Both acidic as well as basic indicators are suitable



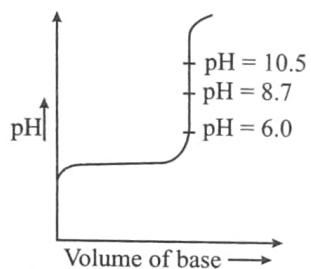
Example: Methyl orange and phenolphthalein

- (ii) Titration of weak base by a strong acid, Only acidic indicators are suitable



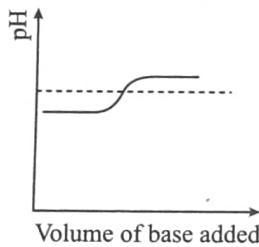
Example: Methyl orange

- (iii) Titration of weak acid by strong base, Only basic indicators are suitable.



Example: Phenolphthalein

- (iv) Titration of weak acid with weak base, No indicators is suitable as such



ACID-BASE TITRATION

| S.No. | Type of titration | pH range of titration | Suitable indicators |
|-------|-------------------|-----------------------|-------------------------------------|
| 1. | SA/SB | 3 – 11 | All indicators (MeOH, HPh etc.) |
| 2. | SA/WB | 3 – 7 | Methyl orange (MeOH) and methyl red |
| 3. | WA/SB | 7 – 11 | Phenolphthalein (HPh) |
| 4. | WA/WB | 6.5 – 7.5 | Phenol red |



Train Your Brain

Example 44: At 25°C pH range of phenolphthalein is 8 – 10. At 100°C pH range of phenolphthalein would be

- (a) pH range remain unaffected by the temperature
- (b) pH range is altered to 8 to 9
- (c) pH range is altered to 7 to 11
- (d) pH range is altered to 8 to 11

Sol. (b) The pH range of the indicator is $pK_{in} \pm 1$. On increase in temperature pK_{in} decreases therefore pH range of indicator decreases.

Example 45: K_b of an acid-base indicator HIn is 10^{-9} . The pH at which its 10^{-3} (M) solution shows the colour change

- (a) 9
- (b) 7
- (c) 5
- (d) 3

Sol. (c) $K_a K_b = 10^{-14}$
or $K_a = K_{in} = 10^{-5}$
 $\therefore [H^+] = 10^{-5}$
or $pH = 5$

Example 46: Indicator used in the titration of sodium carbonate and hydrochloric acid is –

- (a) phenolphthalein
- (b) diphenyl amine
- (c) starch
- (d) methyl orange

Sol. (d) Methyl orange indicator (pH range 3.0 – 4.4) is used for titration of a strong acid with a strong or weak base.



Concept Application

54. Which of the following indicators is best suited in the titration of a weak base versus strong acid?

- (a) Phenolphthalein (8.3 – 10.0)
- (b) Phenol red (6.8 – 8.4)
- (c) Methyl orange (3.1 – 4.4)
- (d) Litmus (4.5 – 8.3)

55. The pink colour of phenolphthalein in alkaline medium is due to

- (a) the acidic form of phenolphthalein
- (b) the anionic form of phenolphthalein
- (c) OH^- of the alkali
- (d) The non conjugated structure of phenolphthalein

Concept Application

Sol. (a) Precipitation occur when $K_{sp} > K_{ip}$
After mixing,

$$[Ag^+] = \frac{1}{2} \times 10^{-4} = 5 \times 10^{-5} M$$

$$[Cl^-] = \frac{1}{2} \times 10^{-4} = 5 \times 10^{-5} M$$

$$K_{ip} = [Ag^+] [Cl^-] = (5 \times 10^{-5})^2 = 2.5 \times 10^{-9}$$

Example 48: Solubility product constants (K_{sp}) of salts of types MX, M_2X , M_3X at temperature T are 4×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} respectively. Solubility (mol dm⁻³) of the salts at temperature T are in the order -

- (a) MX > M_2X > M_3X
- (b) M_3X > MX > M_2X
- (c) M_2X > M_3X > MX
- (d) MX > M_3X > M_2X

Sol. (d) Solubility (S_1) of

$$MX = \sqrt{K_{sp}} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4} M$$

Solubility (S_2) of

$$M_2X = \left(\frac{K_{sp}}{4} \right)^{1/3} = \left(\frac{3.2 \times 10^{-14}}{4} \right)^{1/3} = 2 \times 10^{-5} M$$

Solubility (S_3) of

$$M_3X = \left(\frac{K_{sp}}{27} \right)^{1/4} = \left(\frac{2.7 \times 10^{-15}}{27} \right)^{1/4} = 10^{-4} M$$

$$\therefore S_1 > S_3 > S_2$$

Example 49: The solubility product K_{sp} of the sparingly soluble salt Ag_2CrO_4 is 4×10^{-12} . The solubility of the salt is-

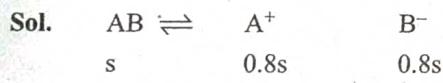
- (a) $1 \times 10^{-12} mol L^{-1}$
- (b) $2 \times 10^{-6} mol L^{-1}$
- (c) $1 \times 10^{-6} mol L^{-1}$
- (d) $1 \times 10^{-4} mol L^{-1}$

Sol. (d) $K_{sp} = 4s^3$

$$4 \times 10^{-12} = 4s^3$$

$$s = 10^{-4}$$

Example 50: Compound AB gets 80% ionised. What should be the solubility of AB, calculate if its solubility product is 6.4×10^{-9} ?



$$K_{sp} = [A^+][B^-]$$

$$6.4 \times 10^{-9} = 0.8s \times 0.8s$$

$$0.64 s^2 = 6.4 \times 10^{-9} \text{ or } s^2 = \frac{6.4 \times 10^{-9}}{0.64} = 10^{-8}$$

$$\therefore s = 10^{-4}$$

58. If solubility product of the base M(OH)³ is 2.7×10^{-11} , the concentration of OH⁻ will be

- (a) 3×10^{-3}
- (b) 3×10^{-4}
- (c) 10^{-3}
- (d) 10^{-11}

59. What is the minimum concentration of SO₄²⁻ required to precipitate BaSO₄ in a solution containing 1.0×10^{-4} mole of Ba²⁺?

$$K_{sp} \text{ for BaSO}_4 = 4 \times 10^{-10}$$

| | |
|---------------------------|--------------------------|
| (a) $4 \times 10^{-10} M$ | (b) $2 \times 10^{-7} M$ |
| (c) $4 \times 10^{-6} M$ | (d) $2 \times 10^{-3} M$ |

60. The solubility in water of a sparingly soluble salt AB₂ is $1.0 \times 10^{-5} mol L^{-1}$. Its solubility product will be -

- (a) 1×10^{-15}
- (b) 1×10^{-10}
- (c) 4×10^{-15}
- (d) 4×10^{-10}

61. If x mol L⁻¹ is the solubility of KAl(SO₄)₂, then K_{sp} is equal to:

- (a) x^3
- (b) $4x^4$
- (c) x^4
- (d) $4x^3$

APPLICATION OF SOLUBILITY PRODUCT (K_{sp})

❖ To find out the solubility (S):

(i) **K_{sp} of AB (Mono-mono, di-di, tri-tri valency) type salt -**

Ex. NaCl, BaSO₄, CH₃COONa, CaCO₃, NaCN, KCN, NH₄CN, NH₄Cl etc.



$$K_{sp} = [A^+][B^-]$$

$$K_{sp} = s^2 \text{ or } s = \sqrt{K_{sp}}$$

(ii) **K_{sp} of AB₂ or A₂B (Mono-di or di-mono valency) type salt -**

Ex. CaCl₂, CaBr₂, K₂S, (NH₄)₂SO₄, K₂SO₄, K₂CO₃ etc.



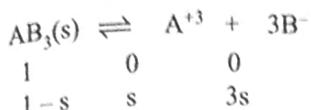
$$K_{sp} = [A^{+2}][B^-]^2$$

$$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$$

$$s = \left(\frac{K_{sp}}{4} \right)^{1/3}$$

(iii) K_{sp} of AB_3 or A_3B (Mono-tri or tri-mono valency) type salt-

Ex. $FeCl_3$, $AlCl_3$, K_3PO_4 etc.

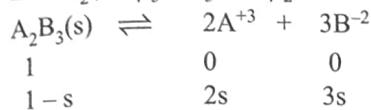


$$K_{sp} = [A^{+3}][B^-]^3 = s \times (3s)^3 = 27s^4 = 27s^4$$

$$s = \left(\frac{K_{sp}}{27} \right)^{\frac{1}{4}}$$

(iv) K_{sp} of A_2B_3 or A_3B_2 (Di-tri or tri-di valency) type salt –

Ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$ etc.



$$K_{sp} = [A^{+3}]^2[B^{-2}]^3 = 2s \times 2s \times 3s \times 3s \times 3s = 108s^5$$

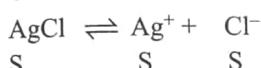
$$s = \left(\frac{K_{sp}}{108} \right)^{\frac{1}{5}}$$

❖ Common ion effect on solubility:

Important point: Solubility of substances always decreases in the presence of common ion.

Illustration 1

(i) Find out the solubility of $AgCl$ in the presence of C $NaCl$ solution?

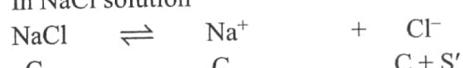


(Let solubility of $AgCl$ is S mol L^{-1})

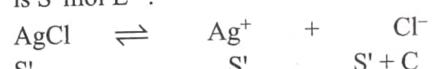
$$K_{sp} = [Ag^+][Cl^-]$$

$$K_{sp} = S^2$$

In $NaCl$ solution



Let solubility of $AgCl$ in the presence of $NaCl$ solution is S' mol L^{-1} .



According to L.M.A.

$$K_{sp} = [Ag^+][Cl^-]$$

$$K_{sp} = S'(S' + C) = S'^2 + S'C$$

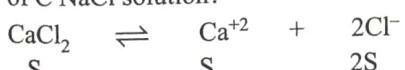
(Neglecting the higher power terms of S')

$$K_{sp} = S'C$$

$$S' = \frac{K_{sp}}{C}$$

Illustration 2

(ii) Find out the solubility of $CaCl_2$ solution in the presence of C $NaCl$ solution?



[Let solubility of $CaCl_2$ is S mol L^{-1}]

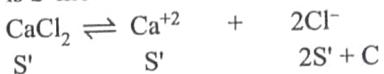
$$K_{sp} = [Ca^{+2}][Cl^-]^2$$

$$= 4S^3$$

For $NaCl$ solution



Let solubility of $CaCl_2$ in the presence of $NaCl$ solution is S' mol L^{-1} .



According to L.M.A.

$$K_{sp} = [Ca^{+2}][Cl^-]^2$$

$$K_{sp} = S'(2S' + C)^2 = S'(4S'^2 + 4S'C + C^2)$$

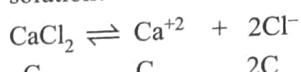
$$K_{sp} = 4S'^3 + 4S'^2C + S'C^2$$

(Neglecting the higher power terms of S')

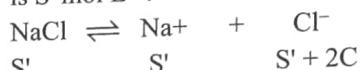
$$S' = \frac{K_{sp}}{C^2}$$

Illustration 3

(iii) Find out the solubility of $NaCl$ in the presence of C $CaCl_2$ solution?



Let solubility of $NaCl$ in the presence of $CaCl_2$ solution is S' mol L^{-1} .



According to L.M.A.

$$K_{sp} = [Na^+][Cl^-]$$

$$K_{sp} = S'(S' + 2C) = S'^2 + 2S'C$$

(Neglecting the higher power terms of S')

$$S' = \frac{K_{sp}}{2C}$$

❖ Group precipitation

(i) $K_{sp} > K_{ip} \Rightarrow$ Unsaturated } No precipitation

(ii) $K_{sp} = K_{ip} \Rightarrow$ Saturated }

(iii) $K_{sp} < K_{ip} \Rightarrow$ Super saturated \Rightarrow precipitation

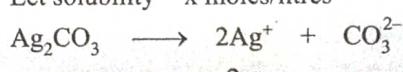


Train Your Brain

Example 51: At $25^\circ C$ what will be the solubility of silver carbonate in 0.1 M Na_2CO_3 solution. At this temperature K_{sp} of silver carbonate is 4×10^{-13} :

- (a) 2×10^{-7} (b) 2×10^{-6}
 (c) 10^{-6} (d) 10^{-7}

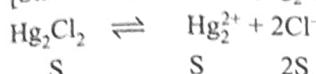
Sol. (c) Let solubility = x moles/litres



IMPORTANT POINTS

(a) Hg^{+1} (us) \rightarrow Unstable in aqueous solution.

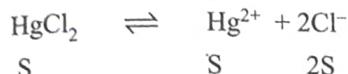
[Stable in dimer form (Hg_2^{2+}) $\Rightarrow \text{Hg}_2\text{Cl}_2$]



$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 \\ = (\text{S})(2\text{S})^2$$

$$K_{sp} = 4\text{S}^3$$

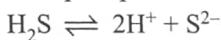
(b) Hg^{2+} (ic) $\rightarrow \text{HgCl}_2$ \rightarrow stable in aqueous solution



$$K_{sp} = 4\text{S}^3$$

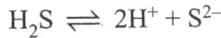
(c) For precipitation of II group, H_2S gas is passed in acidic medium to decrease S^{2-} concentration by common ion effect. So that ionic product of cations of group II and S^{2-} ions exceed the solubility product of their corresponding metal sulphides. Therefore only the cations of group II gets precipitated. But the sulphides of the cation of the other groups (III, IV & V) are not precipitated under these conditions because their solubility products are quite high.

When H_2S gas is directly passed through solution then IVth group is also precipitated with IInd group.



$K_{sp,II} < K_{sp,IV} < [\text{radicals of II}^{\text{nd}} \text{ and IV group}] [\text{S}^{2-}]$

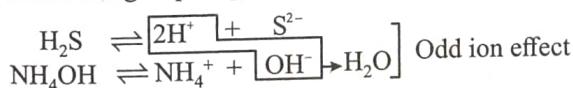
When H_2S gas pass in acidic medium [H^+] then only IInd group radicals are precipitated.



$K_{sp,II} < [\text{radicals of II}^{\text{nd}} \text{ and IV group}] [\text{S}^{2-}] < K_{sp,IV}$

(d) For precipitation of group III, NH_4OH is added in the presence of NH_4Cl to decrease the concentration of OH^- by common ion effect so ionic product of cations of group III and hydroxides ions exceed the solubility product of their corresponding metal hydroxides and only group III cations will precipitated. On the other hand cations of group IV, V and VI, which require large concentration of OH^- due to their high solubility product, will not be precipitated.

(e) In IV group, H_2S gas is passed in basic medium to increase S^{2-} ion concentration by odd ion effect, so that the ionic product of cations of group IV and S^{2-} ions exceed the solubility product of their corresponding metal sulphide and hence gets precipitated.



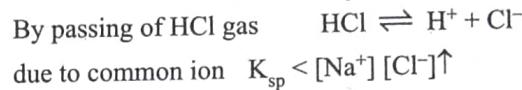
(f) In V group, order of K_{sp} and precipitation is –



PRECIPITATION OF SOAP AND SALT (NaCl)

(i) **Precipitation of NaCl (common salt):** For the precipitation of NaCl, HCl gas passed in saturated solution of NaCl to increase the concentration of Cl^- ion by common ion, so ionic product of concentration of Na^+ and Cl^- ion is more than K_{sp} of NaCl and NaCl easily precipitated.

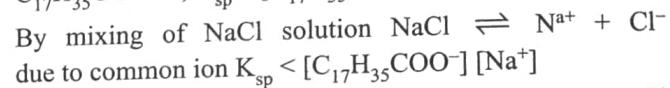
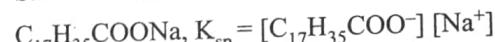
Saturated solution of NaCl $K_{sp} = [\text{Na}^+] [\text{Cl}^-]$



(ii) **Precipitation of soap:** For precipitation of soap, NaCl mixed in saturated solution of soap to increase the concentration of Na^+ ion by common ion. So ionic product of concentration of Na^+ and stearate ions is more than K_{sp} of soap and soap is easily precipitated.

Ex. $\text{C}_{17}\text{H}_{35}\text{COONa}$ (Sodium stearate)

Saturated solution of



Ex: Solubility products of M(OH)_3 and M(OH)_2 are 10^{-23} and 10^{-14} respectively. Which will be precipitated first on adding NH_4OH , if M^{2+} and M^{3+} both the ions are in solution?

(a) M^{2+}

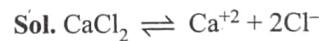
(b) M^{3+}

(c) Both M^{2+} and M^{3+} together

(d) Precipitation will not take place.

Ans. (b)

Ex: Solubility of CaCl_2 is 4×10^{-8} , then find out its K_{sp} and its new solubility in the presence of 10^{-2} M Ca(OH)_2 .



1 s 2s (Initial solubility = s)

$$K_{sp} = 4s^3 = 4(4 \times 10^{-8})^3 = 256 \times 10^{-24} \quad \dots(i)$$



C 0 0

0 C 2C



1 s' + C 2s' (New solubility = s')

$$K_{sp} = [\text{Ca}^{+2}][\text{Cl}^-]^2$$

$$= [s' + C][2s']^2 = 4s'^3 + 4s'^2C \quad (s'^3 = \text{negligible})$$

$$K_{sp} = 4s'^2C \quad \dots(ii)$$

$$\text{From equation (i) and (ii)} \quad s' = \sqrt{\frac{K_{sp}}{4C}} = \sqrt{\frac{256 \times 10^{-24}}{4 \times 10^{-2}}} = \sqrt{64 \times 10^{-22}}$$

$$s' = 8 \times 10^{-11} \text{ mol L}^{-1}$$

Short Notes

Chemical Equilibrium

Consider a reversible reaction,



At Equilibrium State

Rate of forward reaction (r_f) = rate of backward reaction (r_b)

So, at equilibrium,

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{K_f}{K_b}$$

In terms of active mass

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

In terms of partial pressure

$$K_x = \frac{[X_C]^c [X_D]^d}{[X_A]^a [X_B]^b}$$

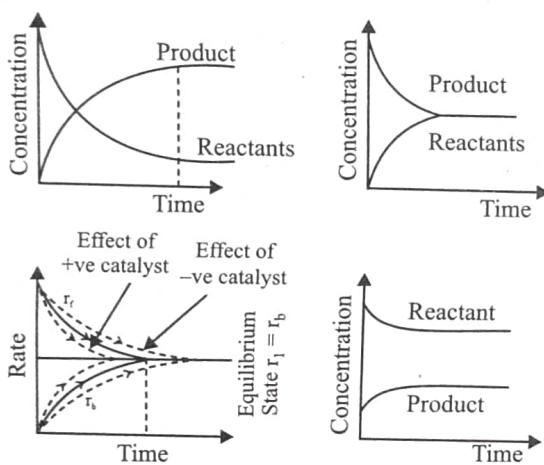
In terms of mole fraction

$$K_p = K_C (RT)^{\Delta n_g}$$

While determining Δn_g take only gaseous species.

The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.

Graphs



Unit of Equilibrium constant

$$K_C = (\text{mol L}^{-1})^{\Delta n_g}; K_p = (\text{atm})^{\Delta n_g}$$

Chemical Equilibrium

| Effect due to change in | | $\Delta n_g = 0$ $A \rightleftharpoons B$ | $\Delta n_g > 0$ $A \rightleftharpoons 2B$ | $\Delta n_g < 0$ $2A \rightleftharpoons B$ |
|-------------------------|-------------------------------|--|---|---|
| Concentration | (i) $\uparrow [A]$ | Forward direction | Forward direction | Forward direction |
| | (ii) $\downarrow [A]$ | Backward direction | Backward direction | Backward direction |
| Pressure | (i) \uparrow in pressure | Unchanged | Backward direction | Forward direction |
| | (ii) \downarrow in pressure | Unchanged | Forward direction | Backward direction |

| | | | | |
|---------------------|--|---|--|--|
| Temperature | (i) ↑ in Endothermic (ii) ↑ in Exothermic | Forward direction Backward direction | Forward direction Backward direction | Forward direction Backward direction |
| Dissociation | (i) ↑ in pressure (ii) ↑ in volume | Unchanged Unchanged | Dissociation Decreases Dissociation Increases | Dissociation Increases Dissociation Decreases |
| Mixing of inert gas | (i) at constant P (ii) at constant V | Unchanged Unchanged | Dissociation Increases Unchanged | Dissociation Decreases Unchanged |

Relationship between Equilibrium Constant K, Reaction Quotient Q and Gibbs Energy G

$\Delta G = \Delta G^\circ + RT \ln Q$... (i) where, ΔG° = Standard free energy difference between the products and reactant, T = Absolute temperature in kelvin, R = Universal gas constant.

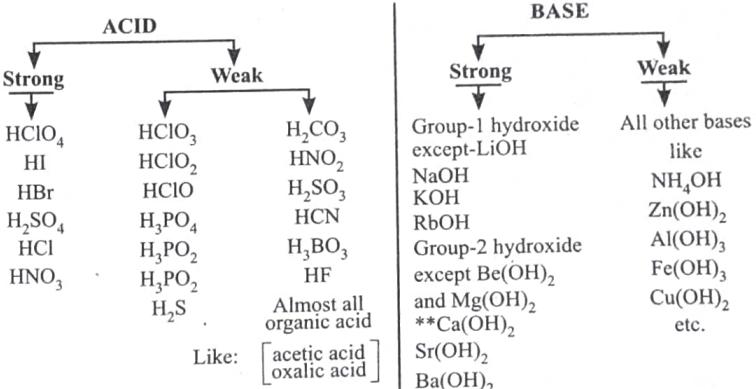
At equilibrium, when $\Delta G = 0$ and $Q = K_c$, then equation (i) becomes

$$0 = \Delta G^\circ + RT \ln K_c \text{ or } \Delta G^\circ = -RT \ln K_c \text{ or } \ln K_c = (-\Delta G^\circ / RT)$$

Case I: If $\Delta G^\circ < 0$, then $(-\Delta G^\circ / RT)$ is positive, i.e., $e^{(-\Delta G^\circ / RT)} > 1$ hence $K_c > 1$, which implies a spontaneous reaction, i.e., the reaction proceeds in the forward reaction.

Case II: If $\Delta G^\circ > 0$, then $(-\Delta G^\circ / RT)$ is negative, i.e., $e^{(-\Delta G^\circ / RT)} < 1$, hence $K_c < 1$, which implies a non-spontaneous reaction or the reaction proceeds in the forward direction to a very small extent i.e., only a very small quantity of product is formed.

Ionic Equilibrium



Acid Base Theories (Arrhenius Concept)

Acid

Which produce H^+ ion in aqueous solution. e.g. HCl, H_2SO_4 , $HClO_4$, H_3PO_4 , CH_3COOH but H_3BO_3 is not a Arrhenius acid.

Major Limitation: Defined only in water solvent.

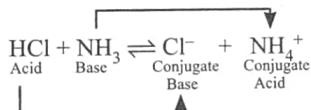
Base

Which produce OH^- ion in aqueous solution. e.g. NaOH, $Mg(OH)_2$, $Ba(OH)_2$.

Bronsted – Lowry Concept

Acid: Which gives H^+ in any solvent.

Base: Which accepts H^+ in any solvent



Major Limitation: Does not explain acidic behaviour of aprotic acids e.g. SO_2 , CO_2 , $AlCl_3$, $SiCl_4$

- ❖ To find conjugate base of any Acid → Remove one H^+
 - ❖ To find conjugate acid of any Base → add one H^+
 - ❖ Water is Amphiprotic solvent (can accept as well as lose H^+)
- $$H_2O \rightleftharpoons H^+ + OH^-$$
- $$H_2O + H^+ \rightleftharpoons H_3O^+$$

Lewis Theory

Acid

Types of Lewis Acid

Lewis acid is an electron pair acceptor.

Base

Types of Lewis Base

Lewis base is an electron pair donor.

1. Having Incomplete octet:
 BF_3 , BCl_3 , $B(OH)_3$, $AlCl_3$ etc.

1. Neutral molecule having lone pair
 $\ddot{N}H_3$, $R-\ddot{N}H_2$, $R_2-\ddot{N}H$,
 $H-\ddot{O}-H$, $R-\ddot{O}-R$ etc.

| | |
|----|---|
| 2. | Having vacant d-orbitals: SF ₄ , SF ₆ , SnCl ₂ , SnCl ₄ etc. |
| 3. | Having multiple bonds between atoms of different EN: CO, SO ₂ , SO ₃ etc. |
| 4. | Cations Ag ⁺ , Li ⁺ , Al ⁺³ , Mg ²⁺ False cations (which cannot act as Lewis acid): NH ₄ ⁺ , H ₃ O ⁺ , PH ₄ ⁺ etc. |

2. **Anions:**
O²⁻, SO₄²⁻, CO₃²⁻, Cl⁻, Br⁻, I⁻, CH₃COO⁻ etc.
 ♦ All the Lewis bases are Bronsted bases but all the Lewis acids are not Bronsted acids.
 ♦ All Arrhenius acids are Bronsted acid but it is not so for bases.

Ostwald's Dilution Law

OSTWALD'S DILUTION LAW

(Only for weak electrolytes)

$$\alpha \propto \sqrt{\text{dilution}}$$

dilution $\uparrow \Rightarrow \alpha \uparrow$

Explanation of water



K_w = Ionic product of water

$$pK_w = pH + pOH$$

K = dissociation constant of water

$$K = \frac{K_w}{[\text{H}_2\text{O}]} [\because [\text{H}_2\text{O}] = 55.5]$$

FOR PURE WATER

$$1. [\text{H}^+] = [\text{OH}^-]$$

$$2. \text{pH} = \text{pOH}$$

$$3. (\text{pH})_{\text{pure water}} = \frac{pK_w}{2}$$

♦ pH of an acidic solution is always less than pH of pure water.

♦ pH of an basic solution is always greater than pH of pure water.

Hydrolysis of Salts

| Salt | Hydrolysis | Resulting solution | Hydrolysis constant (K _h) | Degree of hydrolysis (h) | pH |
|---------------------------|---------------------------|---|---|----------------------------|--|
| Weak acid and Strong base | Anionic | Alkaline pH > 7 | k _w / k _a | $h = \sqrt{\frac{K_h}{C}}$ | $\text{pH} = \frac{1}{2}[\text{pK}_w + \text{pK}_a + \log C]$ |
| Strong acid and Weak base | Cationic | Acidic pH < 7 | k _w / k _b | $h = \sqrt{\frac{K_h}{C}}$ | $\text{pH} = \frac{1}{2}[\text{pK}_w - \text{pK}_b - \log C]$ |
| Weak acid and Weak base | Anionic and Cationic both | Neutral, pH = 7 (If K _a = K _b) | k _w / (k _a . k _b) | $h = \sqrt{K_h}$ | $\text{pH} = \frac{1}{2}[\text{pK}_w + \text{pK}_a - \text{pK}_b]$ |

Buffer Solutions

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called **buffer solutions**.

Buffers are classified into two categories:

- ♦ **Simple buffers:** These are the solutions of salts of weak acid and weak base. For example, CH₃COONH₄ (ammonium acetate).
- ♦ **Mixed buffers:** These are the mixtures of two solutions. These are further of two types:
 - ♦ **Acidic buffers:** These are the solutions of mixtures of weak acid and salt of this weak acid with strong base. For example, CH₃COOH + CH₃COONa. They have pH value lesser than 7.

♦ **Basic buffers:** These are the solutions of mixtures of weak base and salt of this weak base with strong acid. For example, NH₄OH + NH₄Cl. They have the pH value more than 7.

♦ pH of an acidic buffer:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{pK}_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

♦ pH of an basic buffer:

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]} = \text{pK}_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]}$$

$$\text{Buffer capacity} = \frac{\text{No. of moles of acid or base added per litre of buffer}}{\text{Change in pH}}$$

$$\text{Thus, } K_p = \frac{P_{CO} \cdot P_{Cl_2}}{P_{COCl_2}} = \frac{Px^2}{(1-x^2)} \quad \dots(i)$$

$$\text{Also } P = \frac{\rho RT}{m(\text{observed})} \quad (\rho = \text{density})$$

This gives observed molar mass of COCl_2

$$= \frac{\rho RT}{P} = \frac{1.162 \times 8.314 \times 724}{101.325} = 69 \text{ g mol}^{-1}$$

$$\rho(\text{density}) \text{ g/dm}^3 = \text{kg/m}^3$$

$$(a) \text{ Using equation } x = \frac{D-d}{d} = \frac{99-69}{69}$$

$$\therefore x = 0.435$$

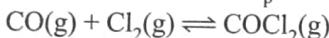
$$(b) P = 101.325 \text{ kPa} = 1 \text{ atm}$$

$$\text{hence, from (i) } K_p = \frac{Px^2}{(1-x^2)} = \frac{1(0.435)^2}{[1-(0.435)^2]}$$

$$K_p = 0.233$$

$$(c) \Delta G^\circ = -2.303 RT \log K_p \\ = -2.303 \times 8.314 \times 724 \log 0.233 \\ = 8770 \text{ J mol}^{-1}$$

3. Pure phosgene gas (COCl_2), 3.00×10^{-2} mol, was placed in a 1.50 L container. It was heated to 800 K, and at equilibrium pressure of CO was found to be 0.497 atm. Calculate the equilibrium constant K_p for the reaction.

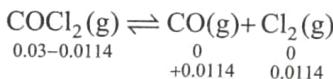


Sol. Initial mol of COCl_2 (g) = 0.03 mol

Equilibrium pressure of CO(g) = 0.497 atm

\therefore Number of moles of CO(g) at equilibrium

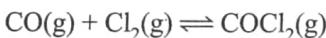
$$= \frac{PV}{RT} = \frac{0.497 \times 1.5}{0.0821 \times 800} = 0.0114 \text{ mol}$$



$$K_p = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{\left(\frac{0.0114}{1.5}\right)\left(\frac{0.0114}{1.5}\right)}{\left(\frac{0.0186}{1.5}\right)} = 4.66 \times 10^{-3}$$

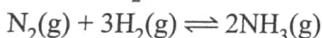
$$K_p = K_c(RT)^{\Delta n} = 4.66 \times 10^{-3} \times (0.0821 \times 800) = 0.306$$

For the reaction



$$K_p = \frac{1}{K_c} = \frac{1}{0.306} = 3.27$$

4. Following equilibrium is studied by taking 1 mol of N_2 and 3 mol of H_2 in 1 L flask at a given temperature:



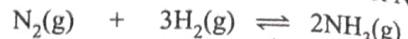
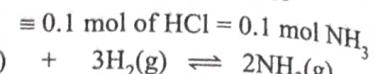
$\text{NH}_3\text{(g)}$ formed at equilibrium is neutralised by 100 mL of 1 M HCl. Calculate equilibrium constant K_c .



1 mol of NH_3 = 1 mol of HCl

0.1 mol of NH_3 = 0.1 mol of HCl

100 mL of 1 M HCl \equiv 100 millimole of HCl



Initial : 1 3 0

At eq (1-x) (3-3x) 2x

Thus, $2x = 0.1 \therefore x = 0.05 \text{ mol}$, $V = 1 \text{ L flask}$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3} = \frac{4x^2 V^2}{27(1-x)^4} = \frac{4 \times (0.05)^2}{27(0.95)^4}$$

$$K_c = 0.0018$$

5. For the reaction, $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$, calculate the equilibrium constant at 298 K. Given that the values of ΔH° and ΔS° of the reaction at 298 K are 77.2 kJ mol^{-1} and $122 \text{ JK}^{-1} \text{ mol}^{-1}$.

Sol. Using the relation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= 77200 - 298 \times 122$$

$$= 40844 \text{ J mol}^{-1}$$

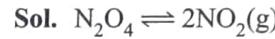
Let the equilibrium constant be K_{eq} . We know that,

$$\Delta G^\circ = -2.303 RT \log K_{eq}$$

$$\text{or } \log K_{eq} = \frac{\Delta G^\circ}{2.303 \times 8.314 \times 298} = -\frac{40844}{2.303 \times 8.314 \times 298} = -7.158$$

$$K_{eq} = 6.95 \times 10^{-8}$$

6. The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.



$$\text{Mol. mass of } \text{N}_2\text{O}_4 = (28 + 64) = 92$$

$$\text{Vapour density, } D = \frac{92}{2} = 46$$

Let the degree of dissociation be x

Given, $d = 30$

Applying the relationship,

$$x = \frac{D-d}{d} = \frac{(46-30)}{30} = \frac{16}{30} = 0.533$$

Degree of dissociation = 53.3%

7. N_2O_4 is 25% dissociated 37°C and one atmospheric pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C .

Sol. (i) $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$

Initial 1 0

At equilibrium (1-x) 2x

Total moles = $(1-x) + 2x = (1+x)$

$$P_{\text{N}_2\text{O}_4} = \left(\frac{1-x}{1+x}\right)P, P_{\text{NO}_2} = \frac{2x}{(1-x)}P$$

Given $x = 0.25$ and $P = 1 \text{ atm}$

$$P_{\text{N}_2\text{O}_4} = \left(\frac{1-0.25}{1+0.25}\right) \times 1 = 0.6 \text{ atm}$$

$$P_{NO_2} = \left(\frac{2 \times 0.25}{1 + 0.25} \right) \times 1 = 0.4 \text{ atm}$$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{0.4 \times 0.4}{0.6} = 0.267 \text{ atm}$$

(ii) Let the degree of dissociation of N_2O_4 at 0.1 atm be 'a' then,

$$P_{N_2O_4} = \left(\frac{1 - \alpha}{1 + \alpha} \right) \times 0.1 \text{ and } P_{NO_2} = \frac{2\alpha}{(1 + \alpha)} \times 0.1$$

$$K_p = \frac{\left(\frac{2\alpha}{1 + \alpha} \right)^2 \times (0.1)^2}{\left(\frac{1 - \alpha}{1 + \alpha} \right) \times 0.1} = \frac{4\alpha^2 \times 0.1}{(1 - \alpha)(1 + \alpha)} = \frac{0.4\alpha^2}{(1 - \alpha^2)}$$

$$\text{or } 0.267 = \frac{0.4\alpha^2}{(1 - \alpha)^2} \text{ or } 0.267 = 0.667\alpha^2$$

$$\alpha = 0.632$$

Hence, dissociation of $N_2O_4 = 63.2\%$

8. Calculate the S^{2-} ion concentration in a saturated solution (0.1 M) of H_2S whose pH was adjusted to 2 by the addition of HCl. ($K_a = 1.1 \times 10^{-21}$)



$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \quad \text{or, } [S^{2-}] = \frac{K_a[H_2S]}{[H^+]^2}$$

$$\text{pH} = 2; \text{ so, } [H^+] = 1 \times 10^{-2} \text{ M}$$

H_2S is a weak electrolyte, so, $[H_2S] = 0.1 \text{ M}$

$$[S^{2-}] = 1.1 \times 10^{-18} \text{ M}$$

9. How many gram moles of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 8.5 using 0.01g formula mass of NaCN? K_a for HCN = 4.1×10^{-10}

Sol. Let a mole of HCl be added. It will combine with NaCN to form HCN.



$$[\text{NaCN}] = (0.01 - a)$$

$$[\text{HCN}] = a$$

Applying the equation,

$$\text{pH} = \log \frac{[\text{NaCN}]}{[\text{HCN}]} - \log K_a$$

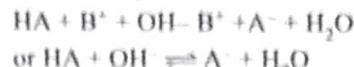
$$8.5 = \log \frac{0.01 - a}{a} - \log 4.1 \times 10^{-10}$$

$$\text{So, } \log \frac{(0.01 - a)}{a} = 8.5 + 0.6127 - 10.0 = 1.1127$$

$$\frac{(0.01 - a)}{a} = 0.1296$$

$$\text{or } a = \frac{0.01}{1.1296} = 0.0089 \text{ mole}$$

10. A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.



$$K = \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]}$$

In the above reaction

$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$\text{So, } K = \frac{1}{K_h}$$

We know that,

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.0 \times 10^{-4}} = 10^{-10}$$

11. The solubility product of $\text{Ca}(\text{OH})_2$ at 25°C is 4.42×10^{-5} mole³ litre⁻³. A 500ml of saturated solution of $\text{Ca}(\text{OH})_2$ is mixed with equal volume of 0.4M NaOH solution. How much $\text{Ca}(\text{OH})_2$ in milligrams is precipitated?

$$\text{Sol. } K_{sp} (\text{Ca}(\text{OH})_2) = 4.42 \times 10^{-5} \text{ mol}^3 \text{ l}^{-3}$$

For a saturated solution, $4s^3 = 4.42 \times 10^{-5}$

$$s = 2.23 \times 10^{-2} = 0.0223 \text{ M} = [\text{Ca}^{2+}]$$

$$[\text{OH}^-] = 2s = 0.0446 \text{ M}$$

$$\text{Now, } \frac{500 \times 0.0446 + 500 \times 0.4}{1000} = [\text{OH}^-]_{\text{new}} = 0.2223$$

$$[\text{Ca}^{2+}][\text{OH}^-]_{\text{new}}^2 = 4.42 \times 10^{-5}$$

$$[\text{Ca}^{2+}]_{\text{remaining}} = 8.94 \times 10^{-4}$$

$$[\text{Ca}^{2+}]_{\text{original}} = 0.0223 \times \frac{500}{1000} = 111.5 \times 10^{-4}$$

$$\therefore \text{ppt} = 111.5 \times 10^{-4} - 8.94 \times 10^{-4} = 102.46 \times 10^{-4}$$

$$\text{MW } [\text{Ca}(\text{OH})_2] = 74 \text{ g}$$

$$\text{wt. in mg} = 102.46 \times 10^{-4} \times 74 \times 10^3 = 758.2 \text{ mg}$$

12. The solubility product of BaSO_4 and BaCrO_4 at 25°C are 1×10^{-10} and 2.4×10^{-10} respectively. Calculate the simultaneous solubilities of BaSO_4 and BaCrO_4 .

$$\text{Sol. Solubility of } \text{BaSO}_4 = x$$

$$\text{Solubility of } \text{BaCrO}_4 = y$$

$$(x + y). x = 10^{-10}$$

$$(x + y). y = 2.4 \times 10^{-10} \Rightarrow y = 2.4 x$$

$$\therefore (x + 2.4x). x = 10^{-10}$$

$$3.4x^2 = 10^{-10}$$

$$\Rightarrow x = 5.42 \times 10^{-6} \text{ M}$$

$$y = 1.3 \times 10^{-5} \text{ M}$$

13. Calculate change in pH of 1 L buffer solution containing 0.10 Mole each of NH_3 and NH_4Cl upon addition of

(i) 0.02 mole of dissolved gaseous HCl.

(ii) 0.02 mole of dissolved NaOH. (Assuming volume to be constnat). $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$



$$0.1 - 0.02 \quad 0.02 \quad 0.02$$

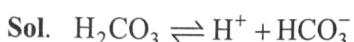
$$\text{Net NH}_4\text{Cl} = 0.1 + 0.02 = 0.12$$

$$\text{Net NH}_3 = 0.08$$

$$\Delta\text{pH} = \log \frac{[\text{salt}]}{[\text{base}]} = \log \frac{0.12}{0.08} = 0.1761$$

(ii) Same as above, $\Delta\text{pH} = 0.1761$

14. The pH of blood stream is maintained by a proper balance of H_2CO_3 and NaHCO_3 concentrations. What volume of 5 M NaHCO_3 solution, should be mixed with 10 ml sample of blood, which is 2 M in H_2CO_3 in order to maintain a pH of 7.4? K_a for H_2CO_3 in blood is 7.8×10^{-7} .



$$K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

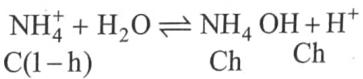
$$\text{pH} = \text{pk}_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$7.4 = 7 - \log 7.8 + \log \left(\frac{5V}{20} \right)$$

$$\Rightarrow V = 78.37 \text{ mL}$$

15. Calculate the amount of NH_4Cl required to be dissolved in 500 ml water to have $\text{pH} = 4.5$ [k_b for $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$].

Sol. $[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.5} = 3.162 \times 10^{-5} \text{ M}$



$$C(1-h) \quad \text{Ch} \quad \text{Ch}$$

$$K_h = Ch^2 = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

$$h = \frac{K_h}{Ch} = \frac{K_h}{[H^+]} = \frac{5.5 \times 10^{-10}}{3.162 \times 10^{-5}} = 1.74 \times 10^{-5}$$

$$C = \frac{[H^+]}{h} = \frac{3.162 \times 10^{-5}}{1.74 \times 10^{-5}} = 1.8 \text{ mol/L}$$

$$500 \text{ ml of H}_2\text{O contains } \frac{1.8}{2} = 0.9 \text{ mole of NH}_4\text{Cl}$$

$$\text{Mass in NH}_4\text{Cl gm} = 0.9 \times 53.5 = 48.15 \text{ g}$$

16. Calculate the pH of each of the following solutions

(a) 100 ml of 0.1 M CH_3COOH mixed with 100 ml of 0.1 M NaOH.

(b) 100 ml of 0.1 M CH_3COOH mixed with 50 ml of 0.1 M NaOH.

(c) 50 ml of 0.1 M CH_3COOH mixed with 100 ml of 0.1 M NaOH.



$$1 \text{mole} \quad 1 \text{mole} \quad 1 \text{mole} \quad 1 \text{mole}$$

$$\text{m. moles of CH}_3\text{COOH} = 0.1 \times 100 = 10$$

$$\text{m. moles of NaOH} = 100 \times 0.1 = 10$$

Therefore, m. moles of CH_3COONa is 10

Now in the solution, only salt CH_3COONa is present therefore, pH of solution can be calculated by hydrolysis of CH_3COONa

CH_3COONa is a salt of weak acid with strong base

$$\text{pH} = 7 + \frac{1}{2}\text{pK}_a + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2} \times 4.75 + \frac{1}{2} \log \left(\frac{10}{200} \right)$$

$$= 8.72$$

(b)



$$\begin{array}{cccc} \text{Initial m. mole} & 10 & 5 & 0 \\ \text{m. moles after reaction} & 10-5 & 0 & 5 \end{array}$$

Since in the solution, mixture of CH_3COOH and CH_3COONa is present, therefore, solution is an acid buffer and pH can be calculated as

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} \quad \text{pH} = 4.75 + \log \left(\frac{\frac{5}{150}}{\frac{5}{150}} \right)$$

$$\boxed{\text{pH} = 4.75}$$

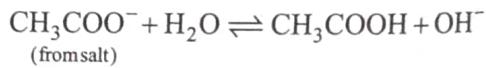
(c)



$$\begin{array}{cccc} \text{Initial m. mole} & 10 & 5 & 0 \\ \text{m. moles after reaction} & 0 & (10-5) & 5 \end{array}$$

$$\begin{array}{cccc} & 0 & (10-5) & 5 \end{array}$$

Now in the solution strong base NaOH and salt of weak acid with strong base is present. We can assume that OH^- ions concentration from the hydrolysis of salt is negligible because hydrolysis of CH_3COONa is suppressed by the presence of strong base NaOH.



$$\therefore [\text{OH}^-] = \left[\frac{5}{150} \right] = \left(\frac{1}{30} \right)$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log \left(\frac{1}{30} \right) = \log 30 = 1.4771$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - 1.4771 = 12.52$$

Exercise-1 (Topicwise)

CHEMICAL EQUILIBRIUM

Properties of equilibrium, active mass, homogeneous & heterogeneous equilibrium (theoretical)

1. In chemical reaction $A \rightleftharpoons B$, the system will be known in equilibrium when
 - A completely changes to B
 - 50% of A changes to B
 - The rate of change of A to B and B to A on both the sides are same
 - Only 10% of A changes to B
2. If a system is at equilibrium, the rate of forward to the reverse reaction is
 - Less
 - Equal
 - High
 - At equilibrium
3. The active mass of 64 gm of HI in a two litre flask would be
 - 2
 - 1
 - 5
 - 0.25
4. Under a given set of experimental conditions, with increase in the concentration of the reactants, the rate of a chemical reaction
 - Decreases
 - Increases
 - Remains unaltered
 - First decreases and then increases
5. Theory of 'active mass' indicates that the rate of chemical reaction is directly proportional to the
 - Equilibrium constant
 - Properties of reactants
 - Volume of apparatus
 - Concentration of reactants
6. Which of the statement is false?
 - The greater the concentration of the substances involved in a reaction, the lower the speed of the reaction.
 - The point of dynamic equilibrium is reached when the reaction rate in one direction just balances the reaction rate in the opposite direction.
 - The dissociation of weak electrolyte is a reversible reaction.
 - The presence of free ions facilitates chemical changes.

HOMOGENEOUS EQUILIBRIUM: K_c

7. For the system $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant is

| | |
|-------------------------------------|-------------------------------------|
| <i>(a)</i> $\frac{[3A][2B]}{[C]}$ | <i>(b)</i> $\frac{[3C]}{[3A][2B]}$ |
| <i>(c)</i> $\frac{[A]^3[B]^2}{[C]}$ | <i>(d)</i> $\frac{[C]}{[A]^3[B]^2}$ |
8. In the reversible reaction $A+B \rightleftharpoons C+D$, the concentration of each C and D at equilibrium was 0.8 mole/litre, then the equilibrium constant K_c will be

| | |
|----------------|-----------------|
| <i>(a)</i> 6.4 | <i>(b)</i> 0.64 |
| <i>(c)</i> 1.6 | <i>(d)</i> 16.0 |
9. 4 moles of A are mixed with 4 moles of B. At equilibrium for the reaction $A+B \rightleftharpoons C+D$, 2 moles of C and D are formed. The equilibrium constant for the reaction will be

| | |
|--------------------------|--------------------------|
| <i>(a)</i> $\frac{1}{4}$ | <i>(b)</i> $\frac{1}{2}$ |
| <i>(c)</i> 1 | <i>(d)</i> 4 |
10. For the system $A(g) + 2B(g) \rightleftharpoons C(g)$, the equilibrium concentrations of (A) = 0.06 mole/litre, (B) = 0.12 mole/litre, (C) = 0.216 mole/litre. The K_{eq} for the reaction is

| | |
|-------------------------------|----------------|
| <i>(a)</i> 250 | <i>(b)</i> 416 |
| <i>(c)</i> 4×10^{-3} | <i>(d)</i> 125 |
11. Partial pressures of A, B, C and D on the basis of gaseous system $A + 2B \rightleftharpoons C + 3D$ are A = 0.20; B = 0.10; C = 0.30 and D = 0.50 atm. The numerical value of equilibrium constant is

| | |
|------------------|------------------|
| <i>(a)</i> 11.25 | <i>(b)</i> 18.75 |
| <i>(c)</i> 5 | <i>(d)</i> 3.75 |
12. For the reaction $A+2B \rightleftharpoons C$, the expression for equilibrium constant is

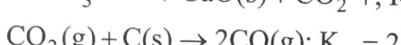
| | |
|-----------------------------------|----------------------------------|
| <i>(a)</i> $\frac{[A][B]^2}{[C]}$ | <i>(b)</i> $\frac{[A][B]}{[C]}$ |
| <i>(c)</i> $\frac{[C]}{[A][B]^2}$ | <i>(d)</i> $\frac{[C]}{2[B][A]}$ |
13. 2 moles of PCl_5 were heated in a closed vessel of 2 litre capacity. At equilibrium, 40% of PCl_5 is dissociated into PCl_3 and Cl_2 . The value of equilibrium constant is

| | |
|------------------|-----------------|
| <i>(a)</i> 0.266 | <i>(b)</i> 0.53 |
| <i>(c)</i> 2.66 | <i>(d)</i> 5.3 |
14. Unit of equilibrium constant for the reversible reaction is $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

| | |
|--------------------------------|-----------------------------|
| <i>(a)</i> mol^{-1} litre | <i>(b)</i> mol^{-2} litre |
| <i>(c)</i> mol litre $^{-1}$ | <i>(d)</i> None of these |

HOMOGENEOUS EQUILIBRIUM: K_p

$$\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO(s)} + \text{CO}_2 \uparrow; K = 8 \times 10^{-2}$$



(a) $\frac{x^2}{(1-x)^2}$ (b) $\frac{(1+x)^2}{(1-x)^2}$
 (c) $\frac{x^2}{(2+x)^2}$ (d) $\frac{x^2}{1-x^2}$

20. For the equilibrium, $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, which of the following expression is correct?

 - $K_p = \left(P_{\text{CaO}} + P_{\text{CO}_2} / P_{\text{CaCO}_3} \right)$
 - $K_p = P_{\text{CO}_2}$
 - $K_p \times \left(P_{\text{CaO}} \times P_{\text{CO}_2} \right) \cdot P_{\text{CaCO}_3}$
 - $$\frac{K_p [\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

RELATION BETWEEN K_p AND K_c

21. In which of the following reaction, the value of K_p will be equal to K_C ?

 - (a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
 - (b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
 - (c) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
 - (d) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

22. The relation between equilibrium constant K_p and K_c is

 - $K_c = K_p (RT)^{\Delta n_g}$
 - $K_p = K_c (RT)^{\Delta n_g}$
 - $K_p = \left(\frac{K_c}{RT}\right)^{\Delta n_g}$
 - $K_p - K_c = (RT)^{\Delta n_g}$

23. For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{heat}$

(a) $K_p = K_c (RT)$ (b) $K_p = K_c (RT)$
 (c) $K_p = K_c (RT)^{-2}$ (d) $K_p = K_c (RT)^{-1}$

24. In which of the following equilibrium, the value of K_p less than K_c ?

 - $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
 - $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 - $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
 - $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

25. For which of the following reactions $K_p = K_c$?

 - $2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$
 - $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
 - $\text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{HCl}(g)$
 - $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

26. For the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

 - $K_p = K_c$
 - $K_p = K_c (\text{RT})^{-1}$
 - $K_p = K_c (\text{RT})$
 - $K_p = K_c (\text{RT})^2$

27. For the reaction $2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$
 $(K_c = 1.8 \times 10^{-6} \text{ at } 184^\circ), (R = 0.0831 \text{ kJ mol}^{-1}\text{K}^{-1})$

K_c and K_p are related to each other by

 - K_p is greater than
 - K_p is less than
 - $K_p = K_c$
 - Whether K_p is greater than, less than or equal to
 K_c depends upon the total gas pressure

28. The reaction between N_2 and H_2 to form ammonia has $K_c = 6 \times 10^{-2}$ at the temperature $500^\circ C$. The numerical value of K_p for this reaction is

- (a) 1.5×10^{-5} (b) 1.5×10^5
 (c) 1.5×10^{-6} (d) 1.5×10^6

REACTION QUOTIENT AND ITS APPLICATIONS

PROPERTIES OF EQUILIBRIUM CONSTANT

44. The vapour density of completely dissociated NH_4Cl would be

 - Slight less than half that of NH_4Cl
 - Half that of NH_4Cl
 - Double that of NH_4Cl
 - Determined by the amount of solid NH_4Cl in the experiment

45. If dissociation for reaction, $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ is 20% at 1 atm pressure, K_p for the equilibrium reaction is

| | |
|----------|----------|
| (a) 0.04 | (b) 0.05 |
| (c) 0.07 | (d) 0.06 |

HETEROGENEOUS EQUILIBRIUM

LE-CHATELIER'S PRINCIPLE

48. In the manufacture of ammonia by Haber's process,

$$\text{N}_2(\text{g}) + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3(\text{g}) + 92.3 \text{ kJ}$$

which of the following conditions is unfavourable?

 - Increasing the temperature
 - Increasing the pressure
 - Reducing the temperature
 - Removing ammonia as it is formed

49. For the reaction $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$, the position of equilibrium can be shifted to the right by

 - Increasing the temperature
 - Doubling the volume of vessel
 - Addition of Cl_2 at constant volume
 - Addition of equimolar quantities of PCl_3 and PCl_5

50. What is the effect of halving the pressure by doubling the volume on the following system at 500°C ?

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$
 - Shift to product side
 - Shift to product formation
 - Liquefaction of HI
 - No effect

- 51.** In equilibrium,

$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$$

The equilibrium constant may change when

 - CH_3COO^- are added
 - CH_3COOH is added
 - Catalyst is added
 - Mixture is heated

52. In the reaction $\text{A}_2(\text{g}) + 4\text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}_4(\text{g})$, $\Delta H < 0$. The formation of AB_4 will be favoured at

 - Low temperature, high pressure
 - High temperature, low pressure
 - Low temperature, low pressure
 - High temperature, high pressure

53. For the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, the equilibrium constant changes with

 - Total pressure
 - Catalyst
 - The amounts of H_2 and I_2 taken
 - Temperature

4. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) - \text{Q cals}$

In the above reaction, which is the essential condition for the higher production of NO?

 - High temperature
 - High pressure
 - Low temperature
 - Low pressure

5. For the reaction,

$$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$$

at a given temperature, the equilibrium amount of CO_2 can be increased by

 - Adding a suitable catalyst
 - Adding an inert gas
 - Decreasing the volume of the container
 - Increasing the amount $\text{CO}(\text{g})$

6. Which of the following reactions proceed at low pressure?

 - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 - $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$

THERMODYNAMIC OF EQUILIBRIUM AND MISCELLANEOUS

57. For a system in equilibrium, $\Delta G = 0$ under conditions of constant

 - (a) Temperature and pressure
 - (b) Temperature and volume
 - (c) Energy and volume
 - (d) Pressure and volume

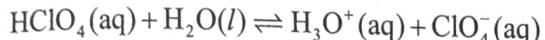
58. A reaction attains equilibrium when the free energy change accompanying it is

- (a) Positive and large (b) Zero
(c) Negative and large (d) Negative and small

IONIC EQUILIBRIUM

Acid Base Concept

59. Review the equilibrium and choose the correct statement.



- (a) HClO_4 is the conjugate acid of H_2O
(b) H_3O^+ is the conjugate base of H_2O
(c) H_2O is the conjugate acid of H_3O^+
(d) ClO_4^- is the conjugate base of HClO_4

60. Which of the following can act both as Bronsted acid and Bronsted base?

- (a) Cl^- (b) HCO_3^-
(c) H_3O^+ (d) OH^-

61. An example of a Lewis acid is

- (a) NaCl (b) MgCl_2
(c) AlCl_3 (d) SnCl_4

62. With reference to protonic acids, which of the following statements is correct?

- (a) PH_3 is more basic than NH_3 .
(b) PH_3 is less basic than NH_3 .
(c) PH_3 is equally basic as NH_3 .
(d) PH_3 is amphoteric while NH_3 is basic.

63. Dissociation of H_3PO_4 takes place in following steps

- (a) 1 (b) 2
(c) 3 (d) 4

64. Water is a

- (a) Amphoteric acid (b) Aprotic solvent
(c) Protophobic solvent (d) None of these

65. According to Bronsted principle, an aqueous solution of HNO_3 will contain

- (a) NO_2^- (b) NO_3^-
(c) NO_2^+ (d) NO^+

66. The species which acts as a Lewis acid but not a Bronsted acid is

- (a) NH_2^- (b) O^{2-}
(c) BF_3 (d) OH^-

PROPERTIES OF WATER, pH SCALE, AUTOPROTOLYSIS

67. The unit of ionic product of water, K_w is

- (a) $\text{Mol}^{-1}\text{L}^{-1}$ (b) $\text{Mol}^{-2}\text{L}^{-2}$
(c) $\text{Mol}^{-2}\text{L}^{-1}$ (d) $\text{Mol}^2\text{L}^{-2}$

68. At 90°C , pure water has $[\text{H}_3\text{O}^+] = 10^{-6}$. The value of K_w at this temperature will be

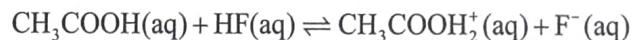
- (a) 10^{-6} (b) 10^{-12}
(c) 10^{-14} (d) 10^{-8}

69. The pH of 1N H_2O is

- (a) 7 (b) > 7
(c) < 7 (d) 0

DIFFERENTIATING EFFECT OF SOLVENT

70. In the equilibrium:



- (a) F^- is the conjugate acid of CH_3COOH
(b) F^- is the conjugate base of HF
(c) CH_3COOH is the conjugate acid of $\text{CH}_3\text{COOH}_2^+$
(d) $\text{CH}_3\text{COOH}_2^+$ is the conjugate base of CH_3COOH

71. Which of the following is a conjugated acid-base pair?

- (a) HCl , NaOH (b) NH_4Cl , NH_4OH
(c) H_2SO_4 , HSO_4^- (d) KCN , HCN

72. The conjugate acid of is HPO_4^{2-}

- (a) H_3PO_4 (b) H_3PO_3
(c) H_2PO_4^- (d) PO_4^{3-}

73. The conjugate acid of NH_2^- is

- (a) NH_3 (b) NH_4^+
(c) NH_2OH (d) PO_4^{3-}

74. Among the following, the weakest base is

- (a) H^- (b) CH_3^-
(c) CH_3O^- (d) Cl^-

pH calculation: Strong acid solutions, Strong base solutions, Solutions containing mixture of two or more strong acids, Solutions containing mixture of two or more strong bases, Solutions containing mixture of strong acid and strong base, mixture of S.A. and W.A., S.B. and W.B.

75. Aqueous solution of HCl has the pH = 4. Its molarity would be

- (a) 4 M (b) 0.4 M
(c) 0.0001 M (d) 10 M

76. What is the pH value of $\frac{\text{N}}{1000}$ KOH solution?

- (a) 10^{-11} (b) 3
(c) 2 (d) 11

77. pH + pOH equal to (at 25°C)

- (a) Zero (b) Fourteen
(c) A negative number (d) Infinity

78. Which one of the following solution has pH 12?

- (a) 0.01M KOH (b) 1N KOH
(c) 1N NaOH (d) 1N $\text{Ca}(\text{OH})_2$

79. pH values of HCl and NaOH solutions each of strength $\frac{\text{N}}{100}$ will be respectively

- (a) 2 and 2 (b) 2 and 12
(c) 12 and 2 (d) 2 and 10

80. What will be the pH of a 10^{-8} M HCl solution?

- (a) 8.0
- (b) 7.0
- (c) 6.98
- (d) 14.0

81. pH of completely dissociated 0.005 M H_2SO_4 is

- (a) 3
- (b) 4
- (c) 2
- (d) 5

82. The pH of a 0.02 M solution of hydrochloric acid is

- (a) 2.0
- (b) 1.7
- (c) 0.3
- (d) 2.2

83. NaOH(aq), HCl(aq) and NaCl(aq) concentration of each is 10^{-3} M. Their pH will be, respectively

- (a) 10, 6, 2
- (b) 11, 3, 7
- (c) 10, 2, 6
- (d) 3, 4, 7

84. The pH of a 10^{-10} molar HCl solution is approximately

- (a) 10
- (b) 7
- (c) 1
- (d) 14

Ostwald dilution law, pH calculation : Solutions of weak monoprotic acid, Solutions of weak monoacidic base

85. Electrolytes when dissolved in water dissociate into their constituent ions. The degree of dissociation of an electrolyte increases with

- (a) Increasing concentration of the electrolyte
- (b) Decreasing concentration of the electrolyte
- (c) Decreasing temperature
- (d) Presence of a substance yielding a common ion

86. An electrolyte

- (a) Gives complex ions in solution
- (b) Dissociates in water to give ions
- (c) Is ionized in the solid state
- (d) Generates ions on passing electric current

87. A monoprotic acid in 1.00 M solution is 0.01% ionised. The dissociation constant of this acid is

- (a) 1×10^{-8}
- (b) 1×10^{-4}
- (c) 1×10^{-6}
- (d) 10^{-5}

88. Which one is strongest electrolyte out of the following?

- (a) NaCl
- (b) CH_3COOH
- (c) NH_4OH
- (d) $\text{C}_6\text{H}_{12}\text{O}_6$

89. If α is the degree of ionization, C is the concentration of a weak electrolyte and K_a is the acid ionization constant, then the correct relationship between α , C and K_a is

- (a) $\alpha^2 = \sqrt{\frac{K_a}{C}}$
- (b) $\alpha^2 = \sqrt{\frac{C}{K_a}}$
- (c) $\alpha = \sqrt{\frac{K_a}{C}}$
- (d) $\alpha = \sqrt{\frac{C}{K_a}}$

90. The extent of ionization increases

- (a) With the increase in concentration of solute
- (b) On addition of excess water to solution
- (c) On decreasing the temperature of solution
- (d) On stirring the solution vigorously

91. For a weak acid HA, Ostwald's dilution law is represented by the equation

$$(a) K_a = \frac{\alpha c}{1-\alpha^2} \quad (b) K_a = \frac{\alpha^2 c}{1-\alpha}$$

$$(c) \alpha = \frac{K_a c}{1-c} \quad (d) K_a = \frac{\alpha^2 c}{1-\alpha^2}$$

92. Concentration of CN^- in 0.1 M HCN, is $[K_a = 4 \times 10^{-10}]$

- (a) 2.5×10^{-6} M
- (b) 4.5×10^{-6} M
- (c) 6.3×10^{-6} M
- (d) 9.2×10^{-6} M

93. 0.02 M monobasic acid dissociates 2%. Hence, pH of the solution is

- (a) 0.3979
- (b) 1.3979
- (c) 1.699
- (d) 3.3979

94. The pH of 0.1 M acetic acid is 3, the dissociation constant of acid will be

- (a) 1.0×10^{-4}
- (b) 1.0×10^{-5}
- (c) 1.0×10^{-3}
- (d) 1.0×10^{-8}

95. The pH value of decinormal solution of NH_4OH which is 20% ionised, is

- (a) 13.30
- (b) 14.70
- (c) 12.30
- (d) 12.95

SALT HYDROLYSIS, pH CALCULATION: SOLUTIONS OF SALT OF MONOPROTIC ACID AND MONOACIDIC BASE, COMMON ION EFFECT

96. Which is the correct alternate for hydrolysis constant of NH_4CN ?

- (a) $\sqrt{\frac{K_w}{K_a}}$
- (b) $\frac{K_w}{K_a \times K_b}$
- (c) $\sqrt{\frac{K_b}{c}}$
- (d) $\frac{K_a}{K_b}$

97. An aqueous solution of CH_3COONa will be

- (a) Acidic
- (b) Alkaline
- (c) Neutral
- (d) None of these

98. In which of the following salt hydrolysis takes place?

- (a) KCl
- (b) NaNO_3
- (c) CH_3COOK
- (d) K_2SO_4

99. Which of the following aqueous solution will have a pH less than 7.0?

- (a) KNO_3
- (b) NaOH
- (c) FeCl_3
- (d) NaCH

100. The pH of a 0.001 M NaOH will be

- (a) 3
- (b) 2
- (c) 11
- (d) 12

101. When 10 ml of 0.1 M acetic acid ($pK_a = 5.0$) is titrated against 10 ml of 0.1M ammonia solution ($pK_b = 5.0$), the equivalence point occurs at pH

- (a) 5.0
- (b) 6.0
- (c) 7.0
- (d) 9.0

102. A solution of $MgCl_2$ in water has pH
(a) < 7 (b) > 7
(c) 7 (d) 14.2

103. Which of the following salt is acidic?
(a) Na_2SO_4 (b) $NaHSO_4$
(c) Na_2SO_3 (d) Na_2S

BUFFER SOLUTION

104. An acidic buffer solution can be prepared by mixing solution of

 - (a) Ammonium acetate and acetic acid
 - (b) Ammonium chloride and hydrochloric acid
 - (c) Sulphuric acid and sodium sulphate
 - (d) Acetic acid and sulphuric acid

105. The pH of a simple sodium acetate buffer is given by
[Salt]

$$105. \text{ The pH of a simple sodium acetate buffer is given by}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}; K_a \text{ of acetic acid} = 1.8 \times 10^{-5}$$

If $[Salt] = [Acid] = 0.1 \text{ M}$, the pH of the solution would be about

106. Which of the following solutions can act as buffer?

 - (a) 0.1 molar aq. NaCl
 - (b) 0.1 molar aq. $\text{CH}_3\text{COOH} + 0.1$ molar NaOH
 - (c) 0.1 molar aq. ammonium acetate
 - (d) None of the above

107. Which of the following solutions cannot act as a buffer?

 - $\text{NaH}_2\text{PO}_4 + \text{H}_3\text{PO}_4$
 - $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
 - $\text{HCl} + \text{NH}_4\text{Cl}$
 - $\text{H}_3\text{PO}_4 + \text{Na}_2\text{HPO}_4$

108. One weak acid (like CH_3COOH) and its strong base together with salt (like CH_3COONa) is a buffer solution. In which pair this type of characteristic is found?

 - (a) HCl and NaCl
 - (b) NaOH and NaNO_3
 - (c) KOH and KCl
 - (d) NH_4OH and NH_4Cl

SOLUBILITY AND TITRATION

110. The solubility product of BaSO_4 at 25°C is 1.0×10^{-9} . What would be the concentration of H_2SO_4 necessary to precipitate BaSO_4 from a solution of 0.01 M Ba^{2+} ions?

- (a) 10^{-9} (b) 10^{-8}
 (c) 10^{-7} (d) 10^{-6}

111. The solubility of CaF_2 is 's' moles/litre. Then, its solubility product is _____

- | | |
|-----------------------------|-----------------------------|
| $(a) \ s^2$ $(c) \ 3s^2$ | $(b) \ 4s^3$ $(d) \ s^3$ |
|-----------------------------|-----------------------------|

- 112.** The solubility of CaF_2 is 2×10^{-4} . Its solubility product is

- (a) 2.0×10^{-4} (b) 4.0×10^{-3}
 (c) 8.0×10^{-12} (d) 3.2×10^{-11}

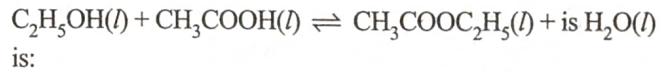


Exercise-2 (Learning Plus)

3. In a chemical equilibrium, the equilibrium constant is found to be 2.5. If the rate constant of backward reaction is 3.2×10^{-2} , the rate constant of forward reaction is -

- (a) 8.0×10^{-2} (b) 4.0×10^{-2}
 (c) 3.5×10^{-2} (d) 7.6×10^{-3}

4. When alcohol $[C_2H_5OH(l)]$ and acetic acid $[CH_3COOH(l)]$ are mixed together in equimolar proportion at $27^\circ C$, 33% of each is converted into ester. Then, the K_C for the equilibrium



5. For the reaction equilibrium:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$; the concentration of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol/L respectively. The value of K_c for the reaction is :

- (a) 3×10^{-3} M (b) 3×10^3 M
 (c) 3.3×10^2 M (d) 3×10^{-1} M

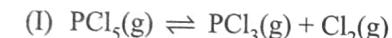
6. The equilibrium constant for the reaction:

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4} . The value of K_c for the reaction,

$NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is:

- (a) 0.02 (b) 50
 (c) 4×10^{-4} (d) 2.5×10^{-2}

7. Consider following reactions in equilibrium with equilibrium concentration 0.01 M of every species



Extent of the reactions taking place is:

- (a) $I > II > III$ (b) $I < II < III$
 (c) $II < III < I$ (d) $III < I < II$

8. The equilibrium constant for the reaction $A(g) + 2B(g) \rightleftharpoons C(g)$ is $0.25 \text{ dm}^6 \text{ mol}^{-2}$. In a volume of 5 dm^3 , what amount of A must be mixed with 4 mol of B to yield 1 mol of C at equilibrium.

- (a) 3 moles (b) 24 moles
 (c) 26 moles (d) None of these

9. 1 mole N_2 and 3 mol H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The equilibrium constant K_p for dissociation of NH_3 is:

- (a) $\frac{1}{0.5} \times (1.5)^3 \text{ atm}^{-2}$ (b) $0.5 \times (1.5)^3 \text{ atm}^2$
 (c) $\frac{0.5 \times (1.5)^3}{3 \times 3} \text{ atm}^2$ (d) $\frac{3 \times 3}{0.5 \times (1.5)^3} \text{ atm}^{-2}$

10. The value of K_p for the reaction, $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$ is 0.03 atm at 427°C , when the partial pressure are expressed in atmosphere, then the value of K_c for the same reaction is

- (a) 5.23×10^{-4} (b) 7.34×10^{-4}
 (c) 3.2×10^{-3} (d) 5.43×10^{-5}

11. $\log \frac{K_p}{K_c} + \log RT = 0$ is a relationship for the reaction :

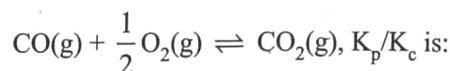
- (a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
 (b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
 (c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
 (d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

12. For the following gaseous equilibrium.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ K_p is found to be equal to K_c . This is attained when temperature is

- (a) 0°C (b) 273 K
 (c) 1 K (d) 12.19 K

13. For the reaction:



- (a) RT (b) $(RT)^{-1}$
 (c) $(RT)^{-1/2}$ (d) $(RT)^{1/2}$

14. At 675 K , $H_2(g)$ and $CO_2(g)$ react to form $CO(g)$ and $H_2O(g)$, K_p for the reaction is 0.16. If a mixture of 0.25 mole of $H_2(g)$ and 0.25 mol of CO_2 is heated at 675 K , mole% of $CO(g)$ in the equilibrium mixture is:

- (a) 7.14 (b) 14.28
 (c) 28.57 (d) 33.33

15. The value of K_p for the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 50. What is the value of K_c ?

- (a) 30 (b) 40
 (c) 50 (d) 70

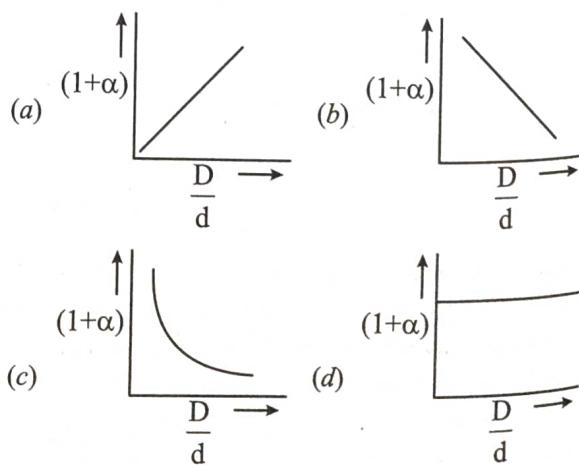
16. PCl_5 dissociation in a closed container is shown as:



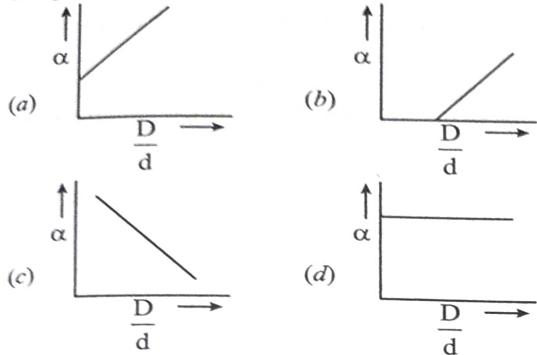
If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is α , the partial pressure of PCl_3 will be:

- (a) $P \left[\frac{\alpha}{\alpha+1} \right]$ (b) $P \left[\frac{2\alpha}{1-\alpha} \right]$
 (c) $P \left[\frac{\alpha}{\alpha-1} \right]$ (d) $P \left[\frac{\alpha}{1-\alpha} \right]$

17. In the dissociation of N_2O_4 into NO_2 , $(1+\alpha)$ values with the vapour densities ratio $\left(\frac{D}{d} \right)$ is as given by: [α -degree of dissociation, D-vapour density before dissociation, d-vapour density after dissociation]



18. In the dissociation of N_2O_4 into NO_2 , α varies with the vapour densities ratio $\left(\frac{D}{d}\right)$ is as given by: [α -degree of dissociation, D-vapour density before dissociation, d-vapour density after dissociation]



19. For the reaction : $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociation α of $HI(g)$ is related to equilibrium constant K_p by the expression:

$$(a) \frac{1+2\sqrt{K_p}}{2} \quad (b) \sqrt{\frac{1+2K_p}{2}}$$

$$(c) \sqrt{\frac{2K_p}{1+2K_p}} \quad (d) \frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$$

20. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, if percentage dissociation of N_2O_4 are 20%, 45%, 65% & 80%, then the sequence of observed vapour densities will be:

- (a) $d_{20} > d_{45} > d_{65} > d_{80}$
 (b) $d_{80} > d_{65} > d_{45} > d_{20}$
 (c) $d_{20} = d_{45} = d_{65} = d_{80}$
 (d) $(d_{20} = d_{45}) > (d_{65} = d_{80})$

21. The vapour density of N_2O_4 at a certain temperature is 30. What is the % dissociation of N_2O_4 at this temperature?

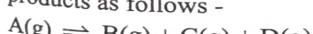
- (a) 53.3 % (b) 106.6 %
 (c) 26.7 % (d) None of these

22. For the reaction,

$A(g) + B(g) \rightleftharpoons C(g) + D(g)$, the degree of dissociation α would be -

- (a) $\frac{\sqrt{K}}{\sqrt{K}+1}$ (b) $\sqrt{K}+1$
 (c) $\sqrt{K} \pm 1$ (d) $\sqrt{K}-1$

23. An unknown compound A dissociates at $500^\circ C$ to give products as follows -



Vapour density of the equilibrium mixture is 50 when it dissociates to the extent of 10%. What will be the molecular weight of Compound A?

- (a) 120 (b) 130
 (c) 134 (d) 140

24. N_2O_4 dissociates as $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at $273 K$ and 2 atm pressure. The equilibrium mixture has a density of 41. What will be the degree of dissociation?

- (a) 14.2% (b) 16.2%
 (c) 12.2% (d) None of these

25. The equation $\alpha = \frac{D-d}{(n-1)d}$ is correctly matched for :

- (a) $A(g) \rightleftharpoons (n/2)B(g) + (n/3)C(g)$
 (b) $A(g) \rightleftharpoons (n/3)B(g) + (2n/3)C(g)$
 (c) $A(g) \rightleftharpoons (n/2)B(g) + (n/4)C(g)$
 (d) $A(g) \rightleftharpoons (n/2)B(g) + C(g)$

26. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_c = 66.9$ at $350^\circ C$ and $K_c = 50.0$ at $448^\circ C$. The reaction has
- (a) $\Delta H = +ve$
 (b) $\Delta H = -ve$
 (c) $\Delta H = zero$
 (d) ΔH sign can not be determined

27. Change in volume of the system does not alter the number of moles in which of the following equilibrium

- (a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
 (b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
 (c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 (d) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

28. For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by:

- (a) Adding a suitable catalyst
 (b) Adding an inert gas
 (c) Decreasing the volume of container
 (d) Increasing the amount of $CO(g)$

29. Given the following reaction at equilibrium,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, some inert gas at constant pressure is added to the system. Predict which of the following facts will be affected?

- (a) More $NH_3(g)$ is produced
 (b) Less $NH_3(g)$ is produced
 (c) No affect on the equilibrium
 (d) K_p of the reaction is decreased

30. For an equilibrium

$H_2O(s) \rightleftharpoons H_2O(l)$ which of the following statement is true?

- (a) The pressure changes do not affect the equilibrium.
 (b) More of ice melts, if pressure on the system is increased.
 (c) More of liquid freezes, if pressure on the system is increased.
 (d) The pressure changes may increase or decrease the degree of advancement of the reaction depending upon the temperature of the system.

31. When a bottle of cold drink is opened, the gas comes out with a fizz due to:

- (a) Decrease in temperature
 (b) Increase in pressure
 (c) Decrease in pressure suddenly which results in decrease of solubility of CO_2 gas in water
 (d) None of these

32. The equilibrium $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is attained at 25°C in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct?
- Concentrations of SO_2 , Cl_2 and SO_2Cl_2 do not change
 - More chlorine is formed
 - Concentration of SO_2 is reduced
 - More SO_2Cl_2 is formed
33. The yield of product in the reaction:
 $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g}) + Q \text{ kJ}$ would be lower at:
- Low temperature and low pressure
 - High temperature & high pressure
 - Low temperature and high pressure
 - High temperature & low pressure
34. What is the effect of the reduction of the volume of the system for the equilibrium?
 $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$
- The equilibrium will be shifted to the left by the increased pressure caused by the reduction in volume.
 - The equilibrium will be shifted to the right by the decreased pressure caused by the reduction in volume.
 - The equilibrium will be shifted to the left by the increased pressure caused by the increase in volume.
 - The equilibrium will be shifted to the right by the increased pressure caused by the reduction in volume.
35. An exothermic reaction is represented by the graph:
-
- (a) $\ln k_p$ vs $1/T$
(b) $\ln k_p$ vs $1/T$
(c) $\ln k_p$ vs $1/T$
(d) $\ln k_p$ vs $1/T$
36. Out of the following, amphiprotic species are
I HPO_3^{2-} II OH^- III H_2PO_4^- IV HCO_3^-
- I, III, IV
 - I and III
 - III and IV
 - All of these
37. Which of the following expression is not true?
- $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$ for a neutral solution at all temperatures.
 - $[\text{H}^+] > [\text{OH}^-]$ for an acidic solution
 - $[\text{H}^+] < [\text{OH}^-]$ for an alkaline solution
 - $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$ for a neutral solution at all temperatures.
38. pOH of H_2O is 7.0 at 298 K . If water is heated at 350 K , which of the following statement should be true?
- pOH will decrease.
 - pOH will increase.
 - pOH will remain 7.0.
 - concentration of H^+ ions will increase but that of OH^- will decrease.
39. Which statement/relationship is correct?
- pH of 0.1 M HNO_3 , 0.1M HCl , 0.1M HI are not equal.
 - $\text{pH} = -\log [\text{H}^+]$
 - The pH of pure water is 7.
 - The value of pK_w at 25°C is 7.
40. One litre of solution contains 10^{-9} moles of OH^- ions at 25°C . Percentage ionisation of water in solution is :
- $1.8 \times 10^{-7} \%$
 - $1.8 \times 10^{-9} \%$
 - $3.6 \times 10^{-9} \%$
 - $1.8 \times 10^{-11} \%$.
41. A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of :
- 3
 - 4
 - 3000
 - 10,000
42. The $[\text{OH}^-]$ in 100.0 ml of 0.016 M-HCl (aq) is:
- $5 \times 10^{12} \text{ M}$
 - $3 \times 10^{-10} \text{ M}$
 - $6.25 \times 10^{-13} \text{ M}$
 - $2.0 \times 10^{-9} \text{ M}$.
43. How many moles of NaOH must be removed from one litre of aqueous solution to change its pH from 12 to 11?
- 0.009
 - 0.01
 - 0.02
 - 0.1
44. Which of the following solution will have pH close to 1.0?
- 100 ml of M/10 HCl + 100 ml of M/10 NaOH
 - 55 ml of M/10 HCl + 45 ml of M/10 NaOH
 - 10 ml of M/10 HCl + 90 ml of M/10 NaOH
 - 75 ml of M/5 HCl + 25 ml of M/5 NaOH.
45. The dissociation constant of acetic acid at a given temperature is 1.69×10^{-5} . The degree of dissociation of 0.01 M acetic acid in the presence of 0.01 M HCl is equal to
- 0.41
 - 0.13
 - 1.69×10^{-3}
 - 0.013
46. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is:
- 4.5
 - 2.5
 - 9.5
 - 7.0
47. Find the pH of solution prepared by mixing 25 ml of a 0.5 M solution of HCl, 10ml of a 0.5 M solution of NaOH and 15 ml of water
- 0.8239
 - 1.0029
 - 1.0239
 - 1.8239



48. Determine degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 11.
 (a) 2% (b) 4% (c) 5% (d) 10%
49. Which of the following has the highest degree of ionisation?
 (a) 1 M NH_3 (b) 0.001 M NH_3
 (c) 0.1 M NH_3 (d) 0.0001 M NH_3
50. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is:
 (a) 1.74×10^{-5} (b) 3.52×10^{-3}
 (c) 6.75×10^{-4} (d) 5.38×10^{-2}
51. The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is:
 (a) 1 (b) 2 (c) 3 (d) 11
52. 1 c.c. of 0.1 N HCl is added to 99 cc solution of NaCl. The pH of the resulting solution will be
 (a) 7 (b) 3 (c) 4 (d) 1
53. The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be
 (a) 100% (b) 50%
 (c) 25% (d) None of these
54. What is the percentage hydrolysis of NaCN in $\frac{N}{80}$ solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$?
 (a) 2.48 (b) 5.26
 (c) 8.2 (d) 9.6
55. Which of the following salts undergoes anionic hydrolysis?
 (a) CuSO_4 (b) NH_4Cl
 (c) AlCl_3 (d) K_2CO_3 .
56. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be:
 (a) 8.58 (b) 4.79
 (c) 7.01 (d) 9.22
57. The pH of 0.1 M solution of the following salts compounds increases in the order :
 (a) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
 (b) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$
 (c) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
 (d) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$
58. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is
 (a) Not a buffer solution and with pH < 7
 (b) Not a buffer solution with pH > 7
 (c) A buffer solution with pH < 7
 (d) A buffer solution with pH > 7
59. If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [$K_a = 2 \times 10^{-4}$]. The pOH of the resulting solution is
 (a) 3.4 (b) 3.7
 (c) 7 (d) 10.3
60. The pH of a solution obtained by mixing 100 ml of 0.2 M CH_3COOH with 100 ml of 0.2 M NaOH would be :
 (pK_a for $\text{CH}_3\text{COOH} = 4.74$)
 (a) 4.74 (b) 8.87
 (c) 9.10 (d) 8.57
61. What volume of 0.2 M NH_4Cl solution should be added to 100 ml of 0.1 M NH_4OH solution to produce a buffer solution of pH = 8.7?
 Given: pK_b of $\text{NH}_4\text{OH} = 4.7$; $\log 2 = 0.3$
 (a) 50 ml (b) 100 ml
 (c) 200 ml (d) None of these
62. A solution is 0.1 M CH_3COOH and 0.1 M CH_3COONa . Which of the following solution will change its pH significantly?
 (a) Addition of water
 (b) Addition of small amount of CH_3COONa with out change in volume
 (c) Addition of small amount of CH_3COOH with out change in volume
 (d) None will change the pH significantly.
63. K_a for HCN is 5×10^{-10} at 25°C. For maintaining a constant pH of 9, the volume of 5 M KCN solution required to be added to 10 ml of 2 M HCN solution, is ($\log 2 = 0.3$)
 (a) 4 ml (b) 8 ml
 (c) 2 ml (d) 10 ml
64. How many gm of solid NaOH must be added to 100 ml of a buffer solution which is 0.1 M each with respect to weak acid HA and salt $\text{Na}^+ \text{A}^-$ to make the pH of solution 5.5. Given $pK_a(\text{HA}) = 5$ (Use antilog (0.5) = 3.16)
 (a) 2.08×10^{-1} (b) 3.05×10^{-3}
 (c) 2.01×10^{-2} (d) None of these
65. When 100 ml of 0.4 M CH_3COOH are mixed with 100 ml of 0.2 M NaOH, the $[\text{H}_3\text{O}^+]$ in the solution is approximately: $[K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}]$
 (a) 1.8×10^{-6} M (b) 1.8×10^{-5} M
 (c) 9×10^{-6} M (d) 9×10^{-5} M.
66. If K_{sp} for HgSO_4 is 6.4×10^{-5} M², then solubility of this substance in mole per m³ is
 (a) 8×10^{-3} (b) 6.4×10^{-5}
 (c) 8×10^{-6} (d) None of these
67. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed.
 (a) 10^{-4} M $\text{Ca}^{2+} + 10^{-4}$ M F^-
 (b) 10^{-2} M $\text{Ca}^{2+} + 10^{-3}$ M F^-
 (c) 10^{-5} M $\text{Ca}^{2+} + 10^{-3}$ M F^-
 (d) 10^{-3} M $\text{Ca}^{2+} + 10^{-5}$ M F^-

Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

1. The two equilibria, $AB \rightleftharpoons A^+ + B^-$ and $AB + B^- \rightleftharpoons AB_2^-$ are simultaneously maintained in a solution with equilibrium constants, K_1 and K_2 respectively. If $[A^+]$ and $[AB_2^-]$ are y and x respectively, under equilibrium produced by adding the substance AB(s) to the solvents, then

 - $k_1/k_2 = \frac{y}{x}(y - x)^2$
 - $k_1/k_2 = \frac{y}{x}(x - y)$
 - $[B^-]_{eq} = y - x$
 - None of these

2. Which of the following statements is (are) correct?

 - (a) An irreversible reaction goes to almost completion.
 - (b) A reversible reaction always goes to completion if carried out in a closed vessel.
 - (c) At equilibrium, the rate of forward reaction becomes equal to that of backward reaction.
 - (d) In the beginning, the rate of backward reaction is much greater than that of forward reaction.

3. (i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; K_1
(ii) $\left(\frac{1}{2}\right)N_2(g) + \left(\frac{1}{2}\right)O_2(g) \rightleftharpoons NO(g)$; K_2
(iii) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; K_3
(iv) $NO(g) \rightleftharpoons \left(\frac{1}{2}\right)N_2(g) + \left(\frac{1}{2}\right)O_2(g)$; K_4

Correct relation between K_1 , K_2 , K_3 and K_4 is/are:

- (a) $K_1 \times K_3 = 1$ (b) $\sqrt{K_1} \times K_4 = 1$
(c) $\sqrt{K_3} \times K_2 = 1$ (d) None of these

4. The value of equilibrium constant of a reversible reaction at a given temperature:

- (a) Depends on the initial concentration of reactants
(b) Depends on the concentration of products at equilibrium
(c) Gets reversed when the mode of representation of the reaction is reversed
(d) Changes when the unit of active mass is changed

5. Which of the following statement is (are) correct?

- (a) The value of equilibrium constant for a particular reaction is constant under all conditions of temperature and pressure.
(b) The unit of K_C for the reaction, $H_2O(l) \rightleftharpoons H_2O(g)$ are mol L⁻¹.
(c) In the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. $[CaCO_3] = [CaO] = 1$
(d) K_p is always greater than K_c for a particular reaction.

6. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium, $NaNO_3(s) \rightleftharpoons NaNO_2(s) + \frac{1}{2}O_2(g)$

- (a) Addition of small amount of $NaNO_2$ favours reverse reaction
(b) Addition of small amount of $NaNO_3$ favours forwards reaction
(c) Increasing temperature favours forward reaction
(d) Increasing pressure favours reverse reaction

7. For the gas phase exothermic reaction,

$A_2(g) + B_2(g) \rightleftharpoons C_2(g)$, carried out in a closed vessel, the equilibrium moles of A_2 can be increased by

- (a) Increasing the temperature
(b) Decreasing the pressure
(c) Adding inert gas at constant pressure
(d) Removing some C_2

8. Consider the equilibrium $HgO(s) + 4I^-(aq) + H_2O(l) \rightleftharpoons HgI_4^{2-}(aq) + 2OH^-(aq)$, which changes will decrease the equilibrium concentration of HgI_4^{2-}

- (a) Addition of 0.1 M $HI(aq)$ (b) Addition of $HgO(s)$
(c) Addition of $H_2O(l)$ (d) Addition of $KOH(aq)$

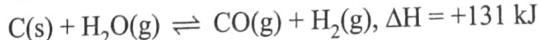
9. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the forward reaction at constant temperature is favoured by
(a) Introducing an inert gas at constant volume
(b) Introducing chlorine gas at constant volume
(c) Introducing an inert gas at constant pressure
(d) Introducing PCl_5 at constant volume.

10. The reactions

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ and $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ are simultaneously in equilibrium in an equilibrium box at constant volume. A few moles of $CO(g)$ are later introduced into the vessel. After some time, the new equilibrium concentration of

- (a) PCl_5 will remain unchanged
(b) Cl_2 will be greater
(c) PCl_5 will become less
(d) PCl_3 will become greater

11. An industrial fuel, 'water gas', which consists of a mixture of H_2 and CO can be made by passing steam over red-hot carbon. The reaction is



The yield of CO and H_2 at equilibrium would be shifted to the product side by:

- (a) Raising the relative pressure of the steam
(b) Adding hot carbon
(c) Raising the temperature
(d) Reducing the volume of the system

12. For the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -198 \text{ kJ}$, the equilibrium concentration of SO_3 will be affected by

- (a) Doubling the volume of the reaction vessel
(b) Increasing the temperature at constant volume
(c) Adding more oxygen to the reaction vessel
(d) Adding helium to the reaction vessel at constant volume

13. Which of the following statements are correct at 25°C?

- (a) pK_a for H_3O^+ is 15.74
(b) pK_b for OH^- is -1.74
(c) $pK_a + pK_b = pK_w$ for HCl & $HOCl$
(d) percentage dissociation of water is $1.8 \times 10^{-7}\%$

14. K_w of H_2O at 373 K is 1×10^{-12} . Identify which of the following is/are correct?

- (a) pK_w of H_2O is 12 (b) pH of H_2O is 6
(c) H_2O at 373K is neutral (d) H_2O at 373K is acidic

15. Which of the following statement(s) is/are correct?

- (a) The pH of $1.0 \times 10^{-8} \text{ M}$ solution of HCl is 8.
(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-} .
(c) Autoprotolysis constant of water increases with increase of temperature.
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralization point $pH = (1/2) pK_a$.

16. Which of following solution can act as buffer?
- $\text{NaCl} + \text{NaOH}$
 - Borax + Boric acid
 - $\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$
 - $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$
17. Equal volumes of following solutions are mixed. In which case the pH of resulting solution will be average value of pH of two solutions?
- Aqueous HCl of pH = 2, aqueous NaOH of pH = 12
 - aqueous HCl of pH = 2, aqueous HCl of pH = 4
 - Aqueous NaOH of pH = 12, aqueous NaOH of pH = 10
 - Aqueous CH_3COOH of pH = 5, aqueous NH_3 of pH = 9. $[K_a(\text{CH}_3\text{COOH}) = K_b(\text{NH}_3)]$
18. A solution contains HCl, Cl_2HCCOOH & CH_3COOH at concentration 0.09 M in HCl, 0.09 M in Cl_2HCCOOH & 0.1 M in CH_3COOH . pH for the solution is 1. Ionization constant of $\text{CH}_3\text{COOH} = 10^{-5}$. What is the magnitude of K for dichloroacetic acid?
- $K_a = 1.25 \times 10^{-2}$
 - $K_a = 2.25 \times 10^{-2}$
 - $K_a = 3.75 \times 10^{-4}$
 - $K_a = 5.75 \times 10^{-2}$
19. Which of the following solutions when added to 1 L of a 0.01 M CH_3COOH solution will cause no change in the degree of dissociation of CH_3COOH and pH of the solution? $K_a = 1.6 \times 10^{-5}$ for CH_3COOH
- 0.6 mM HCOOH ($K_a = 8 \times 10^{-4}$)
 - 0.1 M CH_3COONa
 - 0.4 mM HCl
 - 0.01 M CH_3COOH
20. 100 ml of 0.5 M hydrazoic acid (HN_3 , $K_a = 3.6 \times 10^{-4}$) and 400 ml of 0.1 M cyanic acid (HOOCN , $K_a = 8 \times 10^{-4}$) are mixed. Which of the following is (are) true for the final solution?
- $[\text{H}^+] = 10^{-2} \text{ M}$
 - $[\text{N}_3^-] = 3.6 \times 10^{-3} \text{ M}$
 - $[\text{OCN}^-] = 6.4 \times 10^{-3} \text{ M}$
 - $[\text{H}^+] = 1.4 \times 10^{-2} \text{ M}$
21. K_a values for HA, HB and HD are 10^{-5} , 10^{-7} and 10^{-9} respectively. Which of the following will be correct for decimolar aqueous solutions of NaA , NaB and NaD at 25°C ?
- $(\text{pH})_{\text{NaA}} < (\text{pH})_{\text{NaB}}$
 - $(\text{pH})_{\text{NaD}} < (\text{pH})_{\text{NaB}}$
 - $(\text{pH})_{\text{NaA}} < (\text{pH})_{\text{NaD}}$
 - $(\text{pH})_{\text{NaB}} = 7$
22. 0.1 M CH_3COOH is diluted at 25°C ($K_a = 1.8 \times 10^{-5}$), then which of the following is found to be correct?
- $[\text{H}^+]$ will increase
 - pH will increase
 - Number of H^+ will increase
 - All the above are correct
23. Degree of hydrolysis for a salt of strong acid and weak base is
- Independent of dilution
 - Increases with dilution
 - Increases with decrease in K_b of the bases
 - Decreases with decrease in temperature.
24. When 0.1 mol arsenic acids (H_3AsO_4) is dissolved in 1 L buffer solution of pH = 8, which of the following hold good? For arsenic acid: $K_1 = 2.5 \times 10^{-4}$, $K_2 = 5 \times 10^{-8}$, $K_3 = 2 \times 10^{-13}$. [$<<$ sign denotes that the high concentration is at least 100 times more than the lower one]
- $[\text{H}_3\text{AsO}_4] << [\text{H}_2\text{AsO}_4^-]$
 - $[\text{H}_2\text{AsO}_4^-] << [\text{HAsO}_4^{2-}]$
 - $[\text{HAsO}_4^{2-}] << [\text{H}_2\text{AsO}_4^-]$
 - $[\text{AsO}_4^{3-}] << [\text{HAsO}_4^{2-}]$
25. Which of the following mixtures will act as buffer?
- $\text{H}_2\text{CO}_3 + \text{NaOH}$ (1.5:1 molar ratio)
 - $\text{H}_2\text{CO}_3 + \text{NaOH}$ (1.5:2 molar ratio)
 - $\text{NH}_4\text{OH} + \text{HCl}$ (5 : 4 molar ratio)
 - $\text{NH}_4\text{OH} + \text{HCl}$ (4 : 5 molar ratio)
26. Which of the following is/are correct regarding buffer solution?
- It contains weak acid and its conjugate base.
 - It contains weak base and its conjugate acid.
 - It shows large change in pH on adding small amount of acid or base.
 - All of the above
27. Let the colour of the indicator HIn (colourless) will be visible only when its ionised form (pink) is 25% or more in a solution. Suppose HIn ($pK_a = 9.0$) is added to a solution of pH = 9.6, then predict what will happen? (Take $\log 2 = 0.3$)
- Pink colour will be visible
 - Pink colour will not be visible
 - % of ionised form will be less than 25%
 - % of ionised form will be more than 25%
28. A 2.5 gm impure sample containing weak monoacidic base (Mol. wt. = 45) is dissolved in 100 ml water and titrated with 0.5 M HCl when $\left(\frac{1}{5}\right)^{\text{th}}$ of the base was neutralised, the pH was found to be 9 and at equivalence point, pH of solution is 4.5. Given: All data are at 25°C & $\log 2 = 0.3$. Select correct statement(s).
- K_b of weak monoacidic base is less than 10^{-6} .
 - Concentration of salt (c) at equivalence point is 0.25 M.
 - Volume of HCl used at equivalence point is 100 ml.
 - Weight percentage of base in given sample is 80%.
29. In which of the following solutions, the solubility of AgCN will be greater than that in pure water?
Given: $K_{sp}(\text{AgCN}) = 4 \times 10^{-16}$, $K_a(\text{HCN}) = 5 \times 10^{-10}$
- 0.01 M AgNO_3 solution
 - A buffer solution of pH = 12
 - 0.2 M NH_3 solution
 - A buffer solution of pH = 5

30. The solubility of a sparingly soluble salt A_xB_y in water at $25^\circ C = 1.4 \times 10^{-4} M$. The solubility product is 1.1×10^{-11} . The possibilities are
- $x = 1, y = 2$
 - $x = 2, y = 1$
 - $x = 1, y = 3$
 - $x = 3, y = 1$
31. Which of the following are true for an acid-base titration?
- Indicators catalyse the acid-base reactions by releasing or accepting H^+ ions.
 - Indicators do not significantly affect the pH of the solution to which they are added.
 - Acid-base reactions do not occur in the absence of indicators.
 - Indicators have different colours in dissociated and undissociated forms.
32. If K_{a_1} and K_{a_2} of H_2SO_4 are 10^{-2} and 10^{-6} respectively, then
- $K_{a_1} > K_{a_2}$ because it is easy to abstract H^+ from H_2SO_4 and less easy to abstract H^+ from HSO_4^- .
 - K_{a_1} and K_{a_2} may be measured in acetic acid.
 - K_{a_1} and K_{a_2} are measured in H_2O .
 - the H^+ ion conc. in $0.01 M H_2SO_4$ will be less than $0.02 M$.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 33 to 35): 4.4 grams of CO_2 are introduced into a $0.82 L$ flask containing excess solid carbon at $627^\circ C$, so that the equilibrium



is reached.

The density of equilibrium gaseous mixture corresponds to an average molecular weight of 36.

For the above reaction,

$$K_p = \frac{P_{CO}^2}{P_{CO_2}} \text{ and } K_c = \frac{[CO]^2}{[CO_2]}$$

[$R = 0.082 \text{ L atm mol}^{-1}\text{K}^{-1}$; C = 12, O = 16]

33. Total number of moles of equilibrium gaseous mixture is

- | | |
|--------------------|--------------------|
| (a) $\frac{1}{30}$ | (b) $\frac{2}{15}$ |
| (c) $\frac{1}{15}$ | (d) $\frac{1}{10}$ |

34. K_p of the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, is

- | | |
|------------|------------|
| (a) 6 atm | (b) 12 atm |
| (c) 24 atm | (d) 15 atm |

35. If in the above problem where actually 1.2 g of solid carbon is present initially, how many total moles of CO_2 would have to be introduced initially so that at equilibrium only a trace of carbon remained?

- | | |
|----------|---------|
| (a) 0.25 | (b) 0.7 |
| (c) 0.6 | (d) 0.4 |

Comprehension (Q. 36 to 38):

Le Chatelier's Principle: If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way as to nullify the effect of that change.

Change of pressure: If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. To increase the pressure on the system, the volume has to be decreased proportionately. The total number of moles per unit volume will now be more and the equilibrium will shift in the direction in which there is decrease in number of moles i.e., towards the direction in which there can be decrease in pressure.

Effect of pressure on melting point: There are two types of solids:

- Solids whose volume decreases on melting, e.g., ice, diamond, carborundum, magnesium nitride and quartz.
 $\text{Solid (higher volume)} \rightleftharpoons \text{Liquid (lower volume)}$
 The process of melting is facilitated at high pressure, thus melting point is lowered.
- Solids whose volume increases on melting, e.g., Fe, Cu, Ag, Au, etc.
 $\text{Solid (lower volume)} \rightleftharpoons \text{Liquid (higher volume)}$
 In this case, the process of melting becomes difficult at high pressure; thus melting point becomes high.

Solubility of substances: When solid substances are dissolved in water, either heat is evolved(exothermic) or heat is absorbed (endothermic).



In such cases, solubility increases with increase in temperature. Consider the case of KOH; when this is dissolved, heat is evolved.



In such cases, solubility decreases with increase in temperature.

Solubility of gases in liquids: When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid.

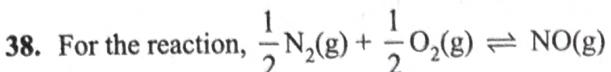
36. A gas 'X' when dissolved in water, heat is evolved. Then, solubility of 'X' will increase at

- Low pressure, high temperature
- Low pressure, low temperature
- High pressure, high temperature
- High pressure, low temperature

37. $Au(s) \rightleftharpoons Au(l)$

Above equilibrium is favoured at:

- High pressure, low temperature
- High pressure, high temperature
- Low pressure, high temperature
- Low pressure, low temperature

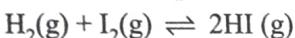


If pressure is increased by reducing the volume of the container, then :

- (a) Total pressure at equilibrium will change.
- (b) Concentration of all the component at equilibrium will change.
- (c) Concentration of all the component at equilibrium will remain same.
- (d) Equilibrium will shift in the forward direction.

Comprehension (Q. 39 to 41): If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from the initial concentrations. Commonly only the initial concentration of reactants are given.

39. In a study of equilibrium,

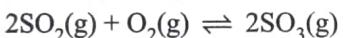


1 mole of H_2 and 3 mole of I_2 gave rise at equilibrium to x mol of HI .

Addition of a further 2 mol of H_2 gave an additional x mol of HI . What is x ?

- | | |
|---------|-------------------|
| (a) 0.5 | (b) 1 |
| (c) 1.5 | (d) None of these |
40. In above problem, what is K_p at the temperature of the experiment?
- | | |
|-------|-------------------|
| (a) 1 | (b) 2 |
| (c) 4 | (d) None of these |

41. In a study of equilibrium,



Starting with 2 mole SO_2 and 1.5 mole O_2 in 5 litre flask, equilibrium mixture required 0.4 mole KMnO_4 in acidic medium. Hence, K_c is:

- | | |
|-----------|-------------------|
| (a) 0.2 | (b) 5.0 |
| (c) 675.0 | (d) None of these |

Comprehension (Q. 42 to 44): Consider a solution of $\text{CH}_3\text{COONH}_4$, which is a salt of weak acid & weak base.

The equilibrium involved in the solution are:



If we add these three reactions, then the net reaction is



Both CH_3COO^- and NH_4^+ get hydrolyzed independently and their hydrolysis depends on

- (i) Their initial concentration
- (ii) The value of K_h which is $\frac{K_w}{K_a}$ for CH_3COO^- and $\frac{K_w}{K_b}$ for NH_4^+ .

Since both of the ions were produced from the same salt, their initial concentrations are same. Therefore, unless & until the value of $\frac{K_w}{K_a}$ and $\frac{K_w}{K_b}$ or K_a and K_b is same, the degree of hydrolysis of ion can't be same.

To explain why we assume that degree of hydrolysis of cation and anion as same, we need to now look at the third reaction i.e., combination of H^+ and OH^- ions. It is obvious that this reaction happens only because one reaction produced H^+ ion and the other produced OH^- ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the equilibrium which has smaller value of equilibrium constant is affected more by the common ion effect. For the same reason if for any reason a reaction is made to occur to a greater extent by the consumption of any one of the product ion, the reaction with the smaller value of equilibrium constant tends to get affected more.

Therefore, we conclude that firstly the hydrolysis of both the ions occurs more in presence of each other (due to consumption of the product ions) than in absence of each other is absence. Secondly, the hydrolysis of the ion which occurs to a lesser extent (due to smaller value of K_h) is affected more than the one whose K_h is greater. Hence, we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolysed in the presence of each other.

42. In the hydrolysis of a salt of weak acid & weak base:

- (a) Degree of hydrolysis of cation and anion is different
- (b) Degree of hydrolysis of cation and anion is same
- (c) Degree of hydrolysis of cation and anion is different and they can never be assumed same.
- (d) Degree of hydrolysis of cation and anion is different but they are very close to each other when they are getting hydrolysed in the presence of each other.

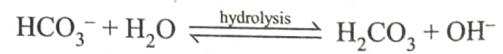
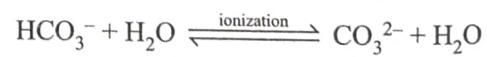
43. For 0.1 M $\text{CH}_3\text{COONH}_4$ salt solution, given:

$$K_a(\text{CH}_3\text{COOH}) = K_b(\text{NH}_4\text{OH}) = 2 \times 10^{-5}$$

In this case, degree of hydrolysis of cation and anion are

- (a) Exactly same
- (b) Slightly different
- (c) Can't say
- (d) Different but can be taken approximately same

44. In a solution of NaHCO_3 , the amphiprotic anion can undergo ionization to form H^+ ion and hydrolysis to form OH^- ion.



To calculate pH, suitable approximation is:

- (a) $[\text{CO}_3^{2-}] = [\text{H}_2\text{CO}_3]$
- (b) Degree of ionization = degree of hydrolysis
- (c) Both (a) and (b)
- (d) Neither (a) nor (b)

Comprehension (Q. 45 to 47): Strontium fluoride (SrF_2) is a sparingly soluble salt. Let s_1 be its solubility (in mol/lit.) in pure water at 25°C , assuming no hydrolysis of F^- ions. Also, let s_2 be its solubility (in mol/lit.) in 0.1 M NaF solution at 25°C , assuming no hydrolysis of F^- ions and no complex formation.

However, it is known that $s_1 : s_2 = 10^6 : 256$. Now, answer the following questions.

45. The K_{sp} value of SrF_2 at 25°C is:

- (a) 2.048×10^{-9} (b) 1.372×10^{-9}
 (c) 1.864×10^{-9} (d) 2.916×10^{-9}

46. The mass of NaF to be added to 100 ml solution of 0.0011 M Sr^{+2} ions to reduce its concentration to $2 \times 10^{-4} \text{ M}$ is: [Assume no hydrolysis of F^- ions]

- (a) 0.42 g (b) 0.063 g
 (c) 0.021 g (d) 0.084 g

47. The solubility of SrF_2 (in mol/L) in a buffer solution of $\text{pH} = 5$ at 25°C is: [Given: K_a for $\text{HF} = \frac{1}{7} \times 10^{-5}$]

- (a) 1.6×10^{-3} (b) 3.2×10^{-3}
 (c) 4.8×10^{-3} (d) 6.4×10^{-3}

MATCH THE COLUMN TYPE QUESTIONS

48. Match the following

| Column-I | | Column-II | |
|--|---|-----------|--|
| A. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ($T = 300^\circ\text{C}$) | p. $\Delta n_g > 0$ | | |
| B. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ ($T = 50^\circ\text{C}$) | q. $K_p < K_c$ | | |
| C. $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$ | r. K_p not defined | | |
| D. $\text{CH}_3\text{COOH}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$ | s. $P_{\text{initial}} > P_{\text{eq}}$ | | |

- (a) A-(s); B-(p); C-(q); D-(r)

- (b) A-(q,s); B-(p); C-(p); D-(r)

- (c) A-(q,s); B-(p,q); C-(p); D-(r)

- (d) A-(q,s); B-(p); C-(p,q); D-(r)

49. Match the following:

| Column-I | | Column-II (K_p/K_c) | |
|---|------------------|----------------------------|--|
| A. $\text{A}_2(\text{g}) + 3\text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}_3(\text{g})$ | p. $(RT)^{-2}$ | | |
| B. $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g})$ | q. $(RT)^0$ | | |
| C. $\text{A}(\text{s}) + 1.5\text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}_3(\text{g})$ | r. $(RT)^{1/2}$ | | |
| D. $\text{AB}_2(\text{g}) \rightleftharpoons \text{AB}(\text{g}) + 0.5\text{B}_2(\text{g})$ | s. $(RT)^{-1/2}$ | | |

- (a) (A)-p; (B)-q; (C)-s; (D)-r

- (b) (A)-q; (B)-p; (C)-s; (D)-r

- (c) (A)-p; (B)-s; (C)-q; (D)-r

- (d) (A)-r; (B)-q; (C)-s; (D)-p

50. Match the following:

| Column-I | | Column-II (factors affecting forward direction) | |
|--|----|--|--|
| A. $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \xrightleftharpoons[\text{Endothermic}]{ } 2\text{AB}(\text{g})$ | p. | High temperature | |
| B. $2\text{AB}_2(\text{g}) + \text{B}_2(\text{g}) \xrightleftharpoons[\text{Exothermic}]{ } \text{AB}_3(\text{g})$ | q. | Low temperature | |
| C. $2\text{AB}_3(\text{g}) + \text{A}_2(\text{g}) \xrightleftharpoons[\text{Exothermic}]{ } 2\text{A}_2(\text{g}) + 3\text{B}_2(\text{g})$ | r. | High pressure | |
| | s. | Low pressure | |
| | t. | Independent of pressure | |

- (a) A-(q,t); B-(q,r); C-(q,s)

- (b) A-(p,r); B-(q,t); C-(q,s)

- (c) A-(p,t); B-(q,r); C-(q,s)

- (d) A-(p,t); B-(q,s); C-(q,t)

51. Match the following:

| Column-I (pH of the resultant solution) | | Column-II (Exist b/w colour transition range of an indicator) | |
|---|----|--|--|
| A. 200 ml of H_2SO_4 solution (specific gravity 1.225 containing 25% H_2SO_4 by weight) + 800 ml of 0.525 M strong triacidic base $\text{X}(\text{OH})_3$ | p. | Phenol Red (6.8 to 8.4) | |
| B. 50 ml of 0.1 M HCO_3^- + 50 ml of 0.8 M CO_3^{2-} (for H_2CO_3): $K_{a_1} = 4 \times 10^{-7}$, $K_{a_2} = 2 \times 10^{-11}$ | q. | Propyl red (4.6 to 6.4) | |
| C. 50 ml of 0.2 M HA (aq) ($K_a = 10^{-5}$) + 50 ml of 0.1 M HCl (aq) + 100 ml of 0.13 M NaOH(aq) | r. | Phenolphthalein (8.3 to 10.1) | |
| | s. | Malachite green (11.4 to 13) | |

- (a) A-(p), B-(s), C-(q)

- (b) A-(s), B-(r), C-(q)

- (c) A-(s), B-(s), C-(r)

- (d) A-(s), B-(s), C-(q)

NUMERICAL TYPE QUESTIONS

52. The value of K_p for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 50. What is the value of K_C ?

53. The equilibrium constant of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 64. If the volume of the container is reduced to one fourth of its original volume, find the value of the equilibrium constant.

54. The equilibrium constant (K_p) for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 16. If the volume of the container is reduced to one half its original volume, find the value of K_p for the reaction at the same temperature.

55. An unknown compound A dissociates at $500^\circ C$ to give products as follows -
 $A(g) \rightleftharpoons B(g) + C(g) + D(g)$

dissociates to the extent to 10%. What will be the molecular weight of compound A?

56. In an equilibrium reaction for which $\Delta G^\circ = 0$, the equilibrium constant K will be _____.

57. Calculate the percentage of hydrolysis in a 0.0100 M solution of KCN. (K_a of HCN = 6.2×10^{-10})

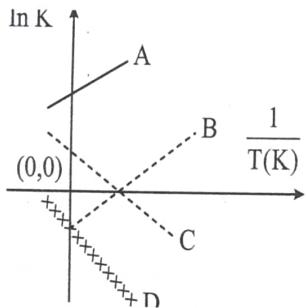
58. Calculate the ratio of degree of dissociation (α_2/α_1) when M acetic acid solution is diluted to 100 times.
[Given: K_a of $CH_3CO_2H = 10^{-5}$ M]

59. Dissociation constant for a weak base BOH is 10^{-5} . calculate the value of pH when it is half neutralized by HCl?

60. Dissociation of H_3PO_4 in H_2O takes place in how many steps?

Exercise-4 (Past Year Questions)

JEE MAIN



Vapour density of the equilibrium mixture is 50 when i dissociates to the extent to 10%. What will be the molecular weight of compound A?

56. In an equilibrium reaction for which $\Delta G^\circ = 0$, the equilibrium constant K will be _____.

57. Calculate the percentage of hydrolysis in a 0.0100 M solution of KCN. (K_a of HCN = 6.2×10^{-10})

58. Calculate the ratio of degree of dissociation (α_2/α_1) when 1 M acetic acid solution is diluted to 100 times.
[Given: K_a of $\text{CH}_3\text{CO}_2\text{H} = 10^{-5}$ M]

59. Dissociation constant for a weak base BOH is 10^{-5} . calculate the value of pH when it is half neutralized by HCl?

60. Dissociation of H_3PO_4 in H_2O takes place in how many steps?

4. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination? (2019)

| Base | Acid | End point |
|-------------|-------------|-----------------------|
| (a) Strong | Strong | Pinkish red to yellow |
| (b) Weak | Strong | Yellow to pinkish red |
| (c) Strong | Strong | Pink to colourless |
| (d) Weak | Strong | Colourless to pink |

5. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} , then the concentration of S^{2-} ions in aqueous solution is: (2018)

(a) 3×10^{-20} (b) 6×10^{-21}
 (c) 5×10^{-19} (d) 5×10^{-8}

7. 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327°C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327°C is ($R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$, Molar mass of S = 32 g mol^{-1} , molar mass of N = 14 g mol^{-1}) (2019)

- (a) $0.242 \times 10^{-4} \text{ atm}^2$ (b) $1 \times 10^{-4} \text{ atm}^2$
 (c) $4.9 \times 10^{-3} \text{ atm}^2$ (d) 0.242 atm^2

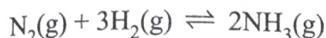
8. For the chemical reaction $X \rightleftharpoons{} Y$, the standard reaction Gibbs energy depends on temperature T (in K) as.

$$D_rG^\circ(\text{kJ mol}^{-1}) = 120 - \frac{3}{8}T$$

The major component of the reaction mixture at T is: (2019)

- (a) Y if $T = 300\text{ K}$ (b) Y if $T = 280\text{ K}$
 (c) X if $T = 350\text{ K}$ (d) X if $T = 315\text{ K}$

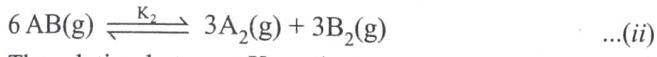
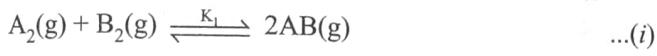
9. Consider the reaction,



The equilibrium constant of the above reaction is K_p . If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $P_{\text{NH}_3} \ll P_{\text{total}}$ at equilibrium) (2019)

- (a) $\frac{3^{3/2} K_p^{1/2} P^2}{16}$ (b) $\frac{K_p^{1/2} P^2}{16}$
 (c) $\frac{K_p^{1/2} P^2}{4}$ (d) $\frac{3^{3/2} K_p^{1/2} P^2}{4}$

10. Consider the following reversible chemical reactions:



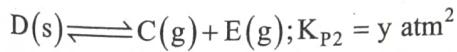
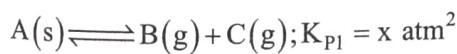
The relation between K_1 and K_2 is (2019)

- (a) $K_1 K_2 = \frac{1}{3}$ (b) $K_2 = K_1^3$
 (c) $K_2 = K_1^{-3}$ (d) $K_1 K_2 = 3$

11. In a chemical reaction $\text{A} + 2\text{B} \rightleftharpoons K 2\text{C} + \text{D}$, the initial concentration of B was 1.5 times of A but the equilibrium concentrations of A and B were found to be equal. The equilibrium, constant (K) for the aforesaid chemical reaction is (2019)

- (a) 4 (b) 16
 (c) 1/4 (d) 1

12. Two solids dissociate as follows:

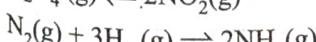
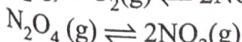
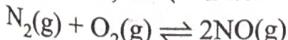


The total pressure when both the solids dissociate simultaneously is (2019)

- (a) $\sqrt{x+y}$ atm (b) $2(\sqrt{x+y})$ atm
 (c) $(x+y)$ atm (d) $x^2 + y^2$ atm

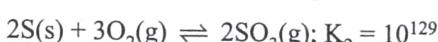
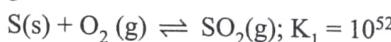
13. The value of K_p/K_c for the following reactions at 300 K are respectively: (2019)

(At 300 K, $RT = 24.62 \text{ dm}^3 \text{ atm mol}^{-1}$)

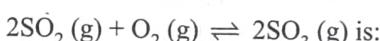


- (a) 1, 24.62 $\text{dm}^3 \text{ atm mol}^{-1}$, 606.0 $\text{dm}^6 \text{ atm}^2 \text{ mol}^{-2}$
 (b) 1, 24.62 $\text{dm}^3 \text{ atm mol}^{-1}$, 1.65 $\text{dm}^{-6} \text{ atm}^{-2} \text{ mol}^2$
 (c) 1, $4.1 \times 10^{-2} \text{ dm}^{-3} \text{ atm}^{-3} \text{ mol}$, 606.0 $\text{dm}^6 \text{ atm}^2 \text{ mol}^{-2}$
 (d) 24.62 $\text{dm}^3 \text{ atm mol}^{-1}$, 606.0 $\text{dm}^6 \text{ atm}^2 \text{ atm}^2 \text{ mol}^{-2}$, $1.65 \times 10^{-3} \text{ dm}^{-6} \text{ atm}^{-2} \text{ mol}^2$

14. For the following reactions, equilibrium constants are given: (2019)



The equilibrium constant for the reaction,

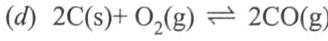
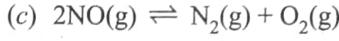
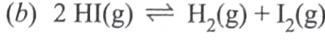
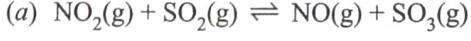


- (a) 10^{181} (b) 10^{154} (c) 10^{25} (d) 10^{77}

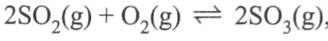
15. The INCORRECT match in the following is: (2019)

- (a) $\Delta G^\circ < 0, K < 1$ (b) $\Delta G^\circ = 0, K = 1$
 (c) $\Delta G^\circ > 0, K < 1$ (d) $\Delta G^\circ < 0, K > 1$

16. In which one of the following equilibrium, $K_p \neq K_c$? (2019)



17. For the reaction, (2019)

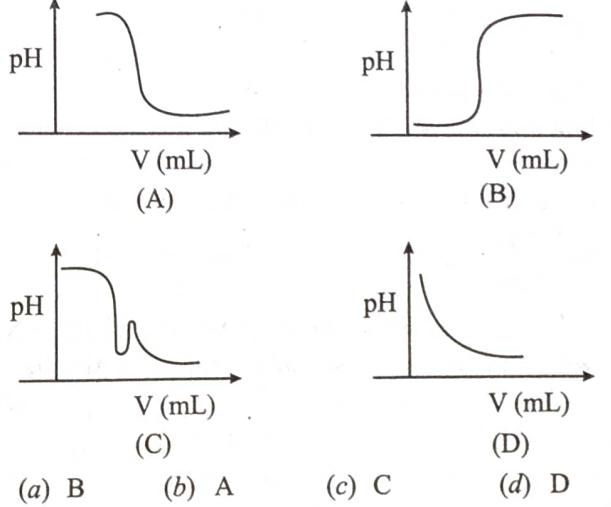


$$\Delta H = -57.2 \text{ kJ mol}^{-1} \text{ and } K_c = 1.7 \times 10^{16}$$

Which of the following statement is INCORRECT?

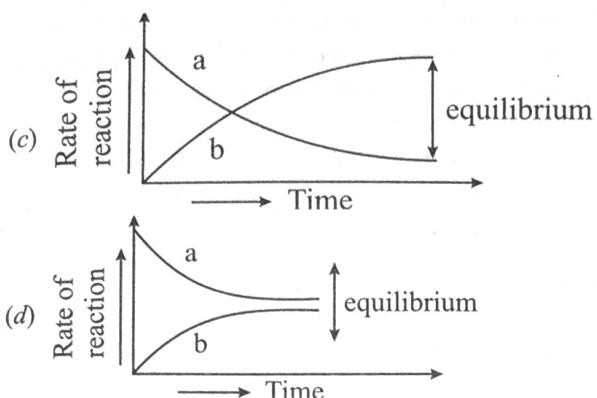
- (a) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.
 (b) The equilibrium will shift in forward direction as the pressure increases.
 (c) The equilibrium constant decreases as the temperature increases.
 (d) The addition of an inert gas at constant volume will not affect the equilibrium constant.

18. In an acid base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment? (2019)



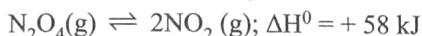
- (a) B (b) A (c) C (d) D

- 19.** Consider the following statements:
- The pH of a mixture containing 400 mL of 0.1 M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3.
 - Ionic product of water is temperature dependent.
 - A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.
 - The Le Chatelier's principle is not applicable to common-ion effect.
- The correct statement are: (2019)
- (I), (II) and (IV)
 - (I), (II) and (III)
 - (II) and (III)
 - (I), and (II)
- 20.** A mixture of 100 mmol of $\text{Ca}(\text{OH})_2$ and 2 g of sodium sulphate was dissolved in water and the volume was made upto 100 mL. The mass of calcium sulphate formed and the concentration of OH^- in resulting solution, respectively are (Molar mas of $\text{Ca}(\text{OH})_2$, Na_2SO_4 and CaSO_4 are 74, 143 and 136 g mol⁻¹ respectively; K_{sp} of $\text{Ca}(\text{OH})_2$, is 5.5×10^{-6}) (2019)
- 1.9 g, 0.28 mol L⁻¹
 - 13.6 g, 0.28 mol L⁻¹
 - 1.9 g, 0.14 mol L⁻¹
 - 13.6 g, 0.14 mol L⁻¹
- 21.** If K_{sp} of Ag_2CO_3 is 8×10^{-12} , the molar solubility of Ag_2CO_3 in 0.1 M AgNO_3 is: (2019)
- 8×10^{-12} M
 - 8×10^{-11} M
 - 8×10^{-10} M
 - 8×10^{-13} M
- 22.** 20 mL of 0.1 M H_2SO_4 is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is (pk_b of $\text{NH}_4\text{OH} = 4.7$) (2019)
- 5.2
 - 9.0
 - 5.0
 - 9.4
- 23.** The pH of rain water is approximately (2019)
- 5.6
 - 7.5
 - 7.0
 - 6.5
- 24.** If solubility product of $\text{Zr}_3(\text{PO}_4)_4$ is denoted by K_{sp} and its molar solubility is denoted by S, then which of the following relation between S and K_{sp} is correct? (2019)
- $S = \left(\frac{K_{sp}}{929} \right)^{1/9}$
 - $S = \left(\frac{K_{sp}}{216} \right)^{1/7}$
 - $S = \left(\frac{K_{sp}}{144} \right)^{1/6}$
 - $S = \left(\frac{K_{sp}}{6912} \right)^{1/7}$
- 25.** The molar solubility of $\text{Cd}(\text{OH})_2$ is 1.84×10^{-5} M in water. The expected solubility of $\text{Cd}(\text{OH})_2$ in a buffer solution of pH = 12 is: (2019)
- 6.23×10^{-11} M
 - 1.84×10^{-9} M
 - $\frac{2.49}{1.84} \times 10^{-9}$ M
 - 2.49×10^{-10} M
- 26.** What is the molar solubility of $\text{Al}(\text{OH})_3$ in 0.2 M NaOH solution? Given that, solubility product of $\text{Al}(\text{OH})_3 = 2.4 \times 10^{-24}$: (2019)
- 12×10^{-23}
 - 12×10^{-21}
 - 3×10^{-19}
 - 3×10^{-22}
- 27.** The pH of a 0.02 M NH_4Cl solution will be (given: $K_b(\text{NH}_4\text{OH}) = 10^{-5}$ and $\log 2 = 0.301$) (2019)
- 4.65
 - 5.35
 - 4.35
 - 2.65
- 28.** Assertion: pH of water increases on increasing temperature. Reason: $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ is an exothermic process. (2020)
- Both assertion and reason are correct and reason is correct explanation of assertion
 - Both assertion and reason are correct and reason is not correct explanation of assertion
 - Assertion is true & reason is false.
 - Both assertion and reason are incorrect.
- 29.** For the reaction, $2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$; the observed rate expression is, rate = $k_f(\text{NO})^2(\text{H}_2)$, then the rate of backward reaction is (2020)
- $k_b(\text{N}_2)(\text{N}_2\text{O})$
 - $k_b(\text{N}_2)(\text{H}_2\text{O})^2 / (\text{NO})$
 - $k_b(\text{N}_2)(\text{H}_2\text{O})_2$
 - $k_b(\text{N}_2)(\text{H}_2\text{O})^2$
- 30.** In the figure shown below reactant A (represented by square) is in equilibrium with product B (represented by circle). The equilibrium constant is: (2020)
-
- 4
 - 8
 - 1
 - 2
- 31.** If the equilibrium constant for $\text{A} \rightleftharpoons \text{B} + \text{C}$ is $K_{eq}^{(1)}$ and that of $\text{B} + \text{C} \rightleftharpoons \text{P}$ is $K_{eq}^{(2)}$. The equilibrium constant for $\text{A} \rightleftharpoons \text{P}$ is (2020)
- $K_{eq}^{(1)} / K_{eq}^{(2)}$
 - $K_{eq}^{(1)} + K_{eq}^{(2)}$
 - $K_{eq}^{(2)} / K_{eq}^{(1)}$
 - $K_{eq}^{(1)}K_{eq}^{(2)}$
- 32.** For the equilibrium $\text{A} \rightleftharpoons \text{B}$, the variation of the rate of the forward (a) and reverse (b) reaction with time is given by (2020)
-



33. For a reaction $X + Y \rightleftharpoons 2Z$, 1.0 mol of X, 1.5 mol of Y and 0.5 mol of Z were taken in a 1 L vessel and allowed to react. At equilibrium, the concentration of Z was 1.0 mol L^{-1} . The equilibrium constant of the reaction is $\frac{x}{15}$. The value of x is _____.

34. Consider the following reaction:



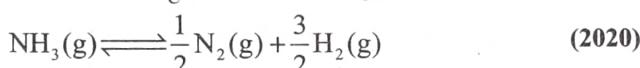
For each of the following cases (a, b), the direction in which the equilibrium shifts is:

(2020)

- (i) Temperature is decreased
- (ii) Pressure is increased by adding N_2 at constant T.
- (a) (i) Towards product, (ii) towards reactant
- (b) (i) Towards reactant, (ii) no change
- (c) (i) Towards reactant, (ii) towards product
- (d) (i) Towards product, (ii) no change

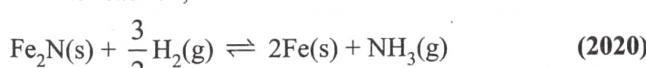
35. The value of K_C is 64 at 800 K for the reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

The value of K_C for the following reaction is



- (a) $1/8$
- (b) $1/64$
- (c) 8
- (d) $1/4$

36. For the reaction,



- (a) $K_C = K_p (\text{RT})^{1/2}$
- (b) $K_C = K_p (\text{RT})$
- (c) $K_C = K_p (\text{RT})^{1/2}$
- (d) $K_C = K_p (\text{RT})^{-1/2}$

37. How many statement are correct about the effect of addition of catalyst at constant temperature?

(2020)

- (A) The equilibrium constant will remain constant
- (B) ΔH of the reaction will remain constant
- (C) R_f and R_b will increase up to same extent
- (D) Equilibrium composition will change
- (a) 1
- (b) 2
- (c) 3
- (d) 4

38. In an experiment starting from 1 mol $\text{C}_2\text{H}_5\text{OH}$, 1 mol CH_3COOH and 1 mol of H_2O , the equilibrium mixture on analysis shows that 50% of acid was esterified; what will be $K_C = ?$

(2020)

39. Two solutions, A and B, each of 100 L was made by dissolving 4 g of NaOH and 9.8 g of H_2SO_4 in water, respectively. The pH of the resultant solution obtained from mixing 40 L of solution A and 10 L of solution B is _____.

(2020)

40. 3 g of acetic acid is added to 250 mL of 0.1 M HCl and the solution made up to 500 mL. To 20 mL of this solution, $\frac{1}{2}$ mL of 5 M NaOH is added. The pH of the solution is _____.

(2020)

(Given: pK_a of acetic acid = 4.75, molar mass of acetic acid = 60 g/mol, $\log 3 = 0.4771$)

Neglect any changes in volume.

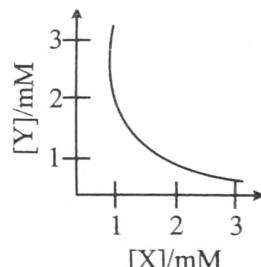
41. The strength of an aqueous NaOH solution is most accurately determined by titrating: (Note: consider that an appropriate indicator is used)

(2020)

- (a) Aq. NaOH in a volumetric flask and concentrated H_2SO_4 in a conical flask
- (b) Aq. NaOH in a burette and aqueous oxalic acid in a conical flask
- (c) Aq. NaOH in a pipette and aqueous oxalic acid in a burette
- (d) Aq. NaOH in a burette and concentrated H_2SO_4 in a conical flask

42. The stoichiometry and solubility product of a salt with the solubility curve given below is, respectively:

(2020)

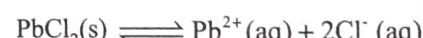


- (a) $\text{X}_2\text{Y}, 2 \times 10^{-9} \text{ M}^3$
- (b) $\text{XY}, 2 \times 10^{-6} \text{ M}^3$

- (c) $\text{XY}_2, 4 \times 10^{-9} \text{ M}^3$
- (d) $\text{XY}_2, 1 \times 10^{-9} \text{ M}^3$

43. The K_{sp} for the following dissociation is 1.6×10^{-5} .

(2020)



Which of the following choices is correct for a mixture of 300 mL 0.134 M $\text{Pb}(\text{NO}_3)_2$ and 100 mL 0.4 M NaCl ?

- (a) $Q = K_{sp}$
- (b) $Q > K_{sp}$
- (c) Not enough data is provided
- (d) $Q < K_{sp}$

44. The solubility product of $\text{Cr}(\text{OH})_3$ at 298 K is 6.0×10^{-31} . The concentration of hydroxide ions in a saturated solution of $\text{Cr}(\text{OH})_3$ will be $x \times 10^{-8}$. Find the value of x (nearest integer).

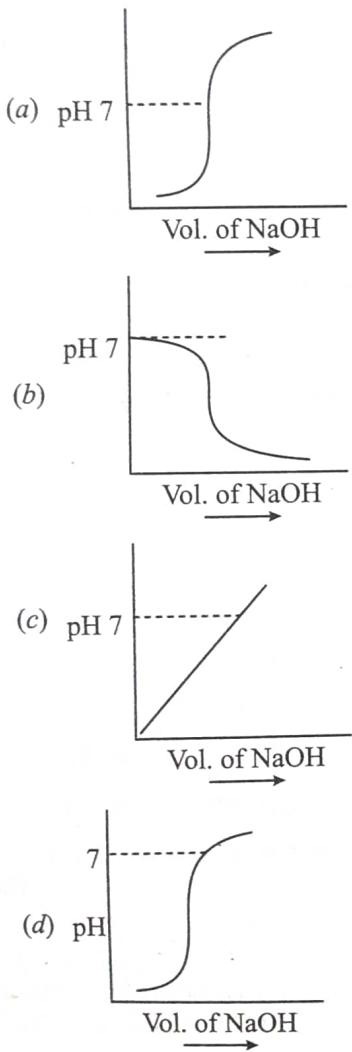
(2020)

45. For the following Assertion and Reason, the correct option is
Assertion (A): When Cu (II) and sulphide ions are mixed, they react together extremely quickly to give a solid.

Reason (R): The equilibrium constant of $\text{Cu}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightleftharpoons \text{CuS}(\text{s})$ is high because the solubility product is low.
(2020)

- (a) (A) is false and (R) is true.
- (b) Both (A) and (R) are true but (R) is not the explanation for (A).
- (c) Both (A) and (R) are true and (R) is the explanation for (A).
- (d) Both (A) and (R) are false.

46. 100 mL of 0.1 M HCl is taken in a beaker and to it 100 mL of 0.1 M NaOH is added in steps of 2 mL and the pH is continuously measured. Which of the following graphs correctly depicts the change in pH?
(2020)



47. An acidic buffer is obtained on mixing
(2020)

- (a) 100 mL of 0.1 M HCl and 200 mL of 0.1 M NaCl
- (b) 100 mL of 0.1 M HCl and 200 mL of 0.1 M CH_3COONa
- (c) 100 mL of 0.1 M CH_3COOH and 100 mL of 0.1 M NaOH
- (d) 100 mL of 0.1 M CH_3COOH and 200 mL of 0.1 M NaOH

48. A soft drink was bottled with a partial pressure of CO_2 of 3 bar over the liquid at room temperature. The partial pressure of CO_2 over the solution approaches a value of 30 bar when 44 g of CO_2 is dissolved in 1 kg of water at room temperature. The approximate pH of the soft drink is _____ $\times 10^{-1}$.
(First dissociation constant of $\text{H}_2\text{CO}_3 = 4.0 \times 10^{-7}$; $\log 2 = 0.3$; density of the soft drink = 1 g mL^{-1})
(2020)

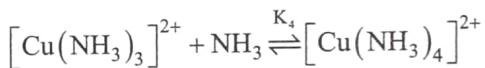
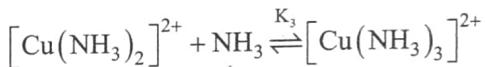
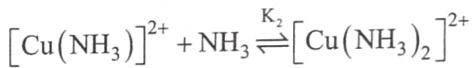
49. If the solubility product of AB_2 is $3.20 \times 10^{-11} \text{ M}^3$, then the solubility of AB_2 in pure water is _____ $\times 10^{-4} \text{ mol L}^{-1}$.
[Assuming that neither kind of ion reacts with water]
(2020)

50. Arrange the following solutions in the decreasing order of pOH
(2020)

- A. 0.01 M HCl
- B. 0.01 M NaOH
- C. 0.01 M CH_3COONa
- D. 0.01 M NaCl

- (a) B > C > D > A
- (b) A > D > C > B
- (c) A > C > D > B
- (d) B > D > C > A

51. The stepwise formation of $(\text{Cu}(\text{NH}_3)_4)^{2+}$ is given below:



The value of stability constants K_1 , K_2 , K_3 and K_4 are 10^4 , 1.58×10^3 , 5×10^2 and 10^2 respectively. The overall equilibrium constant for dissociation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is $x \times 10^{-12}$. The value of x is _____ (Rounded off to the nearest integer)
(2021)

52. At 1990 K and 1 atm pressure, there are equal number of Cl_2 molecules and Cl atoms in the reaction mixture. The value of K_p for the reaction $\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g})$ under the above conditions is $x \times 10^{-1}$. The value of x is _____.
(Rounded off to the nearest integer)
(2021)

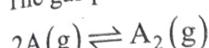
53. For the reaction $\text{A}_{(\text{g})} \rightleftharpoons \text{B}_{(\text{g})}$, the value of the equilibrium constant at 300 K and 1 atm is equal to 100.0. The value of $\Delta_f G$ for the reaction at 300 K and 1 atm in J mol^{-1} is $-xR$, where x is _____. (Rounded off to the nearest integer)
(R = 8.31 J $\text{mol}^{-1}\text{K}^{-1}$ and $\ln 10 = 2.3$)
(2021)

54. A homogeneous ideal gaseous reaction $\text{AB}_2(\text{g}) \rightleftharpoons \text{A}(\text{g}) + 2\text{B}(\text{g})$ is carried out in a 25 litre flask at 27°C. The initial amount of AB_2 was 1 mole and the equilibrium pressure was 1.9 atm. The value of K_p is $x \times 10^{-2}$. The value of x is _____.
(R = 0.08206 dm 3 atm $\text{K}^{-1}\text{mol}^{-1}$)
(2021)



The temperature at which $K_C = 20.4$ and $K_p = 600.0 \text{ K}$. (Round off to the nearest integer) (Assume all gases are ideal and $R = 0.0831 \text{ L bar K}^{-1}\text{mol}^{-1}$) (2021)

56. The gas phase reaction,

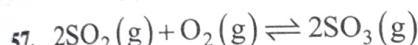


at 400 K has $\Delta G^\circ = +25.2 \text{ kJ mol}^{-1}$.

The equilibrium constant K_C for this reaction is _____ $\times 10^{-2}$.

(Round off to the nearest integer)

(Use : $R = 8.3 \text{ J mol}^{-1}\text{K}^{-1}$, $\ln 10 = 2.3$, $\log_{10} 2 = 0.30$, 1 atm = 1 bar) (antilog(-0.3) = 0.501) (2021)



In an equilibrium mixture, the partial pressures are $P_{\text{SO}_3} = 43 \text{ kPa}$; $P_{\text{O}_2} = 530 \text{ Pa}$ and $P_{\text{SO}_2} = 45 \text{ kPa}$; The equilibrium constant $K_p =$ _____ atm. (2021)

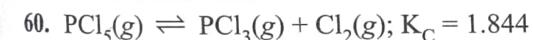
58. Value of K_p for the equilibrium reaction,

$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ at 288 K is 47.9. The K_C for this reaction at same temperature is _____

(Nearest integer) ($R = 0.083 \text{ L bar K}^{-1}\text{mol}^{-1}$) (2021)

59. For the reaction,

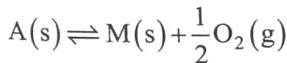
$\text{A} + \text{B} \rightleftharpoons 2\text{C}$, the value of equilibrium constant is 100 at 298 K. If the initial concentration of all the three species is 1 M each, then the equilibrium concentration of C is $x \times 10^{-1} \text{ M}$. The value of x is (2021)



3.0 moles of PCl_5 is introduced in a 1 L closed reaction vessel at 380 K. The number of moles PCl_5 at equilibrium is $\times 10^{-3}$.

(Round off to the nearest integer) (2021)

61. The equilibrium constant for the reaction,



is $K_p = 4$. At equilibrium, the partial pressure of O_2 is atm.

(Round off to the nearest integer) (2021)

62. When 5.1 g of solid NH_4SH is introduced into a two litre evacuated flask at 27 °C, 20% of the solid decomposes into gaseous ammonia and hydrogen sulphide. The K_p for the reaction at 27 °C is $x \times 10^{-2}$. The value of x is _____ (Integer answer)

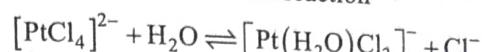
(Given $R = 0.082 \text{ L atm K}^{-1}\text{mol}^{-1}$) (2021)

63. The number of moles of NH_3 , that must be added to 2 L of 0.80 M AgNO_3 in order to reduce the concentration of Ag^+ ions to $5.0 \times 10^{-8} \text{ M}$ ($K_{\text{formation}}$ for $(\text{Ag}(\text{NH}_3)_2)^+ = 1.0 \times 10^8$) is _____.

(Nearest integer)

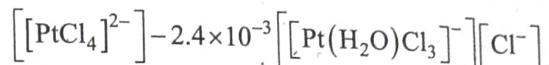
(Assume no volume change on adding NH_3) (2021)

64. The reaction rate for the reaction



was measured as a function of concentration of different species. It was observed that

$$\frac{-d[\text{PtCl}_4]^{2-}}{dt} = 4.8 \times 10^{-5}$$



where square brackets are used to denote molar concentration. The equilibrium constant $K_C =$ _____. (Nearest integer) (2021)

65. The equilibrium constant K_C at 298 K for the reaction, $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$

is 100. Starting with an equimolar solution with concentrations of A, B, C and D all equal to 1M, the equilibrium concentration of D is _____ $\times 10^{-2} \text{ M}$. (Nearest integer) (2021)

66. The OH^- concentration in a mixture of 5.0 mL of 0.0504 M NH_4Cl and 2 mL of 0.0210 M NH_3 solution is $x \times 10^{-6} \text{ M}$. The value of x is _____ (nearest integer) (Given; $K_w = 1 \times 10^{-14}$ and $K_b = 1.8 \times 10^{-5}$) (2021)

67. The solubility product of PbI_2 is 8.0×10^{-9} . The solubility of lead iodide in 0.1 molar solution of lead nitrate is $x \times 10^{-6} \text{ mol/L}$. The value of x is _____ (Round off to the nearest integer) [Given $\sqrt{2} = 1.41$] (2021)

68. The solubility of AgCN in a buffer solution of $\text{pH} = 3$ is X. The value of X is

[Assume: No cyano complex is formed; $K_{\text{sp}}(\text{AgCN}) = 2.2 \times 10^{-16}$ and $K_a(\text{HCN}) = 6.2 \times 10^{-10}$] (2021)

- (a) 0.625×10^{-6} (b) 1.6×10^{-6}
 (c) 2.2×10^{-16} (d) 1.9×10^{-5}

69. The solubility of $\text{Ca}(\text{OH})_2$ in water is:

[Given: The solubility product of $\text{Ca}(\text{OH})_2$ in water = 5.5×10^{-6}] (2021)

- (a) 1.11×10^{-6} (b) 1.77×10^{-6}
 (c) 1.77×10^{-2} (d) 1.11×10^{-2}

70. The pH of ammonia phosphate solution, if pK_a of phosphoric acid and pK_b of ammonium hydroxide are 5.23 and 4.75 respectively, is (2021)

71. Two salts A_2X and MX have the same value of solubility product of 4.0×10^{-12} . The ratio of their molar solubilities i.e. $\frac{S(\text{A}_2\text{X})}{S(\text{MX})} =$ _____.

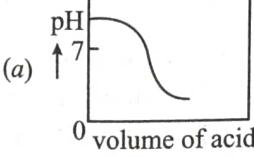
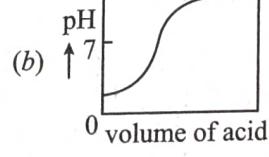
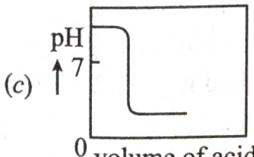
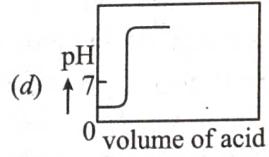
(Round off to the nearest integer). (2021)

72. Sulphurous acid (H_2SO_3) has $\text{Ka}_1 = 1.7 \times 10^{-2}$ and $\text{Ka}_2 = 6.4 \times 10^{-8}$. The pH of 0.588 M H_2SO_3 is _____ (Round off to the nearest integer) (2021)

73. 0.01 moles of a weak acid HA ($K_a = 2.0 \times 10^{-6}$) is dissolved in 1.0 L of 0.1 M HCl solution. The degree of dissociation of HA is $\times 10^{-5}$.

(Round off to the nearest integer)
 [Neglect volume change on adding HA. Assume degree of dissociation $\ll 1$] (2021)

74. In order to prepare a buffer solution of pH 5.74, sodium acetate is added to acetic acid. If the concentration of acetic acid in the buffer is 1.0 M, the concentration of sodium acetate in the buffer is _____ M.
 (Round off to the nearest integer).
 [Given; pK_a (acetic acid) = 4.74] (2021)
75. The solubility of CdSO_4 in water is 8.0×10^{-4} mol L⁻¹. Its solubility in 0.01 M H_2SO_4 is _____
 (Round off to the nearest integer) (Assume that solubility is much less than 0.01 M) (2021)
76. A solution is 0.1 M in Cl^- and 0.001M in CrO_4^{2-} . Solid AgNO_3 is gradually added to it. Assuming that the addition does not cause change in volume and $K_{sp}(\text{AgCl}) = 1.7 \times 10^{-10}$ M² and $K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.79 \times 10^{-12}$ M³. Select correct statement from the following: (2021)
- (a) AgCl precipitates first because its K_{sp} is high.
 - (b) Ag_2CrO_4 precipitates first as its K_{sp} is low.
 - (c) Ag_2CrO_4 precipitates first because the amount of Ag^+ needed is low.
 - (d) AgCl will precipitate first as the amount of Ag^+ needed to precipitate is low.
77. Assuming that $\text{Ba}(\text{OH})_2$ is completely ionised in aqueous solution under the given conditions, the concentration of H_3O^+ ions in 0.005 M aqueous solution of $\text{Ba}(\text{OH})_2$ at 298 K is $x \times 10^{-12}$ mol L⁻¹. Find the value of x. (2021)
78. The molar solubility of $\text{Zn}(\text{OH})_2$ in 0.1 M NaOH solution is $x \times 10^{-18}$ M. The value of x is _____. (Nearest integer)
 (Given: The solubility product of $\text{Zn}(\text{OH})_2$ is 2×10^{-20}) (2021)
79. The pH of a solution obtained by mixing 50 mL of 1 M HCl and 30 mL of 1 M NaOH is $x \times 10^{-4}$. The value of x is _____.
 (Nearest integer) [$\log 2.5 = 0.3979$] (2021)
80. A_3B_2 is a sparingly soluble salt of molar mass M(g mol⁻¹) and solubility x g L⁻¹. The solubility product satisfies $K_{sp} = a \left(\frac{x}{M} \right)^5$. The value of a is _____. (Integer answer) (2021)
81. Given below are two statements.
- Statement-I:** In the titration between strong acid and weak base, methyl orange is suitable as an indicator.
- Statement-II:** For titration of acetic acid with NaOH, phenolphthalein is not a suitable indicator.
- In the light of above statements, choose the most appropriate answer from the options given below. (2021)
- (a) Statement-I is false but Statement-II is true.
 - (b) Statement-I is true but Statement-II is false.
 - (c) Both statement-I and Statement-II are true.
 - (d) Both statement-I and Statement-II are false.
82. K_{a_1} , K_{a_2} and K_{a_3} are the respective ionization constants for the following reactions (a), (b), and (c).
- (a) $\text{H}_2\text{C}_2\text{O}_4 \xrightleftharpoons{K_{a_1}} \text{H}^+ + \text{HC}_2\text{O}_4^-$
- (b) $\text{HC}_2\text{O}_4^- \xrightleftharpoons{K_{a_2}} \text{H}^+ + \text{C}_2\text{O}_4^{2-}$
- (c) $\text{H}_2\text{C}_2\text{O}_4 \xrightleftharpoons{K_{a_3}} 2\text{H}^+ + \text{C}_2\text{O}_4^{2-}$
- The relationship between K_{a_1} , K_{a_2} and K_{a_3} is given as (2022)
- (a) $K_{a_3} = K_{a_1} + K_{a_2}$
 - (b) $K_{a_3} = K_{a_1} - K_{a_2}$
 - (c) $K_{a_3} = K_{a_1} / K_{a_2}$
 - (d) $K_{a_3} = K_{a_1} \times K_{a_2}$
83. At 298 K, the equilibrium constant is 2×10^{15} for the reaction: $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$
 The equilibrium constant for the reaction $\frac{1}{2}\text{Cu}^{2+}(\text{aq}) + \text{Ag(s)} \rightleftharpoons \frac{1}{2}\text{Cu(s)} + \text{Ag}^+(\text{aq})$ is $x \times 10^{-8}$. The value of x is _____. (Nearest integer) (2022)
84. At 600K, 2 mol of NO are mixed with 1 mol of O_2 .
 $2\text{NO}_{(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{2(\text{g})}$
 The reaction occurring as above comes to equilibrium under a total pressure of 1 atm. Analysis of the system shows that 0.6 mol of oxygen are present at equilibrium. The equilibrium constant for the reaction is _____. (Nearest integer) (2022)
85. For a reaction at equilibrium,
 $\text{A(g)} \rightleftharpoons \text{B(g)} + \frac{1}{2}\text{C(g)}$
 the relation between dissociation constant (K), degree of dissociation (α) and equilibrium pressure (p) is given by: (2022)
- (a) $K = \frac{\frac{1}{2} \frac{3}{1}}{\alpha^2 p^2} (1 + \frac{3}{2} \alpha)^{\frac{1}{2}} (1 - \alpha)$ (b) $K = \frac{\frac{3}{1}}{\alpha^2 p^2} (2 + \alpha)^{\frac{1}{2}} (1 - \alpha)$
- (c) $K = \frac{(\alpha p)^{\frac{3}{2}}}{(1 + \frac{3}{2} \alpha)^{\frac{1}{2}} (1 - \alpha)}$ (d) $K = \frac{(\alpha p)^{\frac{3}{2}}}{(1 + \alpha)^{\frac{1}{2}} (1 - \alpha)^{\frac{1}{2}}}$
86. PCl_5 dissociates as
 $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 5 moles of PCl_5 are placed in a 200 litre vessel which contains 2 moles of N_2 and is maintained at 600 K. The equilibrium pressure is 2.46 atm. The equilibrium constant K_p for the dissociation of PCl_5 is $x \times 10^{-3}$. (Nearest integer)
 (Given: R = 0.082 L atm K⁻¹ mol⁻¹; Assume ideal gas behaviour) (2022)

87. The standard free energy change (ΔG°) for 50% dissociation of N_2O_4 into NO_2 at 27 °C and 1 atm pressure is $-x \text{ J mol}^{-1}$. The value of x is _____. J. (Nearest integer) (2022)
 Given: $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$, $\log 1.33 = 0.1239 \ln 10 = 2.3$
88. $2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$
 In an experiment, 2.0 moles of NOCl was placed in a one-litre flask and the concentration of NO after equilibrium is established, was found to be 0.4 mol/L. The equilibrium constant at 30°C is _____ $\times 10^{-4}$. (2022)
89. 4.0 moles of argon and 5.0 moles of PCl_5 are introduced into an evacuated flask of 100 litre capacity at 610 K. The system is allowed to equilibrate. At equilibrium, the total pressure of mixture was found to be 6.0 atm. The K_p for the reaction is (Given $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$) (2022)
 (a) 2.25 (b) 6.24 (c) 12.13 (d) 15.24
90. A box contains 0.90 g of liquid water in equilibrium with vapour at 27 °C. The equilibrium vapour pressure for water at 27 °C is 32.0 torr. When the volume of the box is increased, some of the liquid water evaporates to maintain the equilibrium pressure. If all the liquid water evaporates, then the volume of the box must be _____ litre.
 (Nearest integer)
 (Given: $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$)
 (Ignore the volume of the liquid water and assume water vapour behaves as an ideal gas.) (2022)
91. 20 mL of 0.1 M NH_4OH is mixed with 40 mL of 0.05 M HCl. The pH of the mixture is nearest to:
 (Given: $K_b(\text{NH}_4\text{OH}) = 1 \times 10^{-5}$, $\log 2 = 0.30$, $\log 3 = 0.48$, $\log 5 = 0.69$, $\log 7 = 0.84$, $\log 11 = 1.04$) (2022)
 (a) 3.2 (b) 4.2 (c) 5.2 (d) 6.2
92. Class XII students were asked to prepare one litre of buffer solution of pH 8.26 by their chemistry teacher. The amount of ammonium chloride to be dissolved by the student in 0.2 M ammonia solution to make one litre of the buffer is (Given: $pK_b(\text{NH}_3) = 4.74$; Molar mass of $\text{NH}_3 = 17 \text{ g mol}^{-1}$; Molar mass of $\text{NH}_4\text{Cl} = 53.5 \text{ g mol}^{-1}$) (2022)
 (a) 53.5 g (b) 72.3 g
 (c) 107.0 g (d) 126.0 g
93. At 310 K, the solubility of CaF_2 in water is 2.34×10^{-3} g/100 mL. The solubility product of CaF_2 is _____ $\times 10^{-12}$ (mol/L) 3 .
 Given molar mass: $\text{CaF}_2 = 78 \text{ g mol}^{-1}$ (2022)
94. The plot of pH-metric titration of weak base NH_4OH vs strong acid HCl looks like: (2022)
- (a) 
- (b) 
- (c) 
- (d) 
95. K_a for butyric acid ($\text{C}_3\text{H}_7\text{COOH}$) is 2×10^{-5} . The pH of 0.2 M solution of butyric acid is _____.
 [Given: $\log 2 = 0.30$] (2022)
96. If the solubility product of PbS is 8×10^{-28} , then the solubility of PbS in pure water at 298 K is $x \times 10^{-16} \text{ mol L}^{-1}$. The value of x is _____.
 [Given: $\sqrt{2} = 1.41$] (2022)
97. 200 mL of 0.01 M HCl is mixed with 400 mL of 0.01 M H_2SO_4 . The pH of the mixture is _____. (2022)
 (a) 1.14 (b) 1.78
 (c) 2.34 (d) 3.02
98. Given below are two statements one is labelled as Assertion A and the other is labelled as Reason R:
Assertion A: The amphoteric nature of water is explained by using Lewis acid/base concept.
Reason: Water acts as an acid with NH_3 and as a base with H_2S . (2022)
 (a) Both A and R are true and R is the correct explanation of A
 (b) Both A and R are true but R is NOT the correct explanation of A.
 (c) A is true but R is false
 (d) A is false but R is true
99. 50 mL of 0.1 M CH_3COOH is being titrated against 0.1 M NaOH. When 25 mL of NaOH has been added, the pH of the solution will be _____. $\times 10^{-2}$. (2022)
 [Given: $\text{pK}_a(\text{CH}_3\text{COOH}) = 4.76$; $\log 2 = 0.30$]
100. pH value of 0.001 M NaOH solution is _____. (2022)
101. A student needs to prepare a buffer solution of propanoic acid and its sodium salt with pH = 4. The ratio of $\frac{[\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$ required to make buffer is _____.
 Given: $\text{K}_a(\text{CH}_3\text{CH}_2\text{COOH}) = 1.3 \times 10^{-5}$ (2022)
 (a) 0.03 (b) 0.13
 (c) 0.23 (d) 0.33
102. The solubility of AgCl will be maximum in which of the following solution? (2022)
 (a) 0.01 M KCl (b) 0.01 M HCl
 (c) 0.01 M AgNO_3 (d) Pure water

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103. The thermal dissociation equilibrium of $\text{CaCO}_3(s)$ is studied under different conditions.
 $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$
 For this equilibrium, the correct statement(s) is (are): (2013)
 (a) ΔH is dependent on T
 (b) K is independent of the initial amount of CaCO_3
 (c) K is dependent on the pressure of CO_2 at a given T
 (d) ΔH is independent of the catalyst, if any

Paragraph for Question no. 104 to 105

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:



The standard reaction Gibbs energy “ G° ” of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β . Thus, $\beta_{\text{equilibrium}}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given: $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$) (2016)

104. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{\text{equilibrium}}$, is

(a) $\frac{8\beta_{\text{equilibrium}}}{2 - \beta_{\text{equilibrium}}}$

(b) $\frac{8\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$

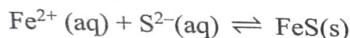
(c) $\frac{4\beta_{\text{equilibrium}}^2}{2 - \beta_{\text{equilibrium}}}$

(d) $\frac{4\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$

105. The INCORRECT statement among the following, for this reaction is

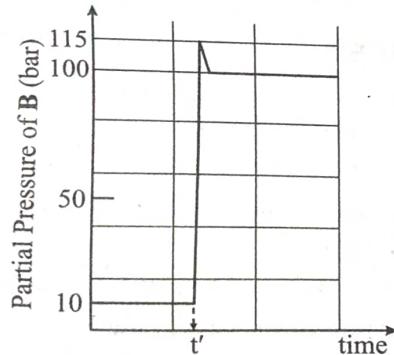
- (a) Decrease in the total pressure will result in formation of more moles of gaseous X.
 (b) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously.
 (c) $\beta_{\text{equilibrium}} = 0.7$
 (d) $K_C < 1$

106. For the following reaction, the equilibrium constant K_c at 298 K is 1.6×10^{17} .



When equal volumes of 0.06 M Fe^{2+} (aq) and 0.2 M S^{2-} (aq) solutions are mixed, the equilibrium concentration of Fe^{2+} (aq) is found to be $Y \times 10^{-17}$ M. The value of Y is _____ (2019)

107. Consider the reaction $A \rightleftharpoons B$ at 1000 K. At time t' , the temperature of the system was increased to 2000 K and the system was allowed to reach equilibrium. Throughout this experiment, the partial pressure of A was maintained at 1 bar. Given below is the plot of the partial pressure of B with time. What is the ratio of the standard Gibbs energy of the reaction at 1000 K to that at 2000 K? (2020)

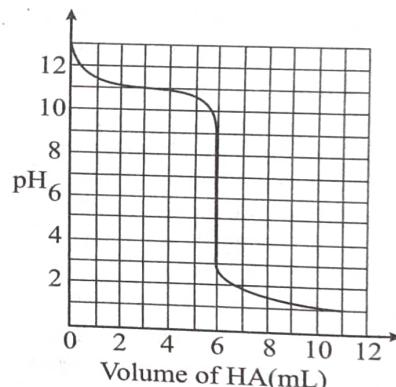


108. The solubility of a salt of weak acid (AB) at pH 3 is $Y \times 10^{-3}$ mol L⁻¹. The value of Y is _____. (Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8}) (2018)

109. 5.00 mL of 0.10 M oxalic acid solution taken in a conical flask is titrated against NaOH from a burette using phenolphthalein indicator. The volume of NaOH required for the appearance of permanent faint pink color is tabulated below for five experiments. What is the concentration, in molarity, of the NaOH solution? (2020)

| Exp No. | Vol. of NaOH (mL) |
|---------|-------------------|
| 1 | 12.5 |
| 2 | 10.5 |
| 3 | 9.0 |
| 4 | 9.0 |
| 5 | 9.0 |

110. A solution of 0.1 M weak base (B) is titrated with 0.1 M of a strong acid (HA). The variation of pH of the solution with the volume of HA added is shown in the figure below. What is the pK_b of the base? The neutralization reaction is given by $B + HA \rightarrow BH^+ + A^-$. (2020)



111. An acidified solution of 0.05 M Zn^{2+} is saturated with 0.1 M H_2S . What is the minimum molar concentration (M) of H^+ required to prevent the precipitation of ZnS ? Use $K_{sp}(\text{ZnS}) = 1.25 \times 10^{-22}$ and overall dissociation constant of H_2S , $K_{NET}(\text{H}_2\text{S}) = K_1 K_2 = 1 \times 10^{-21}$. (2020)

112. Concentration of H_2SO_4 and Na_2SO_4 in a solution is 1 M and 1.8×10^{-2} M, respectively. Molar solubility of PbSO_4 in the same solution is $X \times 10^{-Y}$ M (expressed in scientific notation). The value of Y is _____. [Given: Solubility product of PbSO_4 (K_{sp}) = 1.6×10^{-8} . For H_2SO_4 , K_{a1} is very large and $K_{a2} = 1.2 \times 10^{-2}$] (2022)

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (d) | 3. (d) | 4. (d) | 5. (b) | 6. (a) | 7. (a) | 8. (d) | 9. (a) | 10. (b) |
| 11. (a) | 12. (a) | 13. (b) | 14. (c) | 15. (c) | 16. (a) | 17. (b) | 18. (b) | 19. (c) | 20. (a) |
| 21. (a) | 22. (c) | 23. (a) | 24. (c) | 25. (d) | 26. (c) | 27. (a) | 28. (a) | 29. (b) | 30. (c) |
| 31. (a) | 32. (c) | 33. (c) | 34. (c) | 35. (c) | 36. (c) | 37. (c) | 38. (c) | 39. (b) | 40. (c) |
| 41. (a) | 42. (b) | 43. (a) | 44. (c) | 45. (d) | 46. (b) | 47. (d) | 48. (b) | 49. (c) | 50. (d) |
| 51. (b) | 52. (b) | 53. (d) | 54. (c) | 55. (b) | 56. (b) | 57. (d) | 58. (a) | 59. (c) | 60. (c) |
| 61. (b) | 62. (d) | 63. (a) | 64. (b) | 65. (a) | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (c) | 2. (b) | 3. (d) | 4. (b) | 5. (d) | 6. (a) | 7. (d) | 8. (d) | 9. (c) | 10. (a) |
| 11. (b) | 12. (c) | 13. (a) | 14. (d) | 15. (b) | 16. (a) | 17. (b) | 18. (a) | 19. (c) | 20. (b) |
| 21. (a) | 22. (b) | 23. (c) | 24. (b) | 25. (c) | 26. (c) | 27. (a) | 28. (a) | 29. (a) | 30. (c) |
| 31. (d) | 32. (c) | 33. (d) | 34. (b) | 35. (c) | 36. (d) | 37. (c) | 38. (d) | 39. (c) | 40. (b) |
| 41. (c) | 42. (a) | 43. (a) | 44. (b) | 45. (b) | 46. (d) | 47. (b) | 48. (a) | 49. (c) | 50. (d) |
| 51. (d) | 52. (a) | 53. (d) | 54. (a) | 55. (d) | 56. (c) | 57. (a) | 58. (b) | 59. (d) | 60. (b) |
| 61. (c) | 62. (b) | 63. (c) | 64. (d) | 65. (b) | 66. (c) | 67. (d) | 68. (b) | 69. (a) | 70. (b) |
| 71. (c) | 72. (c) | 73. (a) | 74. (d) | 75. (c) | 76. (d) | 77. (b) | 78. (a) | 79. (b) | 80. (c) |
| 81. (c) | 82. (b) | 83. (b) | 84. (b) | 85. (b) | 86. (b) | 87. (a) | 88. (a) | 89. (c) | 90. (b) |
| 91. (b) | 92. (c) | 93. (d) | 94. (b) | 95. (c) | 96. (b) | 97. (b) | 98. (c) | 99. (c) | 100. (c) |
| 101. (c) | 102. (a) | 103. (b) | 104. (a) | 105. (b) | 106. (c) | 107. (c) | 108. (d) | 109. (a) | 110. (c) |
| 111. (b) | 112. (d) | | | | | | | | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (b) | 3. (a) | 4. (b) | 5. (a) | 6. (b) | 7. (b) | 8. (c) | 9. (b) | 10. (a) |
| 11. (b) | 12. (d) | 13. (c) | 14. (b) | 15. (c) | 16. (a) | 17. (a) | 18. (b) | 19. (d) | 20. (a) |
| 21. (a) | 22. (a) | 23. (a) | 24. (c) | 25. (b) | 26. (b) | 27. (a) | 28. (d) | 29. (b) | 30. (b) |
| 31. (c) | 32. (a) | 33. (d) | 34. (a) | 35. (a) | 36. (c) | 37. (d) | 38. (a) | 39. (c) | 40. (b) |
| 41. (d) | 42. (c) | 43. (a) | 44. (d) | 45. (c) | 46. (c) | 47. (a) | 48. (a) | 49. (d) | 50. (c) |
| 51. (b) | 52. (b) | 53. (b) | 54. (a) | 55. (d) | 56. (c) | 57. (b) | 58. (a) | 59. (d) | 60. (b) |
| 61. (c) | 62. (d) | 63. (c) | 64. (a) | 65. (b) | 66. (d) | 67. (b) | 68. (d) | 69. (a) | 70. (c) |
| 71. (c) | 72. (a) | 73. (d) | 74. (c) | 75. (a) | 76. (c) | 77. (c) | 78. (a) | 79. (a) | 80. (d) |
| 81. (a) | | | | | | | | | |

EXERCISE-3 (JEE ADVANCED LEVEL)

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|-----------|-------------|-------------|-------------|---------------|-------------|------------|-----------|-------------|-------------|
| 1. (a,c) | 2. (a,c) | 3. (a,b) | 4. (c,d) | 5. (b,c) | 6. (c,d) | 7. (b,c) | 8. (c,d) | 9. (c,d) | 10. (c,d) |
| 11. (a,c) | 12. (a,b,c) | 13. (b,d) | 14. (a,b,c) | 15. (b,c) | 16. (b,c,d) | 17. (a,d) | 18. (a) | 19. (a,c,d) | 20. (a,b,c) |
| 21. (a,c) | 22. (b) | 23. (b,c,d) | 24. (a,d) | 25. (a,b,c,d) | 26. (a,b) | 27. (a,d) | 28. (b,c) | 29. (c,d) | 30. (a,b) |
| 31. (b,d) | 32. (a,b) | 33. (b) | 34. (a) | 35. (b) | 36. (d) | 37. (c) | 38. (a,b) | 39. (c) | 40. (c) |
| 41. (b) | 42. (d) | 43. (a) | 44. (c) | 45. (a) | 46. (c) | 47. (b) | 48. (b) | 49. (a) | 50. (c) |
| 51. (d) | 52. [50] | 53. [64] | 54. [16] | 55. [120] | 56. [1] | 57. [4.0%] | 58. [10] | 59. [9] | 60. [3] |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|--------------------|------------|-----------|----------|------------|----------|-----------|------------|----------------------|-----------|
| 1. (b) | 2. (d) | 3. (a) | 4. (b) | 5. (a) | 6. (b) | 7. (d) | 8. (d) | 9. (a) | 10. (c) |
| 11. (a) | 12. (b) | 13. (b) | 14. (c) | 15. (a) | 16. (d) | 17. (a) | 18. (b) | 19. (b) | 20. (a) |
| 21. (c) | 22. (b) | 23. (a) | 24. (d) | 25. (d) | 26. (d) | 27. (b) | 28. (d) | 29. (b) | 30. (d) |
| 31. (d) | 32. (b) | 33. [16] | 34. (b) | 35. (a) | 36. (a) | 37. [3] | 38. [3] | 39. [10.60 to 10.60] | |
| 40. [5.22 to 5.24] | 41. (b) | 42. (c) | 43. (b) | 44. [4] | 45. (b) | 46. (a) | 47. (b) | 48. [37] | |
| 49. [02] | 50. (b) | 51. [1] | 52. [5] | 53. [1380] | 54. [72] | 55. [354] | 56. [2] | 57. [172] | 58. [2] |
| 59. [25] | 60. [1400] | 61. [16] | 62. [6] | 63. [4] | 64. [50] | 65. [182] | 66. [3] | 67. [141] | 68. (d) |
| 69. (d) | 70. [7] | 71. [50] | 72. [1] | 73. [2] | 74. [10] | 75. (64) | 76. (d) | 77. [1] | 78. [2] |
| 79. [6021] | 80. [108] | 81. (b) | 82. (d) | 83. [2] | 84. [2] | 85. (b) | 86. [1107] | 87. [710] | 88. [125] |
| 89. (a) | 90. [29] | 91. (c) | 92. (c) | 93. [108] | 94. (a) | 95. [9] | 96. [282] | 97. (b) | |
| 98. (d) | 99. [476] | 100. [11] | 101. (b) | 102. (d) | | | | | |

JEE Advanced

103. (a,b,d) 104. (b) 105. (c) 106. [8.92 or 8.93] 107. [0.25] 108. [4.47] 109. [0.11] 110. [2.30 to 3.00]
111. [0.20] 112. [6]

CHAPTER

6

Redox Reaction

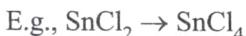
INTRODUCTION

Redox reactions shows vital role in non renewable energy sources. In cell reactions where oxidation and reduction both occurs simultaneously will have redox reaction for interconversion of energy.

CLASSICAL IDEA OF REDOX REACTION

Oxidation

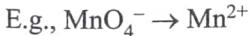
- ❖ Addition of Oxygen or any other electronegative element.
E.g., $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$
- ❖ Removal of Hydrogen e.g., $\text{H}_2\text{S} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{S}$
- ❖ Increase in positive charge e.g., $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$
- ❖ Increase in oxidation number



- ❖ Removal of electron e.g. $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$

Reduction

- ❖ Removal of Oxygen or any other electronegative element.
E.g., $\text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO}$
- ❖ Addition of Hydrogen e.g., $\text{S} + \text{H}_2 \rightarrow \text{H}_2\text{S}$
- ❖ Decrease in positive charge e.g., $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$
- ❖ Decrease in oxidation number



- ❖ Addition of electron e.g. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$

REDOX REACTION IN TERM OF ELECTRON TRANSFER REACTIONS (MODERN IDEA)

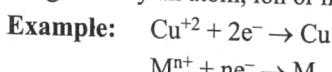
Oxidation

- ❖ De-electronation
- ❖ Oxidation process is those process in which one or more e^- are lost by an atom, ion or molecule.



Reduction

- ❖ Electronation
- ❖ Reduction process is those process in which one or more e^- are gained by an atom, ion or molecule.



Redox Reaction (Oxidation-Reduction): Many chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed as **oxidation-reduction** or **redox reactions**.

or

Those reactions which involve oxidation and reduction both simultaneously are known as oxidation reduction or redox reactions.

or

Those reactions in which increase and decrease in oxidation number of same or different atoms occurs are known as redox reactions.

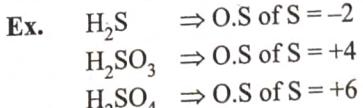
Oxidation State: Oxidation state of an atom in a molecule or ion is the hypothetical or real charge present on an atom due to electronegativity difference.

or

Oxidation state of an element in a compound represents the number of electrons lost or gained during its change from free state into that compound.

Some important points concerning oxidation number

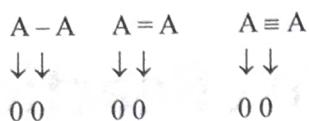
1. Electronegativity values of no two elements are same
 $\text{P} > \text{H} \quad \text{C} > \text{H} \quad \text{S} > \text{C} \quad \text{Cl} > \text{N}$
2. Oxidation number of an element may be positive or negative.
3. Oxidation number may be zero, whole number or a fractional value
 - Ex. $\text{Ni}(\text{CO})_4 \Rightarrow \text{O.S of Ni} = 0$
 - $\text{N}_3\text{H} \Rightarrow \text{O.S of N} = -1/3$
 - $\text{HCl} \Rightarrow \text{O.S of Cl} = -1$
4. Oxidation state of same element can be different in same or different compounds.



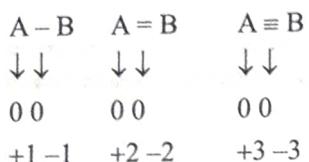
Some helping rules for calculating oxidation number:

(A) In case of covalent bond:

(i) For homoatomic molecule



(ii) For heteroatomic molecule (EN of B>A)



(iii) The oxidation state of an element in its free state is zero.

Example: Oxidation state of Na, Cu, I, Cl, O etc, are zero.

(iv) Oxidation state of atoms present in homoatomic molecules is zero

Ex. H₂, O₂, N₂, P₄, S₈ = zero

(v) Oxidation state of an element in any of its allotropic form is zero.

C_{Diamond}, C_{Graphite}, S_{Monoclinic}, S_{Rhombic} = 0

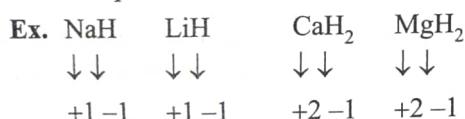
(vi) Oxidation state of all the components of an alloy are 0

(vii) In complex compounds, oxidation state of some neutral molecules (ligands) is zero. Example CO, NO, NH₃, H₂O

(viii) Oxidation state of fluorine in all its compounds is -1

(ix) Oxidation state of IA & IIA group elements are +1 and +2 respectively.

(x) Oxidation state of hydrogen in most of its compounds is +1 except in metal hydrides (-1)



(xi) Oxidation state of oxygen in most of its compounds is -2 except in:

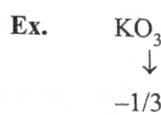
(a) Peroxides $(O_2^{2-}) \rightarrow$ Oxidation state (O) = -1

Ex. H₂O₂, BaO₂

(b) Super Oxides $(O_2^{1-}) \rightarrow$ Oxidation state (O) = -1/2



(c) Ozonide $(O_3^{1-}) \rightarrow$ Oxidation state (O) = -1/3



(d) OF₂ (Oxygen difluoride)



(e) O₂F₂ (dioxygen difluoride)



(xii) Oxidation state of monoatomic ions is equal to the charge present on the ion.

Ex. Mg²⁺ \rightarrow Oxidation state = +2

(xiii) The algebraic sum of oxidation state of all the atoms present in a polyatomic neutral molecule is 0.

Ex. H₂SO₄

If O.S of S is x then

$$2(+1) + x + 4(-2) = 0$$

$$x - 6 = 0$$

$$x = +6$$

Ex. H₂SO₃

If O.S of S is x then

$$2(+1) + x + 3(-2) = 0$$

$$x - 4 = 0$$

$$x = +4$$

(xiv) The algebraic sum of oxidation state of all the atoms in a polyatomic complex ion is equal to the charge present on the ion.

Ex. SO₄²⁻

If O.S of S is x then

$$x + 4(-2) = -2$$

$$x - 8 = -2$$

$$x = +6$$

Ex. HCO₃⁻

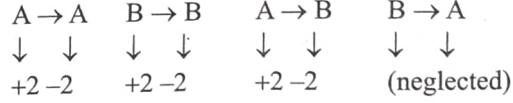
If O.S of C is x then

$$+1 + x + 3(-2) = -1$$

$$x - 5 = -1$$

$$x = +4$$

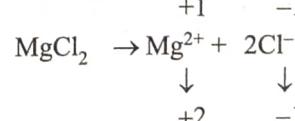
(B) In case of co-ordinate bond (EN of B>A):



(C) In case of Ionic bond:

Charge on cation = O.S of cation

Charge on anion = O.S of anion



OXIDISING AND REDUCING AGENT

❖ **Oxidising agent or Oxidant:** Oxidising agents are those compounds which can oxidise others and reduce itself



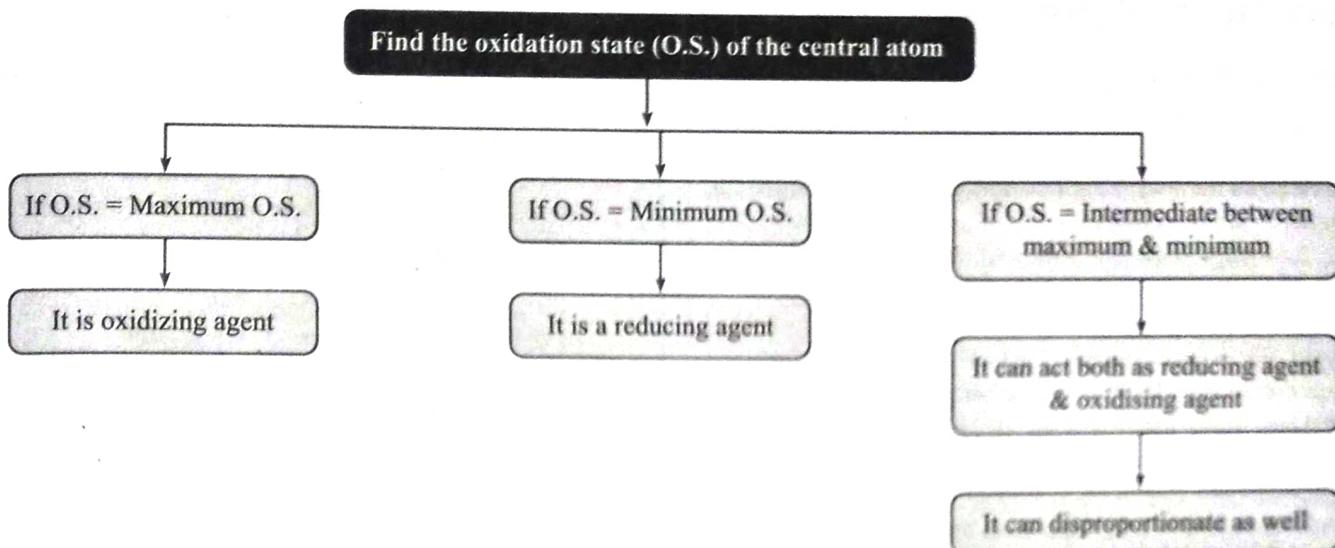
during the chemical reaction. Those reagents in which for an element, oxidation number decreases or which undergoes gain of electrons in a redox reaction are termed as oxidants. e.g. KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 , conc. H_2SO_4 etc. are powerful oxidising agents.

❖ **Reducing agent or Reductant:** Reducing agents are those compounds which can reduce other and oxidise itself during

the chemical reaction. Those reagents in which for an element, oxidation number increases or which undergoes loss of electrons in a redox reaction are termed as reductants. e.g. KI , $\text{Na}_2\text{S}_2\text{O}_3$ etc. are the powerful reducing agents.

Note: There are some compounds also which can work both as oxidising agent and reducing agent e.g., H_2O_2 , HNO_2

How to Identify Whether A Particular Substance is an Oxidising or a Reducing Agent



REDOX REACTION

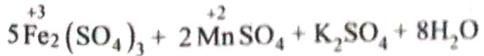
A reaction in which oxidation and reduction simultaneously take place is called a redox reaction

In all redox reactions, the total increase in oxidation number must be equal to the total decrease in oxidation number.

Type of Redox Reaction

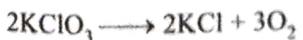
- (i) Intermolecular redox reaction
- (ii) Intramolecular redox reaction
- (iii) Disproportionation reaction
- (iv) Comproportionation reaction

(i) **Intermolecular redox reaction:** A redox reaction in which of oxidising agent and reducing agent belongs to two different molecules of same compound or different compound.



It is intermolecular redox reaction.

(ii) **Intra molecular redox reaction:**



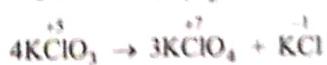
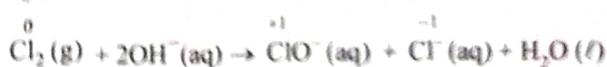
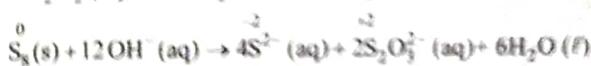
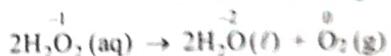
KClO_3 plays a role of oxidant and reductant both. Here, Cl present in KClO_3 is reduced and O present in KClO_3 is oxidized. Since same element is not oxidized and reduced,

so it is not a disproportionation reaction, although it looks like one.

It is called intra molecular redox reaction.

(iii) **Disproportionation Reaction:** A redox reaction in which same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reaction.

Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction. For example:

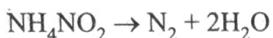


It is a case of disproportionation reaction and Cl atom is disproportionating.

List of some important disproportionation reactions

1. $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$
2. $\text{X}_2 + \text{OH}^-(\text{dil.}) \longrightarrow \text{X}^- + \text{XO}_3^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)
3. $\text{X}_2 + \text{OH}^-(\text{conc.}) \longrightarrow \text{X}^- + \text{XO}_3^{2-}$

(iv) Comproportionation reaction:



Nitrogen in this compound has -3 and $+3$ oxidation number, which is not a definite value. So it is not a disproportionation reaction. It is an example of comproportionation reaction, which is a class of redox reaction in which an element from two different oxidation state gets converted into a single oxidation state. Comproportionation reactions are reverse reactions of disproportionation reactions.

BALANCING OF REDOX REACTIONS

Balancing of Redox Equation

- (a) Ion electron method.
- (b) Oxidation number change method.

(a) Ion electron method: This method was given by Jette and Lamav in 1972.

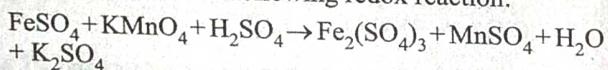
The following steps are followed while balancing redox reaction (equations) by this method.

- (i) Write the equation in ionic form.
- (ii) Split the redox equation into two half reactions, one representing oxidation and the other representing reduction.
- (iii) Balance these half reactions separately and then add by multiplying with suitable coefficients so that the electrons are cancelled. Balancing is done as follows.
- (iv) Add both half reaction and then balance the atoms other than 'O' and 'H'.
- (v) Then balance oxygen atoms by adding H_2O molecules to the side deficient in oxygen. The number of H_2O molecules added is equal to the deficiency of oxygen atoms.
- (vi) Balance hydrogen atoms by adding H^+ ions equal to the deficiency in the side which is the deficient in hydrogen atoms.
- (vii) If the medium of reaction is basic, OH^- ions are added to both sides of balanced equation equal in number of H^+ in balanced equation.
- (viii) Balance the charge by electrons to the side which is rich in +ve charges. i.e. deficiency in electrons. Number of electrons added is equal to the deficiency.
- (ix) Multiply the half equations with suitable coefficients to equalize the number of electrons.
- (x) Add these half equations to get an equation which is balanced with respect to charge and atoms.

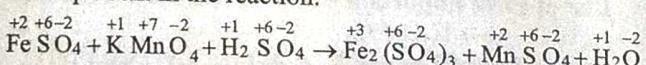


Train Your Brain

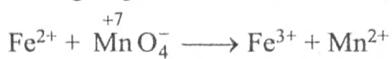
Example 1: Balance the following redox reaction:



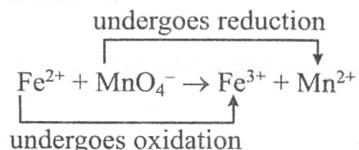
Sol. Step-I: Assign the oxidation number to each element present in the reaction.



Step-II: Now convert the reaction in Ionic form by eliminating the elements or species, which are not undergoing either oxidation or reduction.



Step-III: Now identify the oxidation / reduction occurring in the reaction



Step-IV: Split the Ionic reaction in two half, one for oxidation and other for reduction.

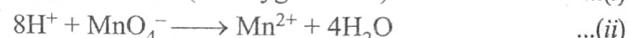


Step-V: Balance the atom other than oxygen and hydrogen atom in both half reactions



Fe & Mn atoms are balanced on both side.

Step-VI: Now balance O & H atom by H_2O & H^+ respectively by the following way: For one excess oxygen atom, add one H_2O on the other side and two H^+ on the same side.

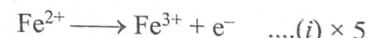


Step-VII: Equation (i) & (ii) are balanced atomwise. Now balance both equations chargewise. To balance the charge, add electrons to the electrically positive side.



Step-VIII: The number of electrons gained and lost in each half-reaction are equalised by multiplying both the half reactions with a suitable factor and finally the half reactions are added to give the overall balanced reaction.

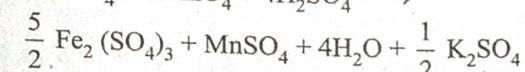
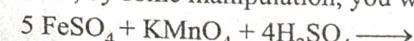
Here, we multiply equation (i) by 5 and (ii) by 1 and add them:



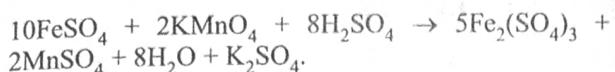
(Here, at this stage, you will get balanced redox reaction in Ionic form)

Step-IX: Now convert the Ionic reaction into molecular form by adding the elements or species, which are removed in step (2).

Now, by some manipulation, you will get:



or



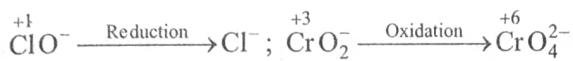
❖ **Balancing in basic medium:** In this case, except step VI, all the steps are same.

We can understand it by the following example.

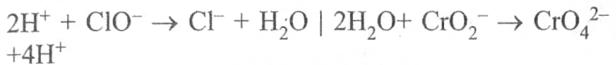
Example 2: Balance the following redox reaction in basic medium:



Sol. By using upto step V, we will get:



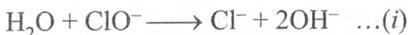
Now, students are advised to follow step VI to balance 'O' and 'H' atom.



Now, since we are balancing in basic medium, therefore add as many as OH^- on both side of equation as there are H^+ ions in the equation.

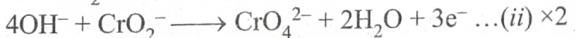
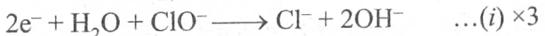


Finally you will get



Now see equation (i) and (ii) in which O and H atoms are balanced by OH^- and H_2O

Now from step VIII



Adding:

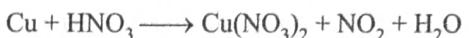


(b) **Oxidation number change method:** This method was given by Jonson. In a balanced redox reaction, total increase in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basis for balancing redox reactions.

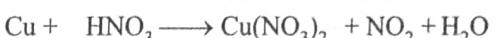
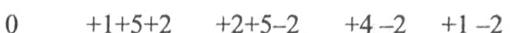
The general procedure involves the following steps:

- Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.
- Select the atom in reducing agent whose oxidation number increases and write the loss of electrons.
- Now cross multiply i.e. multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.
- Balance the number of atoms on both sides whose oxidation numbers change in the reaction.
- In order to balance oxygen atoms, add H_2O molecules to the side deficient in oxygen. Then balance the number of H atoms by adding H^+ ions in the hydrogen.

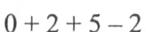
Example 3: Balance the following reaction by the oxidation number method:



Sol. Write the oxidation number of all the atoms.



There is change in oxidation number of Cu and N.

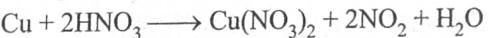


$\text{Cu} \rightarrow \text{Cu}(\text{NO}_3)_2 \dots(i)$ (Oxidation number of Cu is increased by 2)



$\text{HNO}_3 \rightarrow \text{NO}_2 \dots(ii)$ (Oxidation number of N is decreased by 1)

To make increase and decrease equal, eq. (ii) is multiplied by 2.



Balancing nitrates ions, hydrogen and oxygen, the following equation is obtained.



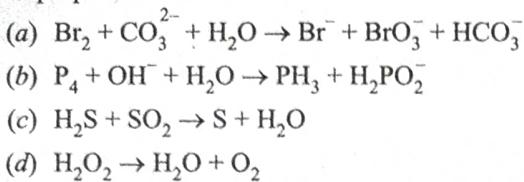
This is the balanced equation.



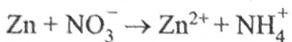
Concept Application

- The oxidation numbers of C in HCN and HNC, respectively, are
 - +2, +2
 - +2, +4
 - +4, +4
 - 2, -2
- The oxidation number of K in KO_2 is:
 - +4
 - +1
 - +1/2
 - 1/2
- What is the oxidation state of Xe in Ba_2XeO_6 ?
 - 0
 - +4
 - +6
 - +8
- When $\text{K}_2\text{Cr}_2\text{O}_7$ is converted into K_2CrO_4 , the change in oxidation number of Cr is
 - 0
 - 6
 - 4
 - 3
- In the reaction: $3\text{Br}_2 + 6\text{CO}_3^{2-} + 3\text{H}_2\text{O} \rightarrow 5\text{Br}^- + \text{BrO}_3^- + 6\text{HCO}_3^-$
 - Bromine is oxidized and carbonate is reduced.
 - Bromine is oxidized and water is reduced.
 - Bromine is both oxidized and reduced.
 - Bromine is neither oxidized nor reduced.

6. Which of the following reaction is not a disproportionation reaction?



7. For the redox reaction,



in basic medium, the coefficients of Zn, NO_3^- and OH^- in the balanced equation, respectively, are:

- $$(a) 4, 1, 7 \quad (b) 7, 4, 1$$
- $$(c) 4, 1, 10 \quad (d) 1, 4, 10$$

APPLICATIONS OF OXIDATION NUMBER

- (a) To compare the strength of acid and base:

Strength of acid \propto Oxidation Number

$$\text{Strength of base} \propto \frac{1}{\text{Oxidation Number}}$$

Example 4: Order of acidic strength in HClO , HClO_2 , HClO_3 , HClO_4 will be

Sol. Oxidation Number of chlorine

| | |
|------------------------------------|----|
| HClO (Hypo chlorous acid) | +1 |
| HClO_2 (Chlorous acid) | +3 |
| HClO_3 (Chloric acid) | +5 |
| HClO_4 (Perchloric acid) | +7 |

\therefore Strength of acid \propto Oxidation Number

So the order will be:



- (b) To determine the oxidising and reducing nature of the substances:

Oxidising agents are the substances which accept electrons in a chemical reaction i.e., electron acceptors are oxidising agent.

Reducing agents are the substances which donate electrons in a chemical reaction i.e., electron donors are reducing agent.

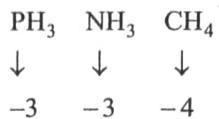
| | | | | | | | | | | | |
|--------------|----|----|----|----|----|----|----|----|----|----|----|
| Highest O.S. | +4 | +5 | +5 | +6 | +7 | +6 | +7 | +8 | +8 | +2 | +1 |
| Elements | C | N | P | S | Cl | Cr | Mn | Os | Ru | O | H |
| Lowest O.S. | -4 | -3 | -3 | -2 | -1 | 0 | 0 | 0 | 0 | -2 | -1 |

- (i) If effective element in a compound is present in maximum oxidation state then the compound acts as oxidising agent.

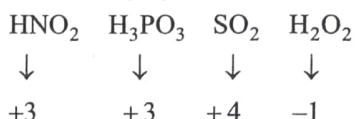
Example:

| | | | | | | |
|-----------------|-----------------------------------|-------------------------|---------------|-------------------------|----------------|-----------------|
| KMnO_4 | $\text{K}_2\text{Cr}_2\text{O}_7$ | H_2SO_4 | SO_3 | H_3PO_4 | HNO_3 | HClO_4 |
| \downarrow | \downarrow | \downarrow | \downarrow | \downarrow | \downarrow | \downarrow |

- (ii) If effective element in a compound is present in minimum oxidation state then the compound acts as reducing agent.



- (iii) If effective element in a compound is present in intermediate oxidation state then the compound can act as oxidising agent as well as reducing agent.

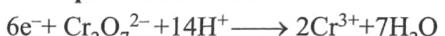


- (c) **To calculate the equivalent weight of compounds:** The equivalent weight of an oxidising agent or reducing agent is that weight which accepts one mole electrons in a chemical reaction or loses one mol electron in chemical reaction.

- (a) Equivalent weight of oxidant

$$= \frac{\text{Molecular weight}}{\text{No. of electrons gained by one mole}}$$

Example: In acidic medium



Here atoms which undergoes reduction is Cr. Its O.S. is decreasing from +6 to +3

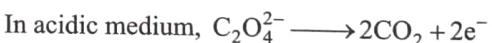
Equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$

$$= \frac{\text{Molecular weight of } \text{K}_2\text{Cr}_2\text{O}_7}{3 \times 2} = \frac{M}{6}$$

Note: [6 in denominator indicates that 6 electrons were gained by $\text{Cr}_2\text{O}_7^{2-}$ as it is clear from the given balanced equation]

- (b) Equivalent weight of a reducant

$$= \frac{\text{Molecular weight}}{\text{No. of electrons lost by one mole}}$$

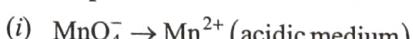


Here, Total electrons lost = 2

$$\text{So, equivalent weight} = \frac{M}{2}$$

- (c) In different conditions a compound may have different equivalent wts. Because, it depends upon the number of electrons gained or lost by that compound in that reaction.

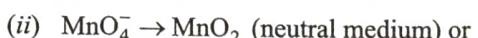
Example:



$$(+7) \quad (+2)$$

Here 5 electrons are taken so equivalent weight

$$= \frac{M}{5} = \frac{158}{5} = 31.6$$

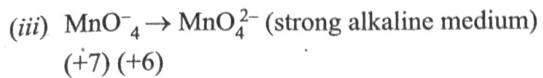


$$(+7) \quad (+4) \text{ (Weak alkaline medium)}$$

Here, only 3 electrons are gained, so eq. wt.

$$= \frac{M}{3} = \frac{158}{3} = 52.7$$

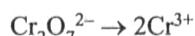
Note: When only alkaline medium is given consider it as weak alkaline medium.



Here, only one electron is gained, so eq. wt. = $\frac{M}{1} = 158$

Note: KMnO_4 acts as an oxidant in every medium although with different strength which follows the order:

Acidic medium > neutral medium > alkaline medium while, $\text{K}_2\text{Cr}_2\text{O}_7$ acts as an oxidant only in acidic medium as follows



$$(2 \times 6) \rightarrow (2 \times 3)$$

Here, 6 electrons are gained so eq. wt. = $\frac{M}{6} = \frac{294}{6} = 49$

(d) **To determine the possible molecular formula of compound:** Since the sum of oxidation number of all the atoms present in a compound is zero, so the validity of the formula can be confirmed.

| Species | Changed to | Reaction | Electrons exchanged or change in O.N. | Eq. wt. |
|---|--|--|---------------------------------------|------------------------|
| MnO_4^- (O.A.) | Mn^{+2} In acidic medium | $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ | 5 | $E = \frac{M}{5}$ |
| MnO_4^- (O.A.) | MnO_2 In neutral medium or weak alkaline medium | $\text{MnO}_4^- + 3\text{e}^- + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{OH}^-$ | 3 | $E = \frac{M}{3}$ |
| MnO_4^- (O.A.) | MnO_4^{2-} Strongly basic medium | $\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$ | 1 | $E = \frac{M}{1}$ |
| $\text{Cr}_2\text{O}_7^{2-}$ (O.A.) | Cr^{3+} In acidic medium | $\text{CrO}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ | 6 | $E = \frac{M}{6}$ |
| MnO_2 (O.A.) | Mn^{2+} In acidic medium | $\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$ | 2 | $E = \frac{M}{2}$ |
| Cl_2 (O.A.) | Cl^- | $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ | 2 | $E = \frac{M}{2}$ |
| CuSO_4 (O.A.) in iodometric titration | Cu^+ | $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$ | 1 | $E = \frac{M}{1}$ |
| $\text{S}_2\text{O}_3^{2-}$ (R.A.) | $\text{S}_4\text{O}_6^{2-}$ | $2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$ | 2 (for two molecules) | $E = \frac{2M}{2} = M$ |
| H_2O_2 (O.A.) | H_2O | $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ | 2 | $E = \frac{M}{2}$ |
| H_2O_2 (R.A.) | O_2 | $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ O.N. of oxygen in H_2O is -1 per atom | 2 | $E = \frac{M}{2}$ |
| Fe^{2+} (R.A.) | Fe^{3+} | $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ | 1 | $E = \frac{M}{1}$ |

Example: To find the n-factor in the following chemical changes.

- (i) $\text{KMnO}_4 \xrightarrow{\text{H}^+} \text{Mn}^{2+}$
- (ii) $\text{KMnO}_4 \xrightarrow{\text{H}_2\text{O}} \text{Mn}^{4+}$
- (iii) $\text{KMnO}_4 \xrightarrow{\text{OH}^- (\text{Concentrated basic medium})} \text{Mn}^{6+}$
- (iv) $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{H}^+} \text{Cr}^{3+}$
- (v) $\text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2$
- (vi) $\text{FeSO}_4 \rightarrow \text{Fe}_2\text{O}_3$
- (vii) $\text{Fe}_2\text{O}_3 \rightarrow \text{FeSO}_4$

Sol. (i) In this reaction, KMnO_4 which is an oxidizing agent, itself gets reduced to Mn^{2+} under acidic conditions.

$$n = |1 \times (+7) - 1 \times (+2)| = 5$$

(ii) In this reaction, KMnO_4 gets reduced to Mn^{4+} under neutral or slightly (weakly) basic conditions.

$$n = |1 \times (+7) - 1 \times (+4)| = 3$$

(iii) In this reaction, KMnO_4 gets reduced to Mn^{6+} under basic conditions.

$$n = |1 \times (+7) - 1 \times (+6)| = 1$$

(iv) In this reaction, $\text{K}_2\text{Cr}_2\text{O}_7$ which acts as an oxidizing agent reduced to Cr^{3+} under acidic conditions. (It does not react under basic conditions.)

$$n = |2 \times (+6) - 2 \times (+3)| = 6$$

(v) In this reaction, $\text{C}_2\text{O}_4^{2-}$ (oxalate ion) gets oxidized to CO_2 when it is reacted with an oxidizing agent.

$$n = |2 \times (+3) - 2 \times (+4)| = 2$$

(vi) In this reaction, ferrous ions get oxidized to ferric ions.

$$n = |1 \times (+2) - 1 \times (+3)| = 1$$

(vii) In this reaction, ferric ions are getting reduced to ferrous ions.

$$n = |2 \times (+3) - 2 \times (+2)| = 2$$

Example: Suppose that there are three atoms A, B, C and their oxidation number are 6, -1, -2, respectively. Then the molecular formula of compound will be

Sol. Since, the charge on a free compound is zero. So

$$+6 = (-1 \times 4) + (-2)$$

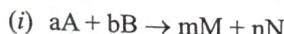
$$+6 = -6$$

$$\text{or } +6 = (-1 \times 2) + (-2 \times 2)$$

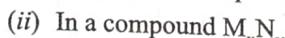
So molecular formula, AB_4C or AB_2C_2 .

Law of Equivalence: The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equivalent and mill equivalent of reactants react in equal amount to give same no. of equivalent or milli equivalents of products separately.

According:



$$\text{m.eq of A} = \text{m.eq of B} = \text{m.eq of M} = \text{m.eq of N}$$



$$\text{m.eq of M}_x\text{N}_y = \text{m.eq of M} = \text{m.eq of N}$$

GOLDEN KEY POINTS

For Acid-base (Neutralization reaction) or redox reaction:

$$\text{N}_1 V_1 = \text{N}_2 V_2 \text{ is always true}$$

But $M_1 V_1 = M_2 V_2$ (may or may not be true)

But $M_1 \times n_1 \times V_1 = M_2 \times n_2 \times V_2$ (always true where n terms represent n-factor)



Train Your Brain

Example 4: Calculate the normality of a solution containing 15.8 g of KMnO_4 in 50 mL acidic solution.

$$\text{Sol. Normality (N)} = \frac{W \times 1000}{E \times V(\text{mL})}$$

where $W=15.8 \text{ g}$, $V=50 \text{ mL}$

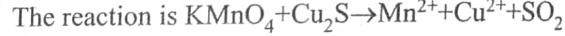
$$E = \frac{\text{Molar mass of } \text{KMnO}_4}{\text{Valence factor}} = \frac{158}{5} = 31.6$$

$$\text{So, N}=10$$

Example 5: Calculate the normality of a solution containing 50 mL of 5M solution $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium.

$$\text{Sol. Normality (N)} = \text{Molarity} \times \text{Valence factor} = 5 \times 6 = 30 \text{ N}$$

Example 6: Find the number of moles of KMnO_4 needed to oxidise one mole Cu_2S in acidic medium.



Sol. From law of equivalence

equivalents of Cu_2S = equivalents of KMnO_4

moles of $\text{Cu}_2\text{S} \times \text{v.f.} = \text{moles of } \text{KMnO}_4 \times \text{v.f.}$

$$1 \times 8 = n_2 \times 5$$

$$n_2 = \frac{8}{5} = 1.6$$

Example 7: In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.15 M NaOH should be added for this requirement?

$$\text{Sol. Amount of NaOH present in 1000 mL of 0.15 M NaOH} = 0.15 \times 40 = 6 \text{ g}$$

$$\therefore 1 \text{ mL of this solution contain NaOH} = \frac{6}{1000} \times 10^{-3} \text{ g}$$

$\therefore 1.184 \text{ g of NaOH will be present in}$

$$= \frac{1}{6 \times 10^{-3}} \times 1.184 = 197.33 \text{ mL}$$

Example 8: Which of the following is/are correct?

$$(a) \text{g mole wt.} = \text{mol. wt. in g} = \text{wt. of } 6.02 \times 10^{23} \text{ molecules}$$

$$(b) \text{mole} = N_A \text{ molecule} = 6.02 \times 10^{23} \text{ molecules}$$

$$(c) \text{mole} = \text{g molecules}$$

$$(d) \text{None of the above}$$

Sol. (a), (b) and (c)

Example 9: Find the average and individual oxidation number of Fe & Pb in Fe_3O_4 & Pb_3O_4 , respectively, which are mixed oxides.

Sol. (i) Fe_3O_4 is mixture of FeO & Fe_2O_3 in 1 : 1 ratio
so, individual oxidation number of Fe = +2 & +3

$$\text{& average oxidation number} = \frac{1(+2) + 2(+3)}{3} = 8/3$$

(ii) Pb_3O_4 is a mixture of PbO & PbO_2 in 2 : 1 molar ratio
so, individual oxidation number of Pb are +2 & +4
& average oxidation number of

$$\text{Pb} = \frac{2(+2) + 1(+4)}{3} = 8/3$$



Concept Application

8. The number of moles of oxalate ion oxidized by one mole of MnO_4^- ion in acidic medium.

- | | |
|-------------------|-------------------|
| (a) $\frac{5}{2}$ | (b) $\frac{2}{5}$ |
| (c) $\frac{3}{5}$ | (d) $\frac{5}{3}$ |

9. The number of moles of KMnO_4 that will be required to react with 2 mol of ferrous oxalate is

- | | |
|-------------------|-------------------|
| (a) $\frac{4}{5}$ | (b) $\frac{2}{5}$ |
| (c) $\frac{6}{5}$ | (d) 1 |

10. The number of moles of ferrous oxalate oxidised by one mole of KMnO_4 in acidic medium is:

- | | |
|-------------------|-------------------|
| (a) $\frac{5}{2}$ | (b) $\frac{2}{5}$ |
| (c) $\frac{3}{5}$ | (d) $\frac{5}{3}$ |

11. How many moles of KMnO_4 are needed to oxidise a mixture of 1 mole of each FeSO_4 & FeC_2O_4 in acidic medium?

- | | |
|-------------------|-------------------|
| (a) $\frac{4}{5}$ | (b) $\frac{5}{4}$ |
| (c) $\frac{3}{4}$ | (d) $\frac{5}{3}$ |

12. Equivalent weight of K_2CrO_4 when it reacts with AgNO_3 to give Ag_2CrO_4 is:

- | | |
|-------------------|-------------------|
| (a) Infinite | (b) M |
| (c) $\frac{M}{2}$ | (d) $\frac{M}{3}$ |

REDOX TITRATION

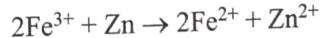
Redox titration is another volumetric technique like neutralization titration, to determine the amount of a specific substance in an unknown sample. This involves oxidation-reduction reaction between the titer and titrant during titration. Oxidation-reduction reaction between ions in the solution can become the basis for the volumetric analysis, provided it fulfills the following conditions.

- (1) There is only one reaction under the given condition
- (2) The reaction goes essentially to completion at equivalence point
- (3) A suitable indicator (or other source) is available to locate the end point

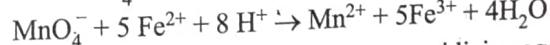
Then number of reactions fulfilling these conditions is very large. Fortunately, however the general principles involved are common to all and a limited study of only a few reactions is sufficient to give a good understanding of the whole redox analysis. Common methods of redox analysis fall in one of the following three categories :

(i) A solution of substance that is readily oxidized is treated by a standard solution of a strong oxidizing agent. Strong oxidizing agent has good affinity for electron, to ensure the completion of reaction at equivalence point. The most widely used strong oxidizing agents for volumetric analysis are MnO_4^- ion in acidic solution, $\text{Cr}_2\text{O}_7^{2-}$ ion in acidic solution, Ce^{4+} ion in acidic solution and MnO_4^- in basic solution.

In analysis of reducing agents by titration with a strong oxidizing agent, it is necessary to pre-treat the sample before the titration, to ensure that all the sought substance is reduced to its lower oxidation state and to ensure that no reducing agent other than the sought material is present in the solution. For example : The iron sample is dissolved and the solution is treated with a strong reducing agent to convert ferric ion into ferrous ions, if present any. The commonly used reducing agent for this purpose is metallic zinc, for which the reaction is

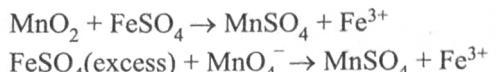


After reduction is complete, the metallic zinc is removed from the solution, which is then titrated by a standard solution of KMnO_4 as



(ii) If the test sample consists of a strong oxidizing agent, it may be analyzed by titration of its solution with a solution of strong reducing agent. The reducing agents commonly used for this purpose are oxalate ion, ferrous ion, are serious acid etc.

Sample of oxidizing agents that are not fairly soluble in water may be analyzed by treating a known weight of the sample with a measured volume of a standard reducing agent and after the reaction is complete, back titrating the excess of reducing agent in the solution with a standard solution of oxidizing agent. A common analysis of this type is determination of MnO_2 in a sample pyrolusite. A weighed portion of pyrolusite is treated with a measured volume of FeSO_4 and excess of FeSO_4 is then back titrated with a standard permanganate solution as



- (iii) Indirect method : Indirect titration is frequently used for the analysis of oxidizing agents. The sample is treated with a solution of KI, and the liberated iodine is titrated by a solution of sodium thiosulphate "Na₂S₂O₃" (hypo solution), which reacts with iodine as



(Applications of Redox Processes)

Titrations based on redox processes are called redox titrations. In these titrations titrate/titrant are oxidising/reducing agents. The calculations made in redox titrations are again based on law of chemical equivalence.

Titrate + Titrant → Products

Meq. of titrate = meq. of titrant (at equivalent point),

$$\text{or } N_1 V_1 = N_2 V_2$$

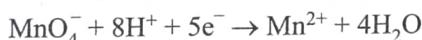
Common oxidising agents which are used in redox titration are given below:

1. Acidified KMnO₄
2. Acidified K₂Cr₂O₇
3. Acidified KIO₃ and KBrO₃
4. Acidified Ce⁴⁺ salts
5. Iodine/Iodide (iodometry and iodometry) etc.

Titration Using Acidified KMnO₄

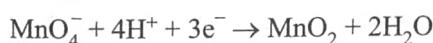
Use of KMnO₄ as oxidising agent in redox titrations was first made by F. Marguerette for the titration of Fe²⁺ ions. It is a powerful oxidant and probably the most widely used of all volumetric oxidising agents. It is readily available and colour of its solution is too intense that an indicator is not ordinarily required and MnO₄⁻ ions act as self indicator. Titrations of MnO₄⁻ are usually carried out in acid medium. The possible reactions are :

In acidic medium:



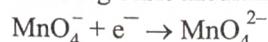
$$E = \frac{M}{5} = \frac{158}{5} = 31.6$$

In weakly basic medium (Faintly alkaline medium) or neutral medium:



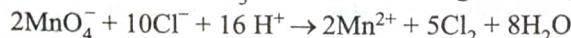
$$E = \frac{M}{3} = \frac{158}{3} = 52.6$$

In strong basic medium:



$$E = \frac{M}{1} = 158$$

Among the common mineral acids H₂SO₄, HCl and HNO₃ only H₂SO₄ is useful for providing acidic medium. HCl cannot be used since Cl⁻ are oxidised to Cl₂ by KMnO₄. On the other-hand HNO₃ itself acts as strong oxidising agent.

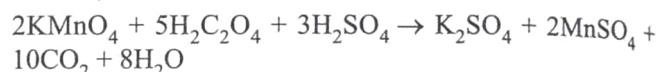


Yet KMnO₄ fulfills almost all the requirements of a good volumetric oxidising agent but it has some limitation also.

The multiplicity of possible reactions at a time, cause uncertainty regarding the stoichiometry of a permanganate oxidation. Also permanganate solution have limited stability and need occasional stabilisation.

Some important titrations using KMnO₄ are given below:

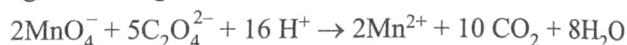
- (a) KMnO₄ vs. oxalic acid :



Titrant Titrate

oxidising reducing

agent agent



Reaction is slow initially and needs elevated temperature but after some time Mn²⁺ (Product) catalyse the reaction. (Autocatalysis)

Medium: acidic (by H₂SO₄).

End point: Light pink colour of MnO₄⁻ solution, KMnO₄ acts as self indicator.

At equivalence point :

(i) 2m-mol KMnO₄ reacts with 5m-mol oxalic acid.

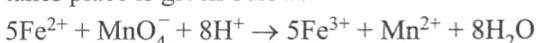
(ii) meq. of KMnO₄ = meq. of oxalic acid

$$N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = N_{\text{oxalic acid}} \times V_{\text{oxalic acid}}$$

$$(iii) \frac{1}{2} \times M_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = \frac{1}{5} \times M_{\text{oxalic acid}} \times V_{\text{Oxalic acid}}$$

- (b) KMnO₄ vs. Fe²⁺ ions :

Fe²⁺ is readily oxidised by MnO₄⁻ to Fe³⁺. The reaction which takes place is given below:



Reducing agent and oxidising agent

In the laboratory, for practical purposes ferrous ammonium sulphate is taken as a source of Fe²⁺ ions. In the determination of Fe content in iron ores, the whole iron content present in a definite amount of its solution is first converted into Fe²⁺ by using suitable reducing agent like SnCl₂.

End point: MnO₄⁻ acts as self indicator and light pink colour of solution indicates end point.

At equivalent point :

(i) 1mol MnO₄⁻ reacts with 5 mol Fe²⁺.

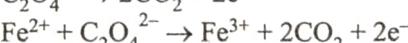
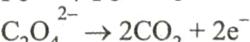
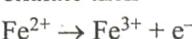
(ii) Meq. of MnO₄⁻ = Meq. of Fe²⁺

$$\text{or } N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = N_{\text{Fe}^{2+}} \times V_{\text{Fe}^{2+}}$$

$$\text{or } 5 \times M_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = 1 \times M_{\text{Fe}^{2+}} \times V_{\text{Fe}^{2+}}$$

$$(\because N_{\text{KMnO}_4} = 5 \times M_{\text{KMnO}_4}, N_{\text{Fe}^{2+}} = M_{\text{Fe}^{2+}})$$

Note: If titration is being carried out with solution of ferrous oxalate then



$$\text{so } E_{\text{Fe-oxalate}} = \frac{M}{3}$$

(E = Equivalent mass)



(c) Estimation of Fe^{2+} and Fe^{3+} ions in a solution:

In this estimation, the solution is titrated twice. First without reduction in which only Fe^{2+} reacts and Fe^{3+} remains unreacted. In second step same volume of solution is taken. Fe^{3+} ions are reduced to Fe^{2+} and then titrated. Here

- In I step : Meq. of KMnO_4 (let x) = Meq. of Fe^{2+}
- In II step : Meq. KMnO_4 (y) = Meq. of Fe^{2+} + Meq. of Fe^{3+} and Meq. of Fe^{3+} ($y-x$)

(d) Analysis of sample containing oxalic acid and sodium oxalate :

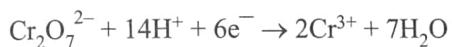
Same volume of solution are titrated separately with NaOH and KMnO_4 solution

Meq. of NaOH = Meq. of oxalic acid

and Meq. of KMnO_4 = Meq. of oxalic acid + Meq. of sodium oxalate

Titration Using Acidified $\text{K}_2\text{Cr}_2\text{O}_7$

In volumetric analysis $\text{Cr}_2\text{O}_7^{2-}$ is also used commonly as oxidant yet weaker than MnO_4^- , Ce^{4+} etc. In most of its applications, it is reduced to Cr^{3+} .

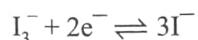


$$E_{\text{Cr}_2\text{O}_7^{2-}} = \frac{M_{\text{Cr}_2\text{O}_7^{2-}}}{6} = \frac{296}{6} = 49$$

These titrations are made in 1–2 N acid solution. In neutral or alkaline medium, it is not used. In alkaline medium orange $\text{Cr}_2\text{O}_7^{2-}$ changes to yellow CrO_4^{2-} .

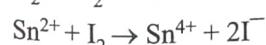
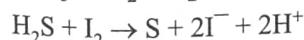
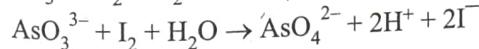
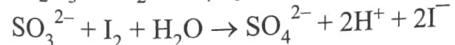
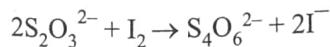
Iodometry and Iodimetry

Iodine acts as mild oxidising agent and is used for titrating several analysis. The titrations are based, upon following half reaction

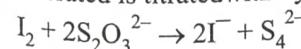


These titrations fall into two categories :

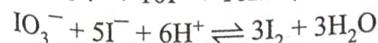
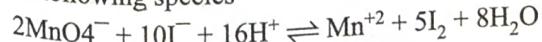
- (a) **Iodimetry:** In these titrations, standard I_2 solution is used to titrate easily oxidisable substances. It includes the estimations of thiosulphates, sulphite arsenite etc.



- (b) **Iodometry:** In iodometric titrations as oxidising agent is allowed to react with excess of KI (or I^-) solution. The I_2 liberated is titrated with hypo solution.



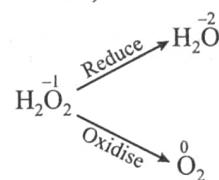
I_2 finds use for selective determination of strong reducing agents. Availability of a sensitive and reversible indicator for iodine makes these titrations useful. It includes the estimations of following species



VOLUME STRENGTH OF H_2O_2 , HARDNESS OF WATER

Hydrogen peroxide (H_2O_2)

H_2O_2 can behave both like oxidising and reducing agent in both the mediums (acidic and basic).



Oxidising agent : $(\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O})$

- (a) Acidic medium : $2\text{e}^- + 2\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O}$

v.f. = 2

- (b) Basic medium : $2\text{e}^- + \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^-$

v.f = 2

Reducing agent : $(\text{H}_2\text{O}_2 \rightarrow \text{O}_2)$

- (a) Acidic medium : $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$

v.f = 2

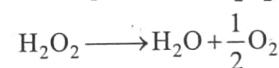
- (b) Basic medium : $2\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^-$

v.f = 2

Volume strength of H_2O_2 : Strength of H_2O_2 is represented as 10V, 20 V, 30 V etc.

20V H_2O_2 means one litre of this sample of H_2O_2 on decomposition gives 20L of O_2 gas at STP.

Decomposition of H_2O_2 is given as :



1 mole $\frac{1}{2} \times 22.4 \text{ L O}_2$ at STP

= 34 g = 11.2 L O_2 at STP

$$\text{Molarity of H}_2\text{O}_2 (\text{M}) = \frac{\text{Volume strength of H}_2\text{O}_2}{11.2}$$

Strength (in g/L) : Denoted by S

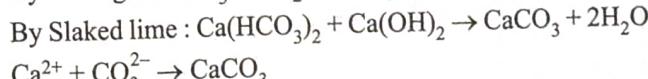
Strength = Molarity \times Mol. wt = Molarity \times 34

Hardness of water (Hard water does not give lather with soap)

Temporary hardness - due to bicarbonates of Ca & Mg

Permanent hardness - due to chlorides & sulphates of Ca & Mg. There are some methods by which we can soften the water sample.

- (a) By boiling : $2\text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{CO}_3^{2-}$ or



- (b) By Washing Soda : $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$

- (c) By ion exchange resins : $\text{Na}_2\text{R} + \text{Ca}^{2+} \rightarrow \text{CaR} + 2\text{Na}^+$

- (d) By adding chelating agents like $(\text{PO}_3)_3^-$ etc.

Measurement of Hardness

Hardness is measured in terms of ppm (parts per million) of CaCO_3 or equivalent to it.

$$\text{Hardness in ppm} = \frac{\text{Mass of } \text{CaCO}_3}{\text{Total mass of solution}} \times 10^6$$



Train Your Brain

Example 10: KMnO_4 solution is to be standardised by titration against $\text{As}_2\text{O}_3(s)$. A 0.1097 g sample of As_2O_3 requires 26.10 ml of the KMnO_4 solution for its titration. What are the molarity and normality of the KMnO_4 solution?

Sol. $\text{Mn}^{7+} + 5\text{e}^- \rightarrow \text{Mn}^{2+}$ (Reduction)
 $\text{As}_2^{3+} \rightarrow 2\text{As}^{5+} + 4\text{e}^-$ (oxidation)
 $\therefore \text{Meq. of As}_2\text{O}_3 = \text{meq of KMnO}_4$

$$\frac{0.1097}{198} \times 1000 = 26.10 \times N$$

$$\frac{1}{4} \quad (\text{E}_{\text{As}_2\text{O}_3} = M/4)$$

$$\therefore N_{\text{KMnO}_4} = 0.085$$

$$\therefore M_{\text{KMnO}_4} = \frac{0.085}{5} = 0.017$$

Example 11: 100 ml solution of FeC_2O_4 and FeSO_4 is completely oxidized by 60 ml of 0.02 M KMnO_4 in acid medium. The resulting solution is then reduced by Zn and dil. HCl. The reduced solution is again oxidized completely by 40 ml 0.02 M KMnO_4 . Calculate normality of FeC_2O_4 and FeSO_4 in mixture.

Sol. Consider the redox reaction

| | |
|----------------------------|--|
| FeC_2O_4 : | $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ (oxidation) |
| (N ₁) | $\text{C}_2^{3+} \rightarrow 2\text{C}^{4+} + 2\text{e}^-$ (Reduction) |

$$\text{FeC}_2\text{O}_4 \rightarrow \text{Fe}^{3+} + 2\text{CO}_2 + 3\text{e}^- \quad (\text{V.f.} = 3)$$

$$100(N_1 + N_2) = 60 \times 0.02 \times 5$$

$$(N_1 + N_2) = 3 \times 0.02 \quad \dots(1)$$

| | |
|-------------------|---|
| FeSO_4 : | $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ (V.f. = 1) |
| (N ₂) | |

$$\text{KMnO}_4 : \text{Mn}^{7+} + 5\text{e}^- \rightarrow \text{Mn}^{2+}$$

The resulting solution now contains only Fe^{3+} ions because CO_2 escapes out. The solution is reduced to Fe^{2+} by Zn and dil. HCl. KMnO_4 oxidises these Fe^{2+} again, therefore meq. of Fe^{2+} from FeC_2O_4 + meq. of Fe^{2+} from FeSO_4 = meq. of KMnO_4

$$100 \left(\frac{N_1}{3} + N_2 \right) = 40 \times 0.02 \times 5$$

$$\left(\frac{N_1}{3} + N_2 \right) = 2 \times 0.02 \quad \dots(2)$$

$$\frac{2N_1}{3} = 0.02$$

$$N_1 = 0.03, N_2 = 0.03$$

Example 12: 0.84 g iron are containing X percent of iron was taken in a solution containing all the iron in ferrous state. The solution required X ml of a potassium dichromate solution for oxidation of iron content to ferric state. Calculate the strength of potassium solution.

Sol. $\text{Fe} \xrightarrow{\text{Valence factor} = 2} \text{Fe}^{2+} + 2\text{e}^- \xrightarrow[\text{by Cr}_2\text{O}_7^{2-}]{\text{Valence factor} = 1} \text{Fe}^{3+} + \text{e}^-$
(oxidation)

$$6\text{e}^- + \text{Cr}_2^{6+} \rightarrow 2\text{Cr}^{3+} \quad (\text{Reduction})$$

$$W_{\text{Fe}} = \frac{0.84X}{100} \quad (\text{Given})$$

$$\text{Meq. of Fe}^{2+} \text{ in solution (V.f.} = 1) = \text{meq. of K}_2\text{Cr}_2\text{O}_7$$

$$= X.N_{\text{K}_2\text{Cr}_2\text{O}_7} \quad (\text{V. f Fe}^{2+} = 1)$$

$$\therefore \text{meq. of Fe}^{2+} \text{ in solution (valence factor} = 2) = 2.X.N$$

or Meq. of Fe = 2.X.N

$$= \frac{0.84X}{100 \times 56/2} \times 1000 = 2.X.N \Rightarrow N = 0.15$$

$$S_{\text{K}_2\text{Cr}_2\text{O}_7} = N \times E = 0.15 \times 49$$

$$(E = \frac{249}{6} = 49) \quad (E = \text{equivalent})$$

Example 13: What was of $\text{K}_2\text{Cr}_2\text{O}_7$ is required to produce 5.0 litre CO_2 at 75°C and 1.07 atm pressure from excess of oxalic acid. Also report the volume of 0.1 N NaOH required to neutral the CO_2 evolved.

Sol. $\text{Cr}_2^{6+} + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}$
 $\text{C}_2^{3+} \rightarrow 2\text{C}^{4+} + 2\text{e}^-$
meq. of $\text{K}_2\text{Cr}_2\text{O}_7$ = meq. of CO_2 formed
= mole of $\text{CO}_2 \times 1000 \times 1$ (V.f for $\text{CO}_2 = 1$)
 $= \frac{PV}{RT} \times 1 \times 1000 = \frac{1.07 \times 5 \times 1000}{0.0821 \times 348} = 187.3$
 $\therefore \frac{W_{\text{K}_2\text{Cr}_2\text{O}_7}}{M/6} \times 1000 = 187.3$
or $w_{\text{K}_2\text{Cr}_2\text{O}_7} = \frac{187.3 \times M}{6 \times 1000} = \frac{187.3 \times 294}{6 \times 1000}$
 $w = 9.18 \text{ g} \quad (M_{\text{K}_2\text{Cr}_2\text{O}_7} = 294)$
 $\text{CO}_2 + \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \quad (\text{V.f. for CO}_2 = 2)$
Also meq. of NaOH = meq. of CO_2 of valence factor 2
 $0.1 \times V = 187.3 \times 2 = 3.746 \text{ L}$

Example 14: 2.480 g of KClO_3 are dissolved in conc. HCl and the solution was boiled. Chlorine gas evolved in the reactions was then passed through a solution of KI and liberated iodine was titrated with 100 ml of hypo. 12.3 ml of same hypo solution required 24.6 ml of 0.5 N iodine for complete neutralization. Calculate % purity of KClO_3 sample.



Also meq. of I_2 = meq. of hypo = 100×1

$$[\because N_{\text{Hypo}} \times 12.3 = 24.6 \times 0.5, \therefore N_{\text{Hypo}} = 1]$$

$$\text{Also m M of Cl}_2 = \text{mM of I}_2 = \frac{100}{5} = 50$$

$$\text{Also mM of KClO}_3 = \frac{2 \times \text{mM of Cl}_2}{6} = \frac{2 \times 50}{6} = \frac{50}{3}$$

$$\therefore \frac{w_{\text{KClO}_3}}{122.5} \times 1000 = \frac{50}{3} \Rightarrow w_{\text{KClO}_3} = 2.042$$

[milli-mole (mM) = (mass \times 1000) (mol. mass)]

$$\therefore \% \text{ KClO}_3 = \frac{2.042}{2.48} \times 100 = 82.34\%$$

Example 15: 0.00012% MgSO_4 and 0.000111% CaCl_2 is present in water. What is the measured hardness of water and millimoles of washing soda required to purify water 1000 L water?

Sol. Basis of calculation = 100 g hard water

$$\text{MgSO}_4 = 0.00012 \text{ g} = \frac{0.00012}{120} \text{ mole}$$

$$\text{CaCl}_2 = 0.000111 \text{ g} = \frac{0.000111}{111} \text{ mole}$$

\therefore equivalent moles of CaCO_3

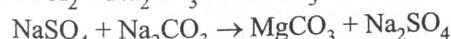
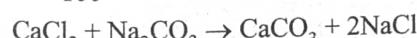
$$= \left(\frac{0.00012}{120} + \frac{0.000111}{111} \right) \text{mole}$$

\therefore mass of CaCO_3

$$= \left(\frac{0.00012}{120} + \frac{0.000111}{111} \right) \times 100 = 2 \times 10^{-4} \text{ g}$$

Hardness (in terms of ppm of CaCO_3)

$$= \frac{2 \times 10^{-4}}{100} \times 10^6 = 2 \text{ ppm}$$



\therefore Required Na_2CO_3 for 100g of water

$$= \left(\frac{0.00012}{120} + \frac{0.000111}{111} \right) \text{mole}$$

$$= 2 \times 10^{-6} \text{ mole}$$

\therefore Required Na_2CO_3 for 1000 litre water

$$= \frac{2 \times 10^{-6}}{100} \times 10^6 = \frac{2}{100} \text{ mol} (\because d_{\text{H}_2\text{O}} = 1 \text{ g/ml})$$

$$= \frac{20}{1000} \text{ mole} = 20 \text{ mmole}$$

Back Titration

In neutralization methods of analysis, if end point is exceeded by adding extra acid or base than required for neutralization, additional acid or bases left un-neutralized are determined back by titrating the residual solution against a standard acid or alkali.

Consider titration of a 25ml solution of CH_3COOH against a standard 0.1M alkali solution. If 20ml alkali is exactly required to reach the equivalence point, this gives an idea that $20 \times 0.1 = 2$ meq of acid was present in the 25ml of its solution.

If, by mistake, end point is exceeded in the titration by adding 25ml of alkali, the original solution will become alkaline due to additional 0.5meq of base present unneutralized in the solution as shown below:



Initial meq. 2.0 2.5 0.0 0.0

Final meq. 0.0 0.5 2.0

The excess base is determined by titrating them back with a known solution of standard acid viz. HCl or H_2SO_4 .



Train Your Brain

Example 16: 9.0 g of an ammonia solution is treated with 50ml 0.5 N H_2SO_4 solution, 20ml of 0.1 N NaOH is required for back titration. What is the percentage of ammonia in the solution?

Sol. meq. of acid taken initially = $50 \times 0.5 = 25$

meq. of NaOH used up in back titration = $20 \times 0.1 = 2$

meq. of H_2SO_4 reacted with $\text{NH}_3 = 25.00 - 2.00 = 23$

= meq of NH_3

\Rightarrow Mass of ammonia = $23 \times 10^{-3} \times 17 = 0.391 \text{ g}$

\Rightarrow Mass percentage of ammonia = $\frac{0.391}{9} \times 100 = 4.34$

Short Notes

$$1. \text{ Number of moles of molecules} = \frac{\text{wt. in g}}{\text{Mol. wt.}}$$

$$\text{Number of moles of atoms} = \frac{\text{wt. in g}}{\text{Atomic mass}}$$

$$\text{Number of moles of gases} = \frac{\text{Volume at STP}}{\text{Standard molar volume}}$$

$$\text{Number of moles of particles, e.g. atoms, molecular ions etc.} = \frac{\text{Number of particles}}{\text{Avogadro's No.}}$$

$$\text{Moles of solute in solution} = M \times V(L)$$

$$2. \text{ Equivalent wt. of element} = \frac{\text{Atomic wt.}}{\text{Valency}}$$

$$\text{Equivalent wt. of compound} = \frac{\text{Mol. wt.}}{\text{Total charge on cation or anion}}$$

$$\text{Equivalent wt. of acid} = \frac{\text{Mol wt.}}{\text{Basicity}}$$

$$\text{Equivalent wt. of base} = \frac{\text{Mol wt.}}{\text{Acidity}}$$

$$\text{Equivalent wt. of an ion} = \frac{\text{Formula wt.}}{\text{Charge on ion}}$$

$$\text{Equivalent wt. of acid salt} = \frac{\text{Molecular wt.}}{\text{Replaceable H atom in acid salt}}$$

$$\text{Equivalent wt. of oxidizing or reducing agent} = \frac{\text{Mol. wt.}}{\text{Change in oxidation number per mole}}$$

$$\text{No. of equivalent} = N \times V(L) = \frac{\text{wt. in g}}{\text{eq. wt.}}$$

$$3. \text{ Molarity (M)} = \frac{W_s \times 1000}{M_s \times V} = \frac{x \times d \times 10}{M_s}$$

where

W_s = wt. of solute in g

M_s = Mol. wt. of solute

x = % by mass of solute

d = density of solution in g/ml

V = volume of solution in ml

$$4. \text{ Normality (N)} = \frac{W_s \times 1000}{E_s \times V} = \frac{x \times d \times 10000}{E_s}$$

W_s = wt. of solute in g.

E_s = eqv. wt. of solute

V = volume of solution in ml

x = % by mass of solute

d = density of solution in g/ml

$$5. \text{ Moles} = M \times V(L) = \frac{\text{wt. of solute}}{\text{Mol. wt.}}$$

$$\text{Millimoles} = M \times V(\text{ml}) = \frac{\text{wt. of solute}}{\text{Mol. wt.}} \times 1000$$

$$\text{Equivalents of solute} = N \times V(L)$$

$$\text{Meq. of solute} = \frac{\text{wt.}}{\text{Eq. wt.}} \times 1000$$

6. Molarity equation:

If a solution having molarity M_1 and volume V_1 is diluted to volume V_2 so that new molarity is M_2 then total number of moles remains the same.

$$M_1 V_1 = M_2 V_2$$

For a balanced equation involving n_1 moles of reactant 1 and n_2 moles of reactant 2.

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

Normality equation : According to the law of equivalence, the substances combine together in the ratio of their equivalent masses

$$\frac{\text{wt. of A}}{\text{wt. of B}} = \frac{\text{eq. wt. of A}}{\text{eq. wt. of B}}$$

$$\Rightarrow \frac{\text{wt. of A}}{\text{eq. wt. of A}} = \frac{\text{wt. of B}}{\text{eq. wt. of B}}$$

Number of gram equivalents of A = Number of gram equivalents of B

$$\text{Number of gram equivalents of A} = \frac{N_A \times V_A}{1000}$$

$$\text{Number of gram equivalents of B} = \frac{N_B \times V_B}{1000}$$

$$\Rightarrow \frac{N_A V_A}{1000} = \frac{N_B V_B}{1000}$$

$$N_A \times V_B = N_B \times V_B$$

The above equation is called normality equation.

7. Normality (N) = Molarity (M) \times n

(where n = n-factor)

For acid-base (neutralization reaction or redox reaction)

$$N_1 V_1 = N_2 V_2 \text{ always true}$$

$$\text{But } M_1 V_1 = M_2 V_2 \text{ (may or may not be true)}$$

$$\text{But } M_1 n_1 V_1 = M_2 n_2 V_2 \text{ (always true where n-terms represent n-factor)}$$

$$8. \text{ Molality (m)} = \frac{\text{Moles of solute}}{\text{wt.of solvent (in kg)}}$$

$$9. \text{ Strength of solution (S)} = N \times \text{Eq.wt.} \\ = M \times \text{mol. wt.}$$

10. In a typical redox reaction :



meq. of an oxidising agent = meq. of a reducing agent

$$11. \text{ From definition of gram-equivalents } \left(g \text{ meq.} = \frac{g}{E} = N \times V_L \right),$$

it is very clear that, we must be very confident about the concept of equivalent weight (E), for an oxidising or reducing agent.

★ The equivalent weight of an oxidising or reducing agent is defined as:

$$\text{Equivalent weight} = E = \frac{M_0}{x}$$

where M_0 = molecular mass; x = number of electrons transferred (loss or gain) by one mole of oxidising or reducing agent as given by their balanced ionic half reaction.

12. **Variable equivalent weight :** Equivalent weight may be variable in many cases. It may depend upon the medium (acidic/basic); dilute/concentrated solution; whether a reagent is acting as an oxidant or reductant; whether a reagent is acting as an oxidant or an acid; whether a reagent is acting reductant or an acid.

13. A reaction in which same atom is oxidised and reduced at the same time is called as a disproportionation reaction. And the equivalent weight of a compound undergoing disproportionation is:

$$E = \frac{\text{Effective molecular weight of compound}}{\text{Number of e}^- \text{ transfer}}$$

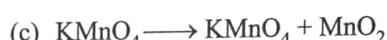
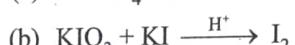
where Effective molecular weight = Total weight in Oxidation half reaction + Total weight in Reduction half reaction.

14. Volume strength is the volume of O_2 given out at S.T.P. by 1 volume solution of H_2O_2 .

$$1 \text{ M } H_2O_2 \equiv 11.2 \text{ vol of } O_2 \text{ at STP}$$

$$\text{or } 1\text{N } H_2O_2 \equiv 5.6 \text{ vol of } O_2$$

15. Avoid use of concept of meq in following cases. (Non-typical Redox reactions).



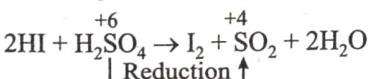
If a reagent (oxidant or reductant) shows different equivalent weights in two different redox reactions in a given problem then apply concept of meq carefully. In fact it is advised to use the mole concept in such cases.

Solved Examples

1. Which of the following reaction represents the oxidising behaviour of H_2SO_4 :

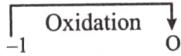
- (a) $2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + SO_2Cl_2$
- (b) $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$
- (c) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$
- (d) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

Sol. (d) Oxidising nature \Rightarrow O.S. decreases



2. In which of the following reaction H_2O_2 acts as reducing agent:

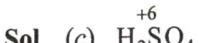
- (a) $2FeCl_2 + 2HCl + H_2O_2 \rightarrow 2FeCl_3 + 2H_2O$
- (b) $Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$
- (c) $2HI + H_2O_2 \rightarrow 2H_2O + I_2$
- (d) $H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$



Oxidation $\Rightarrow H_2O_2 \Rightarrow$ Reducing agent

3. A sulphur containing species that can not be a reducing agent is:

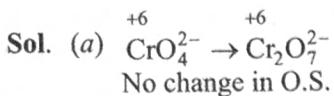
- | | |
|---------------|-------------------|
| (a) SO_2 | (b) SO_3^{-2} |
| (c) H_2SO_4 | (d) $S_2O_3^{2-}$ |



H_2SO_4 because sulphur has its maximum O.S. i.e. +6

4. Which of the following reaction involves neither oxidation nor reduction:

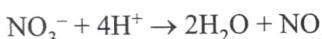
- | | |
|---|--|
| (a) $CrO_4^{2-} \rightarrow Cr_2O_7^{2-}$ | (b) $Cr \rightarrow CrCl_3$ |
| (c) $Na \rightarrow Na^+$ | (d) $2S_2O_3^{2-} \rightarrow S_4O_6^{2-}$ |



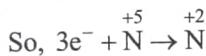
5. Balance the following equations:

- $\text{H}_2\text{O}_2 + \text{MnO}_4^- \longrightarrow \text{Mn}^{2+} + \text{O}_2$ (acidic medium)
 - $\text{Zn} + \text{HNO}_3 \text{ (dil)} \longrightarrow \text{Zn}(\text{NO}_3)_2 + \text{H}_2\text{O} + \text{NH}_4^+$
 - $\text{CrI}_3 + \text{KOH} + \text{Cl}_2 \longrightarrow \text{K}_2\text{CrO}_4 + \text{KIO}_4 + \text{KCl} + \text{H}_2\text{O}$
 - $\text{P}_2\text{H}_4 \longrightarrow \text{PH}_3 + \text{P}_4$
 - $\text{Ca}_3(\text{PO}_4)_2 + \text{SiO}_2 + \text{C} \longrightarrow \text{CaSiO}_3 + \text{P}_4 + \text{CO}$
- Sol.** (a) $6\text{H}^+ + 5\text{H}_2\text{O}_2 + 2\text{MnO}_4^- \longrightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$
- (b) $4\text{Zn} + 10\text{HNO}_3 \text{ (dil)} \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + 3\text{H}_2\text{O} + \text{NH}_4^+$
- (c) $2\text{CrI}_3 + 64\text{KOH} + 27\text{Cl}_2 \longrightarrow 2\text{K}_2\text{CrO}_4 + 6\text{KIO}_4 + 54\text{KCl} + 32\text{H}_2\text{O}$
- (d) $6\text{P}_2\text{H}_4 \longrightarrow 8\text{PH}_3 + \text{P}_4$
- (e) $2\text{Ca}_3(\text{PO}_4)_2 + 6\text{SiO}_2 + 10\text{C} \rightarrow 6\text{CaSiO}_3 + \text{P}_4 + 10\text{CO}$

6. The number of electrons required to balance the following equation are:



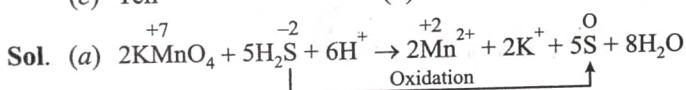
- (a) 2 on right side (b) 3 on left side
(c) 3 on right side (d) 5 on left side



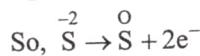
Add 3 electrons on left side.

7. $2\text{KMnO}_4 + 5\text{H}_2\text{S} + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 2\text{K}^+ + 5\text{S} + 8\text{H}_2\text{O}$. In the above reaction, how many moles of electrons would be involved in the oxidation of 1 mole of reductant?

- (a) Two (b) Five
(c) Ten (d) One



$\text{H}_2\text{S} \Rightarrow \text{R.A.} \Rightarrow \text{Reducant}$



2 moles of electrons are involved in oxidation of 1 mole of reductant.

8. In Redox reaction:

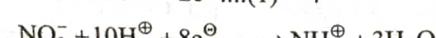
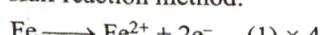


the coefficient of HNO_3 , $\text{Fe}(\text{NO}_3)_2$, NH_4^+ is:

- (a) 1 : 10 : 4 (b) 10 : 4 : 1
(c) 4 : 10 : 1 (d) 10 : 1 : 4



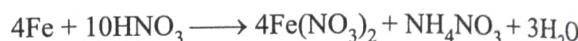
Half reaction method:



Equation (1) $\times 4 +$ (2)



Addⁿ of spectator ion



9. Calculate the normality of a solution containing 13.4 g of Sodium oxalate in 100 mL solution.

$$\text{Sol. Normality} = \frac{\text{wt. in g / eq.wt}}{\text{vol. of solution in litre}}$$

Here, eq. wt. of $\text{Na}_2\text{C}_2\text{O}_4 = 134/2 = 67$

$$\text{so } N = \frac{13.4/67}{100/1000} = 2N$$

10. What volume of 6 M HNO_3 is needed to oxidize 8 g of Fe^{2+} to Fe^{3+} , HNO_3 gets converted to NO ?

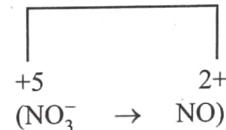
- (a) 8 mL (b) 7.936 mL
(c) 32 mL (d) 64 mL

Sol. Meq. of HNO_3 = Meq. of Fe^{2+}

$$\text{or } 6 \times 3 \times V = \frac{8}{56} \times 1000$$

$$V = 7.936 \text{ mL}$$

n-factor = 3



11. Calculate the normality of a solution obtained by mixing 50 mL of 5 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and 50 mL of 2 M $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium.

Sol. v.f. of $\text{K}_2\text{Cr}_2\text{O}_7$ = 6

$$\text{so } N_f = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

$$= \frac{5 \times 6 \times 50 + 2 \times 6 \times 50}{50 + 50} = 21 \text{ N}$$

12. What volume of 6 M HCl and 2 M HCl should be mixed to get two litre of 3 M HCl?

Sol. Let, the volume of 6 M HCl required to obtain 2 L of 3 M HCl = x L

\therefore Volume of 2 M HCl required = $(2-x)$ L

$$M_1 V_1 + M_2 V_2 = M_3 V_3$$

$$6\text{M HCl} \quad 2\text{M HCl} \quad 3\text{M HCl}$$

$$6 \times (x) + 2 \times (2-x) = 3 \times 2$$

$$\Rightarrow 6x + 4 - 2x = 6 \Rightarrow 4x = 2$$

$$\therefore x = 0.5 \text{ L}$$

Hence, volume of 6 M HCl required = 0.5 L

Volume of 2M HCl required = 1.5 L

13. What weight of Na_2CO_3 of 85% purity would be required to prepare 45.6 mL of 0.235 N H_2SO_4 ?

Exercise-1 (Topicwise)

OXIDATION NUMBER, REDOX, REDUCING AGENT AND OXIDISING AGENT

1. In $\text{Ni}(\text{CO})_4$, the oxidation state of Ni is:

| | |
|-------|-------|
| (a) 4 | (b) 0 |
| (c) 2 | (d) 8 |
2. The oxidation number of nitrogen in NH_2OH is:

| | |
|--------|--------|
| (a) 0 | (b) +1 |
| (c) -1 | (d) -2 |
3. The oxidation number of C in CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 are respectively:

| | |
|-----------------------|-----------------------|
| (a) +4, +2, 0, -2, -4 | (b) +2, +4, 0, -4, -2 |
| (c) -4, -2, 0, +2, +4 | (d) -2, -4, 0, +4, +2 |
4. The oxidation number of Pt in $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ is:

| | |
|--------|--------|
| (a) +1 | (b) +2 |
| (c) +3 | (d) +4 |
5. Oxidation number of C in HNC is:

| | |
|--------|----------|
| (a) +2 | (b) -3 |
| (c) +3 | (d) Zero |
6. Oxidation number of carbon in carbon suboxide (C_3O_2) is :

| | |
|--------------------|--------------------|
| (a) $\frac{+2}{3}$ | (b) $\frac{+4}{3}$ |
| (c) +4 | (d) $\frac{-4}{3}$ |
7. Oxidation number of sulphur in $\text{Na}_2\text{S}_2\text{O}_3$ would be:

| | |
|--------|--------|
| (a) +2 | (b) +4 |
| (c) -2 | (d) 0 |
8. $\frac{-1}{3}$ oxidation state of nitrogen will be obtained in case of:

| | |
|----------------------------------|---|
| (a) Ammonia (NH_3) | (b) Hydrazoic acid (N_3H) |
| (c) Nitric oxide (NO) | (d) Nitrous oxide (N_2O) |
9. Which one of the following is a redox reaction?

| |
|---|
| (a) $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ |
| (b) $2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ |
| (c) $\text{HCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{HNO}_3$ |
| (d) $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ |
10. In the reaction, $\text{Cl}_2 + \text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}_4^- + \text{H}_2\text{O}$, chlorine is:

| |
|----------------------------------|
| (a) Oxidised |
| (b) Reduced |
| (c) Oxidised as well as reduced |
| (d) Neither oxidised nor reduced |

11. Which of the following change represents a disproportionation reaction (s):

| |
|--|
| (a) $\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$ |
| (b) $\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu} + \text{Cu}^{2+} + \text{H}_2\text{O}$ |
| (c) $2\text{HCuCl}_2 \xrightarrow[\text{Water}]{\text{dilution with}} \text{Cu} + \text{Cu}^{2+} + 4\text{Cl}^- + 2\text{H}^+$ |
| (d) All of the above |
12. How many electrons should X_2H_4 liberate so that in the new compound X shows oxidation number of $-\frac{1}{2}$ (E.N. $\text{X} > \text{H}$)

| | |
|--------|-------|
| (a) 10 | (b) 4 |
| (c) 3 | (d) 2 |
13. The reaction $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S} + 2\text{H}_2\text{O}$ manifests:

| |
|--|
| (a) Oxidising action of H_2O_2 |
| (b) Reducing nature of H_2O_2 |
| (c) Acidic nature of H_2O_2 |
| (d) Alkaline nature of H_2O_2 |
14. The compound that can work both as an oxidising as well as reducing agent is:

| | |
|----------------------------------|---------------------------------------|
| (a) KMnO_4 | (b) H_2O_2 |
| (c) $\text{Fe}_2(\text{SO}_4)_3$ | (d) $\text{K}_2\text{Cr}_2\text{O}_7$ |
15. Select the example of disproportionation reaction

| |
|---|
| (a) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HCl}$ |
| (b) $\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$ |
| (c) $4\text{H}_3\text{PO}_3 \rightarrow \text{PH}_3 + 3\text{H}_3\text{PO}_4$ |
| (d) $\text{AgCl} + 2\text{NH}_3 \rightarrow \text{Ag}(\text{NH}_3)_2\text{Cl}$ |
16. Which one of the following is not a redox reaction:

| |
|--|
| (a) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ |
| (b) $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ |
| (c) $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2$ |
| (d) $\text{MnCl}_3 \rightarrow \text{MnCl}_2 + \frac{1}{2}\text{Cl}_2$ |
17. In the reaction: $\text{MnO}_4^- + \text{SO}_3^{2-} + \text{H}^+ \rightarrow \text{SO}_4^{2-} + \text{Mn}^{2+} + \text{H}_2\text{O}$

| |
|--|
| (a) MnO_4^- and H^+ both are reduced |
| (b) MnO_4^- is reduced and H^+ is oxidised |
| (c) MnO_4^- is reduced and SO_3^{2-} is oxidised |
| (d) MnO_4^- is oxidised and SO_3^{2-} is reduced |
18. Select the compound in which the oxidation number of oxygen is -1:

| | |
|---------------------------|----------------------------|
| (a) H_2O | (b) O_2F_2 |
| (c) Na_2O | (d) BaO_2 |



In the above reaction:

- (a) Only oxidation takes place
- (b) Only reduction takes place
- (c) Both the above
- (d) None of the above

20. Match List-I (compound) with List-II (Oxidation state of N) and select the correct answer using the codes given below the list:

| List-I | List-II |
|--------------------------------|-----------|
| A. KNO_3 | (p) - 1/3 |
| B. HNO_2 | (q) - 3 |
| C. NH_4Cl | (r) 0 |
| D. NaN_3 | (s) + 3 |
| | (t) + 5 |
| (a) (A-t), (B-s), (C-q), (D-p) | |
| (b) (A-t), (B-q), (C-s), (D-p) | |
| (c) (A-s), (B-t), (C-p), (D-r) | |
| (d) (A-q), (B-r), (C-s), (D-t) | |

21. In the conversion of Br_2 to BrO_3^- the oxidation state of bromine changes from:

- (a) 0 to 5
- (b) 1 to 5
- (c) 0 to -3
- (d) 2 to 5

22. The sum of oxidation states of sulphur in $H_2S_2O_8$ is:

- (a) +2
- (b) +6
- (c) +7
- (d) +12

23. When H_2 reacts with Na, it acts as:

- (a) Oxidising agent
- (b) Reducing agent
- (c) Both
- (d) None of these

24. Which one is the oxidising agent in the reaction given below.



- (a) H^+
- (b) $Cr_2O_7^{2-}$
- (c) Cr^{++}
- (d) None of these

25. The oxidation number of arsenic atom in H_3AsO_4 is:

- (a) -1
- (b) -3
- (c) +3
- (d) +5

26. In substance $Mg(HXO_3)$, the oxidation number of X is:

- (a) 0
- (b) +2
- (c) +3
- (d) +4

27. Which statement is wrong:

- (a) Oxidation number of oxygen is +1 in peroxides
- (b) Oxidation number of oxygen is +2 in oxygen difluoride
- (c) Oxidation number of oxygen is $-\frac{1}{2}$ in superoxides
- (d) Oxidation number of oxygen is -2 in most of its compound

28. In the reaction: $C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$

HNO_3 acts as:

- (a) An oxidising agent
- (b) An acid
- (c) A reducing agent
- (d) None of these

29. The oxidation number of iron in potassium ferricyanide [$K_3Fe(CN)_6$] is:

- | | |
|-----------|----------|
| (a) Two | (b) Six |
| (c) Three | (d) Four |

30. Which of the following compounds are arranged in increasing oxidation number of S:

- (a) $H_2SO_3, H_2S, H_2SO_4, H_2S_2O_3$
- (b) $H_2S_2O_3, H_2SO_3, H_2S, H_2SO_4$
- (c) $H_2S, H_2SO_3, H_2SO_4, H_2S_2O_3$
- (d) $H_2S, H_2S_2O_3, H_2SO_3, H_2SO_4$

31. Iodine shows the highest oxidation state in the compound:

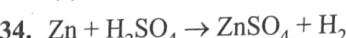
- (a) KI
- (b) KI_3
- (c) IF_5
- (d) KIO_4

32. Oxidation number of Xe in XeF_5^- is:

- (a) +1
- (b) +2
- (c) +3
- (d) +4

33. If in a chemical reaction, Fe^{+2} is converted into Fe^{+3} , then Fe^{+2} :

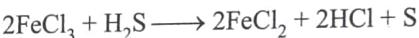
- (a) Gains one electron
- (b) Loses one electron
- (c) Gains one proton
- (d) Loses one proton



Zn undergoes:

- (a) Reduction
- (b) Oxidation
- (c) Both oxidation and reduction
- (d) None of these

35. In the following reaction



- (a) $FeCl_3$ is oxidant
- (b) $FeCl_3$ & H_2S are oxidised
- (c) $FeCl_3$ is oxidised & H_2S is reduced
- (d) None of these

36. Oxidising agents have high:

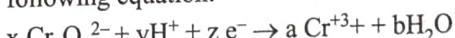
- (a) Reduction potential
- (b) Oxidation potential
- (c) Ionisation potential
- (d) None of these

BALANCING

37. Which of the following reaction is spontaneous oxidation-reduction reaction

- (a) $Mn^{+2} + 5Fe^{+3} + 4H_2O \rightarrow MnO_4^- + 5Fe^{+2} + 8H^+$
- (b) $MnO_4^- + 5Fe^{+3} + 8H^+ \rightarrow Mn^{+2} + 5Fe^{+2} + 4H_2O$
- (c) $MnO_4^- + 5Fe^{+2} + 8H^+ \rightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$
- (d) $Mn^{+2} + 5Fe^{+2} + 4H_2O \rightarrow MnO_4^- + 5Fe^{+3} + 8H^+$

38. Choose the set of coefficients that correctly balances the following equation:



| x | y | z | a | b |
|-------|----|---|---|---|
| (a) 2 | 14 | 6 | 2 | 7 |
| (b) 1 | 14 | 6 | 2 | 7 |
| (c) 2 | 7 | 6 | 2 | 7 |
| (d) 2 | 7 | 6 | 1 | 7 |

Exercise-2 (Learning Plus)

18. For the redox reaction $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$, the correct whole number stoichiometric coefficients of MnO_4^- , $\text{C}_2\text{O}_4^{2-}$ and H^+ are respectively:
 (a) 2, 5, 16 (b) 16, 5, 2
 (c) 5, 16, 2 (d) 2, 16, 5

19. An example of redox process is:
 (a) $\text{CuSO}_4 + \text{Fe} \rightarrow \text{FeSO}_4 + \text{Cu}$
 (b) $\text{Ca(OH)}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$
 (c) $\text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O}$
 (d) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$

20. Consider the following statement in the reaction
 $\text{KIO}_3 + 5\text{KI} + 6\text{HCl} \rightarrow 3\text{I}_2 + 6\text{KCl} + 3\text{H}_2\text{O}$
 (A) KI is oxidised to I_2
 (B) KIO_3 is oxidised to I_2
 (C) KIO_3 is reduced to I_2
 (D) Oxidation number of I increases from (-1) in KI to zero in I_2
 Among these statements
 (a) A, C and D are correct.
 (b) A, B and D are correct.
 (c) B and D are correct.
 (d) A alone is correct.

21. $x\text{NO}_3^- + y\text{I}^- + z\text{H}^+ \rightarrow 2\text{NO} + 3\text{I}_2 + 4\text{H}_2\text{O}$ x, y, z respectively in the above equation are:
 (a) 2, 6, 8 (b) 1, 6, 4
 (c) 0, 6, 8 (d) 2, 3, 4

22. Balance the following equation and choose the quantity which is the sum of the coefficients of reactants and products:
 $\text{KMnO}_4 + \dots \text{H}_2\text{O}_2 + \dots \text{H}_2\text{SO}_4 \rightarrow \dots \text{MnSO}_4 + \dots \text{O}_2 + \dots \text{H}_2\text{O} + \dots \text{K}_2\text{SO}_4$
 (a) 26 (b) 23
 (c) 28 (d) 22

23. In the redox reaction:
 $x\text{MnO} + y\text{PbO}_2 + z\text{HNO}_3 \rightarrow a\text{HMnO}_4 + b\text{Pb(NO}_3)_2 + c\text{H}_2\text{O}$
 (a) x = 2, y = 5, z = 10
 (b) x = 2, y = 7, z = 8
 (c) x = 2, y = 5, z = 8
 (d) x = 2, y = 5, z = 5

24. In the redox reaction:
 $10\text{FeC}_2\text{O}_4 + x\text{KMnO}_4 + 24\text{H}_2\text{SO}_4 \rightarrow 5\text{Fe}_2(\text{SO}_4)_3 + 20\text{CO}_2 + y\text{MnSO}_4 + 3\text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$. The values of x and y are respectively:
 (a) 6, 3 (b) 3, 6
 (c) 3, 3 (d) 6, 6

25. The number of electrons lost or gained during the change:
 $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$
 (a) 2 (b) 4
 (c) 6 (d) 8

26. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{Cr}_2\text{O}_3 + \text{N}_2 + 4\text{H}_2\text{O}$
 In the above reaction the oxidation state of N and chromium changes respectively as:
 (a) -3 to 0 and +6 to +3
 (b) +3 to 0 and +3 to +6
 (c) -4 to 0 and +6 to +2
 (d) Unpredictable

27. How many electrons should A_2H_3 liberate so that in the new compound A shows $-1/2$ oxidation number- (E.N. of A > E.N. of H)
 (a) 2 (b) 3
 (c) 4 (d) 5

28. Number of moles of electrons produced per mole of FeCr_2O_4 in the following redox reaction.
 $\text{FeCr}_2\text{O}_4 + \text{KOH} + \text{O}_2 \rightarrow \text{K}_2\text{CrO}_4 + \text{Fe}_2\text{O}_3$
 (a) 6 (b) 1
 (c) 7 (d) 3

29. Carbon is in the lowest oxidation state in:
 (a) CH_4 (b) CCl_4
 (c) CF_4 (d) CO_2

30. x(g) of the metal gave y g of its oxide. Hence equivalent weight of the metal
 (a) $\frac{y-x}{x} \times 8$ (b) $\frac{x}{(y-x)} \times 8$
 (c) $\frac{x}{y} \times 8$ (d) $\frac{x+y}{x} \times 8$

31. Equivalent weight of Mn^{3+} in the following reaction is (Mn = 55)
 $\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{MnO}_2$
 (a) 27.5 (b) 55
 (c) 110 (d) 165

32. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. Equivalent weight of the metal is:
 (a) 33.25 (b) 3.325
 (c) 12 (d) 20

33. Equivalent weight of FeC_2O_4 in the change, $\text{FeC}_2\text{O}_4 \rightarrow \text{Fe}^{3+} + \text{CO}_2$ is
 (a) M/3 (b) M/6
 (c) M/2 (d) M/1

34. In the ionic equation $2\text{K}^+\text{BrO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{Br}_2 + 6\text{H}_2\text{O} + 2\text{K}^+$, the equivalent weight of KBrO_3 will be (where M = molecular weight of KBrO_3):
 (a) M/5 (b) M/2
 (c) M/6 (d) M/4

37. $(\text{NH}_4)_3\text{PO}_4$ get converted into NO_3^- and PH_3 on reacting with KMnO_4 in acidic medium. If 50 ml of 0.2 M $(\text{NH}_4)_3\text{PO}_4$ solution reacts with 16 ml of KMnO_4 solution, then normality of KMnO_4 solution is
 (a) 5 (b) 8 (c) 10 (d) 20

38. The number of moles of NaOH required to completely react with 20 ml of 0.1 M NaH_2PO_3 solution and 40 ml of 0.1 M NaHCO_3 .
 (a) 8×10^{-3} (b) 2×10^{-3} (c) 4×10^{-3} (d) 6×10^{-3}

Exercise-3 (JEE Advanced Level)

MCQS/COMPREHENSION/MATCHING

- Which of the following are examples of disproportionation reaction:
 - $\text{HgO} \rightarrow \text{Hg} + \text{O}_2$
 - $\text{KClO}_3 \rightarrow \text{KCl} + \text{O}_2$
 - $\text{KClO}_3 \rightarrow \text{KClO}_4 + \text{KCl}$
 - $\text{Cl}_2 + \text{OH}^- \rightarrow \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$
 - Substances which may be oxidized as well as reduced are
 - HCl
 - HClO
 - HClO_3
 - HClO_4
 - Which of the following is a non-redox process?
 - $\text{SO}_4^{2-} \rightarrow \text{SO}_3$
 - $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{CrO}_4^{2-}$
 - $\text{PO}_4^{3-} \rightarrow \text{P}_2\text{O}_7^{4-}$
 - $\text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2$
 - Which of the following is/are peroxide(s)?
 - PbO_2
 - H_2O_2
 - SrO_2
 - BaO_2
 - Which of the following compound does not decolorise an acidified solution of KMnO_4 ?
 - SO_2
 - FeCl_3
 - H_2O_2
 - FeSO_4
 - Consider the redox reaction $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$:
 - $\text{S}_2\text{O}_3^{2-}$ gets reduced to $\text{S}_4\text{O}_6^{2-}$
 - $\text{S}_2\text{O}_3^{2-}$ gets oxidised to $\text{S}_4\text{O}_6^{2-}$
 - I_2 gets reduced to I^-
 - I_2 gets oxidised to I^-
 - The number of moles of KMnO_4 that will be needed to react completely with one mole of ferrous oxalate in acidic solution is
 - $3/5$
 - $2/5$
 - $4/5$
 - 1

8. If mass of KHC_2O_4 (potassium acid oxalate) required to reduce 100 mL of 0.02 M KMnO_4 in acidic medium is x g and to neutralise 100 mL of 0.05 M $\text{Ca}(\text{OH})_2$ is y g, then which of the following options may be correct :

 - If x is 1 g then y is 2 g
 - If x is 5.5g then y is 11 g
 - If x is 2 g then y is 1 g
 - If x is 11 g then y is 5.5 g

9. In the titration of $\text{K}_2\text{Cr}_2\text{O}_7$ and ferrous sulphate, following data is obtained:

V_1 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ solution of molarity M_1 requires V_2 mL of FeSO_4 solution of molarity M_2 .

Which of the following relations is/are true for the above titration:

 - $6 M_1 V_1 = M_2 V_2$
 - $M_1 V_1 = 6 M_2 V_2$
 - $N_1 V_1 = N_2 V_2$
 - $M_1 V_1 = M_2 V_2$

10. Choose the correct statement(s):

 - 1 mole of MnO_4^- ion can oxidise 5 moles of Fe^{2+} ion in acidic medium.
 - 1 mole of $\text{Cr}_2\text{O}_7^{2-}$ ion can oxidise 6 moles of Fe^{2+} ion in acidic medium.
 - 1 mole of Cu_2S can be oxidised by 1.6 moles of MnO_4^- ion in acidic medium.
 - 1 mole of Cu_2S can be oxidised by 1.33 moles of $\text{Cr}_2\text{O}_7^{2-}$ ion in acidic medium.

11. A quantity of 0.5 g of a metal nitrate gave 0.43 g of metal sulphate.

 - The equivalent weight of the metal is 38.
 - The equivalent weight of the metal is 76.
 - The atomic weight of metal may be 76.
 - The atomic weight of metal may be 19.

12. There are two sample of HCl having molarity 1N and 0.25 N. Find volume of these sample taken in order to prepare 0.75 N HCl solution. (Assume no water is used):

 - 20 mL, 10 mL
 - 100 mL, 50 mL
 - 40 mL, 20 mL
 - 50 mL, 25 mL

13. Which of the following samples of reducing agents is / are chemically equivalent to 25 mL of 0.2 N KMnO_4 to be reduced to Mn^{2+} and water:
- 25 mL of 0.2 M FeSO_4 to be oxidized to Fe^{3+}
 - 50 mL of 0.1 M H_3AsO_3 to be oxidized to H_3AsO_4
 - 25 mL of 0.1 M H_2O_2 to be oxidized to H^+ and O_2
 - 25 mL of 0.1 M SnCl_2 to be oxidized to Sn^{4+}
14. 250 ml of 1M I_2 molar is separately reacted with 0.5 M Cu_2S solution, 0.5 M CuS solution and 0.5 M $\text{S}_2\text{O}_3^{2-}$ solution, causing production of Cu^{+2} and SO_4^{2-} in the first two and $\text{S}_4\text{O}_6^{2-}$ in the last case along with iodide ions. Which of the following options is /are correct assuming 100% completion of the reaction?
- 100 ml of Cu_2S solution will be consumed.
 - 125 ml of CuS solution will be consumed.
 - 500 ml of $\text{S}_2\text{O}_3^{2-}$ solution will be consumed.
 - Equivlent weight of I_2 in each of the reactions will be 127.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 15 to 17): Equivalent Mass The equivalent mass of a substance is defined as the number of parts by mass of it which combine with or displace 1.0078 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine.

The equivalent mass of a substance expressed in grams is called gram equivalent mass.

The equivalent mass of a substance is not constant. It depends upon the reaction in which the substance is participating. A compound may have different equivalent mass in different chemical reactions and under different experimental conditions.

(a) **Equivalent mass of an acid:** It is the mass of an acid in grams which contains 1.0078 g of replaceable H^+ ions or it is the mass of acid which contains one mole of replaceable H^+ ions. It may be calculated as:

$$\text{Equivalent mass of acid} = \frac{\text{Molecular mass of acid}}{\text{Basicity of acid}}$$

Basicity of acid = number of replaceable hydrogen atoms present in one molecule of acid

(b) **Equivalent mass of a base:** It is the mass of the base which contains one mole of replaceable OH^- ions in molecule.

$$\text{Equivalent mass of base} = \frac{\text{Molecular mass of base}}{\text{Acidity of base}}$$

Acidity of base = Number of replaceable OH^- ions present in one molecule of the base

(c) **Equivalent mass of an oxidising agent:**

$$(a) \text{Electron concept: Equivalent mass of oxidising agent} = \frac{\text{Molecular mass of oxidising agent}}{\text{Number of electrons gained by one molecule}}$$

(b) **Oxidation number concept:** Equivalent mass of oxidising agent

$$= \frac{\text{Molecular mass of oxidising agent}}{\text{Total change in oxidation number per molecule of oxidising agent}}$$

15. Equivalent mass of $\text{Ba}(\text{MnO}_4)_2$ in acidic medium is: (where M stands for molar mass)

- $M/5$
- $M/6$
- $M/10$
- $M/2$

16. Equivalent mass of $\text{Fe}_{0.9}\text{O}$ in reaction with acidic $\text{K}_2\text{Cr}_2\text{O}_7$, is: (M = Molar mass)

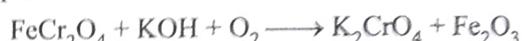
- $7 M/10$
- $10 M/7$
- $7 M/9$
- $9 M/7$

17. Equivalent weight of oxalic acid salt in following reaction is: (Atomic masses: O = 16, C = 12, K = 39)



- 90
- 45
- 64
- 128

Comprehension (Q. 18 to 21): Chromium exists as FeCr_2O_4 in the nature and it contains $\text{Fe}_{0.95}\text{O}$ & other impurity. To obtain pure chromium from FeCr_2O_4 , the ore is fused with KOH and oxygen is passed through the mixture when K_2CrO_4 and Fe_2O_3 are produced.



2 g of ore required 270 mL of O_2 at 273 K and 1 atm for complete oxidation of ore. K_2CrO_4 is precipitated as BaCrO_4 when Barium salt is added. To remaining solution 10 mL of 1 M $\text{K}_4\text{Fe}(\text{CN})_6$ is added when Fe^{3+} ions react with it to form $\text{KFe}[\text{Fe}(\text{CN})_6]$, often called 'Prussian Blue'. To determine excess of $\text{K}_4\text{Fe}(\text{CN})_6$ in solution 7mL of 0.2 N of Fe^{2+} is added when all the $\text{K}_4\text{Fe}(\text{CN})_6$ is precipitated as $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$.

18. Weight of BaCrO_4 precipitated

- 1.64
- 6.29
- 0.82
- 3.29

19. % by mass of $\text{Fe}_{0.95}\text{O}$ in the ore

- 9.6%
- 10.1%
- 8.55%
- 20.2%

20. n factor for $\text{Fe}_{0.95}\text{O}$

- 0.9
- 0.85
- $\frac{2}{0.95}$
- 1.8

21. Weight of impurities present in the ore

- 0.421
- 0.123
- 0.341
- 0.206

Comprehension (Q. 22 to 24): For the reaction: $\text{MnBr}_2 + \text{PbO}_2 + \text{HNO}_3 \rightarrow \text{HMnO}_4 + \text{Pb}(\text{BrO}_3)_2 + \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}$ (Atomic masses: Mn = 55, Br = 80, Pb=208)

22. The equivalent weight of MnBr_2 is

- 107.5
- 215
- 12.65
- 19.55

23. The equivalent weight of PbO_2 is:

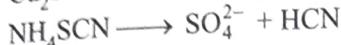
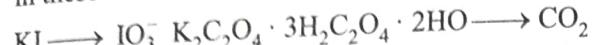
- 120
- 240
- 14.11
- 21.82

24. The equivalent weight of HNO_3 is:

 - (a) 63
 - (b) 55.6
 - (c) 31.5
 - (d) 111.18

MATCH THE COLUMN TYPE QUESTIONS

25. Container-I may contain 1 mol $K_2Cr_2O_7$ or 1 mol $KMnO_4$ in acidic medium. This container-I is mixed with other Container-II, III, IV or V, due to which compound present in these containers undergo following half reaction.



| | | |
|--|-------------------------|-----------------------|
| KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ | KI | Cu_2S |
| Container-I | Container-II | Container-III |
| $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ | NH_4SCN | |
| Container-IV | Container-V | |

Column-I represents the two container which are mixed.

Column-II represents the number of moles of substance which reacts with 1 mol of substance (may be KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$) present in **container-I**.

Match the **Column-I** with **Column-II**.

| Column-I | | Column-II | |
|----------|--------------------------------|-----------|---------------|
| A. | Container-I + Container-III | p. | $\frac{3}{4}$ |
| B. | Container-II + Container-I | q. | $\frac{5}{8}$ |

| | | | |
|----|----------------------------|----|---------------|
| C. | Container-I + Container-V | r. | 1 |
| D. | Container-IV + Container-I | s. | $\frac{5}{6}$ |

- (a) $A \rightarrow p,q; B \rightarrow r,s; C \rightarrow r,s; D \rightarrow p,q$
 (b) $A \rightarrow s,r; B \rightarrow p,q; C \rightarrow r,s; D \rightarrow p,q$
 (c) $A \rightarrow r,q; B \rightarrow r,s; C \rightarrow p,s; D \rightarrow p,q$
 (d) $A \rightarrow s,q; B \rightarrow r,p; C \rightarrow r,s; D \rightarrow p,q$

NUMERICAL BASED QUESTIONS

26. A 458 g sample containing Mn_3O_4 was dissolved and all manganese was converted to Mn^{2+} . In the presence of fluoride ion, Mn^{2+} is titrated with 3 lit of $KMnO_4$ solution (which was 1.25 N against oxalate in acidic medium), both reactants being converted to a complex of Mn(III). What was the % of Mn_3O_4 in the sample?

27. 80 gm of a sample of Anhydrous $CuSO_4$ was dissolved in water and made to 250ml. 25 ml of this solution after taking usual precautions was treated with a little excess of KI solution. A white ppt. of Cu_2I_2 and iodine was evolved. The iodine so evolved required 40 ml of 1 M of hypo solution. What is the approximate purity of $CuSO_4$ solution. [Mol. wt. of $CuSO_4$ = 160]

28. A 0.96 g sample of Fe_2O_3 solid of 50% purity is dissolved in acid and completely reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 mL. An aliquot of 25.0 mL of this solution requires 30 mL of 0.01 M solution of an oxidising agent for titration. Calculate the number of moles of electrons taken up by oxidising agent in the reaction of the above titration.

29. A solution containing 2.68×10^{-3} mol of A^{n+} ions requires 1.61×10^{-3} mol of MnO_4^- for the complete oxidation of A^{n+} to AO_3^- in acidic medium. What is the value of n?

30. 2 × Ratio of moles of oxidant to reductant in the following reaction is _____.
 $CrI_3 + Cl_2 + KOH \longrightarrow K_2CrO_4 + KIO_4 + KCl$

Exercise-4 (Past Year Questions)

JEE MAIN

1. Which of the following reactions is an example of a redox reaction? (2017)

 - $\text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2$
 - $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+ \text{PF}_6^-$
 - $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$
 - $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$

2. Iodine reacts with concentrated HNO_3 to yield along with other products. The oxidation state of iodine in Y is (2019)

4. In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is: (2019)

 - 1
 - 10
 - 2
 - 5

5. Good reducing nature of H_3PO_2 is attributed to the presence of (2019)

 - Two P – OH bonds
 - One P – H bond
 - Two P – H bonds
 - One P – OH bond

6. In order to oxidise a mixture one mole of each of FeC_2O_4 , $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ in acidic medium, the number of moles of KMnO_4 required is: (2019)

 - 3
 - 2
 - 1
 - 1.5

7. The correct order of the oxidation states of the nitrogen in NO , N_2O , NO_2 and N_2O_3 is: (2019)

 - $\text{NO}_2 < \text{N}_2\text{O}_3 < \text{NO} < \text{N}_2\text{O}$
 - $\text{NO}_2 < \text{NO} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}$
 - $\text{N}_2\text{O} < \text{N}_2\text{O}_3 < \text{NO} < \text{NO}_2$
 - $\text{N}_2\text{O} < \text{NO} < \text{N}_2\text{O}_3 < \text{NO}_2$

8. An example of a disproportionation reaction is: (2019)

 - $2\text{K MnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
 - $2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$
 - $2\text{CuBr} \rightarrow \text{CuBr}_2 + \text{Cu}$
 - $2\text{NaBr} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{Br}_2$

9. The oxidation states of transition metal atoms in $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 and K_2FeO_4 , respectively, are x, y and z. The sum of x, y and z is _____. (2020)

10. The redox reaction among the following is (2020)

 - Reaction of H_2SO_4 with NaOH reaction of $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$ with NaOH
 - Reaction of $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$ with AgNO_3
 - Combination of dinitrogen with dioxygen at 2000 K
 - Formation of ozone from atmospheric oxygen in the presence of sunlight

11. Oxidation number of potassium in K_2O , K_2O_2 and KO_2 , respectively, is (2020)

 - +1, +2 and +4
 - +1, +4 and +2
 - +1, +1 and +1
 - +2, +1 and + $\frac{1}{2}$

12. The oxidation states of transition metal atoms in $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 and K_2FeO_4 , respectively, are x, y and z. The sum of x, y and z is _____. (2020)

13. The oxidation states of iron atoms in compounds (a), (b) and (c), respectively, are x, y and z. The sum of x, y and z is _____. (2020)

$\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$ (A) $\text{Na}_4[\text{FeO}_4]$ (B) $[\text{Fe}_2(\text{CO})_9]$ (C)

14. The volume (in mL) of 0.1 N NaOH required to neutralise 10 mL of 0.1 N phosphinic acid is _____. (2020)

15. A 100 mL solution was made by adding 1.43 g of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$. The normality of the solution is 0.1 N. The value of x is _____. (The atomic mass of Na is 23 g/mol) (2020)

16. Consider the following equations: (2020)

$$2\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow x\text{A} + y\text{B}$$

(in basic medium)

$$2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{O}_2 \rightarrow x'\text{C} + y'\text{D} + z'\text{E}$$

(in acidic medium)

The sum of the stoichiometric coefficients x, y, x', y' and z' for products A, B, C, D and E, respectively, is _____. (2020)

17. A 20.0 mL solution containing 0.2 g impure H_2O_2 reacts completely with 0.316 g of KMnO_4 in acid solution. The purity of H_2O_2 (in %) is _____ (mol. wt. of H_2O_2 = 34; mol. wt. of KMnO_4 = 158) (2020)

18. In the given chemical reaction, colors of the Fe^{2+} and Fe^{3+} ions, are respectively: (2021)

$$5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$$
 - Yellow, Orange
 - Yellow, Green
 - Green, Orange
 - Green, Yellow

19. In which one of the following sets all species show disproportionation reaction? (2021)

 - ClO_2^- , F_2 , MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$
 - $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , ClO_2^- and Cl_2
 - MnO_4^- , ClO_2^- , Cl_2 and Mn^{3+}
 - ClO_4^- , MnO_4^- , ClO_2^- and F_2

20. The reaction of sulphur in alkaline medium is the below: (2021)

$$\text{S}_{8(s)} + a\text{OH}_{(aq)}^- \longrightarrow b\text{S}_{(aq)}^{2-} + c\text{S}_2\text{O}_{3(aq)}^{2-} + d\text{H}_2\text{O}_{(l)}$$

The values of 'a' is _____. (Integer answer)

21. $a\text{MnO}_4^- + b\text{C}_2\text{O}_4^{2-} + c\text{H}^+ \rightarrow x\text{Mn}^{2+} + y\text{CO}_2 + z\text{H}_2\text{O}$ If the above equation is balanced with integer coefficients, the value of c is _____. (Round off to the Nearest Integer) (2021)

22. In basic medium CrO_4^{2-} oxidises $\text{S}_2\text{O}_3^{2-}$ to form SO_4^{2-} and itself changes into $\text{Cr}(\text{OH})_4^-$. The volume of 0.154 M CrO_4^{2-} required to react with 40 mL of 0.25 M $\text{S}_2\text{O}_3^{2-}$ is _____. mL. (Rounded-off to the nearest integer) (2021)

23. 15 mL of aqueous solution of Fe^{2+} in acidic medium completely reacted with 20 mL of 0.03 M aqueous $\text{Cr}_2\text{O}_7^{2-}$. The molarity of the Fe^{2+} solution is $\times 10^{-2}$ M (Round off to the Nearest Integer). (2021)

24. In order to oxidise a mixture of one mole of each of FeC_2O_4 , $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ in acidic medium, the number of moles of KMnO_4 required is. (2021)

(a) 2 (b) 1
(c) 3 (d) 1.5

25. 100 ml of a water sample contains 0.81 g of calcium bicarbonate and 0.73 g of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of CaCO_3 is _____.
(molar mass of calcium bicarbonate is 162 g mol⁻¹ and magnesium bicarbonate is 146 g mol⁻¹) (2021)

(a) 5,000 ppm (b) 1,000 ppm
(c) 100 ppm (d) 10,000 ppm

26. 0.4 g mixture of NaOH , Na_2CO_3 and some inert impurities was first titrated with HCl using phenolphthalein as an indicator, 17.5 mL of HCl was required at the end point. After this methyl orange was added and titrated. 1.5 mL of same HCl was required for the next end point. The weight percentage of Na_2CO_3 in the mixture is _____.
(Rounded-off to the nearest integer) (2021)

27. Consider titration of NaOH solution versus 1.25M oxalic acid solution. At the end point following burette readings were obtained.

(i) 4.5 mL (ii) 4.5 mL
(iii) 4.4 mL (iv) 4.4 mL
(v) 4.4 mL

If the volume of oxalic acid taken was 10.0 mL then the molarity of the NaOH solution is _____. M. (Rounded-off to the nearest integer) (2021)

28. 10.0 ml of Na_2CO_3 solution is titrated against 0.2 M HCl solution. The following titre values were obtained in 5 readings.
4.8 ml, 4.9 ml, 5.0 ml and 5.0 ml
Based on these readings, and convention of titrimetric estimation of concentration of Na_2CO_3 solution is _____. mM
(Round off to the Nearest integer) (2021)

29. The neutralization occurs when 10 mL of 0.1 M acid 'A' is allowed to react with 30 mL of 0.05 M base $\text{M}(\text{OH})_2$. The basicity of the acid 'A' is _____. (M is a metal). (2022)

30. Which one of the following is an example of disproportionation reaction? (2022)

(a) $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
(b) $\text{MnO}_4^- + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$
(c) $1\text{OI}^- + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{I}_2$
(d) $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$

JEE ADVANCED

31. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is: (2007)

(a) 3 (b) 4 (c) 5 (d) 6

32. Bleaching powder and bleach solution are produced on a large scale and used in several house hold products. The effectiveness of bleach solution is often measured by iodometry.

25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $\text{Na}_2\text{S}_2\text{O}_3$ was used to reach the end point. The molarity of the household bleach solution is: (2012)

(a) 0.48 M. (b) 0.96 M
 (c) 0.24 M (d) 0.024 M

33. For the reaction : $\text{I}^- + \text{ClO}_3^- + \text{H}_2\text{SO}_4 \rightarrow \text{Cl}^- + \text{HSO}_4^- + \text{I}_2$
 The correct statement(s) in the balanced equation is/are: (2014)

(a) Stoichiometric coefficient of HSO_4^- is 6.
 (b) Iodide is oxidized.
 (c) Sulphur is reduced.
 (d) H_2O is one of the products.

34. In dilute aqueous H_2SO_4 , the complex diaquodioxalato-ferrate(II) is oxidized by MnO_4^- . For this reaction, the ratio of the rate of change of $[\text{H}^+]$ to the rate of change of $[\text{MnO}_4^-]$ is (2015)

35. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is: (2016)

36. The order of the oxidation state of the phosphorus atom in H_3PO_2 , H_3PO_3 , and $\text{H}_4\text{P}_2\text{O}_6$ is (2017)

(a) $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6$
 (b) $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$
 (c) $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_4$
 (d) $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6$

37. To measure the quantity of MnCl_2 dissolved in an aqueous solution, it was completely converted to KMnO_4 using the reaction, $\text{MnCl}_2 + \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{HCl}$ (equation not balanced). Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 g) was added in portions till the colour of the permanganate ion disappeared. The quantity of MnCl_2 (in mg) present in the initial solution is (Atomic weights in g mol⁻¹ Mn = 55, Cl = 35.5) (2018)

ANSWER KEY

CONCEPT APPLICATION

1. (a) 2. (b) 3. (d) 4. (a) 5. (c) 6. (c) 7. (c) 8. (a) 9. (c) 10. (d)
11. (a) 12. (c)

TOPICWISE QUESTIONS

1. (b) 2. (c) 3. (c) 4. (b) 5. (a) 6. (b) 7. (a) 8. (b) 9. (a) 10. (c)
11. (d) 12. (c) 13. (a) 14. (b) 15. (c) 16. (a) 17. (c) 18. (d) 19. (c) 20. (a)
21. (a) 22. (d) 23. (a) 24. (d) 25. (d) 26. (c) 27. (a) 28. (a) 29. (c) 30. (d)
31. (d) 32. (d) 33. (b) 34. (b) 35. (a) 36. (a) 37. (c) 38. (b) 39. (a) 40. (a)
41. (c) 42. (d) 43. (c) 44. (d) 45. (c) 46. (d) 47. (d) 48. (c) 49. (a) 50. (d)
51. (b) 52. (c) 53. (c) 54. (a) 55. (c) 56. (b)

LEARNING PLUS

1. (d) 2. (c) 3. (d) 4. (c) 5. (a) 6. (c) 7. (c) 8. (b) 9. (b) 10. (c)
11. (c) 12. (b) 13. (a) 14. (a) 15. (b) 16. (c) 17. (c) 18. (a) 19. (a) 20. (a)
21. (a) 22. (a) 23. (a) 24. (d) 25. (d) 26. (a) 27. (a) 28. (c) 29. (a) 30. (b)
31. (c) 32. (a) 33. (a) 34. (a) 35. (a) 36. (a) 37. (c) 38. (d)

ADVANCED LEVEL QUESTIONS

1. (c,d) 2. (b,c) 3. (a,b,c) 4. (b,c,d) 5. (b) 6. (b,c) 7. (a) 8. (a,b) 9. (a,c)
10. (a,b,c,d) 11. (a,c) 12. (a,b,c,d) 13. (a,c,d) 14. (a,b,d) 15. (c) 16. (b) 17. (c) 18. (d)
19. (b) 20. (b) 21. (c) 22. (c) 23. (a) 24. (b) 25. (a) 26. [50]
27. [80] 28. [5] 29. [2] 30. [27]

PAST YEAR QUESTIONS

JEE Main

1. (a) 2. (a) 3. (d) 4. (b) 5. (c) 6. (b) 7. (d) 8. (c) 9. [19] 10. (a)
11. (c) 12. [19] 13. [6] 14. [10.00] 15. [10.00] 16. [19.00] 17. [85] 18. (d) 19. (c) 20. [12]
21. [16] 22. [173] 23. [24] 24. (a) 25. (d) 26. (d) 27. [6] 28. [50] 29. [3] 30. (a)

JEE Advanced

31. (d) 32. (c) 33. (a,b,d) 34. [8] 35. [6] 36. (b) 37. [126]

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