

CONTENTS

Details	Page No.
Unit I	1 - 21
Unit II	22 - 45
Unit III	46 - 54
Unit IV	55 - 81
Unit V	82 - 108
Unit VI	109 - 114

Students preparing with WINSOME SERIES
get excellent marks in exam

Our Publication

WINSOME SERIES
ALLAHABAD STATE UNIVERSITY
&

WINSOME SERIES
For Allahabad University

A.U. - B.Sc. 1st Year - Chemistry III Paper - Unit I - I

UNIT - I

1. Write short notes on deviation from ideal behaviour by real gases. (2006)

Ans. Behaviour of Real Gases :-
Deviations from Ideal Behavior :-

We show the deviation of real gas from the ideal behaviour by introducing compressibility factor, Z can be expressed as :

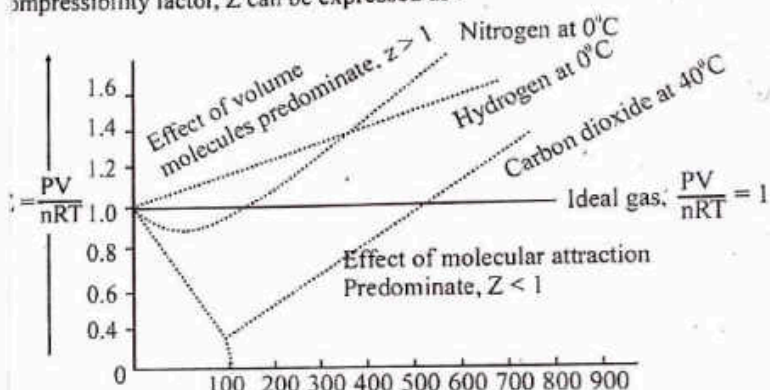


Fig. - A plot of compressibility as a function of P for some gases

$$Z = \frac{PV}{nRT}$$

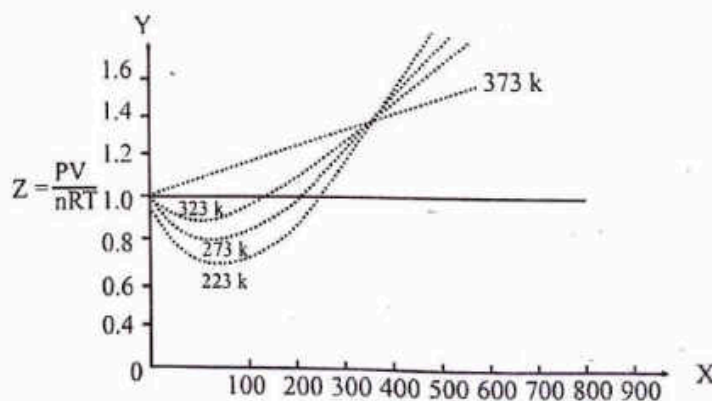


Fig. - A plot of z vs P for N_2 at different temperature
In case of ideal gas $PV = nRT$ hence $Z = 1$
In case of real gas. The value of Z can be < 1 or > 1 .

For more details Visit Us At - www.winsomepublication.in

When $Z < 1$; it refers to negative deviation. It implies that the gas is more compressible than expected from ideal behaviour.

When $Z > 1$, it refers to positive deviation. It implies that the gas is less compressible than expected from ideal behaviour.

Cause of deviation from ideal behaviour is due to two assumptions of kinetic theory of gas that are:

1. The volume occupied by gas molecule is negligibly small as compared to the total volume occupied by the gas.

2. The force of attraction between gas molecule are negligible.

The van der Waal's Equation:-

- The ideal gas equation is not much use at high pressures
- One of the most useful equations to predict the behavior of real gases was developed by Johannes van der Waals (1837-1923)

He modified the ideal gas law to account for:

The finite volume of gas molecules

The attractive forces between gas molecules

$$P = \frac{nRT}{V}$$

(the ideal gas law)

van der Waals equation:-

- The van der Waals constants a and b are different for different gases
- They generally increase with an increase in mass of the molecule and with an increase in the complexity of the gas molecule (i.e. volume and number of atoms)

$$P = \frac{nRT}{V-nb} - \frac{N^2 a}{V^2}$$

(b)

Correction for volume of molecules (decreases volume as a function of the number of molecules)

(a)

Correction for molecular attraction (decreases pressure as volume decreases and the number of molecules increases)

Q.2 Deduce the Vander Wall's equation for real gas. (2007, 16)

Other Related Questions -

Q. Under what condition gasses deviate from ideal gas law. Derive Vander Wall's equation explains its application to real gas and ideal gas. (2011)

Q. Derive Vander Waal equation for one mole of a gas. (2012)

Ans. Vander Waals (1873) encountered the deviation of real gases from ideal behavior and gives two postulate of the kinetic theory. These are as follows:-

- Gaseous molecules are point masses and have no volume.
- Intermolecular attraction between gases molecule is negligible.

That is why, the ideal gas equation $PV = nRT$, which is derived from the kinetic theory, could not hold for real gases. vander Waals gives an idea that

both the pressure P and volume V factors in ideal gas equation needed correction in order to make it applicable to real gasses.

Volume Correction:-

The molecules are non compressible, vander Waals suggested that the volume V changes to volume $(V-b)$, where b is called the excluded volume which is a constant characteristic of each gas. It is also refer to as co-volume and its value depends upon the nature of gas.

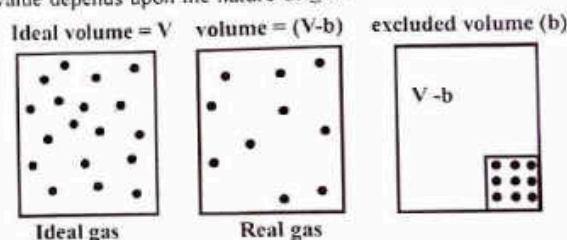


Figure:- volume of real gas

Pressure Correction:-

The other molecules on all sides attract a molecule in the interior of the gas. These attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by the molecules on one side only. Hence it experiences an inward pull. Therefore it strikes the wall with reduced velocity and the actual pressure of the gas p , will be less than the ideal pressure. If the actual pressure P , less than P_{ideal} by a quantity p , we have

$$P = P_{ideal} - p \text{ or } P_{ideal} = P + p$$

p is determined by the force of attraction between molecule (A) striking the wall of container and the molecules (B) pulling them inwards. The net force of the attraction is therefore, proportional to the concentration of (A) type molecules and also of (B) types of molecules. That is

$$P \propto C_A \times C_B \text{ or } P \propto C_A \propto C_B \text{ or } P \propto \frac{n}{V} \times \frac{n}{V} \text{ or } P \propto \frac{n^2}{V^2}$$

Where n is total numbers of gas molecules in the volume V and a is the proportionality constant characteristic of the gas.

Thus the pressure P in the ideal gas equation is corrected as

$$\text{for } n \text{ molecules of gas, } \left(P + \frac{an^2}{V^2} \right)$$

Substituting the values of the corrected pressure and volume in the ideal gas equation $PV = nRT$, we have

$$\left(P + \frac{am^2}{V^2}\right)(V - nb) = nRT$$

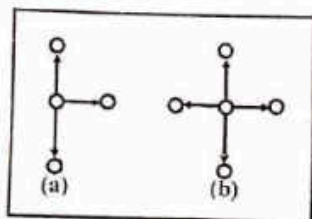


Figure:- (a) a molecule about to strike the wall has net inward pull.
(b) a molecule in the interior of the gas has balanced attraction.

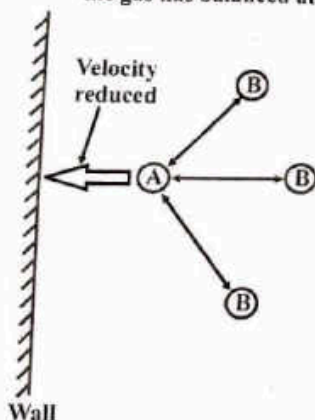


Figure:- The striking molecule A is pulled inward by molecules B which reduce the velocity of A and cause the decrease of pressure

This is known as Vander Waals Equation for n moles of a gas. For 1 mole of a gas ($n = 1$) Vander Wall's Equation becomes

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

constants a and b in Vander Walls Equation are called Vander Wall's Constants.

Note:- Excluded volume is four times the actual volume of the molecules:-

The excluded volume is not equal to the actual volume of the gas molecules. In fact, it is four times the added volumes of the molecules and can be calculated as follows.

Shop Online at www.winsomecollection.co.in

Let us consider two molecules of radius r colliding with each other. Obviously, they cannot approach each other more than a distance $2r$. Therefore, the space indicating by the dotted sphere having sphere $(2r)$ will not be available to all the other molecules of the gas. In other words the dotted spherical space is excluded volume per pair of molecules. Thus

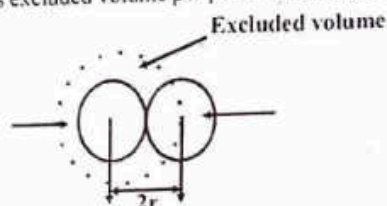


Figure:- excluded volume for a pair of gas molecule

$$\text{Excluded volume for two spherical} = \frac{4}{3}\pi(2r)^3 = 8\left(\frac{4}{3}\pi r^3\right)$$

$$\text{Excluded volume for per molecule } (V_e) = \frac{1}{2} \times 8\left(\frac{4}{3}\pi r^3\right) = 4V_m$$

Where V_m is the actual volume of a single molecule. Therefore, in general, excluded volume of the gas is four times the actual volume of the molecule.

Q.3 Define P_c , V_c , T_c -

(1999)

Ans. Anders (1869) studied the P-T conditions of liquefactions of several gases. He established that for every gas there is a temperature below which the gas can be liquefied but above it the gas defies liquification. This temperature called critical temperature of the gas.

The critical temperature T_c of a gas may be defined as that temperature above which it cannot be liquefied no matter how much the pressure applied.

The critical pressure, P_c is the minimum pressure required to liquefy the gas at its critical temperature.

The critical volume, V_c is the volume occupied by a mole of the gas at critical temperature and critical pressure.

P_c , V_c and T_c are collectively called the critical constant of the gas. All real gases have characteristic constants.

Q.4 Write down the value of Vander Waals critical constants P_c and T_c . (2002)

Ans. The value of P_c is $= \frac{a}{27b^2}$ and $T_c = \frac{8a}{27Rb}$

Where a and b are Vander Walls constant and R is gas constant.

For more details Visit Us At - www.winsomepublication.in

Q.5 Explain critical phenomena on the basis of isotherms of CO₂ gas. Define critical constants and derive the values of P_c , V_c , T_c from Vander Walls equation. (2007)

Other Related Questions -

Q. Derive expressions for critical constants in terms of Van der Waals constants 'a' and 'b'. How are the critical constants interrelated with each other? (2010, 13, 17)

Ans. vander Waals Equation and Critical Constant: -

Thomson (1871) studied the isotherms of carbon dioxide drawn by Andres. He suggested that there should be no sharp points in the isotherms below the critical temperature. These isotherms should really exhibit a complete continuity of state from gas to liquid. He showed a theoretical wavy curve. The curve MLB in figure represents a gas compressed in a way that it would remain stable. The curve MNC represents a super heated liquid. This type of continuity of state is predicted by Vander Wall's cubic equation.

According to figure, for any given value of pressure (P) and temperature (T) there should be three value of Volume (V), these values are indicated by points B, M and C of the wavy curve. The three values of Volume (V) become closer as the horizontal part of the isotherm rises. At the critical point these values becomes identical. This enables the calculation of T_c , P_c and V_c in terms of Vander Wall's Constant. The vander Wall's equation may be written as

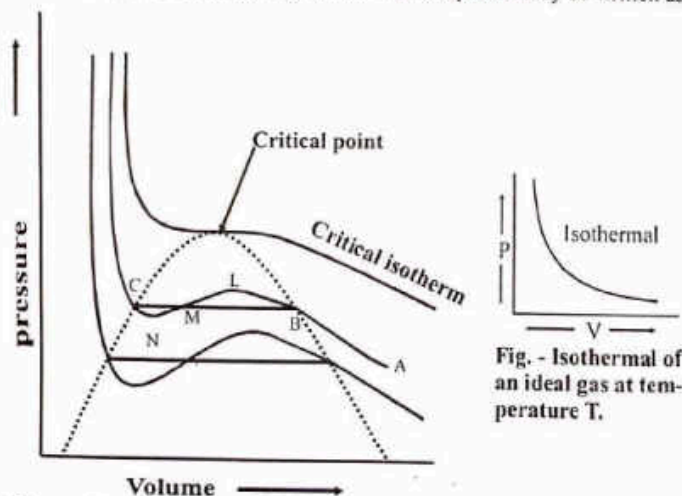


Fig. - Isothermal of an ideal gas at temperature T.

Figure: Isotherm of carbon dioxide according to Vander Wall's Equation.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Shop Online at www.winsomecollection.co.in

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0 \Rightarrow PV^3 - (RT + Pb)V^2 + aV - ab = 0$$

And $(V - V_c)^3 = 0 \Rightarrow V^3 = V_c^3$

At critical point $V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0$ (1)

Thus at critical point vander Wall's equation gives

$$V^3 - \left(\frac{RT_c}{P_c} + b\right)V^2 + \left(\frac{a}{P_c}\right)V - \left(\frac{ab}{P_c}\right) = 0$$
(2)

Equating coefficient of equation (1) and eq. (2)

$$3V_c = \frac{RT_c}{P_c} + b$$
(3)

$$3V_c^2 = \frac{a}{P_c}$$
(4)

$$V_c^3 = \frac{ab}{P_c}$$
(5)

from equation (4) and equation (5)

$$V_c = 3b$$
(6)

substituting the value in equation (4)

$$P_c = \frac{a}{27b^2}$$
(7)

substituting the value of V_c and P_c in equation (3)

$$T_c = \frac{8a}{27Rb}$$
(8)

Knowing a and b which can be deduced from deviation of ideal gas equation. The critical constants can easily be calculated. Conversely, since P_c and T_c can often be determined experimentally with comparative ease, the values may be employed to calculate the constant a and b

$$a = 3V_c^2 P_c \text{ and } b = \frac{V_c}{3}$$

Q.6. With the help of vander Wall's equation explain the behaviour of real gas, when

(i) The pressure is too high

(ii) The temperature is high.

(2016)

Ans. The vander Waal's equation is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$
(i)

For more details Visit Us At - www.winsomepublication.in

$$\text{or } PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

neglecting $\frac{ab}{V^2}$, which is very small quantity, we have

$$PV - Pb + \frac{a}{V} = RT \quad \dots\dots\dots(ii)$$

If P_1 and V_1 represents pressure and volume then the ideal gas equation will be

$$P_1 V_1 = RT \quad \dots\dots\dots(iii)$$

By eq. (ii) and (iii), we get

$$PV - Pb + \frac{a}{V} = RT = P_1 V_1$$

$$\text{or } PV - Pb + \frac{a}{V} = P_1 V_1 \quad \dots\dots\dots(iv)$$

(i) At low pressure: -

The factor Pb is very small and is neglected, so we have $PV + \frac{a}{V} = P_1 V_1$, thus the observed product of pressure and volume is less by $\frac{a}{V}$ than expected for an ideal gas.

(ii) At high pressure: -

The factor $\frac{a}{V}$ can be neglected so from equation (iv), we have $PV - Pb = P_1 V_1$, hence, the observed product is greater by Pb , than expected for an ideal gas.

(iii) At high temperature: -

The factors Pb and $\frac{a}{V}$ are neglected and the equation (iv) becomes $PV = P_1 V_1 = RT$ which is the same as desired.

Q.7 One mole of diethyl ether occupies 15 liters at 27°C calculate the pressure if Vander Walls constant for di ethyl eather are $a = 17.38 \text{ atm liter}^2 \text{ mole}^{-2}$ and $b = 0.134 \text{ liter}^2$ (Imp.)

Ans. As we know

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

dividing by $(V - nb)$ and solving for P

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Here $n = 1$, $R = 0.0821 \text{ liter atm mol}^{-1} \text{ K}^{-1}$, $V = 15\text{L}$ and the values of a and b , we have

$$P = \frac{1 \times 0.0821 \times 500}{15 - (1 \times 0.134)} - \frac{1^2 \times 17.38}{15 \times 15} \quad T = 273 + 227 = 500\text{K}$$

Shop Online at www.winsomecollection.co.in

$$= \frac{41.05}{14.766} - \frac{17.38}{225} = 2.78 - 0.07724 = 2.702 \text{ atm}$$

Q.8 What are the main postulates of the kinetic theory of gas? Deduce and expression for kinetic gas equation. (Imp)

Ans. Postulates: -

The kinetic molecular theory is based on the microscopic model of a gas. The prediction and calculation based on the model agree well with the experimental observations. This establishes the basic correctness of this model.

- (1) A gas consist of a large number of identical molecules of mass (m). the dimension of these molecules are very-very small compares to the space between them. Hence the molecule is treated as point masses.
- (2) There are practically no attractive forces between the molecules. The molecules therefore, move independently.
- (3) The molecules are in a state of ceaseless and random motion, colliding with each other and with the walls of container. The direction of their motions changes only on collision. These collisions are known as elastic collision in which the energy and momentum of the molecule are conserved.
- (4) The pressure of a gas is the result of the collision of the molecules with the walls of the container.
- (5) The average kinetic energy of the colliding molecules is directionally to its temperature.

Average Kinetic energy of the molecules: -

The pressure of the gas in terms of kinetic model is given as

$$P = \frac{1}{3} \left(\frac{N}{V} \right) m \bar{u}^2 \quad \text{where } \bar{u} = \text{root mean square speed.}$$

Using the above relationship and gas law a connection between the average translation kinetic energy, $\frac{1}{2} m \bar{u}^2$, of a molecule at the temperature T of the gas can be derived. Thus we have $(PV = RT)$ for one mole of gas or

$$\frac{1}{3} N_A m \bar{u}^2 = RT$$

$[N = N_A \text{ for one mole of gas} = \text{Avogadro constant}]$

$$\text{or } \frac{1}{2} m \bar{u}^2 = \frac{3}{2} \frac{RT}{N_A}$$

$$\text{Kinetic energy} = \frac{3}{2} KT \quad \left[K = \frac{R}{N_A} = \text{Boltzmann Constant} \right]$$

That is average translation kinetic energy, $(3/2) KT$, of a molecule is directly proportional to the temperature of the gas. Also the average kinetic energy per mole of the gas is equal to $(3/2) RT$.

For more details Visit Us At - www.winsomepublication.in

Q.9 The critical constant for water are $T_c = 647 \text{ K}$, $P_c = 218 \text{ atm}$, $V_c = 0.057 \text{ L/mol}$ calculate vander Waals constant a and b .

Ans. We know that

$$a = 3P_c V_c^2 = 3 \times 218 \times 0.057^2 = 2.112 \text{ L}^2 \text{ atm mol}^{-2}$$

$$b = V_c/3 = 0.057/3 = 0.19 \text{ L mol}^{-1}$$

Q.10 Derive expression for pressure from the kinetic theory of gases and derive Boyle's law, Charler's law form it. (2005, 06)

Other Related Questions -

Q. Show that the value of Boyle Temperature (T_b) may be calculated with the help of van der Wall's equation. (2018)

Ans. Boyle's Law:-

The kinetic molecular model assumes that pressure of a gas is due to the collision of the gas molecule with the walls of the container. The more of the frequency of collision, the higher would be the pressure. The reduction in the volume of the gas, increase the value of (N/V) to which pressure is directly proportional in the above model. Therefore as the volume of the gas is reduced the pressure increases, or in other words, the pressure is inversely proportional to the volume.

We have already derived that

$$\text{or } P = \frac{2}{3} \left(\frac{N}{V} \right) \frac{1}{2} m \bar{u}^2 = \frac{2}{3} \left(\frac{N}{V} \right) \frac{3}{2} K T$$

$$\text{or } PV = NKT$$

$$P \propto \frac{1}{V}$$

Form this equation it can be seen that at a constant temperature for fixed number of gas molecules the pressure is inversely proportional to volume.

Charle's Law:-

From the above relation $PV = NKT$, it can be seen that at constant pressure and for constant amount of gas $n = (N/N_A)$, volume is directly proportional to the temperature which is the statement of the Charl's Law.

Q.11. Derive the virial equation of state and hence show that Boyle's temperature is a/R_b . (Imp.)

Ans. Any variable quantity 'y' can be expressed irrespective of any theory with more and more accuracy by an algebraic expression (polynomial) of the type

$$Y = A + Bx + Cx^2 + Dx^3 \dots\dots\dots$$

By including more and more terms in higher powers of x such an approach has been used by various investigators to express $\frac{PV}{RT}$ (which also equal to Z) either as a function of $1/V$ or as a function of P as shown by the following equation.

$$\frac{PV}{RT} = Z = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \dots\dots\dots (1)$$

Where B , C , D are constant depending on temperatures respectively called II, III, IV Virial Coefficient of gas. Since the contribution from the square cubes offer higher powers are necessarily smaller than the 1st two terms The equation reduced to $PV = \text{constant}$

At a temperature at which $B = 0$ this temperature for any gas is called boyle temperature.

The virial equation coefficient can be expressed in terms of vander Wall's equation as by arranging vander Wall's Constant.

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \Rightarrow P = \frac{RT}{V - b} - \frac{a}{V^2}$$

multiplying by V

$$PV = \frac{RT}{V - b} V - \frac{a}{V}$$

dividing by RT

$$\frac{PV}{RT} = \frac{V}{V - b} - \frac{a}{RTV} = \left(\frac{V - b}{V} \right)^{-1} - \frac{a}{RTV} = \left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{RTV} \dots\dots\dots (2)$$

now eq. (2) is the binomial series $\left(1 - \frac{b}{V} \right)^{-1}$ which can be expressed as

$$\frac{PV}{RT} = 1 + \frac{b}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} \dots\dots\dots - \frac{a}{RTV}$$

neglecting higher terms

$$= 1 + \frac{b}{V} - \frac{a}{RTV} + \frac{b^2}{V^2} + \frac{b^3}{V^3}$$

$$\frac{PV}{RT} = 1 + \frac{1}{V} \left(b - \frac{a}{RT} \right) + \frac{b^2}{V^2} + \frac{b^3}{V^3}$$

comparing this eq. with eq. (1) for $n = 1$ we get

$$B(T) = \left(b - \frac{a}{RT} \right), C(T) = b^2$$

and $D(T) = b^3$ etc.

From experiment of real gas it is found that II virial coefficient is negative at low temperature reaches at maximum and then decreases the temperature at which II virial coefficient maximum is called the Boyle temperature.

$$PV = RT \left\{ 1 + \frac{b - \frac{a}{RT}}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots \right\}$$

Comparing this equation with virial equation of state

$$PV = RT \left(1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \dots \right)$$

Since in the Vander Waals equation is very small, the term involving V^2 , V^3 , ... etc can be neglected so the Vander Waals equation can be written in the virial term as

$$PV = RT \left(1 + \frac{b - \frac{a}{RT}}{V} \right)$$

Since at Boyle temperature the II virial coefficient is zero

$$b - \frac{a}{RT_b} = 0 \quad (\text{where } T_b \text{ is Boyle temperature})$$

$$\text{Or } b - \frac{a}{RT_b} = 0 \Rightarrow b = \frac{a}{RT_b} \Rightarrow \boxed{T_b = \frac{a}{Rb}}$$

Where T_b is Boyle temperature of the gas obeying van der Waals equation.

Q.12 Give the Maxwell's Law of distribution of molecular velocities.

(2006)

Other Related Questions-

Q. Explain Maxwell's distribution law of molecular velocities after giving mathematical expression and graph.

(2012)

Ans. Maxwell worked out the distribution of molecules between different possible velocities by applying probability consideration

$$\frac{dn_c}{n} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-\frac{MC^2}{2RT}} C^2 dC$$

Where dn_c = number of molecules having velocity between C and $(C + dC)$, n = total number of molecules, M = molecular mass, T = temperature on absolute scale.

Shop Online at www.winsomecollection.co.in

Out of a total n molecules having the velocities between C and $C + dC$.

$$\text{Or } \frac{1}{n} \frac{dn_c}{dC} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-\frac{MC^2}{2RT}} \cdot C^2$$

$$\frac{1}{n} \frac{dn_c}{dC} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-\frac{E}{RT}} \cdot C^2$$

Where $e^{-\frac{E}{RT}}$ is called Boltzmann factor, $\frac{1}{n} \frac{dn_c}{dC}$ give the probability of finding molecules having velocity C .

The distribution can be graphically represented as

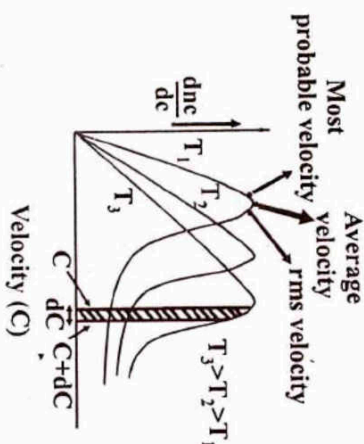


Fig. - Distribution of molecular speeds in a gas at different temperatures

From above graph we see that

- Fraction of the molecules to high to low velocity is very small
- There is a certain velocity for which the fraction of the molecule is maximum most probably velocity, which depends upon the volume of the gas at given temperature.

Effect of temperature on distribution.

The Boltzmann factor increases markedly with increases in temperature most probably velocity is increases with increase in temperature or in other words rise in temperature the fraction of molecules having high velocities considerably.

Q.13. Calculate critical constant of a gas if values of its vander Waals constants, 'a' and 'b' are $0.75 \text{ dm}^6 \text{ atm mol}^{-2}$ and $2.26 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$, respectively.

(2008)

Ans. $V_c = 3b = 3(0.0226 \text{ dm}^3 \text{ mol}^{-1}) = 0.0678 \text{ dm}^3 \text{ mol}^{-1}$

$$P_c = \frac{a}{27b^2} = \frac{0.751 \text{ dm}^6 \text{ atm mol}^{-2}}{27(2.26 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})^2} = 54.5 \text{ atm}$$

For more details Visit Us At - www.winsomepublication.in

$$T_c = \frac{8a}{27Rb} = \frac{8(0.751 \text{ dm}^6 \text{ atm mol}^{-2})}{27(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(2.26 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})}$$

$$= 120 \text{ K}$$

Q.14. Write Berthelot's equation of state for real gases. (2007, 16)

Ans. For real gas Berthelot proposed the following empirical equation to explain the behaviour of real gas

$$\left\{ P + \frac{a}{(TV_m^2)} \right\} (V_m - b) = RT$$

This equation basically the correction of Vander Waals equation except that correction factor, however this equation is quite accurate for the molar mass of the gas.

Q.15. If pressure, volume and temperature of one mole of a gas are

related as $\left(P + \frac{a}{V^2} \right) (V - b) = RT$, show that

- (i) P is a state function and
(ii) dp is an exact differential

Ans. $\left(P + \frac{a}{V^2} \right) (V - b) = RT$

Let P be a state function of two variable (V and T) of system

$$P = f(V, T)$$

Since P is state function hence differential of P will be an exact differential can be written as

$$dP = \left(\frac{\partial P}{\partial V} \right)_T dV + \left(\frac{\partial P}{\partial T} \right)_V dT \quad \dots\dots\dots(i)$$

ideal gas equation $PV = RT$

So $P = \frac{RT}{V}$

$$\left(\frac{\partial P}{\partial V} \right)_T = -\frac{RT}{V^2} \quad \text{and} \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V}$$

Putting in eq.(i)

$$dP = \left(-\frac{RT}{V^2} \right) dV + \left(\frac{R}{V} \right) dT$$

Shop Online at www.winsomecollection.co.in

According to enter reciprocal relation dP will be exact differential if

$$\left[\frac{\partial(RT/P^2)}{\partial T} \right]_V = \left[\frac{\partial(R/V)}{\partial V} \right]_T$$

If $-\frac{R}{V^2} = \frac{-R}{V^2}$ which is true. So dP will be exact differential.

Q.16. Write the short note on Law of corresponding states. (2006, 11, 14, 17, 18)

Ans. Law of corresponding state:-

Experimentally it has been concluded that all gases give the same type of isotherm as carbon dioxide near the critical point. The actual position of the critical isotherm varies with the critical constants of the gas. If for each different gas a suitable scale of pressure, volume and temperature is selected, it will be possible that all the other isotherms would coincide. Under such circumstances we should have one isothermal diagram and one fundamental equation for all gases.

If the pressure, volume and temperature of a gas are expressed in terms of the critical pressure, volume and temperature respectively, thus,

$P = \pi P_c$, $V = \phi V_c$ and $T = \theta T_c$ substituting these values in Vander Waal's equation, becomes

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2} \right) (\phi V_c - b) = R \theta T_c$$

Substituting $P_c = a/27b^2$, $V_c = 3b$, $T_c = 8a/27Rb$

$$\left(\frac{\pi a}{27b^2} + \frac{a}{9\phi^2 b^2} \right) (3\phi b - b) = \frac{8a\theta}{27b}$$

$$\frac{a}{27b^2} \left(\pi + \frac{3}{\phi^2} \right) b(3\phi - 1) = \frac{8a\theta}{27b}$$

$$\left(\pi + \frac{3}{\phi^2} \right) (3\phi - 1) = 8\theta$$

The quantities π , ϕ and θ are called the reduced pressure, volume and temperature respectively.

This equation is known as the reduced of state and is independent on the nature of the substances as it does not contain the critical constants. It is applicable to all substances in the liquid or gaseous state. According to the reduced temperature and pressure, they will also have the same reduced volume.

This statement is known as the law of corresponding states and the

For more details Visit Us At - www.winsomepublication.in

substances under such conditions are said to be in corresponding states.

Q.17. Compare among the Root mean square speed, Average speed and most probable speed with mathematical details (equations). (2012)

Ans.

- (i) The average velocity V_{av}
 (ii) The root mean square velocity (V_{rms})
 (iii) The most probable velocities V_{mp}

$$(a) \bar{V} = \sqrt{\frac{8RT}{\pi M}} \quad (b) \quad V_{rms} = \sqrt{\frac{3RT}{M}} \quad (c) \quad V_{mp} = \sqrt{\frac{2RT}{M}}$$

Root mean square speed, average speed and the most probable speed have following relationship:

$$u_{rms} > u_{av} > u_{mp}$$

The ratio between the three speeds is given below:

$$u_{mp} : u_{av} : u_{rms} :: 1 : 1.128 : 1.224$$

Q.18. Oxygen has density of 1.429 g/litre at N.T.P. Calculate root mean square and average velocities of oxygen molecules. (2012)

Ans. Root mean square velocity

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.315 \times 298}{16}} = 21.55$$

Average Velocity

$$V = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.315 \times 298}{3.14 \times 16}} = 19.86$$

Q.19. Compare inversion temperature (T_i) and Boyle's temperature (T_b) mathematically. (2012)

Ans. The Boyle's temperature (T_b) and inversion temperature (T_i) are related to the two van der Waals constants as:

$$T_b = \frac{a}{bR} = \frac{1}{2} T_i$$

Note:

Boyle's temperature is the temperature at which the gases obey the ideal gas laws over a wide range of pressures.

Inversion temperature is the temperature at which the Joule Thompson coefficient changes its sign i.e., from positive to negative or vice versa.

Q.20. Calculate the van der Waals constants a and b , If $T_c = 31^\circ\text{C}$, $P_c = 72.8$ atm. and $R = 0.082 \text{ atm dm}^3\text{K}^{-1}\text{mol}^{-1}$. (2015)

Sol. Give $T_c = 31^\circ\text{C} = 304 \text{ K}$, $P_c = 72.8 \text{ atm}$ and $R = 0.082 \text{ atm dm}^3\text{K}^{-1}\text{mol}^{-1}$

$$\text{Now } T_c = \frac{8a}{27Rb} \Rightarrow \frac{a}{b} = \frac{27RT_c}{8} = \frac{304 \times 0.082 \times 27}{8}$$

$$\Rightarrow \frac{a}{b} = 84.13 \Rightarrow a = 84.13b$$

$$\text{We know that } P_c = \frac{a}{27b^2}$$

$$\Rightarrow a = 27b^2 P_c \Rightarrow 84.13b = 27b^2 \times 72.8$$

$$\Rightarrow b = \frac{84.13}{27 \times 72.8} = 0.042 \text{ L mol}^{-1}$$

$$\text{Hence } a = 84.13 \times 0.042 = 3.53 \text{ L}^2\text{atm mol}^{-2}$$

Q.21. Write short note on critical constants. (2015)

Ans. Critical Constants:-

Critical Temperature T_c - The critical temperature is the maximum temperature at which a gas can be liquefied i.e. the temperature above which a liquid can not exist.

Critical Pressure P_c - The critical pressure is the minimum pressure required to cause liquefaction at the temperature T_c .

Critical Volume V_c - The critical volume is the volume occupied by one mole of a gas at critical temperature T_c and critical pressure P_c .

Q.22. For an ideal gas $V = \frac{RT}{P}$, show that dV is an exact differential.

Ans. We know that work differential dw is calculated as: (2016)

$$dw = PdV \quad \dots\dots\dots(1)$$

since volume V is a state function i.e. it is independent of the path [$V = f(T, P)$] hence dV is an exact differential. Therefore

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

For an ideal gas, we know that $PV = RT$ which means: $V = RT/P$.

Q.23. The Vander Waal's constant ' b ' for CO_2 is $4.28 \times 10^{-2} \text{ dm}^3\text{mol}^{-1}$. If CO_2 molecule is assumed to be spherical then calculate its molecular diameter. (2018)

Sol. For 1 mole of the gas,

$$b = 4N_A V_m$$

where N is Avagadro's number and v_m is actual volume of the gas molecule

$$v_m = \frac{n}{4V} = \frac{0.4428}{4 \times 6.022 \times 10^{23}} \text{ litres} \\ = 1.777 \times 10^{-26} \text{ litres} = 1.777 \times 10^{-23} \text{ cm}^3$$

But $v_m = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \left(\frac{\sigma}{2} \right)^3$

$$\therefore \sigma^3 = \frac{6v_m}{\pi} = \frac{6 \times 1.777 \times 10^{-23}}{3.143} = 33.92 \times 10^{-24}$$

which gives $\sigma = 3.24 \times 10^{-8} \text{ cm}$ or $3.24 \text{ \AA}$

Q.24. At 340K and atmospheric pressure N_2O_4 is 66% dissociated into NO_2 . What volume of 10g N_2O_4 occupy under these conditions. (2018)

Sol. $10 \text{ g } \text{N}_2\text{O}_4 = 10/92 = 0.1087 \text{ mol of } \text{N}_2\text{O}_4$
As N_2O_4 is 66% dissociated, so the mol of undissociated N_2O_4

$$= 0.187 \times \frac{34}{100} = 0.03696$$

Now find out the volume of N_2O_4 use the following equation.

$$PV = nRT$$

Here $n = 0.03696 \text{ mol}$, $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$, $T = 340 \text{ K}$, $P = 1 \text{ atm}$

Hence $V = \frac{0.03696 \times 0.082 \times 340}{1} = 1.03 \text{ L}$

Q.25. Average root mean square, most probable and average speeds are in the order of increasing value. Discuss the effects of temperature and pressure on these speeds. (2018)

Ans. Average root mean square (C_{rms}), most probable (C_{mp}) and average speeds (C_{av}) the relationship among velocities are :

$$C_{mp} : C_{av} : C_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} \\ = 1 : 1.128 : 1.224$$

In Average root mean square, most probable and average speeds the temperature are in the temperature in square root. So that the average root mean square, most probable and average speed varies as the square root of the absolute temperature.

Root mean square (rms) velocity is mathematically defined as

Shop Online at www.winsomecollection.co.in

$$C_{rms} = \sqrt{3RT/M} \quad \dots\dots\dots(i)$$

where R is universal gas constant, T is absolute temperature and M is the molar mass of the gas.

It is clearly evident from the expression that at constant temperature rms speed is going to be constant.

If the gas is considered to be an ideal gas equation (i) can be rewritten as follows

$$V_{(rms)} = \sqrt{3RT/M} = \sqrt{3Pv/M} \quad \dots\dots\dots(ii)$$

since for 1 mole of an ideal gas $Pv = RT$, where P and v are pressure and volume of the gas respectively.

now when pressure is doubled at constant temperature then volume becomes half and the product Pv remains constant (Boyle's law) and hence rms speed remains same. The effect of temperature and pressure for most probable and average speeds a similar explanation can be apply as above.

Q.26. Write short note on collision frequency and mean free path. (2018)

Ans. **Collision Number:-**

It can be shown on kinetic considerations that in a gas the number of molecules with which a single molecule will collide per unit time is given by $\sqrt{2} \pi d^2 \bar{v} \cdot \rho$ where $\bar{v}$ is the average velocity of the molecules and ρ is the number density, i.e., the number of molecules per unit volume of the gas. This expression, evidently, gives the number of collisions suffered by a single molecule per unit time per unit volume of the gas. This is known as the collision number. Thus

$$Z_1 = \sqrt{2} \pi d^2 \bar{v} \cdot \rho \quad \dots\dots\dots(i)$$

The total number of molecules colliding per unit time per unit volume of the gas is, therefore given by $\sqrt{2} \pi d^2 \bar{v} \cdot \rho$. Since each collision involves two molecules, the number of collisions of like molecules occurring per unit time per unit volume of the gas is given by

$$Z_{11} = \frac{1}{2} (\sqrt{2} \pi d^2 \bar{v} \rho^2) = \frac{1}{\sqrt{2}} (\pi d^2 \bar{v} \rho^2) \quad \dots\dots\dots(ii)$$

Collision Frequency - The number Z_{11} in eq.(ii) gives the collision frequency of the gas. Thus, **collision frequency** is the number of the molecular collision occurring per unit time per unit volume of the gas.

It readily follows that the number of collisions of molecules of type 1 with those of type 2, would be given by

$$Z_{12} = \frac{1}{\sqrt{2}} (\pi d^2 \bar{v} \rho_1 \rho_2) \quad \dots\dots\dots(iii)$$

For more details Visit Us At - www.winsomepublication.in

where r_1 and r_2 are the number densities of molecules of type 1 and 2, respectively. The number density ρ is equal to P/kT , as shown below:

For an ideal gas, $PV = nRT = nN_A kT$

$$P = nN_A kT/V = NkT/V \quad \dots\dots\dots(iv)$$

where $N (= nN_A)$ is the total number of molecules in n moles of the gas. Since N is the number of molecules per unit volume, hence $\rho = N/V$. Thus, $P = \rho kT$.

$$\rho = P/kT$$

Eq.(i) and (ii) may thus be written as

$$Z_1 = \sqrt{2} \pi d^2 \gamma P / kT \quad \dots\dots\dots(v)$$

$$\text{and } Z_{11} = \frac{\pi d^2 \gamma P^2}{\sqrt{2} (kT)^2} \quad \dots\dots\dots(vi)$$

It may be noted that while units of Z_1 are s^{-1} , those of Z_{11} are $s^{-1}m^{-3}$.

Mean Free Path :-

At a given temperature, a molecule travels in a straight line before collision with another molecule. The distance travelled by the molecule before collision is termed free path. The free path for a molecule varies from time to time. The mean distance travelled by a molecule between two successive collisions is called the Mean Free Path. It is denoted by λ . If l_1, l_2, l_3 are the free paths for a molecule of a gas, its free path

$$\lambda = \frac{l_1 + l_2 + l_3 + \dots\dots\dots + l_n}{n}$$

where n is the number of molecules with which the molecule collides. Evidently, the number of molecular collisions will be less at a lower pressure, lower density and longer will be the mean free path. The mean free path is also related to the viscosity of the gas

The mean free path, λ , is given by the expression

$$\frac{\eta}{Z} = \lambda = \eta \sqrt{\frac{3}{P d}}$$

where P = pressure of the gas, d = density of the gas, η = coefficient of viscosity of the gas

Q.27. Show that mean free path is inversely proportional to pressure. (2019)

Ans. The average distance covered by a molecule between two successive collisions is called mean free path and is denoted by λ .

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 n}$$

where n = no. of molecules/cc. Again, if P and T denote the pressure and temperature of the gas, from kinetic theory,

$$P \times 10^{-3} = nRT/N_A$$

Shop Online at www.winsomecollection.co.in

$$n = \frac{N_0 \times 10^{-3}}{R} \times \frac{P}{T} = K' \left(\frac{P}{T} \right)$$

$$\lambda = \frac{1 \times T}{\sqrt{2} \pi \sigma^2 K' P} = K_1 \left(\frac{T}{P} \right)$$

Thus mean free path is directly proportional to temperature and inversely to pressure.

Q.28. Show that excluded volume for each molecule of a gas is four times the actual volume of each molecule. (2019)

Ans. Consider the molecules A and B of equal radius r of any gas. Two molecules when touching from any direction will always have their centres separated by $2r$. This means that effective volume occupied by two molecules

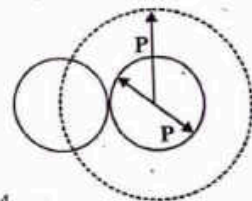
$$\text{is } \frac{4}{3} \pi (2r)^3 \text{ i.e. } 8 \cdot \frac{4}{3} \pi r^3$$

The effective volume occupied by

$$\text{each molecule} = \frac{1}{2} \cdot 8 \cdot \frac{4}{3} \pi r^3 = 4 \cdot \frac{4}{3} \pi r^3$$

$$\text{The volume of the individual isolated molecule} = \frac{4}{3} \pi r^3$$

Thus the excluded volume is four times the actual volume of a molecule.



Winsome Publication

Invite writers for publishing of their books.

Interested candidates send their resume as email

winsomepublication@rediffmail.com

or

Contact Us at - 9935951901

For more details Visit Us At - www.winsomepublication.in

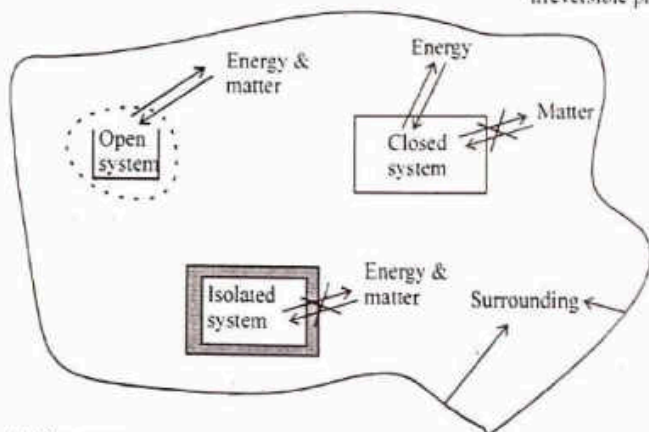
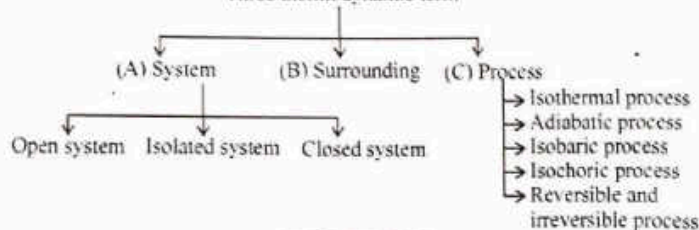
Unit II

Thermodynamics and Thermochemistry

The thermodynamics deals with the study of flow of heat, it deals with energy changes accompanying physical and chemical processes. Thermodynamics is based on three generalization called the first, second and third law of thermodynamics. These laws based on human experienced; there is no formal proof of these laws. In other word we can say, "the branch of science which deals with the study of different forms of energy and the quantitative relationships between them is known as Thermodynamics.

Terminology of thermodynamics: -

Three thermodynamic term



(A) System: -

A system will be defined as any specified portion of a matter in the universe, which is under study.

(i) Isolated system: -

A system, which can exchange neither energy nor matter with its surroundings, is called Isolated system.

(ii) Closed system: -

A system, which can exchange energy but not matter with its surrounding is called a closed system.

(iii) Open system: -

A system, which can exchange matter as well as energy with its surrounding is said to be open system, consider in the operation of water placed in a open beaker, the water vapour will exchange in to the surrounding while heat acquired. Following vaporization will be observed from the surrounding hence it is open system.

(B) Surrounding: -

The rest of the universe, which might be in a position to exchange energy and matter with the system, is called surrounding.

(C) Process: -

When a thermodynamic system changes from one state to another the operation is called a Process.

(i) Isothermal process ($\Delta T = 0$): -

A process is said to be isothermal if the temperature of the system remains constant during each step of the process that is $\Delta T = 0$.

(ii) Adiabatic process: -

A process is said to be adiabatic if no heat enters or leave the system during each step of the process that is $\Delta Q = 0$.

(iii) Isobaric process: -

A process is said to be isobaric if the pressure of the system remains constant during each step of the change in the state out the system that is $\Delta P = 0$.

(iv) Isochoric process: -

A process is said to be isochoric if the volume of the system remains constant during each step of the process that is $\Delta V = 0$.

(v) Reversible and irreversible process: -

A process carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposite force is called a reversible process. A process, which does not take place infinitesimally slowly is said to be irreversible process.

Q.1. Write short note on extensive and intensive properties. (2009, 15)

Ans: Extensive properties: -

These are those properties, which depend upon the quantity of the matter contained in the system. The common examples of these properties are mass, volume and heat capacity. Besides these, some other properties, which is thermodynamic parameter e.g. - internal energy, enthalpy, entropy, Gibbs free energy etc.

Intensive properties: -

These are those properties, which depends only upon the nature of the substance and are independent of the amount of the substance present in the

system. The common examples of these properties are temperature, pressure, refractive index, viscosity, density, surface tension, specific heat, freezing point, boiling point etc.

Q.2 Define state functions. Explain why the quantities work (w) and heat (q) are not the state functions? (2009)

Related Questions -

Q. What do you mean by state function and path function. (Imp.)

Ans: Path function and state function:-

The physical and thermodynamic properties, which depend upon only initial and final state is termed as state function. In such case we can calculate only difference in contrast path function, which determined each and every instant. Example of state function is Internal energy (dE), Enthalpy, Entropy, free energy etc.

It is interesting to note that a state function is an exact differential while the differential of path function is inexact differential. An exact differential is that which can be integrated between appropriate limits to give a definite value. For example internal energy is state function because of

$$\int_{E_1}^{E_2} dE = E_2 - E_1$$

In contrast absorbed energy and work done are path function and which cannot be integrated.

Q.3. State the first law of thermodynamics and obtain a mathematical formulation of the law.

Related Questions -

Q. State "First law of thermodynamics". (2008, 12)

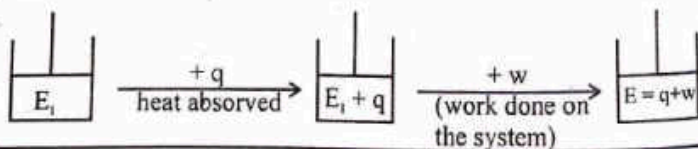
Ans: First law of thermodynamics:-

The first law of thermodynamics is simply the law of conservation of energy, which states "Energy can neither be created nor destroyed although it may be converted from one form to another." Or the total energy of the universe (i.e. system and surrounding) remains constant although it may undergo transformation from one form to another form.

Mathematical formulation:-

(i.e. relationship between internal energy work and heat).

The internal energy of a system can be increased in two ways. As given in figure.



For more details Visit Us At - www.winsomepublication.in

- (i) By supplying heat to the system.
(ii) By doing work on the system.

Suppose the internal energy of the system = E_1
If it absorbed heat q , its internal energy become = $E_1 + q$
If further work w is done on the system, the internal energy will further increase and become = $E_1 + q + w$.

Let us call this final internal energy as E_2 then

$$E_2 = E_1 + q + w \quad \text{or} \quad E_2 - E_1 = q + w$$

$$\text{Or } \Delta E = q + w$$

Above equation is mathematical formulation of the 1st law of thermodynamics.

If the work done is the work of expansion, then w would be (-) sign.

Hence above equation is as

$$\Delta E = q - w$$

$$\therefore w = P\Delta V$$

$$\Rightarrow \Delta E = q - P\Delta V$$

Q.4 Find the expression for work done in isothermal reversible expansion.

Ans. Isothermal Reversible Expansion:-

Reversibility and maximum work:- Let us consider an ideal gas kept in a cylinder fitted with frictionless and weightless piston. The external pressure applied on the gas is P , suppose the gas expands (V increase) reversibility from V_1 to V_2 at constant T .

$$dW_{\text{rev}} = (P - dP)A \cdot dl \quad \dots\dots(1)$$

dl is infinitesimally small displacement of piston, A = cross-section,

since $A \cdot dl = dV$

$$\text{Hence } dW_{\text{rev}} = (P - dP)dV$$

$\therefore dP$ is very-very small so it is neglected.

$$dW_{\text{rev}} = PdV \quad \dots\dots(2)$$

total amount of work done by the gas will be obtained by integrating eq(2).

$$\int dW_{\text{rev}} = \int_{V_1}^{V_2} PdV \Rightarrow W_{\text{rev}} = \int_{V_1}^{V_2} PdV \quad \left[\because \text{for one mole of an ideal gas} \right]$$

$$PV = RT \Rightarrow P = \frac{RT}{V}$$

since T is constant.

$$W_{\text{rev}} = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT(\ln V)_{V_1}^{V_2} = RT(\ln V_2 - \ln V_1)$$

$$\Rightarrow W_{\text{rev}} = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{V_1}{V_2}$$

$$\text{At constant } T \quad P_1 V_1 = P_2 V_2 \Rightarrow \frac{V_1}{V_2} = \frac{P_2}{P_1}$$

Shop Online at www.winsomecollection.co.in

Substituting in eq.(1) we get

$$q_p = q_v + \Delta nRT$$

Q.7. Show that for a constant volume process $dq = dE$ and for a constant pressure process $dq = dH$. (2016)

Ans. If we use the definition of the enthalpy H of a gas:

$$H = E + P V$$

Then: $dH = dE + PdV + V dP$

Substitute into the first law equation:

$$dq = dH - V dP - PdV + PdV$$

$$dq = dH - V dP$$

is an alternate way to present the first law of thermodynamics. For an ideal gas, the equation of state is written:

$$PV = R T$$

where R is the gas constant. The heat transfer of a gas is equal to the heat capacity times the change in temperature; in differential form:

$$dq = C dT$$

If we have a constant volume process, the formulation of the first law gives:

$$dE = dq = C (constant volume) dT$$

Similarly, for a constant pressure process, the formulation of the first law gives:

$$dH = dq = C (constant pressure) dT$$

Q.8. Show that the decrease in Gibbs free energy at constant temperature and pressure is equal to the net work over and above the mechanical work. (Imp.)

Ans: Energy of the system, which does not increase even in isothermal and isobaric process, is called as Gibbs free energy or thermodynamical potential.

The free energy G is defined by the relation

$$G = H - TS \quad \dots\dots\dots(1)$$

The values G , H and S depend on the state of the system. If three function of the eq.(1) at on constant temperature in two different states of the system are G_1 , H_1 , S_1 and G_2 , H_2 , S_2 then by relation we have

$$G_1 = H_1 - TS_1 \quad \dots\dots\dots(ii)$$

$$G_2 = H_2 - TS_2 \quad \dots\dots\dots(iii)$$

Subtracting eq.(ii) by eq.(iii) we get

$$G_2 - G_1 = H_2 - H_1 - TS_2 + TS_1$$

$$\Delta G = \Delta H - T\Delta S \quad \dots\dots\dots(iv)$$

As we know $\Delta H = \Delta E + P\Delta V$

Putting the value of ΔH in eq.(iv) we get

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad \dots\dots\dots(v)$$

Another relation as we know i.e. $\Delta A = \Delta E - T\Delta S$

Putting ΔA value in eq.(v) we get

$$\Delta G = \Delta A + P\Delta V \quad \dots\dots\dots(vi)$$

And also $\Delta A = - W_{rev}$ Putting ΔA value in eq.(vi) we get

.....(vii)

Using the first law of thermodynamics, show that

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v \text{ and } C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (2006, 18)$$

Show that $C_p - C_v = R$ for one mole of an ideal gas. (2016)

Heat capacity:-

It is the capacity of the system to absorb and store the energy. It is defined, as the heat required to increasing the temperature of the system by one degree.

It is expressed in two-way (a) specific heat (b) molar heat capacity.

Specific heat - The amount of heat absorbed by 1 gm of a substance to raise its temperature by 1°C it is defined by C hence

$$C = \frac{q}{m(T_2 - T_1)}$$

Where q = heat absorbed by m gm of substance to increase its temperature from T_1 to T_2 .

Molar heat capacity:-

The amount of heat absorb by one mole of substance to raise its temperature by 1°C, it is denoted by C.

The heat capacity is the rate of change of heat with T that is

$$C = \frac{dq}{dT} \quad \left[\text{from the first law of thermodynamics} \right] \\ \Rightarrow C = \frac{dE + PdV}{dT} \quad [dq = dE + PdV] \quad \dots\dots\dots(1)$$

At constant volume $dV = 0$

$$\text{(2007 equation (1) becomes } C = \frac{dE}{dT} \quad \dots\dots\dots(2)$$

In terms of partial differential eq.(2) become

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v$$

At constant pressure from eq.(1)

$$C = \frac{dE + PdV}{dT}$$

Since P is constant

$$C = \frac{dE}{dT} + P \left(\frac{dV}{dT} \right)$$

Shop Online at www.winsomecollection.co.in

$$\Delta G = -W_{\text{rev}} + P\Delta V$$

Multiplying both side of eq.(vii) by (-) sign

$$-\Delta G = W_{\text{rev}} - P\Delta V$$

Hence - ΔG is the measure of maximum net work that can be obtained from system at constant temperature and pressure. G is known as Gibbs free energy.

Remark:- Sign Convention -

- (i) Work done on the system, W is positive.
- (ii) Work done by the system, W is negative.
- (iii) Heat absorbed by the system, q is positive.
- (iv) Heat given out by the system, q is negative.

Q.9. Explain the meaning of internal energy of a system.

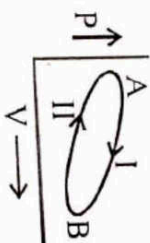
Ans: Every substance is associated with a definite amount of energy, which depends upon its chemical nature or temperature pressure, and volume the energy is known as intrinsic or internal energy. The change in intrinsic energy is a measurable quantity.

Let E_A and E_B be the energies of the systems state A and B respectively. Suppose a system while undergoing change from state A to state B absorb heat q from surroundings and also performs some work equal to W the change in the internal energy ΔE accompanying the above process will be by

$$\Delta E = E_B - E_A$$

$$\Rightarrow \Delta E = q - W \quad \dots\dots\dots(1)$$

eq.(1) is a mathematical statement of the 1st law of thermodynamics.

**Q.10. Show that for an ideal gas:**

$$\left(\frac{\partial C_v}{\partial V} \right)_T = 0$$

Related Questions:-
Q. Show that:

$$C_p - C_v = \left[P + \left(\frac{\partial E}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P \quad (2010, 13, 15)$$

Q. Define 'heat capacity' of a system and obtain expression for heat capacities at constant volume and constant pressure. Show that for ideal gas

$$C_p - C_v = R$$

(2008, 2011)

Q. Heat capacity of a system is defined as

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

$$\Rightarrow C_p = \left(\frac{\partial E}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p \quad \dots(4)$$

Now $H = E + PV$

Differentiating this eq. with respect to temperature at constant P we get

$$\left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial E}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p \quad \dots(5)$$

Comparing equation (4) and eq.(5) we get

$$\Rightarrow C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

Relation between C_p and C_v :-

The heat capacity is the rate of change of heat with temperature.

From the first law of Thermodynamics

$$dq = dE + PdV \Rightarrow C = \frac{dE + PdV}{dT}$$

Since P is constant hence

$$C_p = \left(\frac{\partial E}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p$$

$$\text{Also } C_v = \left(\frac{\partial E}{\partial T} \right)_v$$

$$\Rightarrow C_p - C_v = \left(\frac{\partial E}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial E}{\partial T} \right)_v \quad \dots\dots(1)$$

We know that E is the state function and is regarded as a function of any two of variables P, V and T. If we write E as a function of V and T, then

$$E = f(V, T)$$

Hence change in E i.e. dE can be expressed as

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

Dividing this equation by dT, keeping P as a constant, we get

For more details Visit Us At - www.winsomepublication.in

$$\left(\frac{\partial E}{\partial T} \right)_p = \left(\frac{\partial E}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p \quad \dots\dots\dots(2)$$

from eq. (1) and eq. (2)

$$C_p - C_v = \left(\frac{\partial E}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p \quad \dots\dots\dots(3)$$

For an ideal gas -

i) The variation of E with respect to V at constant T is zero. That is

$$\left(\frac{\partial E}{\partial V} \right)_T = 0 \quad \dots\dots\dots(4)$$

ii) For 1 mole of gas

$$PV = RT$$

Differentiating with respect to T at constant pressure, we get

$$P \left(\frac{\partial V}{\partial T} \right)_p = R \left(\frac{\partial T}{\partial T} \right)_p \Rightarrow P \left(\frac{\partial V}{\partial T} \right)_p = R \quad \dots\dots(5)$$

from eq.(3), (4) and (5) we get

$$C_p - C_v = R$$

Alternate derivation of $C_p - C_v = R$

$$\text{As } H = E + PV$$

Differentiating with respect to T

$$\frac{dH}{dT} = \frac{dE}{dT} + \frac{d(PV)}{dT}$$

For one mole of gas $PV = RT$

$$\Rightarrow \frac{dH}{dT} = \frac{dE}{dT} + \frac{d(RT)}{dT} = \frac{dE}{dT} + R \frac{dT}{dT} = \frac{dE}{dT} + R$$

$$\therefore \frac{dH}{dT} = C_p \text{ and } \frac{dE}{dT} = C_v$$

$$\Rightarrow C_p = C_v + R$$

$$\Rightarrow C_p - C_v = R$$

Q.11. What is the inversion temperature and deduce the Joule Thomson effect. (Imp.)

Other Related Questions-

Q. Write short notes on inversion temperature. (2014)

Q. Explain Joule-Thomson coefficient. (2017)

Ans: Joule Thomson effect:-

If a stream of gas at high pressure is allowed to expand by passing through a porous plug into a vacuum on a region of low pressure it gets cool.

Shop Online at www.winsomecollection.co.in

the temperature below which a gas become cooler on expansion is known as Inversion Temperature (T_i).
The change of temperature produced when gas is made to expand from a region of high pressure to a region of extremely low pressure is known as Joule Thomson Effect. The cooling effect is due to decrease in the kinetic energy of the gases molecules since a part of this energy is used up in overcoming van der Waals forces of attraction existing between the molecules during expansion. Joule Thomson effect is very small when a gas approaches ideal behaviour, Joule Thomson effect is zero. Thus when an ideal gas expands in a vacuum, there is neither absorption nor evolution of heat i.e. ($Q = 0$) further when an ideal gas expand in a vacuum it does no work, hence $W = 0$.

Then $H = f(T)$
On differentiating

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

The condition of μ_{JT} effect is

$$dH = 0$$

By definition of C_P

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

from the above eq. we get

$$0 = C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \Rightarrow C_P dT = - \left(\frac{\partial H}{\partial P} \right)_T dP$$

$$\Rightarrow \frac{dT}{dP} = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T \Rightarrow \left(\frac{dT}{dP} \right)_H = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T$$

$$\Rightarrow \mu = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T \dots \dots \dots (iv)$$

In eq. (4) $\left(\frac{\partial H}{\partial P} \right)_T$ is a measure of intermolecular forces in the gas. Hence

sign of μ depends on sign of $\left(\frac{\partial H}{\partial P} \right)_T$ thus if

i) $\left(\frac{\partial H}{\partial P} \right)_T$ is positive then μ will be negative.

ii) $\left(\frac{\partial H}{\partial P} \right)_T$ is negative then μ will be positive.

Q.12. On account of Joule Thomson experiment so that the Joule Thomson Effect is Isoenthalpic and derive Joule Thomson coefficient. (1m)

Other Related Questions -
Q. Explain Joule Thomson coefficient. (20)

Q. Write short note on Joule - Thomson Coefficient. (2016)

Ans: Joule Thomson Coefficient (μ_{JT}):-

The experimental technique used by Joule Thomson for deriving mathematical relation between the lowering of temperature and the fall of pressure of a gas expansion is shown in figure.

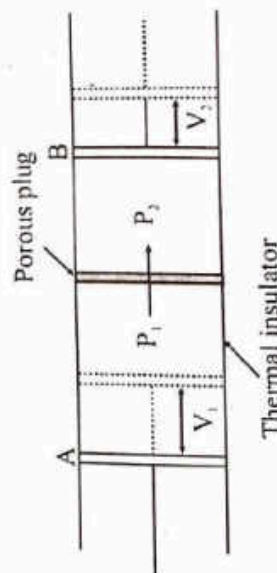


Fig. - Joule Thomson Experiment

A tube made of non-conducting material is fitted with a porous plug in which a tube between the two piston A and B

Work done on the system at piston A = $P_1 V_1$

Work done by the system at piston B = $P_2 V_2$

Net work done by the system = $P_2 V_2 - P_1 V_1$ (1)

Since the expansion of the gas has taken place adiabatically the internal energy of the system falls from E_1 to E_2 i.e. $q = 0$

$$\therefore \Delta E = q - w \Rightarrow \Delta E = -w \dots \dots \dots (2)$$

From eq. (1) and eq. (2) we get

$$E_1 - E_2 = P_2 V_2 - P_1 V_1 \Rightarrow E_1 + P_1 V_1 = E_2 + P_2 V_2$$

For more details Visit Us At - www.winsomepublication.in

Using another approximation for real gas

$$V = \frac{RT}{P}$$

then eq.(ii) becomes

$$V = \frac{RT}{P} - \frac{a}{P \times \frac{RT}{P}} + b \Rightarrow V = \frac{RT}{P} - \frac{a}{RT} + b$$

Differentiating this eq. with respect to T at constant pressure we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \left(\frac{\partial T}{\partial T}\right)_P - \frac{a}{R} \left(\frac{\partial T^{-1}}{\partial T}\right)_P + \left(\frac{\partial b}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} + 0 \quad \dots\dots\dots(iii)$$

writing eq.(i) again

$$PV = RT - \frac{a}{V} + Pb \Rightarrow RT = PV - Pb + \frac{a}{V}$$

Using another approximation for real gas

$$V = \frac{RT}{P}$$

$$RT = P(V-b) + \frac{aP}{RT}$$

Dividing by PT we get

$$\frac{R}{P} = \frac{V-b}{T} + \frac{a}{RT^2} \quad \dots\dots\dots(iv)$$

From eq.(iii) and eq.(iv) we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{a}{RT^2} + \frac{a}{RT^2} = \frac{V-b}{T} + \frac{2a}{RT^2}$$

Multiplying both sides by T

$$T\left(\frac{\partial V}{\partial T}\right)_P = (V-b) + \frac{2a}{RT}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b \quad \dots\dots\dots(v)$$

Q.13. Explain Joule-Thomson coefficient. Deduce expression for Joule-Thomson coefficient for real gases in terms of van der Waals constants 'a' and 'b'. (2007)

Other Related Questions -

Q. Explain Joule-Thomson coefficient.

Show that the Joule-Thomson coefficient for a Van der Waals gas is given by :

$$\mu_{J,T} = \frac{1}{C_p} \left(\frac{a}{RT} - b \right). \quad (2010)$$

Q. Define Joule Thomson Coefficient. Prove that for a Vander Wall Gas the Joule Thomson Coefficient is given by $\frac{1}{C_p} \left[\frac{2a}{RT} - b \right]$.

Q. Give a thermodynamic analysis of Joule Thomson Coefficient and show that for a perfect gas Joule Thomson Coefficient vanishes and give heating and cooling effects for real gas.

Q. Define inversion temperature. Show that for a van der Waals gas, the inversion temperature is given by $T_i = \frac{2a}{Rb}$. (2013)

Q. Explain Joule-Thomson coefficient and show that of an ideal gas. (2015)

Q. Show that for an ideal gas the Joule-Thomson coefficient ($\mu_{J,T}$) is zero while for a gas obeying Van der Waals equation, it is given by

$$\mu_{J,T} = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right) \quad (2017)$$

Ans: The magnitude of effect is expressed in terms of Joule Thomson Coefficient (μ), which is defined as the rate of change in temperature with pressure at constant enthalpy mathematically defined as

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H$$

Vander Wall equation for 1 mole of gas is

$$\left(P + \frac{a}{V^2} \right) (V-b) = RT \Rightarrow PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

since a and b are small then $\frac{ab}{V^2}$ can be neglected.

$$PV = RT - \frac{a}{V} + Pb \quad \dots\dots\dots(i)$$

$$\Rightarrow V = \frac{RT}{P} - \frac{a}{PV} + b \quad \dots\dots\dots(ii)$$

By the definition of enthalpy

$$H = E + PV \Rightarrow dH = dE + PdV + VdP \quad \text{.....(vi)}$$

From second law of thermodynamics

$$dS = \frac{dq}{T} \quad \text{.....(vii)}$$

But from first law of thermodynamics

$$dq = dE + PdV \quad \text{.....(viii)}$$

$$\Rightarrow dS = \frac{dE + PdV}{T} \Rightarrow TdS = dE + PdV$$

substituting the value in eq.(vi) we get

$$dH = TdS + VdP \quad \text{.....(ix)}$$

$$VdP = dH - TdS$$

$$\Rightarrow V = \left(\frac{\partial H}{\partial P} \right)_T - T \left(\frac{\partial S}{\partial P} \right)_T \quad \text{.....(x)}$$

But we know that

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad [\text{Maxwell Relation}]$$

Putting this value in eq.(x) we get

$$V = \left(\frac{\partial H}{\partial P} \right)_T + T \left(\frac{\partial V}{\partial T} \right)_P \quad \text{.....(xi)}$$

From eq.(v) and eq.(xi) we get

$$- \left(\frac{\partial H}{\partial P} \right)_T = \frac{2a}{RT} - b \quad \text{.....(xii)}$$

$$\therefore \mu = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T \quad \text{.....(xiii)}$$

From eq.(xii) and eq. (xiii) we get

$$\mu = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right)$$

Now we can conclude that if

$$(i) \frac{2a}{RT} > b \text{ then } \mu \text{ is positive.}$$

$$(ii) \frac{2a}{RT} < b \text{ then } \mu \text{ is negative.}$$

For more details Visit Us At - www.winsomepublication.in

$$(iii) \frac{2a}{RT} = b \text{ then } \mu = 0$$

the temperature under this condition is called inversion temperature denoted by T_i . Hence

$$\text{when } \mu = 0 \text{ then } \frac{2a}{RT_i} = b$$

$$\Rightarrow T_i = \frac{2a}{Rb}$$

Joule Thomsan Coefficient For Ideal Gas:-

The enthalpy is given by the relation

$$H = E + PV \quad \text{.....(i)}$$

Now substituting the eq.(i) in eq. $C_p \left(\frac{\delta T}{\delta P} \right)_H = - \left(\frac{\delta H}{\delta P} \right)_T dP$, we get

$$\left(\frac{\delta T}{\delta P} \right)_H = - \frac{1}{C_p} \left[\frac{\delta(E + PV)}{\delta P} \right]_T \quad \text{.....(ii)}$$

$$\left(\frac{\delta T}{\delta P} \right)_H = - \frac{1}{C_p} \left[\left(\frac{\delta E}{\delta P} \right)_T + \left(\frac{\delta PV}{\delta P} \right)_T \right]$$

Multiplying and dividing the first factor of right hand side by δV ,

$$\left(\frac{\delta T}{\delta P} \right)_H = - \frac{1}{C_p} \left[\left(\frac{\delta E}{\delta V} \right)_T \left(\frac{\delta V}{\delta P} \right)_T + \left(\frac{\delta PV}{\delta P} \right)_T \right]$$

In case of ideal gas,

$$\left(\frac{\delta E}{\delta V} \right)_T = 0 \quad \text{from eq.(ii)}$$

$$\left(\frac{\delta T}{\delta P} \right)_H = - \frac{1}{C_p} \left(\frac{\delta(PV)}{\delta P} \right)_T \quad \text{.....(iii)}$$

At constant temperature,

$$PV = \text{constant}$$

$$\text{Hence } \left(\frac{\delta(PV)}{\delta P} \right)_T = 0, \text{ putting in eq.(iii)}$$

$$\left[\frac{\delta T}{\delta P} \right]_H = 0 = \mu_{JT} \quad \text{.....(iv)}$$

Shop Online at www.winsomecollection.co.in

Thus for an ideal or perfect gas, Joule-Thomson-Coefficient is zero,

Q.14. Calculate the work done during reversible isothermal expansion of one mole of an ideal gas at 27°C from a volume of 15 dm³ to a volume of 30 dm³ ($R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$).

Ans. $W = -nRT \ln \frac{V_2}{V_1}$

$n = 1 \text{ mole}$ $T = 27 + 273 = 300 \text{ K}$

$V_1 = 15 \text{ dm}^3$

$V_2 = 30 \text{ dm}^3$

$R = 8.314 \text{ KJ}^{-1} \text{ mole}^{-1}$

$$W = -2.303nRT \log \frac{V_2}{V_1} = -2.303 \times 1 \times 8.314 \times 300 \log \frac{30}{15}$$

$W = -1728.98 \text{ J}$

Q.15. Calculate the work done during reversible isothermal expansion of one mole of an ideal gas at 37°C from a volume of 20 dm³ to a volume of 30 dm³ ($R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$). (2011)

Ans. $W = -nRT \ln \frac{V_2}{V_1} = -(1 \text{ mole}) (8.314 \text{ JK}^{-1}) (310) \ln \left(\frac{30 \text{ dm}^3}{20 \text{ dm}^3} \right)$

$$= -(2.303 \times 1 \times 310 \times 8.314) \log \frac{3}{2} = -1045.2 \text{ J}$$

Q.16. Show that for an ideal gas $\left(\frac{\partial H}{\partial P} \right)_T = 0$. (2011)

Ans. For an ideal gas

$$H = E + PV$$

For Ideal gas $PV = nRT$

So $H = E + nRT$

Since E is a function of T for Ideal gas

$$E = f(T)$$

Hence, $H = f(T) + nRT$ (i)

Equation (i) means that H is a function of T , i.e.

$$H = f(T) \text{(ii)}$$

Differentiating eq.(ii) with respect to P at constant T , we get

$$\left(\frac{\partial H}{\partial P} \right)_T = 0$$

Q.17. Compare isothermal and adiabatic expansion of an ideal gas and
For more details Visit Us At - www.winsomepublication.in

show that

(i) $P_{\text{adiab.}} < P_{\text{iso.}}$ and (ii) $V_{\text{adiab.}} < V_{\text{iso.}}$ (2011)

Ans. Let us consider isothermal and adiabatic expansion of an ideal gas from initial volume V_o and pressure P_o to a common final volume V_f . If P_{iso} and $P_{\text{adiab.}}$ are the final pressures, then

$$P_o V_o = P_{\text{iso}} V_f \quad \text{for isothermal expansion}$$

$$\text{and } P_o V_o^\gamma = P_{\text{adiab.}} V_f^\gamma \quad \text{for adiabatic expansion}$$

Accordingly $V_f/V_o = P_o/P_{\text{iso}}$ (i)

and $(V_f/V_o)^\gamma = P_o/P_{\text{adiab.}}$

Since for expansion $V_f > V_o$ and also for all gases $\gamma > 1$, hence

$$(V_f/V_o)^\gamma > (V_f/V_o) \quad \text{.....(ii)}$$

$$P_o/P_{\text{adiab.}} > P_o/P_{\text{iso.}} \text{ or } P_{\text{adiab.}} < P_{\text{iso.}} \quad \text{.....(iii)}$$

The above conclusion receives support from the argument that since adiabatic expansion, there is a fall of temperature, hence, according to the Charles law ($P \propto T$ at constant V), there is a corresponding fall of pressure so that $P_{\text{adiab.}} < P_{\text{iso.}}$

Now let us consider the expansions in which the final pressure P_f is the same in both cases. If V_{iso} and $V_{\text{adiab.}}$ are the final volumes in isothermal and adiabatic expansions, respectively, then

$$P_o V_o = P_f V_{\text{iso}} \quad \text{for isothermal expansion}$$

and $P_o V_o^\gamma = P_f V_{\text{adiab.}}^\gamma$ for adiabatic expansion

Accordingly, $P_o/P_f = V_{\text{iso}}/V_o$ and $P_o/P_f = (V_{\text{adiab.}}/V_o)^\gamma$ (iv)

for eq.(vi) $V_{\text{iso}}/V_o = (V_{\text{adiab.}}/V_o)^\gamma$ (v)

or $\ln(V_{\text{iso}}/V_o) = \gamma \ln(V_{\text{adiab.}}/V_o)$

Since $\gamma > 1$, it follows that

$$V_{\text{adiab.}}/V_o < V_{\text{iso}}/V_o \text{ or } V_{\text{adiab.}} < V_{\text{iso.}} \quad \text{.....(vi)}$$

This conclusion also receives support from the argument that since in adiabatic expansion, there is a fall of temperature, hence according to the Charles law ($V \propto T$ at constant P), there is a corresponding decrease in volume so that $V_{\text{adiab.}} < V_{\text{iso.}}$

Q.18. Write short note on cyclic rule. (2012, 13, 18)

Ans. Consider the set of state variables $\{x, y, z\}$, of which any two may be considered independent. The differentials dx and dy then become

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz$$

$$dy = \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz$$

so that $dx = \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z dx + \left[\left(\frac{\partial x}{\partial z} \right)_y + \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \right] dz$

This relationship applies to any $\{dx, dy\}$. In particular, if we choose to make $dz = 0$, then the coefficients of dx must be equal. Hence, we obtain the familiar chain rule

Shop Online at www.winsomecollection.co.in

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

which can be extracted to an arbitrary number of derivatives, all evaluated with the same constraints, simply by linking each denominator with the next numerator until the chain is closed upon itself; e.g.

$$\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_w \left(\frac{\partial z}{\partial s}\right)_w \left(\frac{\partial s}{\partial t}\right)_w \left(\frac{\partial t}{\partial w}\right)_s = 1$$

Alternatively, if we choose $dx = 0$, then the coefficient of dz must vanish, so that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_s \left(\frac{\partial z}{\partial x}\right)_s = -1$$

This relation is known as cyclic rule.

Q.19. One mole of an ideal gas is expanded isothermally and reversibly at 27°C from a volume of 2.28 m^3 to 4.56 m^3 . Calculate q , w , ΔE and ΔH for this process. (2012)

Sol. Temperature $T = 27^\circ\text{C} = 27 + 273 = 300\text{ K}$

Since the process is Isothermal,

Therefore, $\Delta E = 0$ and $\Delta H = 0$ (as for an isothermal expansion of an ideal gas $\Delta E = 0$ and $\Delta H = 0$)

As work done in reversible isothermal expansion is given by:

$$\begin{aligned} w &= -2.303nRT \ln(V_2/V_1) \\ &= -2.303(1\text{ mol})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(300\text{ K}) \log(4.56\text{ m}^3/2.28\text{ m}^3) \\ &= -1729.15\text{ J} \end{aligned}$$

From first law, $\Delta U = q + w$

Since $\Delta U = 0$, $q = -w = 1729.15\text{ J}$

Q.20. Differentiate $H = E + PV$ with respect to V at constant T to show that

$$\left(\frac{\partial H}{\partial V}\right)_T = 0 \text{ for an ideal gas.} \quad (2013)$$

Sol. We know that

$$H = E + PV$$

Differentiating w. r. t. V at constant T

$$\begin{aligned} \left(\frac{\partial H}{\partial V}\right)_T &= \left(\frac{\partial E}{\partial V}\right)_T + P \left(\frac{\partial V}{\partial V}\right)_T + V \left(\frac{\partial P}{\partial V}\right)_T \\ &= \left(\frac{\partial E}{\partial V}\right)_T + P + V \left(\frac{\partial P}{\partial V}\right)_T \end{aligned} \quad \dots(1)$$

$$\text{For an ideal gas } \left(\frac{\partial E}{\partial V}\right)_T = 0 \quad \dots(2)$$

For 1 mole of an ideal gas

$$PV = RT$$

$$PdV + VdP = RdT$$

At constant temperature, $dT = 0$

$$\therefore PdV + VdP = 0$$

$$\text{or } P + V \left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \dots(3)$$

Form equations (1); (2) and (3) we get

$$\left(\frac{\partial H}{\partial V}\right)_T = 0$$

This was to be proved.

Q.21. Explain the term bond energy. (2013, 19)

Sol. The bond energy is defined as the average amount of energy (per mole) required to break a particular bond in a molecule producing free atoms or radicals. Thus, the C - H bond energy is one fourth the amount required to dissociate 1 mole of methane (CH_4) into gaseous carbon and hydrogen atoms. It is possible that different energies are required to remove the four hydrogen atoms successively from a methane molecule and so the bond energies are mean value. Due to this reason the value of bond energy may vary from one compound to another.

Q.22. Show that $T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$. (2013, 17)

Ans. Reversible adiabatic expansion of an ideal gas -

In adiabatic changes there is no heat transfer between system and surroundings.

$$\therefore dq = 0$$

By First law of thermodynamics

$$dq = dE + PdV$$

For adiabatic process

$$0 = dE + PdV \Rightarrow PdV = -dE$$

$$\text{Since } \frac{dE}{dT} = C_V \text{ or } \Delta E = C_V \Delta T = C_V (T_2 - T_1)$$

$$\text{Hence } PdV = -C_V dT \quad \dots(i)$$

For one mole of an ideal gas

$$PV = RT \Rightarrow P = RT/V \quad \dots(ii)$$

From eq.(i) and (ii)

$$RT \left(\frac{dV}{V}\right) = -C_V dT \Rightarrow \frac{dV}{V} = -\frac{C_V}{R} \left(\frac{dT}{T}\right)$$

Integrating above eq. we get

$$\int_{V_1}^{V_2} \frac{dV}{V} = -\frac{C_V}{R} \int_{T_1}^{T_2} \frac{dT}{T} \Rightarrow \ln \frac{V_2}{V_1} = -\frac{C_V}{R} \ln \left(\frac{T_2}{T_1} \right) \quad \dots (iii)$$

$$\ln \frac{V_2}{V_1} = \ln \left(\frac{T_1}{T_2} \right)^{\frac{C_V}{R}} \Rightarrow \frac{V_2}{V_1} = \left(\frac{T_1}{T_2} \right)^{\frac{C_V}{R}}$$

$$\Rightarrow V_1 T_1^{\frac{C_V}{R}} = V_2 T_2^{\frac{C_V}{R}}$$

$$\Rightarrow V T^{\frac{C_V}{R}} = \text{constant} \quad \dots (iv)$$

Another form of eq.(iv) as follows

$$\text{From eq.(iii)} \quad \ln \frac{V_2}{V_1} = \frac{C_V}{R} \ln \left(\frac{T_1}{T_2} \right)$$

Now $C_p - C_V = R$

$$\ln \frac{V_2}{V_1} = \frac{C_V}{(C_p - C_V)} \ln \frac{T_1}{T_2} \Rightarrow \frac{C_p - C_V}{C_V} \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2}$$

$$\Rightarrow \left(\frac{C_p}{C_V} - 1 \right) \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2} \Rightarrow (\gamma - 1) \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2}$$

$$\Rightarrow \ln \left(\frac{V_2}{V_1} \right)^{\gamma-1} = \ln \frac{T_1}{T_2} \Rightarrow \left(\frac{V_2}{V_1} \right)^{\gamma-1} = \frac{T_1}{T_2}$$

$$\Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

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

Q.23. Write short notes on Bond energy and resonance energy.

(2014, 15, 19)

Other Related Questions -

Q. Explain the bond energy and resonance energy. Give applications of these energies. (2018)

Ans. The heat of formation of carbon monoxide from solid carbon and gaseous oxygen is 26.8 kcal, and so the bond energy is 210 cal. This value is much higher than the normal C=O value and it shows the presence of a triple bond. Taking the heat of formation of carbon dioxide as 94.0 cal; the energy of each C-O bond is 168 kcal. On comparing this value with the value of C=O, the possibility of resonance is found, with a triple bonded structure making an appreciable contribution. If the structure of carbon dioxide were O=C=O. The heat of formation from gaseous atomic carbon and oxygen should be about $2 \times 150 = 300$ kcal, assuming each bond to have the energy of normal C=O linkage. The heat of formation of $O^+ = C = O^-$ should involve that of a single and triple carbon oxygen bond, the former is 70 kcal, and later may be assumed

For more details Visit Us At - www.winsomepublication.in

equal to that in carbon monoxide i.e. 210 kcal, so that the total is at least 280 kcal. From these two values it appears that resonance should occur. Since the actual energy of formation of carbon dioxide is $2 \times 168 = 336$ kcal, the stabilizing energy due to resonance is about $336 - 300 = 36$ kcal mole. That is to say, as a consequence of resonance an additional 36 kcal are required to dissociate/mole of carbon dioxide into its constituent atoms.

The existence of resonance in benzene has been explained in the same way. The heat of formation from gaseous atoms is 1036 kcal, but the sum of energies of six C-H, three C-C and three C=C linkage is only 999 kcal, including a resonance energy of 40 kcal. It is of interest to compare the observed and calculated heat of formation of cyclo-hexane, the former is 1398 kcal. The comparison of observed and calculated bond energies was used by L. Pauling and J. Sherman to evaluate the resonance energies in a number of organic compounds.

Resonance energy = Actual or experimental heat of formation - heat of formation calculated from bond energy data.

Q.24. Show that the work done by the system in an isothermal reversible expansion of an ideal gas is greater than the work done in an isothermal irreversible expansion. (2017)

Ans. Isothermal Irreversible Expansion Of an Ideal Gas: -

When a gas expands against a constant external pressure ($P_{\text{ext}} = \text{constant}$). There is considerable difference between the gas pressure (inside the cylinder) and the external pressure. The temperature does not change during this process.

$$W = -\int_{V_1}^{V_2} P_{\text{ext}} dV = -P_{\text{ext}} \int_{V_1}^{V_2} dV = -P_{\text{ext}} (V_2 - V_1) = -P_{\text{ext}} \Delta V$$

Work done in Isothermal Reversible Expansion of an Ideal Gas: -

As a small amount of work done δW on reversible expansion of a gas through a small volume dV against an external pressure 'P' can be given as $dW = -PdV$

So the total work done when the gas expands from initial volume V_1 to final volume V_2 is given as

$$\int dW = \int_{V_1}^{V_2} PdV$$

As according to ideal gas equation $PV = nRT$

$$P = \frac{nRT}{V}$$

So $W_{\text{rev}} = \int_{V_1}^{V_2} nRT dV$ (as temperature is constant)

$$\text{So } W_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -2.303nRT \log_{10} \left(\frac{V_2}{V_1} \right)$$

Shop Online at www.winsomecollection.co.in

$$W_{\text{rev}} = -2.303nRT \log_{10} \left(\frac{P_1}{P_2} \right)$$

Here negative sign indicates work of expansion and it is maximum and greater than work in the irreversible process.

Q.25. Show that:

$$q_p = q_v + \Delta n_g RT \quad (2017)$$

Ans. For a reaction at constant pressure, such as that taking place in an open coffee-cup calorimeter, the heat flow is equal to the change in enthalpy. If a reaction is carried out at constant volume (as is the case in a sealed bomb calorimeter) and there is no mechanical or electrical work involved, no work is done. Under these conditions, with $w = 0$, the heat flow is equal to the change in energy, ΔE . Hence we have

$$\Delta H = q_p \quad \Delta E = q_v \quad \dots\dots(i)$$

(q_p = heat flow at constant pressure, q_v = heat flow at constant volume).

Almost always, when you carry out a reaction in the laboratory, you do so at constant pressure, that of the atmosphere.

We can obtain a relation between ΔH and ΔE for a chemical reaction at constant temperature by starting with defining equation relating enthalpy, H , and energy E

$$H = E + PV$$

Where V is the volume at pressure P . It follows that

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

To evaluate $\Delta(PV)$ for a reaction note that

the PV product for a liquid or solid can be ignored, since their molar volume is

- typically only about 0.1 of that for a gas.
- gasses taking part in the reaction can be assumed to obey the ideal gas law, $PV = nRT$.

It follows that

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

where Δn_g is the change in number of moles of gas when the reaction takes place.

Finally, we obtain the relation

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

$$\Rightarrow q_p = q_v + \Delta n_g RT$$

Q.26 For adiabatic reversible expansion of an ideal gas, show

$$\text{that: } w = n\bar{C}_v (T_2 - T_1) \quad (2017)$$

Ans. Work done in reversible adiabatic expansion of an ideal gas:

$$q_p = 0$$

$$\Delta E = w = \int_{T_1}^{T_2} n\bar{C}_v dT = n\bar{C}_v (T_2 - T_1)$$

For more details Visit Us At - www.winsomepublication.in

Q.27. Show that numerically the work in the reversible isothermal expansion of an ideal gas is greater than for a van der Waals gas. (2018)

Ans. We know that for an ideal gas, work done w is given as:

$$W_{\text{ideal}} = -nRT \ln(V_2/V_1)$$

And for 'a' van der Waals Gas, work done is given as:

$$W_{\text{vdw}} = -nRT \ln \left(\frac{V_2 - nb}{V_1 - nb} \right) + an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

If $V \gg nb$, then above equation will reduce to:

$$W_{\text{vdw}} = -nRT \ln \left(\frac{V_2}{V_1} \right) + an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

Hence, numerically

$$W_{\text{ideal}} - W_{\text{vdw}} = -an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right) = \frac{an^2 (V_2 - V_1)}{V_1 V_2}$$

Hence for the expansion of a gas, $V_2 > V_1$, which shows that numerically the work of expansion in the reversible isothermal expansion of an ideal gas is greater than van der Waals Gas.

Q.28. Calculate q , w , ΔU and ΔH for the reversible isothermal expansion of one mole of an ideal gas at 27°C from the volume 10 dm^3 to 20 dm^3 . (2019)

Ans. Temperature $T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$

Since the process is isothermal, therefore $\Delta U = 0$ and $\Delta H = 0$ (as for an isothermal expansion of an ideal gas $\Delta U = 0$ and $\Delta H = 0$).

As work done in reversible isothermal expansion is given by:

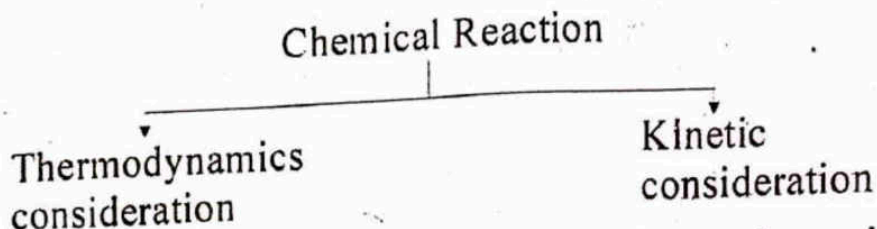
$$\begin{aligned} W &= -nRT \ln(V_2/V_1) \\ &= -(1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln(20 \text{ dm}^3/10 \text{ dm}^3) \\ &= -1728.8 \text{ J} \end{aligned}$$

From first law, $\Delta U = q + W$

Since $\Delta U = 0$, $q = -W = 1728.8 \text{ J}$

Shop Online at www.winsomecollection.co.in

Chemical Kinetics



Each chemical reaction is characterized by thermodynamic and kinetic consideration.

Chemical kinetics means about the relative stability and concentration of reactants and product at equilibrium. The studies have also been useful in working out for getting maximum yields of several industrial products that is kinetic part.

Rate of a Reaction: -

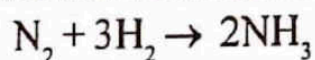
(i) $A \rightarrow \text{product}$

$$R_t = -\frac{d(A)}{dt}$$

(ii) $A + B \rightarrow C + D$

$$R_t = -\frac{d(A)}{dt} = -\frac{d(B)}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

The idea of rate in chemistry is the same as in every day life, such as the rate of flow of water through a tap, the rate at which a car travels etc. For a chemical reactions the average reaction rate may be defined as the change in the concentration of reactants and products per unit. The positive sign indicates that a concentration of products increases with the time for a reaction.



$$\text{Reaction rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

This needs to a forward definition of the reaction rate as “the time derivatives of the concentration divided by the appropriate stoichiometric coefficient and converted to constant number.”

In case of gasses reaction, since concentration of any gas component would be proportional to the partial pressure. The reaction rate can be expressed for the above reaction as

$$\text{Reaction rate} = -\frac{dp_{N_2}}{dt} = -\frac{1}{3} \frac{dp_{H_2}}{dt} = \frac{1}{2} \frac{dp_{NH_3}}{dt}$$

Q.1 Write the differential rate equations of the following reactions :

For more details Visit Us At - www.winsomepublication.in

- (i) $2A + B \rightarrow \text{Products}$
 (ii) $A + 2B + 2C \rightarrow \text{products}$
 (iii) $3A + B \rightarrow 2C + D + 2E$
 Ans. (i) $2A + B \rightarrow \text{Products}$:-

$$\text{Reaction rate} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

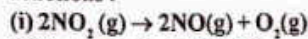
- (ii) $A + 2B + 2C \rightarrow \text{products}$:-

$$\text{Reaction rate} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = -\frac{1}{2} \frac{d[C]}{dt}$$

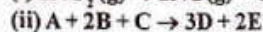
- (iii) $3A + B \rightarrow 2C + D + 2E$:-

$$\text{Reaction rate} = -\frac{1}{3} \frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} = \frac{1}{2} \frac{d[E]}{dt}$$

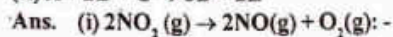
Q.2 Write the differential rate equations for the following single step reactions:



(2016)



(2006)



$$\text{Reaction rate} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$$



$$\text{Reaction rate} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = -\frac{d[C]}{dt} \\ = \frac{1}{3} \frac{d[D]}{dt} = \frac{1}{2} \frac{d[E]}{dt}$$

Q.3 Write short notes on the following:

(i) Order Of reaction.

(2004)

(ii) Molecularity of a reaction.

(2004)

(iii) Differentiation Between Order and Molecularity.

(2014)

(iv) Pseudo Order Reaction.

(Imp)

Ans. (i) Order Of reaction:-

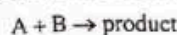
Order may be defined as sum of the power to which the concentration term should be raised in order to express the rate of reaction.

$A \rightarrow \text{product}$

$$r = K C_A^0$$

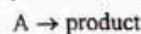
Shop Online at www.winsomecollection.co.in

Where r = rate, K = rate constant, C_A^0 concentration term.
 Above is the zero order reaction



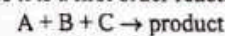
$$r = K C_A^1 C_B^1$$

since $(1+1) = 2$, hence it is a second order reaction.



$$r = K C_A^1$$

Hence it is a first order reaction



$$r = K C_A^1 C_B^1 C_C^1$$

since $(1+1+1) = 3$, hence it is a third order reaction.

as $r = K C_A^1 C_B^2$, $(1+2) = 3$ third order reaction

$$r = K C_A^3 \text{ third order reaction}$$

$$r = K C_A^2 C_B^1, (2+1) = 3 \text{ third order reaction}$$

In short if the rate of a reaction varies as the n^{th} power of concentration of A and m^{th} power of the concentration of B then the order of reaction is $(n+m)$, the order of reaction may not always be a whole number, it may be a fractional quantity also.

$$r = K C_A^n C_B^m \text{ order} = (n+m), r = K C_A^n C_B^{m/2} \text{ order} = (n+m/2)$$

(ii) Molecularity of a reaction:-

Chemical reaction may be classified in two types

(1) Elementary reaction

(2) Complex reaction

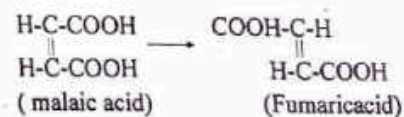
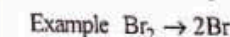
An elementary reaction is a simple reaction, which occurs, in a single step. A complex reaction is one, which occurs in two or more steps.

Molecularity of an elementary reaction:-

The molecularity of an elementary reaction is defined as the number of reactant molecules involved in a reaction, the elementary reaction having molecularity 1, 2, 3 are called unimolecular, bimolecular and termolecular reaction.

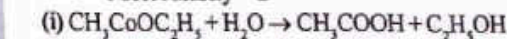
(a) Mono Molecular Reaction:-

$$\text{Molecularity} = 1$$

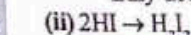


(b) Bimolecular reaction:-

$$\text{Molecularity} = 2$$



Ethy acetate acetic acid ethyl alcohol



For more details Visit Us At - www.winsomepublication.com

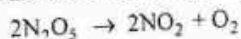
(c) Termolecular Reactions:-

Molecularity- 3

- (i) $2\text{NO} + \text{O}_3 \rightarrow 2\text{NO}_2$
 (ii) $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$

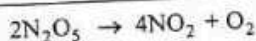
Molecularity of a Complex Reaction:-

Most complex reactions occur in a series of steps, each step is an elementary reaction. The stepwise sequence of elementary reactions that converts reactants and products is called mechanism of reaction. In any mechanism some of the steps will be fast and other will be slow. The slowest step is the rate-determining step.



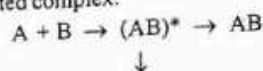
Which is a complex reaction it occurs in the following steps.

- Step I - $2\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + 2\text{NO}_3$ (fast)
 Step II - $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$ (slow)
 Step III - $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$ (fast)



Step II is the rate determining step and has molecularity 2.

By the transition state theory, which consider the formation of an activated complex from the reactants defined molecularity as equal to the number of molecules, atoms or ions of the reactants used in forming the activated complex.



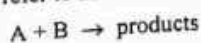
↓
activated complex

(iii) Differentiation Between Order and Molecularity:-

- (i) Order is an experimentally deduced number where as molecularity is a theoretically deduced number.
 (ii) Order and molecularity not necessarily equal for complex reactions they are generally different.
 (iii) The order of the reaction being an experimental value can be fractional where as the molecularity of the molecules participating in a reaction can be whole numbers only thus rate law for the reaction.

(iv) Pseudo Order Reaction:-

A reaction in which one of the reactant is present in a large extent shows an order different from the experimental order, which is not the actual one is referred to as "Pseudo order reaction" for e.g. let



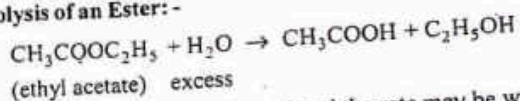
$$\text{Rate} = k[\text{A}][\text{B}]$$

Shop Online at www.winsomecollection.co.in

As 'B' is present in large excess the concentration remains constant during the reaction, thus we have

$$\text{Rate} = k'[\text{A}]$$

Thus the actual order is '2' but in practice it will be first order hence the reaction is said to be "Pseudo first order" for e.g.

Hydrolysis of an Ester:-

Here a large excess of water is used and the rate may be written as

$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$$

$$\text{Rate} = k'[\text{CH}_3\text{COOC}_2\text{H}_5]$$

The reaction is actually second order but in practice it is found to be first order hence this is a pseudo first order reaction.

Q.4 Define the terms of rate and order a reaction.

(2008, 13, 16)

Ans. (i) Rate of a Reaction:-

The rate by which concentration of reacting molecule decreases which respect to time or the rate by which concentration of product molecule increases with respect to time is called rate of reaction.

In other words the rate of reaction is defined as the change of concentration with respect to time during the course of any chemical reaction
 Unit of rate = $\text{Mole lit}^{-1} \text{sec}^{-1}$

(ii) Order of Reaction:-

The number of reactant molecule whose concentration change determines the rate of reaction is called the order of reaction.

In other words, the order of a reaction is the sum of the exponents to which the concentration terms are raised in the rate law expression. E.g.,
 order of reaction = (m + n)

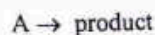
Order of reaction can be determined only on the basis of experiment. These value may be zero, whole number, fractional or even number.

Q.5 Derive expression for the rate constant of a zero order reaction.

(2006, 0)

Ans. Zero Order Reaction:-

A reaction is said to be of zero order if its rate is independent of the concentration of the reactant.



Reaction rate is given by equation

$$= \frac{d[\text{A}]}{dt} = k[\text{A}]^0 = k$$

For more details Visit Us At - www.winsomepublication.in

At any instant if 'x' is the amount of 'A' transform into products the rate of formation of products is given by

$$\frac{dx}{dt} = K[a-x]^0 = K$$

Separating the variables and integrating we get

$$x = Kt + I \quad \{I = \text{integrating constant}\}$$

When $x = 0, t = 0$ then $I = 0$

$$\text{Hence } x = Kt$$

Thus this is the general rate of equation for zero order reaction.

Characteristic of Zero Order Reaction:-

(i) The concentration of the products increases linearly with time plot of 'x' with respect of time 't' will be a straight line passing through origin.

(ii) The units of zero order rate constant K are concentration / time, $K = x/t$

e.g. photo chemical combination of H_2 and Cl_2 .

Q.6 $A \xrightleftharpoons[k_{-1}]{k_1} B$ For the above first order reversible reaction, derive the integrated rate expression

$$K = \frac{2.303}{t} \log \frac{x_e}{x_e - x}$$

where $K = (k_1 + k_{-1})$ and x_e is the concentration of B at equilibrium. (2005)

Other Related Questions -

Q. For a first-order reversible reaction $A \xrightleftharpoons[k_{-1}]{k_1} B$, derive the integrated rate expression

$$(k_1 + k_{-1}) = \frac{2.303}{t} \log \frac{X_e}{X_e - X}$$

where X_e is the concentration of B at equilibrium. (2007, 2011, 13)

Q. Derive an expression for the rate constant of a first-order reaction. (2015)

Q. Derive integrated rate equation for the rate constant of a first order reaction. (2017)

Q. Discuss the kinetics of a first order reversible reaction,

$A \xrightleftharpoons[k_{-1}]{k_1} B$ and derive the rate equation for $(k_1 + k_{-1})$ as

$$(k_1 + k_{-1}) = \frac{2.303}{t} \log \frac{x_e}{x_e - x}$$

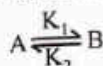
where x_e is the concentration of B at equilibrium. (2017)

Shop Online at www.winsomecollection.co.in

Q. For a first order reversible reaction $A \xrightleftharpoons[k_{-1}]{k_1} B$, derive the integrated rate expression. (2019)

Ans. kinetics of first order opposing reactions:

Opposed or reversible reaction are those reaction in which forward and backward reaction taking place simultaneously. For example,



Initial constant (when $t = 0$)

$$a \quad 0$$

constant after time t ($a - x$)

$$x$$

Equilibrium constant ($a - x$)

$$b \quad xb$$

where K_1 = velocity constant of forward reaction

K_2 = Velocity constant backward reaction.

Rate of forward reaction = $K_1(a - x)$

Rate of backward reaction = K_2x

Net rate formation of B at time t = forward rate - backward rate

$$\text{As } \frac{dx}{dt} = K_1(a - x) - K_2x \quad \text{.....(i)}$$

At the equilibrium stage $x = x_e$ and $\frac{dx}{dt} = 0$

$$\text{So } K_1(a - x_e) - K_2x_e = 0 \text{ or } K_1(a - x_e) = K_2x_e \quad \text{.....(ii)}$$

$$\text{or } K_2 = \frac{K_1(a - x_e)}{x_e} \quad \text{.....(iii)}$$

From equilibrium (i) and (iii)

$$\frac{dx}{dt} = K_1(a - x) - K_1 \frac{(a - x_e)}{x_e} x$$

$$= K_1 \left[\frac{a \cdot x_e - x \cdot x_e - ax + x \cdot x_e}{x_e} \right]$$

$$\frac{dx}{dt} = K_1 \frac{a(x_e - x)}{x_e} \quad \text{.....(iv)}$$

Integrating equation (iv)

For more details Visit Us At - www.winsomepublication.in

$$\int \frac{dx}{(x_b - x)} = \frac{aK_1}{x_b} \int dt + c$$

$$-\ln(x_b - x) = \frac{aK_1}{x_b} t + c \quad \dots\dots\dots(v)$$

when $x=0$ $t=0$

So $-\ln x_b = c$

Putting $-\ln x_b$ value in equation (v) we get.

$$-\ln(x_b - x) = \frac{aK_1}{x_b} t - \ln x_b$$

$$\ln x_b - \ln(x_b - x) = \frac{aK_1 t}{x_b}$$

$$\ln \left(\frac{x_b}{x_b - x} \right) = \frac{aK_1 t}{x_b}$$

$$K_1 = \frac{x_b}{at} \ln \left(\frac{x_b}{x_b - x} \right) = \frac{2.303x_b}{at} \log \left(\frac{x_b}{x_b - x} \right) \quad \dots\dots\dots(vii)$$

The equation (vii) give K_1 in terms of easily measured quantities.

From equation (ii)

$$K_1(a - x_b) = K_2x_b$$

$$x_b(K_1 + K_2) = aK_1$$

$$\therefore (K_1 + K_2) = \frac{aK_1}{x_b} \quad \dots\dots\dots(viii)$$

from equation (vii) & (viii) we get

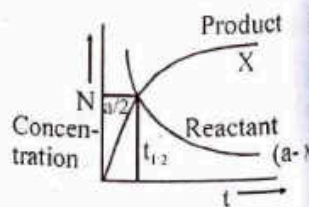
$$(K_1 + K_2) = \frac{2.303}{t} \log \left(\frac{x_b}{x_b - x} \right) \quad \dots\dots\dots(ix)$$

Characteristics of First Order Reaction: -

(I) equation (vii) shows that the concentration of the first order reaction decreases exponentially with the time for a first order reaction the concentration of the reactant decreases and that of the product increases exponentially with time as shown in the figure.

The intersection point of the two curves corresponds to the condition

$$a - x = x \Rightarrow a = 2x \quad x = a/2$$



This point corresponds to the completion of half of the reaction, the corresponding time 't' is called the half life time of the reaction, the expression for the half life time $t_{1/2}$ of the first order reaction is obtained by putting $t_{1/2}$ in place of 't' and $a/2$ in place of 'x' in eq.

$$\Rightarrow K = \frac{2.303}{t} \log \frac{a}{a-x} \Rightarrow K = \frac{2.303}{t_{1/2}} \log \frac{a}{a-a/2}$$

$$\Rightarrow t_{1/2} = \frac{2.303}{K} \log \frac{a}{a/2} \Rightarrow t_{1/2} = \frac{2.303}{K} \log 2$$

$$\Rightarrow t_{1/2} = \frac{2.303}{K} \times 0.3010 \Rightarrow t_{1/2} = \frac{0.693}{K} \quad \dots\dots\dots(viii)$$

Hence the time required for the completion of a definite fraction of the reaction is independent of initial concentration of reaction.

(2) The term $a/(a-x)$ being dimensionless, the units 'K' are independent of the units in which the concentration are measured. The units of 'K' are those of $(\text{time})^{-1}$.

$$\therefore K = \frac{2.303}{t} \log \frac{a}{a-x} \Rightarrow \frac{Kt}{2.303} = \log a - \log(a-x)$$

$$(3) \log(a-x) = \log a - \frac{Kt}{2.303}$$

$$y = C + mx$$

Thus a plot of $\log(a-x)$ Vs time t must be a straight line, the slope of line equals to $(-K/2.303)$

A few example of the reaction that obey first order reaction are

- (i) The composition of H_2O_2 in aqueous solution.
- (ii) Hydrolysis of ethyl acetate.
- (iii) Inversion of cane sugar.

$$K = \frac{2.303}{t} \log \frac{a}{a-x} \text{ can be change to}$$

For the decomposition of H_2O_2 , $K = \frac{2.303}{t} \log \frac{V_0}{V_t}$, where V_0 and V_t is the volume at t

(a) $a = 0$ and $t = t$ respectively.

(b) For the decomposition of NH_4NO_2 (Ammonium Nitrate).

$$K = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}, \text{ where } V_\infty \text{ is volume when } t = \infty$$

(c) For decomposition of ethyl acetate. $K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$

(d) For the optical rotation of sucrose in HCl. $K = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$, where r_0 is optical rotation when $t = 0$ and $t = t$ respectively.

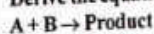
Q.7. For a second order reaction, prove that

$$k_2 = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

Other Related Question -

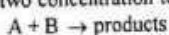
Q. Obtain an expression for the rate constant of second order reaction in which initial concentrations of the reactants are not equal.

Q. Derive the equation for a second order reaction when



Ans. **Second Order Reaction:-**

A reaction is said to be a second order reaction when its rate depends upon two concentration terms.



The reaction rate may be expressed as

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{dx}{dt} = K[A][B]$$

If 'a' and 'b' be the initial amount of A and B and at any instant x amount of each have reacted then

$$\frac{dx}{dt} = K(a-x)(b-x)$$

Where K is the rate constant for this reaction and (a-x) and (b-x) concentrations of A and B at any specific instant separating the variables

$$\frac{dx}{(a-x)(b-x)} = K dt$$

separating into partial fraction

$$\frac{1}{b-a} \left\{ \frac{dx}{a-x} - \frac{dx}{b-x} \right\} = K dt$$

Integrating and converting the logarithm to the base 10.

$$\frac{2.303}{b-a} \{-\log(a-x) + \log(b-x)\} = Kt + I$$

at $t = 0$, $x = 0$

$$I = \frac{2.303}{b-a} \log \frac{b}{a}$$

Substituting the value of I in the above eq. we get

$$Kt = \frac{2.303}{(b-a)} \left\{ \log \left(\frac{b-x}{a-x} \right) - \log \frac{b}{a} \right\}$$

$$K = \frac{2.303}{t(b-a)} \log \frac{a(b-x)}{b(a-x)} \quad \dots\dots\dots(1)$$

Equation (1) is the general rate eq. for second order reaction the reaction will not hold good when the concentration of both the reactants are equal i.e. $[A] = [B]$ or $a = b$

The differential rate expression for equal concentration of both the reactant is

$$\frac{dx}{dt} = K'(a-x)^2 \quad \Rightarrow \quad \frac{dx}{(a-x)^2} = K' dt$$

Integrating the eq. we get

$$\frac{1}{(a-x)} = K't + I$$

at $t = 0$, $x = 0$ then $I = \frac{1}{a}$

$$K't = \frac{1}{(a-x)} - \frac{1}{a} = \frac{x}{a(a-x)}$$

$$K' = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad \dots\dots\dots(2)$$

Characteristics of Second Order Reaction:-

- 1) The unit of K for a second order reaction is $\text{time}^{-1} \text{concentration}^{-1}$.
- 2) when $a \neq b$ we know that the general equation of second order rate is

$$K = \frac{2.303}{t(b-a)} \log \frac{a(b-x)}{b(a-x)}$$

the above eq. may be written as

$$\log \frac{a(b-x)}{b(a-x)} = \frac{K(b-a)}{2.303} \cdot t$$

$$y = mx$$

We see that this is the eq. of a straight line passing through origin and its slope is

$$m = \frac{K(b-a)}{2.303}$$

Q.8 How can order of a reaction be determined by Van't Hoff's differential method? (2006)

Ans. According to this method divided by the Vant Haff the rate 'r' of a nth order reaction is given by $r = K_n C^n$

Taking log we get

$$\log r = \log K_n + n \log C$$

Which is the form of $r = C + mx$

Thus if the double logarithmic ppt of rate Vs concentration give the straight line then the slope give the value of n and the intercept gives the $\log K_n$ also if r_1 and r_2 are the rates at two different reactant concentrations C_1 and C_2 then.

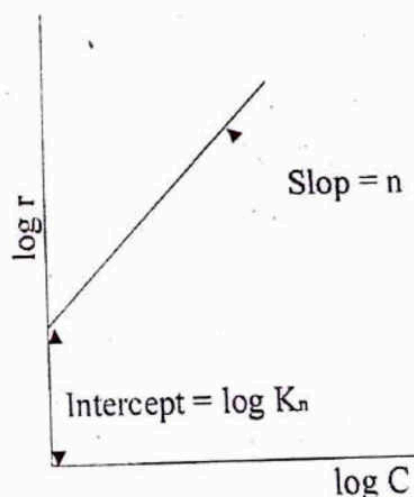
$$\frac{r_1}{r_2} = \frac{-dC_1 / dt}{-dC_2 / dt}$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{K_n C_1^n}{K_n C_2^n} = \left(\frac{C_1}{C_2} \right)^n$$

taking log we get,

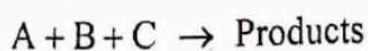
$$\log \frac{r_1}{r_2} = n \log \frac{C_1}{C_2}$$

$$n = \frac{\log \frac{r_1}{r_2}}{\log \frac{C_1}{C_2}}$$



Ostwald's Isolation Method: -

This method is used for determining the order of complicated reaction by isolating one of the reactant. Let a reaction be



The order of the reaction with respect to A, B and C is determine by taken it in large excess. The order of the reaction is then determine by using any one of the method describe earlier likewise the order of the reaction is determine with respect to B and C if n_A , n_B and n_C are the order of the reaction w.r.t. A, B and C respectively then the expression

$$n = n_A + n_B + n_C$$

Radioactive disintegration follows first order reaction: - (Imp.)

Radioactive disintegration is very similar to a chemical reaction of the first order kinetics, because its rate of reaction varies as the concentration of one molecular species only.

Let us consider a reaction



Where K = rate constant, E = energy of activation, R and T = used notations
 If K_1 and K_2 are the values of the rate constant at temperature T_1 and T_2 respectively, one can derive from Arrhenius equation.

$$\log \frac{K_2}{K_1} = \frac{E}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Q.9 Derive equation $k = Ae^{-E/RT}$ from Van't Hoff equation. Where A is the frequency factor and E is activation energy and k is the rate constant. (2017)

Ans. Derivation of Arrhenius Equation: -

Let us consider following reversible reaction



Rate of the forward reaction = $K_1 [A] [B]$, Rate of the backward reaction = $K_2 [C] [D]$

At equilibrium $K_1 [A] [B] = K_2 [C] [D]$

$$\Rightarrow \frac{K_1}{K_2} = \frac{[C] [D]}{[A] [B]} \text{ or } K_C = \frac{[C] [D]}{[A] [B]}, \text{ where } K_C = \frac{K_1}{K_2} \quad \dots\dots\dots(2)$$

As we know from the thermodynamics, Vant Haff equation

$$\frac{d \ln K_C}{dT} = \frac{\Delta E}{RT^2} \quad \dots\dots\dots(3)$$

Substituting the value of K_C from eq. (2) in eq. (3), we get

have

$$\frac{d \ln \frac{K_1}{K_2}}{dT} = \frac{\Delta E}{RT^2} \Rightarrow \frac{d \ln K_1}{dT} - \frac{d \ln K_2}{dT} = \frac{\Delta E}{RT^2} \quad \dots\dots\dots(4)$$

Vant Haff proposed that the above eq. could be split into two equation follows

$$\frac{d \ln K_1}{dT} = \frac{E_1}{RT^2} + I \quad \dots\dots\dots(5)$$

$$\frac{d \ln K_2}{dT} = \frac{E_2}{RT^2} + I \quad \dots\dots\dots(6)$$

s for a
at two
nt (K)

where $\Delta E = E_1 - E_2$ and I is constant. It was observed that I was independent of temperature. Therefore I must be equal to zero in eq.(5) and eq.(6)

$$\frac{d \ln K_1}{dT} = \frac{E_1}{RT^2} \quad \dots\dots\dots(7)$$

by the

$$\frac{d \ln K_2}{dT} = \frac{E_2}{RT^2} \quad \dots\dots\dots(8)$$

For more details Visit Us At - www.winsomepublication.com.

Integrating eq.(7) and eq.(8) we get.

$$\ln K_1 = -\frac{E_1}{RT} + \text{constant A} \quad \dots\dots\dots(9)$$

$$\text{and } \ln K_2 = -\frac{E_2}{RT} + \text{constant A} \quad \dots\dots\dots(10)$$

eq. (9) and eq. (10) can be written as

$$K = Ae^{-E/RT} \quad \dots\dots\dots(11)$$

$$\text{In general } K = Ae^{-E/RT} \quad \dots\dots\dots(12)$$

Equation (12) is known as integrated form of Arrhenius equation.

Q.10 The half-life period for a certain first-order reaction is 2.5×10^3 S. How long will it take for 1/5 of the reactant to be left behind? (2006)

$$\text{Ans. As we know } t_{1/2} = \frac{0.693}{k}$$

$$\therefore t_{1/2} = 2.5 \times 10^3 \text{ s}$$

$$\text{So } K = \frac{0.693}{2.5 \times 10^3} = 0.277 \times 10^{-3} \text{ s}^{-1}$$

Rate of first order reaction

$$K = \frac{2.303}{t} \log \frac{A_0}{A}$$

$$\text{So } 0.277 \times 10^{-3} = \frac{2.303}{t} \log \frac{1}{\frac{1}{5}} \Rightarrow 0.277 \times 10^{-3} = \frac{2.303}{t} \log 5$$

$$t = 5.8 \times 10^3 \text{ s}$$

Q.11 The rate constant of a reaction of 27°C and 37°C are $1.3 \times 10^{-3} \text{ S}^{-1}$ and $2.6 \times 10^{-3} \text{ sec}^{-1}$ respectively. Determine its activation energy and the frequency factor. (2007)

$$\text{Ans. } \begin{array}{l} T_1 = 27^\circ\text{C} \quad K_1 = 1.3 \times 10^{-3} \text{ S}^{-1} \quad T_1 = 27 + 273 = 300\text{K} \\ T_2 = 37^\circ\text{C} \quad K_2 = 2.6 \times 10^{-3} \text{ sec}^{-1} \quad T_2 = 37 + 273 = 310\text{K} \end{array}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \frac{1.3 \times 10^{-3}}{2.6 \times 10^{-3}} = \frac{E_a}{2.303 \times 8.318} \times \left[\frac{310 - 300}{310 \times 300} \right]$$

Shop Online at www.winsomecollection.co.in

$$E_a = 5.36 \text{ kJ/mol}^{-1}$$

Q.12 A reaction is first order. After 350 S, 28% of reactant remains. What is the rate constant of the reaction? How long will it take 90% of the material to reactance? (2007)

$$\text{Ans. We know } K = \frac{2.303}{t} \log \frac{A_0}{A}$$

$$K = \frac{2.303}{t} \log \frac{100}{100 - 72} \quad (\text{Let us assume 100\% of material initial time.})$$

$$K = 3.6 \times 10^{-3} \text{ S}^{-1}$$

Time taken when 90% of material reactant

$$K = \frac{2.303}{t} \log \frac{A_0}{A}$$

$$3.6 \times 10^{-3} = \frac{2.303}{t} \log \frac{100}{100 - 10}$$

$$t = 639 \text{ S.}$$

Q.13 Show that in the case of a unimolecular reaction, the time required for 99.9% of the reaction to take place is ten times that required for half the reaction.

Ans. For 50% reaction

$$K_1 = \frac{2.303}{t_1} \log \frac{100}{100 - 50}$$

$$K_1 = \frac{2.303}{t_1} \log 2$$

$$K_1 = \frac{2.303}{t_1} 0.30$$

$$\frac{K_2}{K_1} = \frac{t_1}{t_2} = 10 \quad \text{or} \quad t_1 = 10t_2$$

For 99.9%

$$K_2 = \frac{2.303}{t_2} \log \frac{100}{100 - 99.9}$$

$$K_2 = \frac{2.303}{t_2} \log \frac{100}{0.1}$$

$$K_2 = \frac{2.303}{t_2} \times 3$$

Q.14 Half life period for a first order reaction is 100 minutes. How long will it take period for a 75% of the reactant to react? (2015)

Ans. The reaction is of first order

$$K = \frac{2.303 \times 0.3010}{T} = \frac{2.303 \times 0.3010}{10} \quad \dots\dots(i)$$

For more details Visit Us At - www.winsomepublication.in

$$K = \frac{2.303}{T} \log \frac{a}{(a-x)}$$

Let $a = a$, $x = 3a/4$, $a-x = a/4$, $T = ?$

$$K = \frac{2.303}{T} \log \frac{a}{a/4} = \frac{2.303}{T} \log 4 = \frac{2.303}{T} \times 0.6021 \quad \dots\dots(ii)$$

equating eq.(i) and (ii)

$$\frac{2.303 \times 0.3010}{10} = \frac{2.303}{T} \times 0.6021 \Rightarrow T = 20 \text{ minutes}$$

Q.15 Energy of activation and its determination. (2009, 2008)

Other Related Questions -

Q. Write short notes on Energy of activation. (2014, 17)

Q. What is activation energy? Describe a method for the determination of activation energy for a chemical reaction. Calculate activation energy for a chemical reaction whose velocity constant is tripled when temperature is raised from 22°C to 32°C. (2004, 2010)

Ans. Activation Energy: -

Activation energy is defined as minimum energy necessary to cause a reaction between the colliding molecules. Calculation of E_a using Arrhenius equation.

1st method $\ln K = \ln A - E/RT$

Above equation is just like to $y = mx + b$

Thus if we plot the natural logarithmic of K against $1/T$ we get a straight line. From the slope of the line we conclude the value of eq.

$$\text{slope} = \frac{E_a}{R}$$

Hence by this eq. we calculate the activation energy.

2nd method - By following equation we can calculate activation energy, - from eq. taking logarithmic form

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Numeical: -

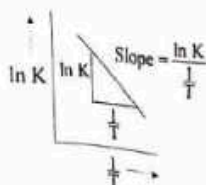
Now we are given that

$$T_1 = 22^\circ\text{C} = 273 + 22 = 295 \text{ K}, K_1 = K \text{ (say)}$$

$$\text{When } T_2 = 32^\circ\text{C} = 273 + 32 = 305 \text{ K}, K_2 = K \text{ (say)}$$

Substituting these values in the eq.

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

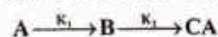


$$\log \frac{3K}{K} = \frac{E_a}{2.303 \times 8.314} \left[\frac{305 - 295}{305 \times 295} \right]$$

$$\Rightarrow \log 3 = 0.4771 = \frac{E_a}{19.147} \times \frac{10}{89979}$$

$$\Rightarrow E_a = 82.2 \text{ KJ mol}^{-1}$$

Q.16 What are consecutive reactions? Discuss the kinetics of the first-order consecutive reactions:

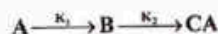


(2006, 2008, 2010, 2012)

Other Related Question -

Q. Write short note on First order consecutive reactions. (2016)

Ans. It is defined as the reaction which proceeds from reactants to final products through one or more Intermediate stages. The overall reaction is a result of several successive or consecutive steps. The consecutive or successive reactions may be represented as each step or stage has its own reaction rate and velocity constant.



Initial conc. $a \quad 0 \quad 0$

Conc. after time $t \quad x \quad y \quad z$

The rate of disappearance of A is given by

$$-dx/dt = K_1 \cdot x \Rightarrow -dx/x = K_1 \cdot dt$$

$$-\int \frac{dx}{x} = k \int dt + C \Rightarrow -\ln x = K_1 t + C$$

When $t = 0$ and $x = a$ we get

$$-\ln a = 0 + C \Rightarrow C = -\ln a$$

$$-\ln x = k_1 t - \ln a \Rightarrow \ln a - \ln x = k_1 t$$

$$\ln x - \ln a = -k_1 t \Rightarrow \ln (x/a) = -k_1 t$$

$$x/a = e^{-k_1 t} \Rightarrow x = a \cdot e^{-k_1 t} \quad \dots\dots\dots(1)$$

in equation 1 satate conc. of A fall off exponentially with time

Rate of formation of B = $k_1 x$

Rate of formation of B = $k_2 x$

so the rate of consumption of B = rate of consumption of B into C - Rate of formation of B

$$-dy/dt = k_2 y - k_1 x$$

from equation (1) and (2) we get

$$-dy/dt = k_2 y - k_1 a e^{-k_1 t} \quad \dots\dots\dots(2)$$

Equation 2 is the differential equation of first order.

Q.17. Derive expressions for $t_{1/2}$ in a

(i) Zero order reaction (ii) Second order reaction. (2011, 15)

Ans. Half-life period (Zero order): - Half life period ($t_{1/2}$) is the time in which half of the substance has reacted.

This implies that

$$\text{When } [A] = \frac{A_0}{2} \text{ and } t = \frac{t}{2} \quad \dots\dots\dots(i)$$

And we know

$$K = \frac{1}{t} \{ [A]_0 - [A] \} \quad \dots\dots\dots(ii)$$

Putting half life condition i.e. (i) in (ii)

$$t_{1/2} = \frac{1}{k} \left\{ \frac{[A]_0 - [A_0/2]}{2} \right\} = \frac{A_0}{2k}$$

$$\text{i.e. } t_{1/2} = \frac{A_0}{2k}$$

(ii) We know that second order reaction

$$K_2 = \frac{1}{t} \left[\frac{1}{a-x} - \frac{1}{a} \right] = \frac{1}{t} \left[\frac{x}{a(a-x)} \right]$$

putting the half life condition i.e. $x = a/2$, $t = t_{1/2}$

$$\text{Hence } K_2 = \frac{1}{t_{1/2}} \left[\frac{a/2}{a(a - a/2)} \right] = \frac{1}{t_{1/2}} \times \frac{a/2}{a(a/2)} = \frac{1}{at_{1/2}}$$

$$\text{Thus } t_{1/2} = \frac{1}{K_2 a}$$

Q.18. Write short note on side reactions. (2012)

Other Related Questions:-

Q. Write short note on parallel reaction. (2013)

Q. Write note on Kinetics of parallel reactions. (2017)

Ans. Parallel or Competing Reaction or side reactions:-

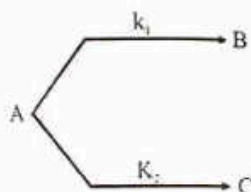
The reaction in which a substance reacts or decomposes in more than one way are called parallel or side reactions.

$$(-d[A])/dt = (k_1 + k_2)[A] = k_{av}[A]$$

$$k_1 = \text{fractional yield of B} \times k_{av}$$

$$k_2 = \text{fractional yield of C} \times k_{av}$$

If $k_1 \gg k_2$ then



$A \rightarrow B$ main and

$A \rightarrow C$ is side reaction

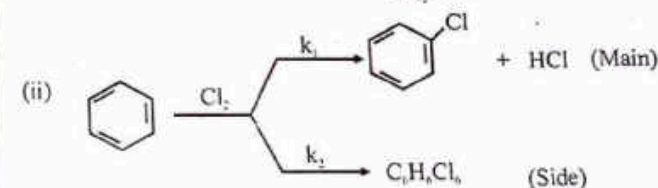
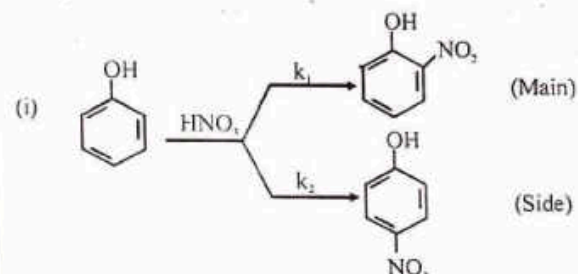
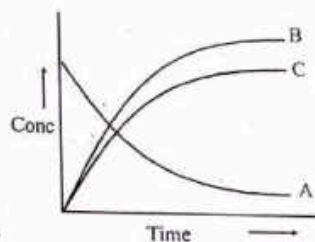
Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

$$x/y = k_1/k_2$$

$$\text{i.e., } \frac{d[B]/dt}{d[C]/dt} = \frac{k_1}{k_2}$$

Variation of concentration A, B and C with time may be graphically represented as, shown in figure

Example:



Q.19. The rate constants of a reaction is $1.5 \times 10^7 \text{ s}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ s}^{-1}$ at 100°C . Evaluate A and E_a . (2012)

Other Related Questions:-

Q. The rate constant of a reaction are $1.5 \times 10^{-6} \text{ s}^{-1}$ and $4.5 \times 10^{-6} \text{ s}^{-1}$ at 300 K and 350 K , respectively. Calculate energy of activation (E_a) of the reaction. (2015)

Ans. Given as $T_1 = 50 + 273 = 323 \text{ K}$, $K_1 = 1.5 \times 10^7 \text{ s}^{-1}$

$T_2 = 100 + 273 = 373 \text{ K}$, $K_2 = 4.5 \times 10^7 \text{ s}^{-1}$

$$\text{Now } \log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

For more details Visit Us At - www.winsomepublication.in

Shop Online at www.winsomecollection.co.in

$$\Rightarrow \log \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{2.303 \times 8.318} \left(\frac{373 - 323}{373 \times 323} \right)$$

$$\Rightarrow E_a = 3.792 \times 10^3$$

Q.20 Derive an expression for the rate constant of a bimolecular gaseous reaction on the basis of collision theory. (2012, 16)

Other Related Questions -

Q. Write short note on collision theory of bimolecular reactions in gases. (2014)

Q. On the basis of collision theory derive the expression for the rate constant when bimolecular collisions are taking place between dissimilar molecules. (2018)

Ans. **Collision Theory for Bimolecular Reactions:-**

A chemical reaction takes place only by collision between the reacting molecules. But not all collisions are effective. In actual practice, rate of the reaction is much smaller than the number of collisions between the reactant molecules. In order to overcome this discrepancy it is assumed that molecules are activated and only those molecules possessing energy greater than or equal to the threshold energy are able to form the product.

The reaction rate constant (k) depends upon the number of effective collisions per cc second.

$$\text{i.e. } k = Zf \quad \dots\dots(i)$$

where Z = number of molecules per cc taking part in the collision

f = fraction of molecules that are activated

According to kinetic theory of gases, fraction of molecules possessing energy greater than a particular value is given as

$$f = \frac{\Delta N}{N} = e^{-E_a/RT} \quad \dots\dots(ii)$$

Using eq.(i) and (ii), we get

$$k = Ze^{-E_a/RT} \quad \dots\dots(iii)$$

Using this equation, rate constant of various gaseous bimolecular reactions were calculated. For simple elementary reactions like decomposition of HI, the theoretical and experimental values were found to be in good agreement. For the other reactions, the theoretical values were found to be greater than the observed value. To account for relatively smaller value of rate constants, collision theory was modified.

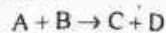
According to modified theory, the essential requirements for a reaction to occur are:

- (i) collision between the reactant molecules
- (ii) activation of molecules i.e. must possess sufficient kinetic energy to cause a reaction.

Shop Online at www.winsomecollection.co.in

(iii) proper orientation at the time of collision i.e. direct contact between the atom involved in the forming and breaking of bonds.

For a reaction,



$$k = f p z$$

.....(iv)

where p = probable fraction of collision with proper orientation. This probability factor is a measure of discrepancy between simple collision theory and experimental results.

Using eq. (ii) and (iv)

$$k = z p e^{-E_a/RT}$$

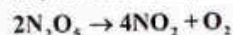
Value of p varies between 1 to 10^{-9} .

when $p = 1$, reaction obeys collision theory.

Limitation of collision theory:- Though it is logical and correct but still

- (i) is applicable to simple gaseous reactions only.
- (ii) For complex reactions, the experimental rate constants are quite different from the calculated value.
- (iii) It is supposed that only the kinetic energy of the colliding molecules contribute to the energy required for passing the energy barrier. There is no justification for ignoring other forms of energy associated with moving molecules i.e. rotational and vibrational energies.
- (iv) It does not talk about how a simple collision results in the breaking up of old bonds and formation of new bonds resulting in the product formation.

Q.21. N_2O_5 decomposes according to the equation,



The rate can be expressed as

$$\frac{-d[N_2O_5]}{dt} = k_1[N_2O_5], \quad \frac{d[NO_2]}{dt} = k_2[N_2O_5]$$

$$\text{and } \frac{d[O_2]}{dt} = k_3[N_2O_5]$$

How are k_1 , k_2 and k_3 related?

(2013)

Sol.
$$\text{Rate} = \frac{K_1[N_2O_5]}{2K_3(K_2 + K_3)}$$

Q.22 First-order reaction is found to be 15% completed in 20 minutes. Calculate the time taken to complete 75% of the reaction. (2013)

Sol. The equation rate of first order reaction is

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

For more details Visit Us At - www.winsomepublication.in

have $a - x = a - 0.15a = 0.85a$ and $t = 20$ minutes

$$\therefore k = \frac{2.303}{20} \log \frac{a}{0.85a} = \frac{2.303}{20} \times 0.07 = 0.008$$

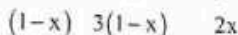
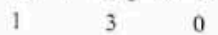
using again first order reaction equation.

$$0.008 = \frac{2.303}{t} \log \frac{a}{a - 0.75a} = \frac{2.303}{t} \log 4$$

$$\Rightarrow t = \frac{2.303}{0.008} \times 0.602 = 173.3 \text{ minutes.}$$

Q.23. A mixture of $N_2(g)$ and $H_2(g)$ in the mole ratio of 1:3 contains 16% $NH_3(g)$ at equilibrium at 480 K and total pressure of 1 atm. Calculate K_p for the reaction. (2014)

Ans. Now the reaction is



given $2x = 16/100 = 0.16 \Rightarrow x = 0.16/2 = 0.08$

Total mols = $1 - x + 3 - 3x + 2x = 4 - 2x = 4 - 2(0.08) = 3.94$

Total pressure = 1

$$\therefore p_{N_2} = \frac{(1-0.08) \times 1}{3.94} = 0.2335 \text{ atm}$$

$$p_{NH_3} = \frac{2x \times 1}{3.94} = \frac{2 \times 0.08 \times 1}{3.94} = 0.04 \text{ atm}$$

$$p_{H_2} = \frac{3(1-0.08) \times 1}{3.94} = 0.70 \text{ atm}$$

Q.24. Show that in a first-order reaction half life period is half of the time for 75% of the reaction. (2014)

Sol. For 50% reaction, we have

$$K = \frac{2.303}{T} \times 0.3010 \quad \dots (i)$$

For 75% reaction,

$$a = 100, x = 75, a - x = 25$$

$$K = \frac{2.303}{t} \log \frac{100}{25} = \frac{2.303}{t} \log 4 = \frac{2.303}{t} \times 0.6020 \quad \dots (ii)$$

Equating eq. (i) and (ii)

Shop Online at www.winsomecollection.co.in

$$\frac{2.303}{T} 0.3010 = \frac{2.303}{t} \times 0.6020$$

$$\frac{t}{T} = \frac{0.6020}{0.3010} = 2$$

i.e., the time required for 50% reaction is half that for 75% reaction.

Q.25. The rate constant of a reaction becomes double on changing temperature from 20°C to 30°C. Calculate the energy of activation. (2016)

Ans. Using eq.

$$\log \frac{K_2}{K_1} = \frac{E}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Here $k_2/k_1 = 2$, $R = 2.0 \text{ cal}$, $T_2 - T_1 = 10$

$T_1 = 273 + 20 = 293^\circ \text{K}$ and $T_2 = 273 + 30 = 303^\circ \text{K}$

$$\therefore \log 2 = \frac{E}{2.303 \times 2} \times \frac{10}{293 \times 303}$$

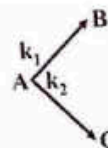
$$\Rightarrow E = \frac{0.3010 \times 2.303 \times 2 \times 293 \times 303}{10}$$

$$= 12308.3 \text{ Cal/mole} = 12.3 \text{ KCal/mole}$$

Q.26. Write short note on parallel reactions. (2015)

Ans. In parallel reactions a reactant undergoes two or more concurrent reactions to give different products. The grouping might be expanded to include two or more reactants undergoing reaction to give a common product. Parallel reaction are also called competitive reactions.

Q.27. Discuss the kinetics of the first-order parallel reactions:

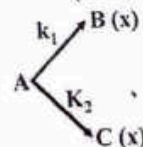


Explain clearly how the values of k_1 and k_2 can be determined, separately. (2010)

Sol. First order parallel reaction

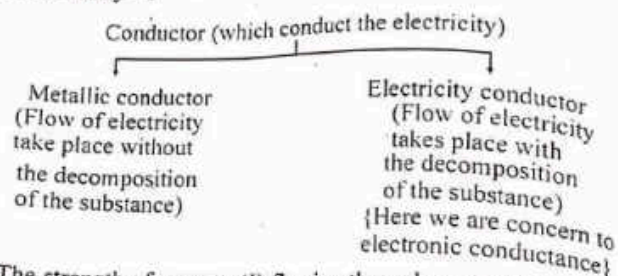
At initial state (a)

x is the amount which decompose after time T then



For more details Visit Us At - www.winsomepublication.in

Electrochemistry-I



The strength of current (I) flowing through a conductor is governed by Ohm's Law, which states that the current strength (I) flowing through a conductor is governed by Ohm's Law, which states that the current strength (I) flowing through a conductor at a given temperature is proportional to the potential difference (E) and inversely proportional to the resistance (R).

$$\text{Mathematically } I = \frac{E}{R} \text{ or } R = \frac{E}{I}$$

The resistance of a conductor of uniform cross section is directly proportional to its length (ℓ) and inversely proportional to cross-section (A) it is measured is Ohm (Ω)

$$R \propto \frac{\ell}{A} \text{ or } R = \rho \frac{\ell}{A}$$

Where ρ is resistivity or specific resistance and may be defined as the resistance in Ohm of a conductor of cm length and one cm cross section. Then, $R = \rho$ $\ell = 1 \text{ cm}, A = 1 \text{ cm}^2$

Q.1 Define specific conductance and equivalent conductance. Explain clearly why on dilution the specific conductance decrease but the equivalent conductance increases? (2006, 13, 17)

Other Related Questions -

Q. Define conductance, specific conductance and equivalent conductance. Explain clearly why on dilution the specific conductance decreases and equivalent conductance increases. (2010)

Q. Explain specific conductance and equivalence conductance. What is the effect of dilution on them? (2011)

Q. Write short note on relation between specific equivalent and molar conductivities and effect of dilution on conductivity. (2012)

For more details Visit Us At - www.winsomepublication.in

Conductance:-

The conductance of any conductor is reciprocal of its resistance R.

$$C = \frac{1}{R}$$

Specific Conductivity:-

The reciprocal of the specific resistance is called specific conductivity or conductance. It is represented by K (kappa),

$$\text{Thus, } K = \frac{1}{\rho} \quad \therefore R = \rho \frac{\ell}{a} \Rightarrow \rho = \frac{Ra}{\ell}$$

$$\text{Then, } K = \frac{\ell}{Ra}$$

Since resistance (R) is reciprocal of electrical conductance (C) which is expressed in Ohm^{-1} or rho. The unit of electrical conductance is called Siemen (S) Thus equation may be represented as

$$K = \frac{\ell \times C}{a}$$

$$\text{Thus if } \ell = 1 \text{ cm } a = 1 \text{ cm}^2 \Rightarrow \boxed{K = C}$$

In such way if $\ell = 1 \text{ cm } a = 1 \text{ cm}^2$ then conductance is termed as specific conductance.

Since $\frac{\ell}{a}$ = cell constant then we can write

$$\boxed{K = \text{cell constant} \times \text{observed conductivity}}$$

Molar Conductance:-

By measuring conductance of electrolytes solutions a quantity known as molar conductance is used. It is defined as the conducting power of all the ions produce by one mole of an electrolyte in a given solution. It is denoted by λ_m or μ and A_m at infinite dilution.

$$\mu = K \times V \quad \mu = K \times \frac{1000}{C} = K \times \frac{1000}{M}$$

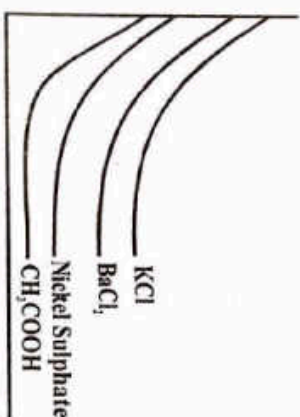
Variation of Molar Conductance With Dilution:-

Molar conductance of an electrolyte increases with increase the dilution this is due to increase in the degree of dissociation of the electrolyte the increase in the ease of electrolyte like HCl, KCl & BaCl₂ is not so large as in the case of acetic acid or NH₄OH the electrolyte as strong electrolytes while these of 2nd category CH₃COOH, NH₄OH are known as weak electrolyte.

Shop Online at www.winsomecollection.co.in

On plotting the graph of some electrolytes it is seen that in strong electrolytes there is a tendency of molar conductance to approach a certain limiting value when the concentration approach zero.

The molar conductance at this point is known as molar conductance at zero conc. or infinite dilution it is denoted by Λ^∞ . This value in the case of strong electrolyte is obtained by extra plot. This molar conductance graph to zero concentration, when the molar conductance is says Λ^∞ , the degree of dissociation α is given



$$\alpha = \frac{\Lambda_m}{\Lambda^\infty} = \frac{\text{Molar conductance at given conc.}}{\text{Molar conductance at infinite dilution}}$$

Equivalent Conductance (λ or Λ):-

Equivalent conductivity of a solution at a dilution V may be defined as the conductance of all the ions produced from one gram equivalent of the electrolyte dissolved in V cc of the solution when the distance between the two electrode is one cm and the area of the electrodes is so large that whole of the solution is contain of between them.

$\lambda = K \times V$ Where K = Specific conductivity, V = Volume of solution in cc containing 1 gram of equivalent of the electrolyte.

$$\lambda = K \times \frac{1000}{x}$$

Where x = normality or weight of solute.

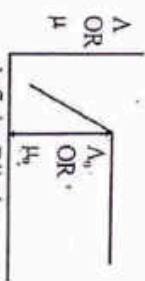
Effect Of dilution on the conductivity:-

The conductivity of a solution is due to presence of ions in the solution and greater the number of ions, the greater will be the total conductivity. On diluting a solution this has different effects on specific conductivity and equivalent (and also molecular) conductivity. The specific conductivity decreases on dilution, while those of equivalent conductivity and molecular

For more details Visit Us At - www.winsomepublication.in

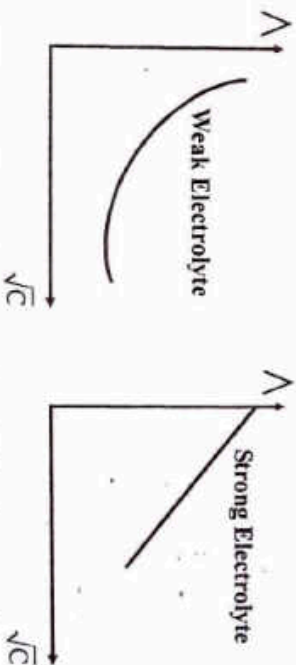
conductivity increases and attains a maximum value at infinite dilution known as equivalent or molecular conductivity at infinite dilution. The decrease in the value of specific conductivity on dilution is due to the fact that the number of ions present per cc's, decreases while equivalent or molecular conductivity will increase as it is numerically equal to the product of specific conductivity and the dilution. The variation of equivalent or molecular conductivity with dilution can be expressed by the curve shown in figure.

By the study of the curve it may be concluded that on increasing the dilution, the value of equivalent or molecular conductivity will increase and attains a maximum value and then there is no change in this maximum value on further dilution because at this dilution the electrolyte is completely ionised and this maximum value is known as equivalent or molecular conductivity at infinite dilution represented by Λ_0 or μ_0 respectively.



Q.2 How does equivalent conductance vary with concentration in the case of (i) strong electrolyte and (ii) weak electrolytes.

Ans:



The equivalent conductance of a solution does vary linearly with concentration this variation can be studied by plotting Λ values against the square root of conc. it has been found that variation of equivalent conductance with $\sqrt{C}$ depends upon the nature of electrolyte the behaviour differ for strong and weak electrolytes.

Strong electrolyte are completely ionized at all concentration the increase in equivalent conductance is not due increase in the number in forces of attraction between ion ions of equivalent charge at high concentration the force of attraction between the opposite ions increase consequently it effects the speed of ions with which they move towards oppositely charge towards this phenomenon is called ionic interference as the solution becomes more and dilute the equivalent conductance increase till it reaches a limiting value this value is known as equivalent conductance at infinite dilution or zero

Shop Online at www.winsomecollection.co.in

conc. The variation of equivalent conductance in same cases can be represented by the imperial equation

$$\lambda = \lambda^{\infty} - K\sqrt{C} \quad \left\{ \text{which is like } \lambda = C + mx \right\}$$

Here K is constant when λ is plotted against $\sqrt{C}$ it gives a straight line which is true for strong electrolyte.

Q.3 State and explain the transport number of an ion. Describe Hittorf's method of determining the transport number of an ion. (2009, 2011)

Other Related Questions:-

Q. Write short notes on the Transport number. (2008)

Q. What is transport number? How will you determine transport number of an ion by Hittorf's method? (2007, 14, 16)

Q. What is transport number of an ion? Discuss moving boundary method for its determination. (2005)

Q. Define transport number. How will you determine transport number of an ion? Give one method. (2019)

Ans. The fraction of that current carried by the cation or the anion is termed as its transport number or Hittorf's number. If v_+ represents the speed of migration of the cation and v_- that of the anion.

$$\text{Transport number of cation} = \frac{v_+}{v_+ + v_-}$$

$$\text{Transport number of anion} = \frac{v_-}{v_+ + v_-}$$

If t_+ is transport number of cation t_- is transport number of anion

$$\text{Then } t_+ = \frac{v_+}{v_+ + v_-} \text{ and } t_- = \frac{v_-}{v_+ + v_-}$$

v_+ = speed of cation, v_- = speed of anion

$$\frac{t_+}{t_-} = \frac{v_+}{v_-}$$

$$t_+ + t_- = 1$$

If speed ratio $\frac{v_+}{v_-}$ be denoted by γ then $\gamma = \frac{t_+}{t_-} = \frac{t_+}{1 - t_+}$

$$t_+ = \frac{1}{1 + \gamma}$$

Determination Of Transport Number:-

There are two methods for determination of transport number of an ion.

For more details Visit Us At - www.winsomepublication.in

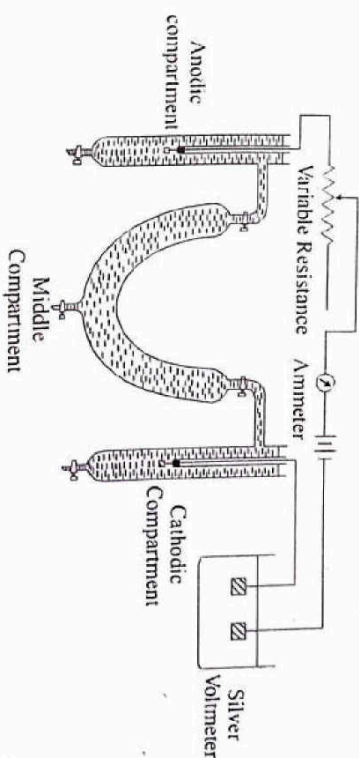
- (i) Hittorf's method
- (ii) Moving boundary method

Hittorf's Method:-

In this method the determination of transport number is based on Hittorf's rule. According to this rule the loss of conc. around any electrode is proportional to the speed of ion moving away from that electrode i.e.

$$\text{Full around anode} = \frac{\text{Speed of cation}}{\text{Speed of anion}} = \frac{v_+}{v_-}$$

The transport number of anion is calculated from the changes in conc. around the electrode experimentally. The apparatus used in this method consist of two vertical glass tube joint through a U tube in the middle, all the three tube are provided with stop corks at the bottom. The U tube is also provided with stop corks at the top of the two limbs. The silver anode is shield in a glass tube and the cathode is the piece of freshly silvered foil. The apparatus is filled with the solution of HgNO_3 and the static current is passed for two to three hours.



When the current has been passed for about 3 hours the stop corks at the top of U tube are closed. The whole liquid in the anode compartment is carefully drained into a weighed flask and its weight determined its silver content is determined by titrating against a standard solution of potassium thiocyanate. If there is no change in conc. of the solution in the U tube then this means experiment has been successfully performed.

For Numerical Calculations:-

Two different cases may arise.

Case I:- When electrodes are Unattachable

After passing electric current -

Let the weight of anodic solution taken out = ag

Weight of AgNO_3 present in it by titration = bg

Weight of water = (a - b)g

Before passing electric current

Shop Online at www.winsomecollection.co.in

Let weight of AgNO_3 in (a-b) of water before passing electric current be = c_g

$\therefore$ Fall in concentration = $(c-b)$ of AgNO_3

$$= \frac{c-b}{170} \text{ g eqvt. of } \text{AgNO}_3$$

$$= \frac{c-b}{170} \text{ g eqvt. of } \text{Ag} = d \text{ (say)}$$

Suppose the weight of Ag deposited in Ag coulometer be = $w.g$

$$= \frac{w}{100} \text{ g eqvt. of } \text{Ag} = w \text{ (say) g eqvt. of } \text{Ag}$$

$$\text{Transport no. of } \text{NO}_3^- \text{ ion} \left(t_{\text{NO}_3^-} \right) = 1 - \frac{d}{w}$$

Case II:-

When electrodes are attackable (Ag electrode are used)
Concentration of anodic solution increase = $(b-c)$ g of AgNO_3

$$= \frac{(b-c)}{170} \times 100 \text{ g of } \text{Ag} = \frac{(b-c)}{170} \text{ g eqvt. of } \text{Ag} = F \text{ (obtain)}$$

If this happen that no Ag^+ ions has migrate from the anode,
Then conc. of Ag^+ ion would have been equal to w

Therefore concentration decrease due migration of Ag^+ ion = $w - F$

$$\text{Hence transport number of } \text{Ag}^+ \text{ ion} (t_{\text{Ag}^+}) = \frac{w-F}{w}$$

$$\text{And transport number of } \text{NO}_3^- \text{ ion} (t_{\text{NO}_3^-}) = \frac{w-F}{w}$$

Q.4 Discuss the moving boundary method for determination of transport number. (Imp.)

Other Related Questions-

Q. How will you determine the transport number with the help of moving boundary method. (2018)

Ans. Moving Boundary Method:-

The moving boundary method is very accurate and has been used directly for precision measurement.

The apparatus consist of a long vertical tube filled with two electrodes at the two ends. The tube filled with a solution of CdCl_2 at the lower end and HCl at the upper end in such a way that there is a sharp boundary between the tubes.

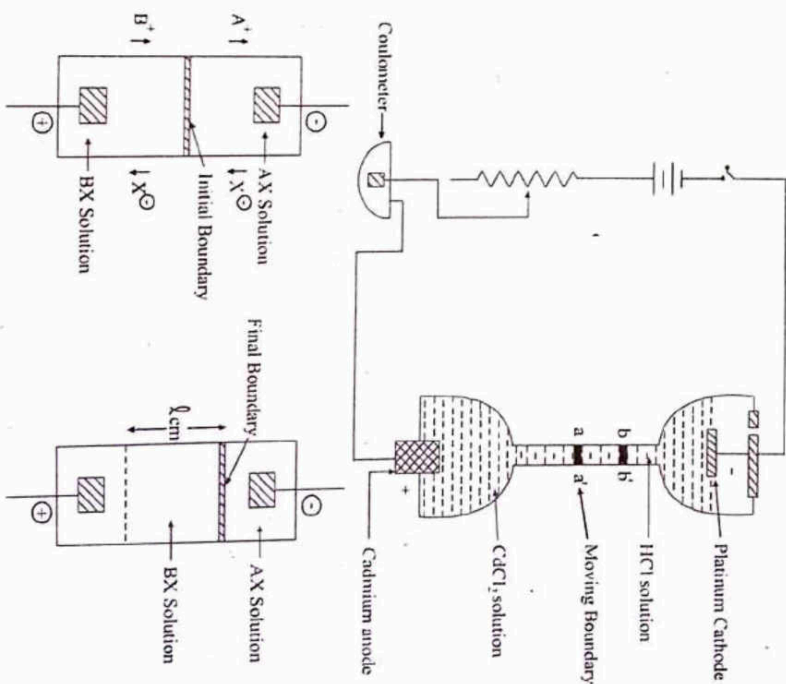
For more details Visit Us At - www.winsomepublication.in

And the anode (cadmium stick) is introduced at the bottom.

In general if the transport number of a cation at is to be determined. The electrolyte (Ax) solution is taken in the upper part of the apparatus and the layer of mother electrolyte Bx having common ion X^- is introduced in the lower part of the apparatus the electrolyte Bx is selected so the velocity of B^+ ion is less than of A^+ ion.

Calculation:-

Suppose the boundary moves through a distance l cm (say from aa' to bb'). Then the volume of the liquid that has moved up A cm^3 when A is the cross-section area of the tube in cm^2 . Let the concentration of the acid be C gram equivalent per liter.



Then the number of gram equivalent of ions carried towards the cathode $\frac{lAC}{1000}$

Since each gram equivalent carries one faraday of electricity the

electricity carried by ions = $\frac{lAC}{1000}$ faradays.

Shop Online at www.winsomecollection.co.in

Consider the total current flows in the same time as measured in a Coulometer also included in the circuit.

$$\text{Then, Transport number of ions} = \frac{\lambda}{\sum \lambda}$$

Q.5 State and explain Kohlrausch law of ionic mobilities. (2006, 11, 16)

Other Related Questions - (2008, 09, 13)

Q. State and explain Kohlrausch's Law. (1mp.)

Q. What is Kohlrausch's Law explain its use for the determination of equivalent conductance of acetic acid at infinite dilution. (2010)

Q. State and explain Kohlrausch's law of independent migration of ions. (2018)

Q. Write short notes on Kohlrausch's law. (2019)

Q. Write short note on Kohlrausch's law and its application. (2019)
Ans. The difference in the conductance of any two cations appears to be about the same irrespective of the nature of anion with which they are associated.

Similarly the difference in the molar conductance at infinite dilution of any two anions is always about the same irrespective of the nature of cation, which they are associated.

Kohlrausch's Law states, "The equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductance of the component ions". Mathematically expressed as,

$$\Lambda_{\infty} = \Lambda_c + \Lambda_a$$

Where Λ_c and Λ_a = equivalent conductance of cation and anion.

Application:-

(i) Calculation of molar conductance at infinite dilution of weak electrolyte -
The application of Kohlrausch law unable to indirect the evaluation the molar conductance of CH_3COOH adding infinite dilution can be obtain from the knowledge of molar conductance at infinite dilution of HCl , CH_3COOH and NaCl as shown below -

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COOH}) - \Lambda_m^0(\text{NaCl})$$

Write in form of ion

$$\begin{aligned} \Lambda_m^0(\text{CH}_3\text{COOH}) + \Lambda_m^0(\text{H}^+) + \Lambda_m^0(\text{Cl}^-) &= \Lambda_m^0(\text{H}^+) + \Lambda_m^0(\text{Cl}^-) + \Lambda_m^0(\text{CH}_3\text{COO}^-) + \Lambda_m^0(\text{Na}^+) - (\Lambda_m^0(\text{Na}^+) + \Lambda_m^0(\text{Cl}^-)) \\ &= \Lambda_m^0(\text{H}^+) + \Lambda_m^0(\text{Cl}^-) + \Lambda_m^0(\text{CH}_3\text{COO}^-) + \Lambda_m^0(\text{Na}^+) - \Lambda_m^0(\text{Na}^+) - \Lambda_m^0(\text{Cl}^-) \\ &= \Lambda_m^0(\text{H}^+) + \Lambda_m^0(\text{CH}_3\text{COO}^-) \\ &= \Lambda_m^0(\text{CH}_3\text{COOH}) \end{aligned}$$

For more details Visit Us At - www.winsomepublication.in

Q.6 Discuss various applications of conductance measurements. (2005, 2011)

Other Related Questions -

Q. Write short note on Conductometric Titrations (1999, 2002)

Q. Give three applications of conductivity measurement with mathematical expressions and proper graphs wherever necessary. (2012)

Q. Write short note on application of conductance measurement in conductometric titrations. (2019)

Ans. Conductometric Titrations:-

This method of analysis is applicable to any titration in which there is sharp change in conductivity at the end point determination of the end point of a titration by means of conductivity measurement is known as conductometric titration.

In conductometric titration the titrate is added from burette and the conductivity readings corresponding to various increments of titrant are plotted against the volume of the titrant. Two curves will be obtained which will intersect each other at a point called end point as equivalent point when the reaction is not quantities there is some curvature in the curve near the end point, which may be due to hydrolysis dissociation of product or appreciable solubility in the case of precipitation reaction. Since resistance and hence conductance changes with temperature, so titration must be done under constant temperature bath.

$$\text{Actual conductivity} = \frac{(v + V)}{V} \times \text{observed conductivity}$$

Where v is the volume of the titrant added, V is the original volume.

Acid-base titrations and redox titrations are often performed in which common indicators are used to locate the end point e.g., methyl orange, phenolphthalein for acid base titrations and starch solutions for iodometric type redox process. However, electrical conductance measurements can also be used as a tool to locate the end point, e.g., in a titration of a HCl solution with the strong base NaOH .

As the titration progresses, the protons are neutralized to form water by the addition of NaOH . For each amount of NaOH added equivalent amount of hydrogen ions is removed. Effectively, the mobile H^+ cation is replaced by the less-mobile Na^+ ion, and the conductivity of the titrated solution as well as the measured conductance of the cell fall. This continues until the equivalence point is reached, at which one obtains a solution of sodium chloride, NaCl . I more base is added, an increase in conductivity or conductance is observed since more ions Na^+ and OH^- are being added and the neutralization reaction no longer removes an appreciable amount of H^+ . Consequently, in the titration of a strong acid with a strong base, the conductance has a minimum at the

Shop Online at www.winsomecollection.co.in

equivalence point. This minimum can be used, instead of an indicator dye, to determine the endpoint of the titration. The conductometric titration curve is a plot of the measured conductance or conductivity values as a function of the volume of the NaOH solution added. The titration curve can be used to graphically determine the equivalence point.

For reaction between a weak acid-weak base in the beginning conductivity decreases a bit as the few available H^+ ions are used up. Then conductivity increases slightly up to the equivalence point volume, due to contribution of the salt cation and anion. (This contribution in case of a strong acid-strong base is negligible and is not considered there.) After the equivalence point is achieved the conductivity increases rapidly due to the excess OH^- ions.

Advantages:-

Over the volumetric titration there are some advantages of conductometric titrations. Conductometric titrations are particularly useful in the case of coloured as turbid liquids where ordinary indicators cannot function. They can be employed for the analysis of all solutions and also for very weak acids.

No special precautions are necessary, as the titration approaches the equivalent point. Since this found graphically.

It is not necessary to measure the actual conductance as we may use any quantity that is proportional to it the same can be plotted against the volume of alkali solution used up.

Q.7. Write short note on theory of acid base indicator in brief. (2014, 18)

Other Related Question:-

Q. Write short note on theory of acid base indicators. (2016, 17, 19)

Ans. The pH value at null point is not exactly 7, but due to hydrolysis, the pH value is either towards acidic side or alkaline side. The indicators change their colour at different pH value i.e. the ionization of indicators depends on the pH value. In a titration, only that particular indicator can be used which changes its colour near the null point.

In the following table, the various indicators are given which are used at different pH-value.

Indicator	pH range	Colour in acidic medium	Colour in alkaline solution
Methyl orange	3.1 to 4.4	Red	Yellow
Congo red	3.0 to 5.0	Violet	Red
Methyl red	4.2 to 6.3	Red	Yellow
Phenol red	6.8 to 8.4	Yellow	Red
Cresol red	7.2 to 8.8	Yellow	Red
Phenolphthalein	8.2 to 10	Colourless	Pink

Q.8. Calculate the effective mobility of a proton in water. The equivalent conductance of H^+ ion at infinite dilution is $349.82 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$. (Imp.)

Ans. Ionic mobility $U = \frac{\lambda_0}{96500}$

$$= \frac{394.82 \text{ ohm cm}^2 \text{ equiv}^{-1}}{96500 \text{ C mol}^{-1}} \text{ or } \frac{\text{S cm}^2 \text{ mol}^{-1}}{\text{V S Sec}} \\ = 4.091 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$$

Q.9. Calculate L^0 value of acetic acid given that L^0 values of HCl, NaCl and CH_3COONa are 426.16, 126.45 and $91.01 \text{ ohm}^{-1} \text{ cm}^2 \text{ equivalent}^{-1}$ respectively.

Ans. Remark:-

During solving such type of Kohlrausch Law problem, your attitude in such a way that how can obtain a desired compound from other compound which equivalent conductance is given.



Writing the equivalent conductance (i.e. ionic form)

$$\begin{aligned} \Lambda_{CH_3COOH}^0 + \Lambda_{H^+}^0 &= \Lambda_{CH_3COO^-}^0 + \Lambda_{Na^+}^0 + \Lambda_{H^+}^0 + \Lambda_{Cl^-}^0 \\ &\quad - (\Lambda_{Na^+}^0 + \Lambda_{Cl^-}^0) \\ &= \Lambda_{CH_3COO^-}^0 + \Lambda_{Na^+}^0 + \Lambda_{H^+}^0 + \Lambda_{Cl^-}^0 - \Lambda_{Na^+}^0 - \Lambda_{Cl^-}^0 \end{aligned}$$

Hence as you add and subtract according you solve

$$\Lambda_{CH_3COOH}^0 = 91.01 + 426.16 - 126.45 = 390.72 \text{ ohm}^{-1} \text{ cm}^2$$

Ostwald's Dilution Law:-

Since weak electrolytes are not completely dissociated, there exists equilibrium between the ions and undissociated molecules of the electrolyte. This equilibrium is called ionic equilibrium. Ostwald applied the law of mass action to the ionic equilibrium of weak electrolytes and derived an equation known as Ostwald's dilution law.

Let us consider an aqueous solution of the weak electrolyte HA at constant temperature. In aqueous solution, HA remains in equilibrium with its ions.



After time t , consider a dissociation take place then,



$$\text{According to law of mass action } K_c = \frac{[H^+][A^-]}{[HA]}$$

Arrhenius Theory:-

Svante Arrhenius in (1887) proposed that when an electrolyte is dissolved in water it undergoes ionisation i.e. the electrolyte molecules break up into electrically charged particles called ions. Complete ionisation does not occur at equilibrium between unionized electrolyte molecules and the ions is established the equilibrium may be represented as



The equilibrium is dynamic nature

When electrolyte solution is diluted the equilibrium is disturbed more electrolyte molecules break up and ions are formed, as the result of which the solution exhibits greater conductivity at some extent at dilution the ionisation is complete. At limiting value of equivalent conductance or equivalent conductance at infinite dilution will be reached. Arrhenius also proposed that the degree of ionisation

$$\alpha = \frac{\Lambda}{\Lambda^\infty}$$

May be expressed as $\alpha = \frac{\Lambda}{\Lambda^\infty}$

Where Λ is equivalent conductance

Λ^∞ is equivalent conductivity at infinite dilution

This expression has been widely used for the estimation of the degree of ionisation of electrolyte.

$$K_c = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K = \frac{\alpha^2 C}{(1-\alpha)} \text{ Mole/liter} \dots\dots\dots (i)$$

The equilibrium constant K_c is called the Dissociation constant or Ionisation constant. If one mole of an electrolyte be dissolved in V liter of the solution then,

$$C = \frac{1}{V}$$

V is known as Dilution for the solution
Substituting the value of C in equation.

$$K = \frac{\alpha^2}{(1-\alpha)V} \dots\dots\dots (ii)$$

This mathematically expression representing the variation of the degree of dissociation with dilution is known as Ostwald's dilution law. The equilibrium constant K is called the dissociation constant or ionization constant of the electrolyte.

In case of dissociation α is very small as is usually the case for weak

electrolytes then $(1-\alpha)$ will become nearly equal to unity and thus the

For more details Visit Us At - www.winsomepublication.in

equation (i) and (ii) becomes

$$K = C\alpha^2 \quad \text{or} \quad K = \frac{\alpha^2}{V}$$

$$\alpha = \sqrt{\frac{K}{C}} \quad \text{or} \quad \alpha = \sqrt{VK}$$

Q.10. Write on short on Buffer solutions. (2007, 10, 13, 15, 19)

Ans: A buffer solution is defined as a solution, which resists any small change in its pH value, even when small amount of the acid or the base are added to it.

Type of buffer solution:-

There are two types of buffer solution, these are -

(i) Solution of single substances - The solution of the salt of weak acid and weak base e.g. ammonium acetate ($\text{CH}_3\text{COONH}_4$) acts as buffer.

(ii) Solution of mixtures - These are further of two types.

(a) Acid buffer - It is the solution of a mixture of a weak acid and a salt of this weak acid with a strong base (e.g. $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$)

(b) Basic Buffer - It is the solution of a mixture of a weak base and a salt of this weak base with a strong acid e.g. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.

Buffer Action:-

The property of a buffer solution to resist any change in its pH value even when small amounts of the acid or the base are added to it is called buffer action.

How a buffer action?

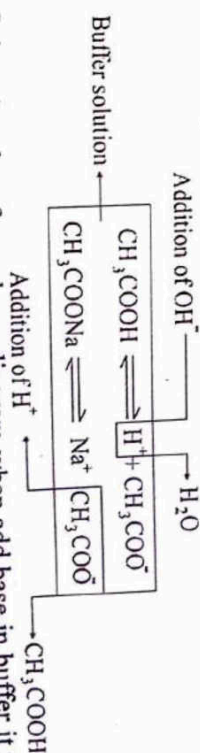
Taking an example of a buffer solution with sodium acetate and acetic acid. The pH of the buffer is governed by the equilibrium.



And also sodium acetate ionizes as



Above mixture when we add acid or base in small amount the following mechanism take place.



It is quite clear from above diagram when add base in buffer it reacts with H^+ and to form H_2O and when acid is added it forms again CH_3COOH and over effect on H^+ or OH^- concentration is nullified. Hence in such a way the buffer solution is termed as Resistance solution.

Q.11. Derive the Henderson equation.

Other Related Questions:-

Q. Derive Henderson's equation for the pH of the buffer solution. (Imp)

Ans: The behavior of weak acids and Buffer is described by the Henderson Hasselbach equation:-

Let a equation



$$\Rightarrow K = \frac{[H^+][A^-]}{[HA]}$$

$$\Rightarrow K[HA] = [H^+][A^-]$$

$$\Rightarrow [H^+] = K \frac{[HA]}{[A^-]}$$

$$\Rightarrow \log H^+ = \log \left\{ K \frac{[HA]}{[A^-]} \right\} = \log K + \log \frac{[HA]}{[A^-]}$$

$$\Rightarrow -\log H^+ = -\log K - \log \frac{[HA]}{[A^-]} \Rightarrow pH = pK - \log \frac{[HA]}{[A^-]}$$

$$\Rightarrow pH = pK + \log \frac{[A^-]}{[HA]}$$

Case 1:- When an acid is exactly half neutralized i.e. $[A^-] = [HA]$

$$\Rightarrow pH = pK + \log (1/1)$$

$\Rightarrow pH = pK$ on half neutralization.

Case 2:- When the ratio $\frac{[A^-]}{[HA]} = 100 : 1$

$$\Rightarrow pH = pK + 2$$

Case 3:- When the ratio $\frac{[A^-]}{[HA]} = 1 : 10$

$$\Rightarrow pH = pK - 1$$

Important physiologic buffers includes $[HCO_3^-]$, $[H_2CO_3]$, Orthophosphate $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and intra cellular proteins.

Q.12. Calculate the pH of a buffer solution containing 0.08 mole of acetic

For more details Visit Us At - www.winsomematerials.com

Ans. Given $pK_a = 1.75 \times 10^{-5}$, salt concentration = 0.08, Acid concentration = 0.12 according Henderson equation

$$pH = pK_a + \log \frac{[salt]}{[acid]} = 1.75 \times 10^{-5} + \log \frac{0.08}{0.12}$$

$$pH = -1.7607$$

Q.13. What is hydrolysis?

(2005)

Ans. The idea that the solution of salts prepared by the combination of equivalent quantities of acid and base will be neutral, is found to be untrue, e.g., a solution of sodium chloride is neutral but the aqueous solution of copper sulphate is acidic and that of potassium cyanide is strongly alkaline. This is due to the fact that the character of the solution (neutral or acidic or alkaline) depends on the relative strengths of acid and base from which the salt is prepared. The salt sodium chloride prepared by the combination of strong acid (HCl) and strong base (NaOH), so the resulting solution is neutral. On the other hand, copper hydroxide a weak base and sulphuric acid is a strong acid so the solution of copper sulphate will be acidic. Similarly the solution of potassium cyanide will be strongly alkaline as hydrocyanic acid is a weak acid and potassium hydroxide is a strong base. This alkalinity or acidity of a solution is due to the tendency of the salt to react with water and is referred as hydrolysis. In other words, we may say that the process of decomposition of salt by water into free acid and free base is termed as hydrolysis or salt hydrolysis.

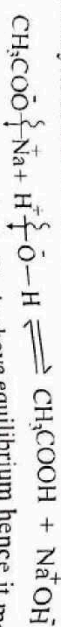
This behaviour of salt is due to the fact that water is slightly ionised into H^+ and OH^- ions. These ions react with the ions given by the salt producing an acid and an alkali. The resulting solution will be either acidic or alkaline as the H^+ or OH^- ions are in excess in solution but the product of H^+ and OH^- ions will be constant.

The equilibrium constant, in case of the decomposition of salts by water into free acid and free base or in the process of salt hydrolysis referred as hydrolysis constant.

Q.14. Derive expressions for (i) hydrolysis constant, (ii) degree of hydrolysis and (iii) pH of an aqueous solution of a salt of weak acid and strong base. (iv) Relation between K_h , K_w and K_a .
Ans. Salt Of Weak Acids And Strong Bases:-
(2006, 17)

In general hydrolysis is a reversible reaction. In this reversible reaction we can apply Law of mass action and obtaining equilibrium constant which is known as hydrolytic constant or hydrolytic constant (K_h)

(i) **Hydrolytic constant** - consider sodium acetate salt in water



Since, Na^+ is common in both side in above equilibrium hence it may be left out and equation can be written as



Applying law of chemical equilibrium and taking the conc. of water as constant

$$K_h = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad \dots\dots\dots(i)$$

(ii) **Degree Of Hydrolysis (a)**:-

Suppose we start with one mole of the salt dissolved in V liter of solution. Then the equilibrium concentration are



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V}$$

If α is small as compared to unity, $(1-\alpha)$ in above equation must be replaced by 1 so that

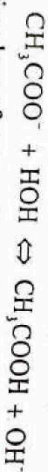
$$K_h = \frac{\alpha^2}{V} \Rightarrow \alpha^2 = K_h V = \frac{K_w}{K_a}$$

$$\alpha = \sqrt{\frac{K_w V}{K_a}} \Rightarrow \alpha = \sqrt{\frac{K_w}{K_a C}}$$

Where C is initial conc. of the salt.

(iii) **pH of aqueous solution of a salt of weak acid and strong base**:-

At equilibrium, we have the equation,



Applying law of mass action,

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \dots\dots\dots(i)$$

A.U. - B.Sc. Ist Year - Chemistry III Paper - Unit V - 99

All equilibrium, $[\text{CH}_3\text{COOH}] = [\text{OH}^-]$ and let the concentration of the salt, $[\text{CH}_3\text{COO}^-]$ is C mol/litre.

Putting in eq. (i)

$$K_h = \frac{K_w}{K_a} = \frac{[\text{OH}^-]^2}{C} \quad \dots\dots\dots(ii)$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]},$$

Putting in eq. (ii)

$$\frac{K_w}{K_a} = \frac{K_w^2}{C[\text{H}^+]^2} \Rightarrow [\text{H}^+]^2 = \frac{K_w \cdot K_a}{C}$$

$$[\text{H}^+] = \left[\frac{K_w \cdot K_a}{C} \right]^{1/2}$$

$$\log [\text{H}^+] = \frac{1}{2} \log K_w + \frac{1}{2} \log k_a - \frac{1}{2} \log C$$

Multiplying by -ve sign

$$-\log [\text{H}^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log k_a + \frac{1}{2} \log C$$

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}k_a + \frac{1}{2} \log C$$

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C \quad \dots\dots\dots(iii)$$

(iv) Relation between K_h , K_w and K_a

The ionic product of water (K_w) is expressed as

$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots\dots\dots(iv)$$

K_a is the dissociation constant of the acid, here acid is



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \dots\dots\dots(v)$$

Dividing equation (ii) by (iii) we get

$$\frac{K_w}{K_a} = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

From equation (i) = K_h

Shop Online at www.winsomecollection.co.in

For more details Visit Us At - www.winsomepublication.in

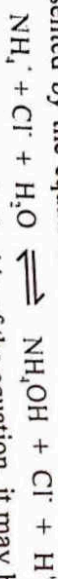
$$K_h = \frac{K_w}{K_a}$$

It is quite clear, the hydrolysis constant K_h of the salt varies inversely as the dissociation constant K_a of the weak acid. Therefore the weak the acid the greater is the hydrolysis constant of the salt.

Q.15. Define salt hydrolysis. Obtain expression for the hydrolysis constant for the salt of strong acid and weak base. (2010)

Ans: Salt Of Weak Bases And Strong Acids:-

The hydrolysis of a salt of a weak base and strong acid may be represented by the equation



Since Cl^- is common both side of the equation, it may be left out and above equation can be written as



(i) Hydrolysis Constant:-

Applying law of mass action to the above hydrolysis reaction. The hydrolysis constant K_h is given by

$$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+][H_2O]}$$

Since H_2O is large excess and it is taken to be constant and hydrolysis constant is reduce to

$$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+]}$$

(ii) Relation K_h , K_w And K_b :-

We know that ionic product of H_2O (K_w) is represent as,

$$K_w = [H^+][OH^-] \quad \dots\dots\dots(i)$$

For dissociation of weak base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$\text{Then, } K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \dots\dots\dots(ii)$$

Divided (i) by equation (ii)

$$\frac{K_w}{K_b} = \frac{[H^+][NH_4OH]}{[NH_4^+]} = K_h$$

$$K_h = \frac{K_w}{K_b}$$

(iii) Degree Of Hydrolysis:-

Let we start with one mole of salt dissolved in V liter of solution. Then the equation when equilibrium attained is



Applying law of mass action

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{(1-\alpha)} = \frac{\alpha^2}{(1-\alpha)V}$$

When α is small ($1 - \alpha$) may be considered as equal to one, then

$$K_h = \frac{\alpha^2}{V} \Rightarrow K_h \times V = \alpha^2 \Rightarrow \alpha = \sqrt{K_h \times V}$$

We know from above equation $K_h = \frac{K_w}{K_b}$

$$\alpha = \sqrt{\frac{K_w \times V}{K_b}} \Rightarrow \alpha = \sqrt{\frac{K_w}{K_b \times C}}$$

(iv) Derivation Of pH:-

$$\text{We know that } [H^+] = \frac{\alpha}{V} = \alpha C$$

Substitution the value of α in equation (i)

$$[H^+] = \sqrt{\frac{K_w}{K_b \times C}} \times C \Rightarrow [H^+] = \sqrt{\frac{K_w C}{K_b}}$$

Taking log

$$\log H^+ = \frac{1}{2} \log K_w + \frac{1}{2} \log C - \frac{1}{2} \log K_b$$

Reversible sign

$$-\log [H^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log C + \frac{1}{2} \log K_b$$

$$\Rightarrow pH = \frac{1}{2} pK_w - \frac{1}{2} \log C - \frac{1}{2} \log pK_b$$

$$\therefore K_w = 1 \times 10^{-14}$$

$$pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

Thus pH of the solution is always being less than 7 solutions will be acidic.

Q.16. Define degree of hydrolysis and derive the relationship between K_a , K_b and K_h for the solution of salt of weak acid and weak base. (2009)

Other Related Question -

Q. Write short note on Hydrolysis of CH_3COONH_4 . (2016)

Ans. Salts Of Weak Acid And weak Bases:-

Such of salt both anion of weak acid (CH_3COO^-) and the cation of weak base (NH_4^+) undergo hydrolysis simultaneously



(i) Hydrolysis Constant:-

Applying law of mass action to the above hydrolysis reaction we have the hydrolysis constant K_h

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+][H_2O]}$$

$[H_2O]$ is very large and is taken to be constant

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \quad \dots\dots\dots(i)$$

(ii) Relation Between K_a , K_b And K_h :-

Applying law of mass action to the ionisation of weak acid, weak base, NH_4OH and water we can write CH_3COOH



$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad \dots\dots\dots(ii)$$



$$K_b = \frac{[OH^-][NH_4^+]}{[NH_4OH]} \quad \dots\dots\dots(iii)$$



$$K_w = [H^+][OH^-] \quad \dots\dots\dots(iv)$$

Dividing (iv) by (iii) and (ii) we have

$$\begin{aligned} \frac{K_w}{K_a \times K_b} &= \frac{[H^+][OH^-][CH_3COOH][NH_4OH]}{[CH_3COO^-][H^+][NH_4^+][OH^-]} \\ &= \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \end{aligned}$$

$$\frac{K_w}{K_a K_b} = K_h$$

Q.17. Show the for ammonium acetate solution, the degree of hydrolysis, x is given by :

$$x = \sqrt{\frac{K_w}{K_a K_b}} \quad (2007, 19)$$

Ans. Relation Between Hydrolysis Constant And Degree Of Hydrolysis:-

Let us start with 1 mole of the salt of a weak acid and base. If α is the degree of hydrolysis the equilibrium concentration are



$$K_h = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V} \times \frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)^2}$$

When α is very small the $(1-\alpha)$ may consider as one, then

$$K_h = \alpha^2 \Rightarrow \alpha^2 = \sqrt{K_h}$$

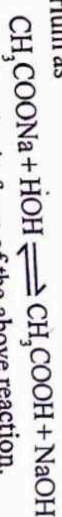
$$K_h = \frac{K_w}{K_a \times K_b} \Rightarrow \alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Q.18. Establish relation between k_a , k_b and k_w in hydrolysis of salts of weak acids and strong bases. (2014)

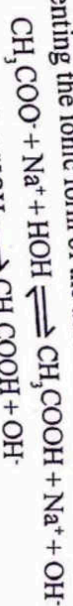
Ans. Hydrolysis of salt of weak acid and strong base:-

The hydrolysis of sodium acetate is represented at

equilibrium as



Representing the ionic form of the above reaction.



or $CH_3COO^- + HOH \rightleftharpoons CH_3COOH + OH^-$

Applying the law of mass action at equilibrium,

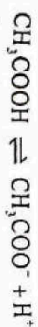
$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \dots\dots(i)$$

Where K_h is the hydrolysis constant.

$$K_h = K \times [\text{H}_2\text{O}]$$

here K is equilibrium constant.

By electrolytic ionization of weak acid,



Applying law of mass actions,

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\Rightarrow [\text{CH}_3\text{COOH}] = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{K_a} \quad \dots\dots(ii)$$

Where K_a is the ionization constant of the acid. Putting the value from eq.(ii) in eq.(i)

$$K_h = \frac{[\text{CH}_3\text{COO}^-][\text{OH}^-][\text{H}^+]}{[\text{CH}_3\text{COO}^-]K_a}$$

$$\text{or } K_h = \frac{[\text{H}^+][\text{OH}^-]}{K_a}$$

$$\text{or } K_h = \frac{K_w}{K_a}$$

where K_w is ionic product of water.

Q.19. Calculate degree of hydrolysis of 0.1 M solution of sodium acetate at 25°C, $K_a = 1.8 \times 10^{-5}$, $K_w = 1 \times 10^{-14}$

Ans: First we decide a given salt is which type here CH_3COONa it must be form from $\text{CH}_3\text{COOH} + \text{NaOH}$ reaction i.e. weak acid and strong base hence we can use the formula (2001)

$$\alpha = \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.1}} = 7.45 \times 10^{-5}$$

Q.20. In what amounts should 0.02 M HCl and 0.02 M monoacid base ($K_a = 8.1 \times 10^{-8}$) be mixed to make a buffer at pH = 7?
Sol. Now (2012)

For more details Visit Us At - www.winsomepublication.in

$$p_{\text{OH}} = p_{K_h} + \log \frac{[\text{Salt}]}{[\text{Base}]} = -\log(8.1 \times 10^{-8}) + \log \frac{(0.02)}{[\text{Base}]}$$

We know that $p_{\text{H}} + p_{\text{OH}} = 14$

$$7 = -\log(8.1 \times 10^{-8}) + \log \frac{(0.02)}{[\text{Base}]}$$

$$\Rightarrow \text{Base amount} = 1.62 \times 10^{-16}$$

Q.21. For the indicator thymol blue pH = 2, when half of the indicator is present in ionic form. Calculate the percentage (%) of the indicator in the unionized form in a solution of $4.0 \times 10^{-3} \text{ M H}^+$ ion. (2012)

Sol. Since at pH = 2.0, half of the indicator is present in the unionized form then

$$[\text{HI}] = [\text{I}^-]$$

$$p_{\text{H}} = pK_{\text{in}} + \log \frac{[\text{I}^-]}{[\text{HI}]}$$

$\therefore \text{I}_n = \text{indicator}$

and we know that

$$p_{K_{\text{in}}} = p_{\text{H}} = 2$$

pH of the solution containing $4.0 \times 10^{-3} \text{ M}$ of H^+ is

$$p_{\text{H}} = -\log(4.0 \times 10^{-3}) = 2.4$$

$$\text{Thus } \log \frac{[\text{I}_n]}{[\text{HI}_n]} = p_{\text{H}} - p_{K_{\text{in}}} = 2.4 - 2.0 = 0.4$$

$$\text{or } \frac{[\text{I}_n]}{[\text{HI}_n]} = 2.5$$

Adding 1 on both side, we get

$$\frac{[\text{I}_n] + [\text{HI}_n]}{[\text{HI}_n]} = 3.5$$

$$\text{or } \frac{[\text{HI}_n]}{[\text{I}_n] + [\text{HI}_n]} = \frac{1}{3.5} = 0.286$$

Thus the percentage of indicator in the unionized form = 28.6

Q.22. To 100 ml of 0.2 M formic acid, $pK_a = 3.77$, is added 10 m mole of solid NaOH. What will be the final pH?

Sol. The given data are

$$pK_a = 3.77$$

$$\text{salt} + \text{acid} = 20 \text{ m mole}$$

The ratio of [salt]/[acid] must be calculated:

10 m mole of NaOH will neutralize 10 m mole of formic acid

Therefore (20 - 10) m mole of acid will be converted to salt:

$$\text{salt} = 10 \text{ m mole in } 100 \text{ ml,}$$

$$\text{acid} = 10 \text{ m mole in } 100 \text{ ml,}$$

Therefore

$$[\text{salt}]/[\text{acid}] = 100 \text{ mM} / 100 \text{ mM} = 1.$$

Substituting in Equation,

$$pH = 3.77 + \log 1, \quad pH = 3.77$$

Q.23. Molar conductance for BaCl_2 , NaCl and NaOH electrolytes at infinite dilution are 280.0×10^{-4} , 126.5×10^{-4} and $248.1 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$, respectively. Calculate molar conductance at infinite dilution for Ba(OH)_2 .

Ans. Ionic form of given species is as and desired to get Ba(OH)_2 :



Looking this ionic form of equation, if we multiply eq.(2) and (3) by two and reverse the eq.(2) and add all the (3) eqs then we get our desired.

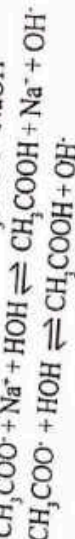
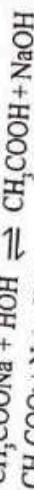


As we have do for getting the desired species we perform same with numerical value and add it.

$$\Lambda_0 \text{Ba(OH)}_2 = 280.0 \times 10^{-4} - 2 \times 126.5 \times 10^{-4} + 2 \times 248.1 \times 10^{-4}$$

$$\Lambda_0 \text{Ba(OH)}_2 = 523.2 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

2.24. Calculate pH of 0.01 M aqueous solution of sodium acetate at 25°C if K_a for acetic acid is 1.75×10^{-5} . (2014)



$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

$$pK_a = -\log K_a = 5 - \log 1.75 = 5 - 0.2430 = 4.760$$

$$\log C = \log 10^{-2} = -2.0$$

$$pH = 7 + \frac{1}{2} (4.760) + \frac{1}{2} (-2.0) = 7 + 2.3780 - 1 = 8.3780$$

For more details Visit Us At - www.winsomepublication.in

Q.25. The specific conductance of a 0.01N solution of acetic acid at 25°C is $1.63 \times 10^{-4} \text{ mho cm}^{-1}$ and the ionic conductance at infinite dilution at the same temperature for H^+ and CH_3COO^- ions are 349.8 and $40.9 \text{ mho cm}^2 \text{ equiv}^{-1}$ respectively. Calculate the dissociation constant of acetic acid at 25°C. Also calculate the H^+ ion concentration in the solution. (2018)

$$\text{Ans. (i) Molar conductance} = \frac{k \times 1000}{C}$$

$$= \frac{1.63 \times 10^{-4} \times 1000}{0.01} = 16.3 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$$

(ii) Degree of dissociation

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$$

$$\Lambda_m^\infty = 16.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m(\text{CH}_3\text{COOH}) = \lambda(\text{H}^+) + \lambda(\text{CH}_3\text{COO}^-)$$

$$= 349.8 + 40.9 = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{16.3}{390} = 0.0423$$

(iii) Dissociation constant (K)

Acetic acid dissociates as



$$\text{Initial concentration} \quad c \quad 0 \quad 0$$

$$\text{Equilibrium conc.} \quad c(1-\alpha) \quad c\alpha \quad c\alpha$$

$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{0.01 \times (0.0423)^2}{1 - 0.0423}$$

$$= 1.86 \times 10^{-5}$$

(iv) H^+ ion concentration



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Let $[\text{H}^+] = X$ then CH_3COO^- also equal to X and

$$\text{CH}_3\text{COOH} = 0.01 - X$$

Substituting these values into expression for the acid dissociation constant gives:

Shop Online at www.winsomecollection.co.in

$$\frac{[X][X]}{0.01 - X} = 1.86 \times 10^{-5}$$

Assuming, as before that (H^+) is so much less than 0.01 mass to be insignificant we rewrite the eq. as

$$\frac{x^2}{0.01} = 1.86 \times 10^{-5}$$

$$\Rightarrow x = \sqrt{0.186 \times 10^{-6}} = 0.431 \times 10^{-3}$$

Thus in 0.01N acetic acid

$$(H^+) = 0.431 \times 10^{-3} N$$

Q.26. The pH of a 0.1 M solution of ammonium chloride is 5.127. Calculate

(i) Degree of hydrolysis (ii) Hydrolysis constant and (iii) Dissociation constant of the base. (2019)

Ans. pH = 5.127 = $-\log[H^+]$

$$\Rightarrow \log[H^+] = 5.127 \Rightarrow [H^+] = \text{antilog of } (-5.127) = 7.4 \times 10^{-6}$$

The hydrolysis reaction is



$$(i) [H^+] = C\alpha = 7.4 \times 10^{-6} \Rightarrow \alpha = \frac{7.4 \times 10^{-6}}{0.1} = 7.4 \times 10^{-5}$$

(ii) The hydrolysis constant

$$K_h = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2$$

$$\Rightarrow K_h = 0.1 (7.4 \times 10^{-5})^2 = 5.56 \times 10^{-10}$$

$$(iii) K_h = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{K_b}$$

$$\Rightarrow K_b = \frac{1 \times 10^{-14}}{K_h} = \frac{1 \times 10^{-14}}{5.56 \times 10^{-10}} = 0.179 \times 10^{-4} = 1.79 \times 10^{-5}$$