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KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed University Established Under Section 3 of UGC Act 1956)
COIMBATORE-21
DEPARTMENT OF CHEMISTRY
B.Sc Chemistry

16CHU401 PHYSICAL CHEMISTRY IV (Electrochemistry) 4H 4C

Instruction Hours/week:L:4 T:0 P:0 Marks: Internal: 40 External: 60 Total:100

Scope

The course deals with different aspects of electrochemistry and fundamentals about the chemical kinetics, catalysis and photochemistry.

Methodology

Blackboard teaching, Power point presentation and group discussion.

Programme Outcome

1.To enable the types of conductance measurements and the factors affecting it
2.To impart knowledge on ionic mobilities and the applications of conductance measurements
3.To understand the order and molecularity of reactions and the integrated rate expressions for different types of first order reactions
4. To Understand the fundamentals of photochemistry

Programme Learning Outcome

1.Students know the types of conductance measurements and the factors affecting it
2.Students learned the applications of conductance measurements
3.Students know the order and molecularity of reactions and the integrated rate expressions for different types of first order reactions

UNIT I

Conductance: Quantitative aspects of Faraday's laws of electrolysis Arrhenius theory of electrolytic dissociation. Conductivity, equivalent and molar conductivity and their variation with dilution for weak and strong electrolytes. Molar conductivity at 29 infinite dilution. Kohlrausch law of independent migration of ions. Debye-Hückel-Onsager equation, Wien effect, Debye-Falkenhagen effect, Walden's rules.

UNIT II

Ionic velocities, mobilities and their determinations, transference numbers and their relation to ionic mobilities, determination of transference numbers using Hittorf and Moving Boundary methods. Applications of conductance measurement: (i) degree of dissociation of weak electrolytes, (ii) ionic product of water (iii) solubility and solubility product of sparingly soluble salts, (iv) conductometric titrations, and (v) hydrolysis constants of salts.

UNIT III

Chemical Kinetics: Order and molecularity of a reaction, rate laws in terms of the advancement of a reaction, differential and integrated form of rate expressions up to second order reactions, experimental methods of the determination of rate laws, kinetics of complex reactions (integrated rate expressions up to first order only): (i) Opposing reactions (ii) parallel reactions and (iii) consecutive reactions and their differential rate equations (steady-state approximation in reaction mechanisms) (iv) chain reactions.

Unit IV

Temperature dependence of reaction rates; Arrhenius equation; activation energy. Collision theory of reaction rates, Lindemann mechanism, qualitative treatment of the theory of absolute reaction rates.

Catalysis: Types of catalyst, specificity and selectivity, mechanisms of catalyzed reactions at solid surfaces. Enzyme catalysis, Michaelis-Menten mechanism, acid-base catalysis.

Unit V

Photochemistry: Characteristics of electromagnetic radiation, Lambert-Beer's law and its limitations, physical significance of absorption coefficients. Laws, of photochemistry, quantum yield, actinometry, examples of low and high quantum yields, photochemical equilibrium and the differential rate of photochemical reactions, photosensitised reactions, quenching. Role of photochemical 34 reactions in biochemical processes, photostationary states, chemiluminescence.

Suggested Readings

Text Books:

1. Atkins, P.W & Paula, J.D. (2011). *Physical Chemistry*. 9th Ed. Oxford University Press.
2. B.R.Puri, L.R.Sharma, Madan S.Pathania, *Principles of physical chemistry*,(2013) Vishal publishing Co, Jalandhar
3. Madan, R.L. (2015). *Chemistry for Degree Students.* India. S. Chand and Company (New Delhi) Pvt, Ltd.

Reference Books

1. Engel, T. & Reid, P. (2012). *Physical Chemistry*. 3rd Ed. Prentice-Hall.
2. Rogers, D. W. (2010). *Concise Physical Chemistry*. Wiley.

KARPAGAM ACADEMY OF HIGHER EDUCATION

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Coimbatore – 641 021.

LECTURE PLAN

DEPARTMENT OF CHEMISTRY

Staff In charge : Dr.G.Ayyannan and H.Revathi
Class : B.Sc Chemistry
Subject : Electrochemistry
Subject Code : 16CHU401
Semester / Year : IV/II

S.No	Lecture Duration Period	Topics to be covered	Support Material/Page Nos
	UNIT I		
1	1	Quantitative aspects of Faraday's laws of electrolysis	T1:759-760
2	1	Arrhenius theory of electrolytic dissociation	T2:485
3	1	Conductivity, equivalent conductivity	T2:526-528
4	1	Molar conductivity and their variation with dilution for weak and strong electrolytes	T2:526-530
5	1	Molar conductivity at infinite dilution	T2:526-530
6	1	Kohlraush law of independent migration of ions	T2;535-536
7	1	Debys-Huckel-Onsager equation	T1:761-764
8	1	Wien effect	T1:761-764
9	1	Debye-Falkenhagen effect	T2:869-870

10	1	Walden's rules	T2:869-870
11	1	Revision and discussion of question papers	
	Total No of hours planned for Unit I-11		
	UNIT-II		
1	1	Ionic velocities	T1:760-762
2	1	Mobilities and their determinations	T1:760-762
3	1	Transference numbers and their relation to ionic mobilities	T2:532-535
4	1	Determination of transference numbers using hittorf method	T2:532-535
5	1	Moving boundary method	T2:534-535
6	1	Applications of conductance measurement	T2:542-544
7	1	Degree of dissociation of weak electrolytes	T2:542
8	1	Ionic product of water	T2:542
9	1	Solubility and solubility product of sparingly soluble salts	T2:543-544
10	1	Conductometric titrations and hydrolysis constants of salts	T2:545-546
11	1	Revision and discussion of question papers	
	Total No of hours planned for Unit II-11		
	UNIT-III		
1	1	Order and molecularity of a reaction	T1:787-790
2	1	Rate laws in terms of the advancement of a reaction	T1:787-790
3	1	Differential and integrated form of rate expressions up to second order reactions	T1:790-795
4	1	Experimental methods of the determination of rate laws	T1;790-795
5	1	Kinetics of complex reactions(integrated rate expressions up to first order only)	T2:224-225

6	1	Opposing reactions	T2:241-242
7	1	Parallel reactions	T2:241-242
8	1	Consecutive reactions	T1:803-804
9	1	Differential rate equations(steady-state approximation in reaction mechanisms)	T1:805-806
10	1	Chain reactions	T2:239-240
11	1	Chain reactions	T2:239-240
12	1	Revision and discussion of question papers	
	Total No of hours planned for Unit III-12		
	UNIT-IV		
1	1	Temperature dependence of reaction rates	T1:799-801
2	1	Arrhenius equation	T1:799-801
3	1	Activation energy	T1:811
4	1	Collision theory of reaction rates	T2:809-810
5	1	Lindemann mechanism	T1:809-810
6	1	Qualitative treatment of the theory of absolute reaction rates	T1:809-815
7	1	Catalysis:Types of catalyst, Specificity and selectivity	T1:876-878
8	1	Mechanisms of catalyzed reactions at solid surfaces	T1:878-880
9	1	Enzyme catalysis	T1:878-880
10	1	Michaelis-Menten mechanism, acid base catalysis	T1:878-880
11	1	Revision and discussion of question papers	
	Total No of hours planned for Unit IV-11		
	UNIT-V		
1	1	Characteristics of electromagnetic radiation	T1:489

2	1	Lambert-Beer’s law and its limitations	T1:490
3	1	Physical significance of absorption coefficients	T1:490-492
4	1	Laws of photochemistry	T2:792-793
5	1	Quantum yield actinometry	T2:798-800
6	1	Examples of low and high quantum yields	T2:798-800
7	1	Photochemical equilibrium	T2:800-805
8	1	The differential rate of photochemical reactions	T2:800-805
9	1	Photosensitised reactions,quenching	T2:804-806
10	1	Role of photochemical reactions in biochemical processes	T2:810-811
11	1	Photostationary states, Chemiluminescence	T2:806-807
12	1	Revision and discussion of question papers	
13	1	ESE question paper discussion	
14	1	ESE question paper discussion	
15	1	ESE question paper discussion	
	Total No of hours planned for Unit V-15		
Total planned hours	60		

SUPPORTING MATERIALS:
Text Books:

T1: Atkins,P.W and Paula,J.D (2011), *Physical Chemistry*, 9th Edition.Oxford university press.

T2: B.R.Puri, L.R.Sharma, Madan S.Pathania, *Principles of physical chemistry*,(2013) Vishal publishing Co, Jalandhar

UNIT-I

SYLLABUS

Conductance: Quantitative aspects of Faraday’s laws of electrolysis Arrhenius theory of electrolytic dissociation. Conductivity, equivalent and molar conductivity and their variation with dilution for weak and strong electrolytes. Molar conductivity at 29 infinite dilution. Kohlrausch law of independent migration of ions. Debye-Huckel-Onsager equation, Wien effect, Debye-Falkenhagen effect, Walden’s rules.

Quantitative aspects of Faraday’s laws of electrolysis

Faraday's First Law of Electrolysis

From the brief explanation above, it is clear that the flow of current through the external battery circuit fully depends upon how many electrons get transferred from negative electrode or cathode to positive metallic ion or cations. If the cations have valency of two like Cu^{++} then for every cation, there would be two electrons transferred from cathode to cation. We know that every electron has negative electrical charge - 1.602×10^{-19} Coulombs and say it is -e. So for disposition of every Cu atom on the cathode, there would be - 2.e charge transfers from cathode to cation. Now say for t time there would be total n number of copper atoms deposited on the cathode, so total charge transferred, would be - 2.n.e Coulombs. Mass m of the deposited copper is obviously function of number of atoms deposited. So, it can be concluded that the mass of the deposited copper is directly proportional to the quantity of electrical charge that passes through the electrolyte. Hence mass of deposited copper m ∝ Q quantity of electrical charge passes through the electrolyte.

Law of Electrolysis states that only, According to this law, the chemical deposition due to flow of current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it. *i.e.* mass of chemical deposition,

$$m \propto Quantity\ of\ electricity,\ Q \Rightarrow m = Z.Q$$

Where, Z is a constant of proportionality and is known as electro-chemical equivalent of the substance.

If we put Q = 1 coulombs in the above equation, we will get Z = m which implies that electro-chemical equivalent of any substance is the amount of the substance deposited on passing of 1 coulomb through its solution. This constant of passing of electro-chemical equivalent is generally expressed in terms of milligram per coulomb or kilogram per coulomb.

Faraday's Second Law of Electrolysis

So far we have learned that the mass of the chemical, deposited due to electrolysis is proportional to the quantity of electricity that passes through the electrolyte. The mass of the chemical, deposited due to electrolysis is not only proportional to the quantity of electricity passes through the electrolyte, but it also depends upon some other factor. Every substance will have its own atomic weight. So for same number of atoms, different substances will have different masses. Again, how many atoms deposited on the electrodes also depends upon their number of valency. If valency is more, then for same amount of electricity, number of deposited atoms will be less whereas if valency is less, then for same quantity of electricity, more number of atoms to be deposited. So, for same quantity of electricity or charge passes through different electrolytes, the mass of deposited chemical is directly proportional to its atomic weight and inversely proportional to its valency.

Faraday's second law of electrolysis states that, when the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight.

Chemical Equivalent or Equivalent Weight

The chemical equivalent or equivalent weight of a substance can be determined by **Faraday’s laws of electrolysis** and it is defined as the weight of that sub tenancy which will combine with or displace unit weight of hydrogen. The chemical equivalent of hydrogen is, thus, unity. Since valency of a substance is equal to the number of hydrogen atoms, which it can replace or with which it can combine, the chemical equivalent of a substance, therefore may be defined as the ratio of its atomic weight to its valency

$$Thus\ chemical\ equivalent = \frac{Atomic\ weight}{Valency}$$

Ostwald’s dilution law

Ostwald’s dilution law is the application of the law of mass action to weak electrolytes in solution. Suppose an acid HA is dissolved in water, it will ionize as under:

Applying law of mass action,

Where K_a is the dissociation (or ionisation) constant of the acid HA and α is its degree of dissociation.This equation is known as **Ostwald’s dilution law equation.** If $\alpha << 1$ then the above equation may be written as:

Thus at constant temperature degree of dissociation of weak electrolyte is directly proportional to square root of its dilution. The value of α can be calculated by measuring conductance of the solution as:

$$\alpha = \frac{\lambda_v}{\lambda_{infty}}$$

Where λ_v is the equivalent conductance at a particular dilution and λ_∞ is equivalent conductance at infinite dilution.

With the help of this equation; $[H+]$ or p^H of the acid solution may be calculated.

If we know the value of α and C for any acid then K_a may be calculated. For example, the value of α for 0.05 N acetic acid is 0.03.

Therefore the value of K_a for acetic acid will be,

$$K_a = \frac{0.05 \times 0.03 \times 0.03}{1 - 0.02}$$

$$4.64 \times 10^{-5}$$

THEORIES OF ACIDS AND BASES

This page describes the Arrhenius, Bronsted-Lowry, and Lewis theories of acids and bases, and explains the relationships between them. It also explains the concept of a conjugate pair - an acid and its conjugate base, or a base and its conjugate acid.

The Arrhenius Theory of acids and bases

- Acids are substances which produce hydrogen ions in solution.
- Bases are substances which produce hydroxide ions in solution.

Neutralization happens because hydrogen ions and hydroxide ions react to produce water.

Limitations of the theory

Hydrochloric acid is neutralised by both sodium hydroxide solution and ammonia solution. In both cases, you get a colourless solution which you can crystallise to get a white salt - either sodium chloride or ammonium chloride.

These are clearly very similar reactions. The full equations are:

In the sodium hydroxide case, hydrogen ions from the acid are reacting with hydroxide ions from the sodium hydroxide - in line with the Arrhenius theory.

However, in the ammonia case, there don't appear to be any hydroxide ions.

You can get around this by saying that the ammonia reacts with the water it is dissolved in to produce ammonium ions and hydroxide ions:

This is a reversible reaction, and in a typical dilute ammonia solution, about 99% of the ammonia remains as ammonia molecules. Nevertheless, there are hydroxide ions there, and we can squeeze this into the Arrhenius theory.

However, this same reaction also happens between ammonia gas and hydrogen chloride gas.

In this case, there aren't any hydrogen ions or hydroxide ions in solution - because there isn't any solution. The Arrhenius theory wouldn't count this as an acid-base reaction, despite the fact that it is producing the same product as when the two substances were in solution.

Weak electrolytes obey Ostwa1d’s dilution law fairly well, but strong electrolytes do not obey

1. **The relaxation effect:** According to this effect, each cation is surrounded by a number of anions and vice versa in solution; which is called ionic atmosphere of the oppositely charged ions. On applying e.m.f., the ion moves towards oppositely charged electrode leaving behind the ionic atmosphere. To form a new ionic atmosphere some time is taken which is called **relaxation time** and this effect of the ionic atmosphere is called **relaxation effect**. Due to this effect the value of λ is not limiting.
2. **The electrophoretic effect:** Since solvent molecules attached to the ionic atmosphere moving in the opposite direction produce friction hence reduce the motion of central ion.

Basics of ionic conduction

The conduction of electricity through an ionic solution is different from metallic conduction in two fundamental ways:

The current is associated with the transport of relatively large and massive hydrated ions, rather than by nearly weightless electrons. Electrons move largely unimpeded through the metal. But ions, with their closely-held waters of hydration and more diffuse secondary hydration shell and oppositely-charged counterions, must disrupt the local hydrogen-bonded water structure as they move through the solution.Transfer of electric charge into and out of the solution occurs at electrodes, and is accompanied by chemical reactions at these interfaces.

Electrolytic conduction involves the transport of electric charge in the form of hydrated ions. Movement of these ions in response to an electric potential gradient is known as migration. Electric charge is measured in units of coulombs. A coulomb is an ampere-second; if a current of 1 amp flows for one minute, the quantity of charge transported will be 3600 C.

When charges migrate in an electric field, thermodynamic work is done. One C of charge moving through a potential difference of one volt results in the performance of one joule of work.

Arrhenius Theory of Electrolytic Dissociation

Arrhenius (1887) put forward the theory of electrolytic dissociation, as a more explicit form of one he had proposed in 1883, which forms the basis of the modern treatment of electrolytes. The assumption made was that when an acid, base or salt is dissolved in water, a considerable portion becomes spontaneously dissociated into positive and negative ions. Considering an electrolyte $A_{\nu+}$ $B_{\nu-}$ which might undergo complete dissociation to form ν_+ positive ions and ν_- negative ions according to the equation

$$A_{\nu+} B_{\nu-} = +\nu_+ A^{z+} + \nu_- B^{Z-}$$

We must calculate the net number of particles that result from a degree of dissociation α. If m is the molality of the electrolyte, α is the degree of dissociation, the concentration of undissociated electrolyte will be m -αm = m(1 - α). In addition, the concentration of A^{z+} and B^{Z-} will be ν_+ αm and ν_- αm, respectively.

Here the concentration of particles is m(1 - α) + (ν_+)αm + (ν_-)αm and let ν be the total number of ions yielded by complete dissociation of the electrolyte, i.e, $\nu = \nu_+ + \nu^-$. With this notation the molality of particles for the partially dissociated electrolyte is m(1-α) + ανm rather than the value of 'm' expected for no dissociation.

The van't Hoff 'I' factor can be written as

$$= \frac{m(1-\alpha)+\alpha\nu m}{m} = 1-\alpha+\alpha\nu$$

From this interpretation of i, one obtains

$$\alpha = \frac{i-1}{\nu-1}$$

This relation can also be used inspite of the relation $\alpha = \Lambda/\Lambda^{\infty}_{m}$, for calculating the degree of dissociation of an electrolyte.

Electrical resistance, conductance, and conductivity

Ionic migration is always impeded by the drag created by the hydration shell as the ions break their way through the hydrogen-bonded water structure. Electrolytic conduction is therefore always associated with a certain amount of electrical resistance. Electrical resistance is defined by Ohm's law $R = V/i$in which V is the potential difference (voltage) and i is the current. Resistance is expressed in ohms, whose symbol is Ω (omega).

Resistance is an extensive property because it depends on the thickness and cross-section area of the material through which the current flows. The intensive analog of resistance is the resistivity ρ (rho), defined as the resistance between opposite faces of a 1-cm cube. Resistivity is usually expressed in ohm-cm.

In working with electrolytic solutions, it is more convenient to use the corresponding reciprocal properties:

$$\text{conductance } \Lambda \text{ (lambda)} = 1/R$$

$$\text{conductivity } \kappa \text{ (kappa)} = 1/\rho$$

The SI unit of conductance is the siemens, indicated by the symbol S.
Conductivity, the reciprocal of the resistivity, is frequently expressed in $\text{ohm}^{-1}\text{cm}^{-1}$ or S cm^{-1}, but the SI units are S m^{-1}.

Conductance measurements

The traditional method of measuring resistance or conductance is by means of a Wheatstone bridge arrangement in which a known resistance is balanced against the unknown resistance. The latter consists of a conductivity cellhaving electrodes of fixed size and spacing. Nowadays it is more common to employ a digital measuring device.

In practical measurements of conductivity, no attempt is made to define the precise dimensions of the conductive path. Instead, the conductance cell is first calibrated by filling it with a standardized solution of potassium chloride, for which extensive conductivity data is available.

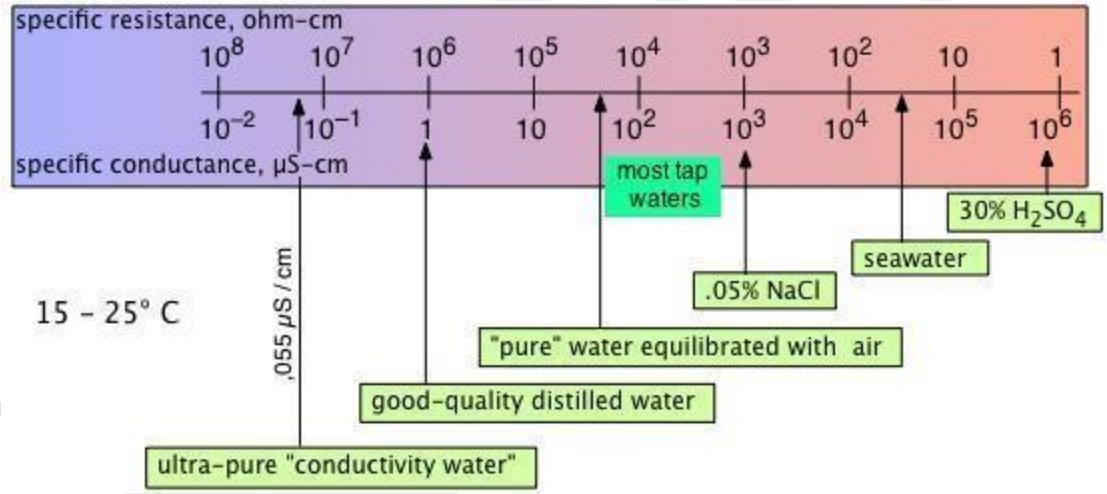
Because resistances can be measured to very high precision, conductance measurements can be extended to very dilute solutions if impurities are guarded against, of which dissolved atmospheric CO_2 is the most common.

Heroic measures may be required to purify water sufficiently: after 42 successive vacuum distillations, Kohlrausch in 1894 obtained a "conductivity water" with $\kappa = 0.043 \times 10^{-6}$ S cm^{-1} at

18°C. Ordinary distilled water in equilibrium with atmospheric CO_2 has a conductivity that is 16 times greater.

It is now known that ordinary distillation cannot entirely remove all impurities from water. Ionic impurities get entrained into the fog created by breaking bubbles and are carried over into the distillate by capillary flow along the walls of the apparatus. Organic materials tend to be steam-volatile ("steam-distilled").

The best current practice is to employ a special still made of fused silica in which the water is volatilized from its surface without boiling. Complete removal of organic materials is accomplished by passing the water vapor through a column packed with platinum gauze heated to around 800°C through which pure oxygen gas is passed to ensure complete oxidation of carbon compounds.



Conductance measurements are widely used to gauge water quality, especially in industrial settings in which concentrations of dissolved solids must be monitored in order to schedule maintenance of boilers and cooling towers.

Molar and equivalent conductivity

The conductance of a solution depends on 1) the concentration of the ions it contains, 2) on the number of charges carried by each ion, and 3) on themobilities of these ions. The latter term refers to the ability of the ion to make its way through the solution, either by ordinary thermal diffusion or in response to an electric potential gradient.

The first step in comparing the conductances of different solutes is to reduce them to a common concentration. For this, we define the conductance per unit concentration which is known as the molar conductivity, denoted by the upper-case Greek lambda:

$$\Lambda = \kappa/c$$

When κ is expressed in S cm^{-1}, C should be in mol cm^{-3}, so Λ will have the units S cm^2. This is best visualized as the conductance of a cell having 1-cm^2 electrodes spaced 1 cm apart that is, of a 1 cm cube of solution. But because chemists generally prefer to express concentrations in mol L^{-1} or mol dm^{-3} (mol/1000 cm^3) , it is common to write the expression for molar conductivity as

$$\Lambda = 1000\kappa/c$$

whose units are S cm2 mol L^{-1}. This corresponds to a 1000 cm–3 cube of solution composed of two 1000-cm2 electrodes, separated again by 1 cm.

But if c is the concentration in moles per liter, this will still not fairly compare two salts having different stoichiometries, such as $AgNO_3$ and $FeCl_3$, for example. If we assume that both salts dissociate completely in solution, each mole of $AgNO_3$ yields two moles of charges, while $FeCl_3$ releases six(i.e., one Fe^{3+} ion, and three Cl^- ions.) So if one neglects the [rather small] differences in the ionic mobilities, the molar conductivity of $FeCl_3$ would be three times that of $AgNO_3$.

Equivalents and equivalent concentration

The most obvious way of getting around this is to note that one mole of a 1:1 salt such as $AgNO_3$ is "equivalent" (in this sense) to 1/3 of a mole of $FeCl_3$, and of ½ a mole of $MgBr_2$.

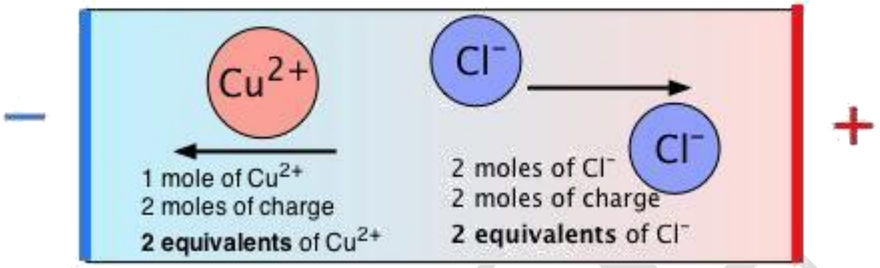
To find the number of equivalents that correspond a given quantity of a salt, just divide the number of moles by the total number of positive charges in the formula unit. (If you like, you can divide by the number of negative charges instead; because these substances are electrically neutral, the numbers will be identical.)

Note that we can refer to equivalent concentrations of individual ions as well as of neutral salts. Also, since acids can be regarded as salts of H^+, we can apply the concept to them; thus a

1M L^{-1} solution of sulfuric acid H_2SO_4 has a concentration of 2 eq L–1.

The following diagram summarizes the relation between moles and equivalents for $CuCl_2$:

The following diagram summarizes the relation between moles and equivalents for $CuCl_2$:



Equivalent conductivity

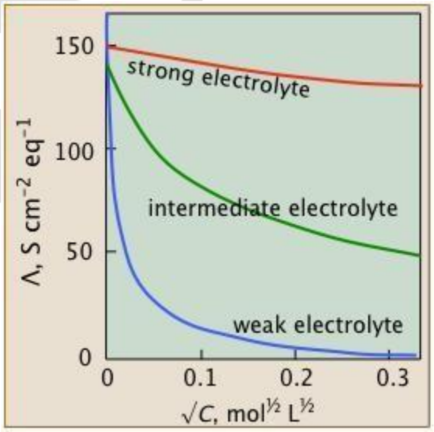
The concept of equivalent concentration allows us to compare the conductances of different salts in a meaningful way. Equivalent conductivity is defined similarly to molar conductivity

$$\Lambda = \kappa/c$$

except that the concentration term is now expressed in equivalents per liter instead of moles per liter. (In other words, the equivalent conductivity of an electrolyte is the conductance per equivalent per liter.)

Electrolytes weak and strong

The serious studies of electrolytic solutions began in the latter part of the 19th century, mostly in Germany and before the details of dissociation and ionization were well understood.



These studies revealed that the equivalent conductivities of electrolytes all diminish with concentration (or more accurately, with the square root of the concentration), but they do so in several distinct ways that are distinguished by their behaviors at very small concentrations. This led to the classification of electrolytes as weak, intermediate, and strong.

You will notice that plots of conductivities vs. √c start at c=0. It is of course impossible to measure the conductance of an electrolyte at vanishingly small concentrations (not to mention zero!), but for strong and intermediate electrolytes, one can extrapolate a series of observations to zero. The resulting values are known as limiting equivalent conductances or sometimes as "equivalent conductances at infinite dilution", designated by Λ°.

Strong electrolytes

These well-behaved systems include many simple salts such as NaCl, as well as all strong acids. The Λ vs. √c plots closely follow the linear relation

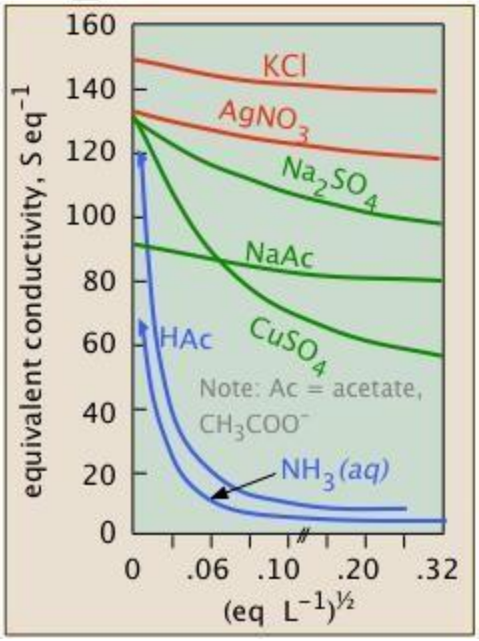
$\Lambda = \Lambda^\circ - b\sqrt{c}$

Intermediate electrolytes

These "not-so-strong" salts can't quite conform to the linear equation above, but their conductivities can be extrapolated to infinite dilution.

Weak electrolytes

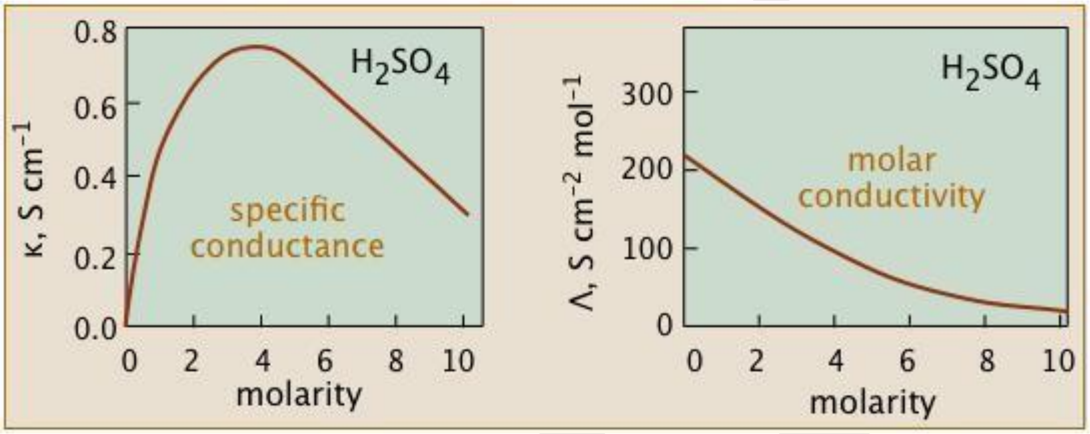
"Less is more" for these oddities which possess the remarkable ability to exhibit infinite equivalent conductivity at infinite dilution. Although Λ° cannot be estimated by extrapolation, there is a clever work-around.



Conductivity diminishes as concentrations increase

Since ions are the charge carriers, we might expect the conductivity of a solution to be directly proportional to their concentrations in the solution. So if the electrolyte is totally dissociated, the conductivity should be directly proportional to the electrolyte concentration.

But this ideal behavior is never observed; instead, the conductivity of electrolytes of all kinds diminishes as the concentration rises.



The non-ideality of electrolytic solutions is also reflected in their colligative properties, especially freezing-point depression and osmotic pressure.

The primary cause of this is the presence of the ionic atmosphere that was introduced above. To the extent that ions having opposite charge signs are more likely to be closer together, we would expect their charges to partially cancel, reducing their tendency to migrate in response to an applied potential gradient.

A secondary effect arises from the fact that as an ion migrates through the solution, its counter-ion cloud does not keep up with it. Instead, new counter-ions are continually acquired on the leading edge of the motion, while existing ones are left behind on the opposite side. It takes some time for the lost counter-ions to dissipate, so there are always more counter-ions on the trailing edge. The resulting asymmetry of the counter-ion field exerts a retarding effect on the central ion, reducing its rate of migration, and thus its contribution to the conductivity of the solution.

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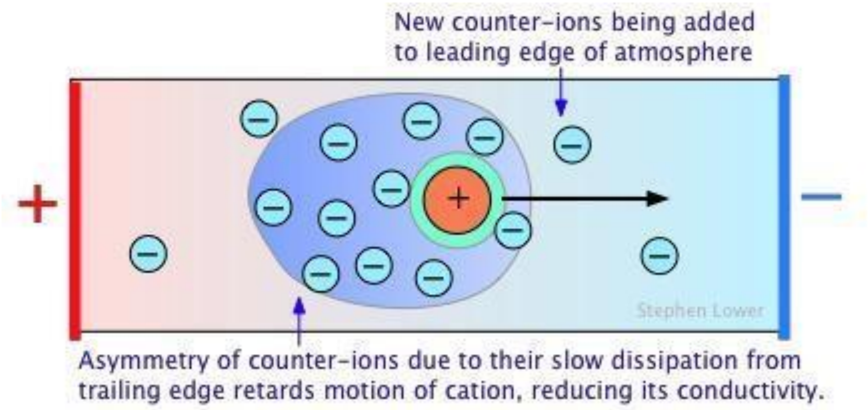
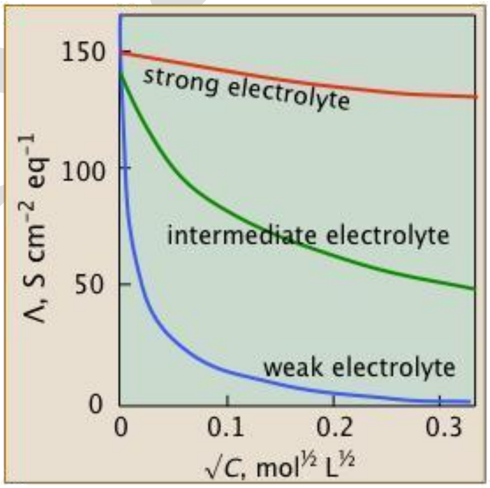


The quantitative treatment of these effects was first worked out by P. Debye and W. Huckel in the early 1920's, and was improved upon by Ostwald a few years later. This work represented one of the major advances in physical chemistry in the first half of the 20th Century, and put the behavior of electrolytic solutions on a sound theoretical basis. Even so, the D-H theory breaks down for concentrations in excess of about 10^{-3} M L^{-1} for most ions.

Many electrolytes are not totally dissociated in solution. The nearly-linear nature of conductivity-vs.-√c plots for strong electrolytes is largely explained by the effects discussed immediately above. The existence of intermediate electrolytes served as the first indication that many salts are not completely ionized in water; this was soon confirmed by measurements of their colligative properties.



The curvature of the plots for intermediate electrolytes is a simple consequence of the LeChatelier effect, which predicts that the equilibrium

$$MX(aq) = M^+(aq) + X^-(aq)$$

will shift to the left as the concentration of the "free" ions increases. In more dilute solutions, the actual concentrations of these ions are smaller, but their fractional abundance in relation to the undissociated form is greater. As the solution approaches zero concentration, virtually all of the MX(aq) becomes dissociated, and the conductivity reaches its limiting value.

Weak electrolytes are dissociated only at extremely high dilution

Hydrofluoric acid	HF	Ka = 10–3.2
Acetic acid	CH_3COOH	Ka = 10–6.3
Bicarbonate ion	$H_3CO–$	Ka = 10–10.3
Ammonia	NH_3	Kb = 10–4.7

Dissociation, of course, is a matter of degree. The equilibrium constants for the dissociation of an intermediate electrolyte salt MX are typically in the range of 1-200. This stands in contrast to the large number of weak acids (as well as weak bases) whose dissociation constants typically range from 10^{-3} to smaller than 10^{-10}. These weak electrolytes, like the intermediate ones, will be totally dissociated at the limit of zero concentration; if the scale of the weak-electrolyte plot (blue) shown above were magnified by many orders of magnitude, the curve would resemble that for the intermediate electrolyte above it, and a value for Λ° could be found by extrapolation. But at such a high dilution, the conductivity would be so minute that it would be masked by that of water itself (that is, by the H^+ and OH^- ions in equilibrium with the massive 55.6 M L^{-1} concentration of water) -making values of Λ in this region virtually unmeasurable.

Kohlrausch's law greatly simplifies estimates of Λ^0.

This principle is known as Kohlrausch's law of independent migration, which states that in the limit of infinite dilution,

Each ionic species makes a contribution to the conductivity of the solution that depends only on the nature of that particular ion, and is independent of the other ions present.

Kohlrausch's law can be expressed as

$\Lambda 0 = \Sigma\, \lambda_0^+ + \Sigma\, \lambda_0^-$

This means that we can assign a limiting equivalent conductivity λ_0 to each kind of ion:

Just as a compact table of thermodynamic data enables us to predict the chemical properties of a very large number of compounds, this compilation of equivalent conductivities of twenty different species yields reliable estimates of the of Λ^0 values for five times that number of salts.

One useful application of Kohlrausch's law is to estimate the limiting equivalent conductivities of weak electrolytes which, as we observed above, cannot be found by extrapolation. Thus for acetic acid CH_3COOH ("HAc"), we combine the λ^0 values for H_3O^+ and CH_3COO^- given in the above table:

$$\Lambda_0 HAc = \lambda_0 H^+ + \lambda_0 Ac^-$$

Movement of a migrating ion through the solution is brought about by a force exerted by the applied electric field. This force is proportional to the field strength and to the ionic charge.

Calculations of the frictional drag are based on the premise that the ions are spherical (not always true) and the medium is continuous (never true) as opposed to being composed of discrete molecules. Nevertheless, the results generally seem to be realistic enough to be useful.

According to Newton's law, a constant force exerted on a particle will accelerate it, causing it to move faster and faster unless it is restrained by an opposing force. In the case of electrolytic conductance, the opposing force is frictional drag as the ion makes its way through the medium. The magnitude of this force depends on the radius of the ion and its primary hydration shell, and on the viscosity of the solution.

Eventually these two forces come into balance and the ion assumes a constant average velocity which is reflected in the values of λ_0 tabulated in the table above.

The relation between λ_0 and the velocity (known as the ionic mobility μ^0) is easily derived, but we will skip the details here, and simply present the results:

Anions are conventionally assigned negative μ^0 values because they move in opposite directions to the cations; the values shown here are absolute values $|\mu^0|$.

As with the limiting conductivities, the trends in the mobilities can be roughly correlated with the charge and size of the ion. (Recall that negative ions tend to be larger than positive ions.)

Cations and anions carry different fractions of the current. In electrolytic conduction, ions having different charge signs move in opposite directions. Conductivity measurements give only the sum of the positive and negative ionic conductivities according to Kohlrausch's law, but they do not reveal how much of the charge is carried by each kind of ion. Unless their mobilities are the same, cations and anions do not contribute equally to the total electric current flowing through the cell.

Recall that an electric current is defined as a flow of electric charges; the current in amperes is the number of coulombs of charge moving through the cell per second. Because ionic solutions contain equal quantities of positive and negative charges, it follows that the current passing through the cell consists of positive charges moving toward the cathode, and negative charges moving toward the anode. But owing to mobility differences, cations and ions do not usually carry identical fractions of the charge.

Debye Huckel Onsager equation

In 1926, Debye, Huckel and onsager worked out mathematically the magnitudes of asymmetry and electrophoretic effects in terms of such factors as valency of the ion, ionic concentration and dielectric constant and viscosity of the medium.

For a given solvent and at a given temperature, Debye-Huckel Onsager equation

$$\wedge_m=\wedge^0_m-(A+B\wedge^0_m)\sqrt{c}$$

Where A and B are the Deby-Huckel constants.

The values of A nad B for water at 25^0C come out to be 60.2 and 0.229, respectively

$$\wedge_m=\wedge^0_m-(60.2+0.229\wedge^0_m)\sqrt{c}$$

Debye –Falkenhagen effect

Debye and Falkenhagen examined the conductance behavior of a solution of a strong electrolyte by applying alternating currents of different frequencies. They predicted that if the frequency of alternating current is high so that the time of oscillation is small in comparison with the relaxation time of the ionic atmosphere, the asymmetry effect will be virtually absent. In other words, the ionic atmosphere around the central ion will remain symmetric. The retarding effect due to asymmetry may, therefore be entirely absent and the conductance may be higher. The conductance of a solution therefore should vary with the frequency of the alternating current used. The higher the frequency the higher the conductance evidently. This effect also known as dispersion of conductance has been verified experimentally.

Wien effect

Speed of an ion in an electric field varies with the applied potential gradient. Thus, under a potential gradient of about 20,000 volt per cm, an ion may have a speed of about 100 cm per sec. the ion, therefore should pass several times through the thickness of the ionic atmosphere during the time of relazation. The moving ion, therefore, will be moving so fast that there will be no time for the ionic atmosphere to be built up. The asymmetry and electrophoretic effects, under these circumstances, may be negligibly small or even absent. Thus, the conductance of a strong electrolyte in aqueous solution increases to a certain limiting value with increase in potential gradient applied.

Walden's rule

An empirical rule suggested by P. Walden (1863–1957) concerning ions in solutions, stating that the product of the molar conductivity, Λ_m, and the viscosity, η, is approximately constant for the same ions in different solvents. Some justification for Walden's rule is provided by the proportional relationship between Λ_m and the diffusion coefficient, D; as D is inversely proportional to the viscosity, Λ_m is inversely proportional to η, which is in accordance with Walden's rule. However, different solvents hydrate the same ions differently, so that both the radius and the viscosity change when the solvent is changed. It is this fact that limits the validity of the rule.

UNIT I

POSSIBLE QUESTIONS

PART- B

(Each carries two marks)

1. What is cell constant?
2. What is meant by strong electrolyte? Give two examples.
3. Define Walden's rules.
4. What is meant by conductance?
5. Define Faraday's 1st law.

PART C

(Each carries Six marks)

1. Derive the Debye-Huckel Onsager equation.
2. Explain the following terms
    (i) Debye- Falkenhagen effect
    (ii) Wien effect
3. Explain the Arrhenius theory of electrolytic dissociation.

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(For the candidates admitted from 2016 & onwards)
II B.Sc. Chemistry
PHYSICAL CHEMISTRY

UNIT I
Multiple choice questions

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
	Unit 1					
1	The unit of specific conductance are	sm^{-1}	sm^{2}	sm	1/rho	sm^{-1}
2	The resistance of 0.01 m solution of an electrolyte was found to be 210 ohm at 25°c. calculate molar conductance of the solution at 25°c cell constant = 0.88 cm^{-1}	0.829 sm^{2} mol^{-1}	0.0419 sm^{2} mol^{-1}	1.829 sm^{2} mol^{-1}	0.0419 sm^{2} mol^{-1}	0.0419 sm^{2} mol^{-1}
3	The fraction of the total current carried by each ions is called	transport number	hittorf's method	kohlrauschs law	wien effect	transport number
4	For the strong electrolytes NaOH, NaCl and $BaCl_2$ the molar ionic conductances are infinite dilution are 248.1x 10^{-4} , 126.5 x 10^{-4} and 280.0 x 10^{-4} sm^{2} mol^{-1} respectively. Calculate λ_m° for $Ba(OH)_2$	523.2x 10^{-4} sm^{2} mol^{-1}	9.45x 10^{-4} sm^{2} mol^{-1}	253.2x 10^{-4} sm^{2} mol^{-1}	183x 10^{-4} sm^{2} mol^{-1}	523.2x 10^{-4} sm^{2} mol^{-1}
5	The degree of dissociation of a weak electrolyte at any dilution can be calculated by the relationship of	$\alpha=\Delta m/\Delta^{\circ} m$	$\alpha=1$	$\alpha=\Delta^{\circ} m/\Delta m$	$\alpha=-1$	$\alpha=\Delta m/\Delta^{\circ} m$
6	which one of the following is a conductance measurements	determination of ionic product of water	conductometric titration	Concetration of solution	Total number of ions	determination of ionic product of water
7	The equilibrium constant K is called	dissociation constant of the electrolyte	dissociation constant of the weak electrolyte	dissociation constant of the acid	dissociation constant of the base	dissociation constant of the electrolyte
8	Fraction of the total current carried by potassium ion in KCl is called	transport number	hittorf's method	kohlrauschs law	wien effect	transport number
9	Who put forward their well known theory of strong electrolytes	Peter debye and E. Huckel	Ostwald	Kohlrausch	Huckel	Ostwald

10	Decrease in molar conductance with increase in concentration is not due to fall the degree of ionisation but to fall in mobilities of ions due to greater	interionic effect	wien effect	viscous effect	interionic effect	interionic effect
11	The drag on the central ion is known as	assymmetry effect	symmetry effect	viscous effect	interionic effect	assymmetry effect
12	The counter current slow down the ion in the same way as counter current in a stream slow down a swimmer this effect is known as	electrophoretic effect	viscous effect	Interionic effect	wein effect	electrophoretic effect
13	The speed of the ion per unit potential gradient is called as	ionic mobility	ionic conductance	Potetial	Conductance	ionic mobility
14	The molar ionic conductance at infinite dilution of silver ions is $61.92x10^{-4}$ sm^2 mol^{-1} at 25°c. Calculate the ionic mobility of Ag ions at 25°c at infinite dilution.	$6.417x10^{-8}$ m^2 v^{-1} s^{-1}	$3.321x10^{-8}$ m^2 v^{-1} s^{-1}	$6.417x10^{-3}$ m^2 v^{-1} s^{-1}	$3.321x10^{-3}$ m^2 v^{-1} s^{-1}	$6.417x10^{-8}$ m^2 v^{-1} s^{-1}
15	Calculate the molar conductance at infinite dilution of an aqueous solution of NaCl at room temperature, given that the mobilities of Na^+ and Cl^- ions at this temperature are 4.26 x 10^{-8} and 6.08 x 10^{-8} $m^2v^{-1}s^1$ respectively	106.71 x 10^{-4} sm^2 mol^{-1}	108.71 x 10^{-4} sm^2 mol^{-1}	106.71 x 10^{-8} sm^2 mol^{-1}	102.71 x 10^{-6} sm^2 mol^{-1}	106.71 x 10^{-4} sm^2 mol^{-1}
16	Calculate ionic mobility of Na^+ ion in 0.1 m aqueous solution of NaCl at 25°c if the diffusion co-efficient of Na^+ ions is 1.30 x 10^{-9} m^2 s^{-1}	$3.2x10^{-8}$ m^2 v^{-1} s^{-1}	$5.06x10^{8}$ m^2 v^{-1} s^{-1}	$5.6x10^{8}$ m^2 v^{-1} s^{-1}	$5.06x10^{-8}$ m^2 v^{-1} s^{-1}	$5.06x10^{-8}$ m^2 v^{-1} s^{-1}
17	According to Kohlrausch's law, conductivity of ions is constant at	fixed temperature	infinite dilution	1 M concentration	all the concentrations	a. fixed temperature
18	Each ions carry a fraction of the total current is called	transport number	hittorf's method	kohlrauschs law	wien effect	transport number
19	In the given equation $a=Y_m$ where Y is called	activity coefficient	mean ionic activity	mean ionic active coefficient	Concentration	activity coefficient
20	Specific conductance is measured in	sm^{-1}	sm^2	sm	1/rho	sm^{-1}
21	In molar conductance λ_m is measured in terms of	k/m	k/c	k/s	k/sa	k/c
22	What is the unit of k (kappa)	sm^{-1}	s^2m^2	$s^{-1}m$	s/m^2	sm^{-1}

23	What is the unit of c (concentration of a solution)?	mol m^2	mol m	mol m^{-3}	mol mK	mol m^{-3}
24	What is the unit of λ_m (Molar conductance)	$Smmol^{-1}$	Sm^2mol^{-1}	Sm mol^{-2}	Sm^2mol^{-2}	Sm^2mol^{-1}
25	The specific conductance of a decimolar solution of potassium chloride at 18°c is 1-12 Sm^{-1}. The resistance of a conductivity cell containing the solution at 18°c was found to be 55 ohm. What is the cell constant ?	6.16 m^{-1}	616 m^{-1}	0.616 m^{-1}	6.16 m^{-1}	6.16 m^{-1}
26	The resistance of 0.5 m solution of an electrolyte in a cell was found to be 45Ω. Calculate the molar conductance of the solution if the electrodes in the cell are 2.2 cm apart and have an area of 3.8 cm^2.	2.572x 10^{-4} Sm^2 mol^{-1}	25.72x 10^{-4} Sm^2 mol^{-1}	257.2x 10^{-2} Sm^2 mol^{-1}	25.72x 10^{-2} Sm^2 mol^{-1}	25.72x 10^{-4} Sm^2 mol^{-1}
27	The specific conductance of water is 7.8x10^{-2} Sm^{-1} and the specific conductance of 0.1 m aqueous solution of KCl is 1.1639 Sm^{-1}. A cell has a resistance of 33.20Ω when filled with 0.1 m KCl solution and 300Ω when filled with 0.1m acetic acid solution . calculate the molar conductance of acetic acid.	53x 10^{-4} Sm^2 mol^{-1}	5.3x 10^{-4} Sm^2 mol^{-1}	2.6x 10^{-4} Sm^2 mol^{-1}	26x 10^{-4} Sm^2 mol^{-1}	5.3x 10^{-4} Sm^2 mol^{-1}
28	An electrolytes Infinite dilution is denoted by	λ°m	1/λ°m	λ°c	1/λ°c	λ°m
29	The specific conductance of 0.01m solution of CH_3COOH was found to be 0.063 Sm^{-1} at 25°c. Calculate the degree of dissociation of acid. Molar conductance of acetic acid at infinite dilution is 390.7x10^{-4} Sm^2 mol^{-1} at 25°c?	0.0472	0.472	0.3852	0.4278	0.0472
30	A potential of 12.0 volts was applied to two electrodes placed 20cm apart. A dilute solution of NH_4Cl was placed between the electrodes when NH_4^+ ions was found to be cover a distance of 1-60cm in one hour. What is the mobility of NH_4^+ ion?	7.24x10^8 m^2 v^{-1} s^{-1}	7.41x10^{-8} m^2 v^{-1} s^{-1}	7.8x10^{-8} m^2 v^{-1} s^{-1}	7.85x10^{-8} m^2 v^{-1} s^{-1}	7.41x10^{-8} m^2 v^{-1} s^{-1}

31	The ionic mobility is extremely small as compared to the speed of gaseous molecule which is about	10^3 ms^{-1}	10^2 ms^{-1}	10^{-2} ms^{-1}	10^{-4} ms^{-1}	10^2 ms^{-1}
32	Ice has tetrahedral structure with each oxygen atom surrounded by four oxygen atom at a distance of	276 pm	284 pm	225 pm	296 pm	276 pm
33	According to Kohlrausch’s law, conductivity of ions at infinite dilutions does not depend on	nature of co-ions	temperature	pressure	concentration	nature of co-ions
34	The measurement of specific conductance of a strong electrolyte is	sm^{-1}	sm^2	sm	1/rho	sm^{-1}
35	Decimolar solution of potassium chloride at 18°c specific conductance is 1-12 Sm^{-1}. The resistance of a conductivity cell containing the solution at 18°c was found to be 55 ohm. What is the cell constant ?	6.16 m^{-1}	616 m^{-1}	0.616 m^{-1}	6.16 m^{-1}	6.16 m^{-1}
36	What is the unit of molar conductance of a strong electrolyte	$Smmol^{-1}$	Sm^2mol^{-1}	Sm mol^{-2}	Sm^2mol^{-2}	Sm^2mol^{-1}
37	Which method is used for determination of transport number?	Hirttorf's method	moving boundary method	Debye method	Hirttorf's method and moving boundary method	Hirttorf's method and moving boundary method
38	The molar ionic conductance at infinite dilution of LiX is found to be 89.2 x $10^{-4}Sm^2$ mol^{-1}. what would be the molar ionic conductance of the halide ion if the molar ionic conductance of Li^+ ion is 38.70x 10^{-4} Sm^2 mol^{-1}	40.8x 10^{-4} Sm^{-1} mol^{-1}	50.5x 10^{-4} Sm^2 mol^{-1}	50.5x 10^{-2} Sm^2 mol^{-1}	40.8x 10^{-2} Sm^{-1} mol^{-1}	50.5x 10^{-4} Sm^2 mol^{-1}
39	Which of the following salts is not sparingly soluble one?	NaCl	AgCl	$BaSO_4$	$PbSO_4$	NaCl
40	Calculate the transport number of Li^+ and Br^- ions when a current flows through an infinitely dilute aqueous solution of LiBr at 25°c, given the ionic mobilities of Li^+ and Br^- ion at infinite dilution are 4.01 x 10^{-8} and 8.09 x 10^{-8} $m^2v^{-1}s^{-1}$ respectively.	0.669	0.996	0.756	0.825	0.669

41	Molar ionic conductance at infinite dilution of Na$^+$ and Cl^{-1} ions are 50.11x10^{-4} and 76.34 x 10^{-4} Sm^{2}mol^{-1} respectively. Calculate the transport number of Na$^+$ and Cl$^-$ ions.	0.396	0.604	1		0.604
42	At 25°c, the specific conductance of 0.01m aqueous solution of acetic acid is 1.63 x 10^{-2}S/m and the molar conductance at infinite dilution is 390.7 x 10^{-4} Sm^2 mol^{-1}. Calculate the degree of dissociation	0.0417	0.317	0.418	0.0418	0.0417
43	The molar conductance at infinite dilution of HCl, NaCl and NaZ are 425x 10^{-4}, 125x 10^{-4} and 80x 10^{-4} Sm^2 mol^{-1} respectively. The specific conductance of 0.001 mol aqueous solution of carbonic acid [HZ] is 3.8 x 10^{-3} Sm$^{-1.}$ calculate the degree of dissociation.	0.18	0.21	0.01	0.1	0.1
44	What is the another method used for the titration of AgNO$_3$ against KCl?	precipitation titration	conductometric titration	permanganometric titration	concentration titration	precipitation titration
45	In Ostwald's dilution law, the equilibrium constant K is called	dissociation constant of the electrolyte	precipitative constant of the electrolyte	transport number	Equilibrium constant	dissociation constant of the electrolyte
46	According to coulombs law which force varies inversely as the dielectric constant of the medium?	electrostatic force	electro magnetic force	Electrode potential	electrolyte concentration	electro magnetic force
47	What is the unit of cell constant?	m^{-1}	m^2	1/m^2	m^3	m^{-1}
48	What is the unit of conductance?	siemen	ohms	Ω^{-1}	ohms m	siemen
49	The Extremely small ionic mobility as compared to the speed of gaseous molecule which is about	10^3 ms^{-1}	10^2 ms^{-1}	10^{-2} ms^{-1}	10^{-4} ms^{-1}	10^2 ms^{-1}
50	Fraction of the total current carried by each ions is also known as	transport number	hittorf's method	kohlrauschs law	wien effect	transport number
51	Specific conductance of a weak electrolyte is measured by	sm^{-1}	sm^2	sm	1/rho	sm^{-1}
52	Conjugate acid-base pairs, if the acid is strong, then base is	strong	weak	neutral	moderate	weak

53	Basic character of NaOH is due to	presence of anions and cations	presence of OH^- ions even in solid state	presence of water of hydration	presence of H^+ ions	presence of OH^- ions even in solid state
54	In the equation $a=Y_m$ where Y is called	activity coefficient	mean ionic activity	mean ionic active coefficient	Concentration	activity coefficient
55	Acetic acid is dissolved in water, the water behaves as	solvent	acid	amphoteric	neutral	solvent
56	The hydronium ion is represented as	H^+	OH^-	H_3O^+	H_2O	H_3O^+
57	The reciprocal of resistivity is known as	molar conductance	specific conductance	equivalent conductance	permittivity	specific conductance
58	Molar conductance decreses with increase in concentration is not due to fall the degree of ionisation but to fall in mobilities of ions due to greater	interionic effect	wien effect	viscous effect	interionic effect	interionic effect
59	Central ion drag in a concentrated or weak electrolytic solution is due to	assymmetry effect	symmetry effect	viscous effect	interionic effect	assymmetry effect
60	Slow down the ion by counter current in the same way as counter current in a stream slow down a swimmer this effect is known as	electrophoretic effect	viscous effect	Interionic effect	wein effect	electrophoretic effect

UNIT-II

SYLLABUS

Ionic velocities, mobilities and their determinations, transference numbers and their relation to ionic mobilities, determination of transference numbers using Hittorf and Moving Boundary methods. Applications of conductance measurement: (i) degree of dissociation of weak electrolytes, (ii) ionic product of water (iii) solubility and solubility product of sparingly soluble salts, (iv) conductometric titrations, and (v) hydrolysis constants of salts

Ionic mobilities:

The equivalent conductances of all electrolytes approach a limiting value at very high dilutions since then all the ions derived from one gram equivalent are taking part in current conduction. Therefore at high dilutions, solutions containing one equivalent of various electrolytes will contain equivalent number of ions. Thus the total charge carried by all the ions will be the same in every case. The conductance of an electrolyte is determined by the total charge of the ions and by the actual speed of the ions. The total charge is constant for equivalent solutions at high dilution. Then the limiting equivalent conductance of an electrolyte must depend only on the ionic velocities. The difference in the speeds of the ions is responsible for the different values of ion conductances. The speed of the charged particle is proportional to the potential gradient (fall of potential per cm). The speeds of ions are specified under a potential gradient of unity (1 V per cm). These speeds are called the mobilities of the ions.

Let U_0^+ and U_0^- be the mobilities of positive and negative ions of an electrolyte at infinite dilution under unit potential gradient. Then the equivalent conductance at infinite dilution must be proportional to the sum of these quantities.

$$\lambda_0 = K (U_0^+ + U_0^-) = KU_0^+ + KU_0^- \qquad (1)$$

where K is the proportionality constant and it is the same for all electrolytes.

The equivalent conductance is the sum of the ionic conductances

$$\lambda_0 = \lambda_0^+ + \lambda_0^- \qquad (2)$$

$$\lambda_0^+ = K\,U_0^+ \text{ and } \lambda_0^- = K\,U_0^- \qquad (3)$$

Imagine a very dilute solution of an electrolyte at a concentration ‘C’ equivalent per litre placed in a cube of 1 cm side with square electrodes of 1 square cm area at opposite faces and let an emf of 1V be applied.

$$\lambda_0 = 1000\,K/\,C = \lambda_0^+ + \lambda_0^- \qquad (4)$$

$$K = C\,(\lambda_0^+ + \lambda_0^-)/\,1000 \qquad (5)$$

When a pd of 1V is applied to a 1 cm cube, the current in amperes is numerically equal to the specific conductance. ($I = E/R = 1 \times 1/C = K$)

$$I = K = C\,(\lambda_0^+ + \lambda_0^-)/\,1000 \qquad (6)$$

This equation represents the number of coulombs flowing through the cube per second. All the cations within a length of U_0^+ cm will pass across a given plane in the direction of the current in 1 second while all the anions within a length of U_0^- cc will pass in the opposite direction. 1 cc of the solution contains C/1000 equivalents. Then a total of $(U_0^+ + U_0^-)\,C/\,1000$ equivalent of cations and anions will be transported by the current in 1 second. Each equivalent of any ion carries one Faraday (F) of electricity. Hence the total quantity carried per second will be

$$F(U_0^+ + U_0^-)\,C/\,1000 \text{ Coulombs.}$$

$$F(U_0^+ + U_0^-)\,C/\,1000 = C\,(\lambda_0^+ + \lambda_0^-)/\,1000 \qquad (7)$$

$$F(U_0^+ + U_0^-) = \lambda_0^+ + \lambda_0^- \qquad (8)$$

The constant K in equation (3) is equal to F. Then

$$\lambda_0^+ = FU_0^+ \quad \text{and} \quad \lambda_0^- = FU_0^- \qquad (9)$$

$$U_0^+ = \lambda_0^+ / F \quad \text{and} \quad U_0^+ = \lambda_0^+ / F \qquad (10)$$

The absolute velocity of any ion in cm/sec under a potential gradient of 1 Volt per cm can be obtained by dividing the ion conductance by the value of Faraday in Coulombs (96500). The above equation gives the ionic mobility at infinite dilution. The values of mobility decrease with increasing concentration, especially for strong electrolytes. (Most of the ions except H^+ and OH^- ions have velocities of about 5×10^{-4} cm per second at 25^0C under a potential gradient of unity)

Influence of temperature on ion conductances

The increase of temperature results in an increase of ion conductance at infinite dilution. The variation of conductance with temperature can be expressed using the equation

$$\Lambda_t^0 = \lambda_{25}^0 [1 + \alpha(t - 25) + \beta(t - 25)^2] \qquad (1)$$

Λ_t^0 is the ion conductance at infinite dilution at the temperature t and λ_{25}^0 is the value at 25^0C. α and β are constants for a given ion in the particular solvent for a narrow temperature range. (The constant β can be neglected and the temperature coefficient α is very close to 0.02 at 25^0C except for H^+ and OH^- ions)

The conductance of an ion depends on its rate of movement and conductance increase with temperature. Hence $\Lambda^0 = Ae^{-E/RT}$ (2)

where A is a constant independent of temperature over a relatively small range, E is the activation energy, R is the gas constant and T is the absolute temperature.

$$\ln \Lambda^0 = \ln A - E/RT \qquad (3)$$

On differentiating the above equation with respect to temperature,

$$\frac{d \ln\Lambda^0}{dT} = \frac{1}{\Lambda^0} \frac{d\Lambda^0}{dT} = \frac{E}{RT^2} \qquad (4)$$

On taking log of equation 1 and differentiating with respect to temperature neglecting β for a narrow temperature range

$$\ln \Lambda_t^{\,0} = \ln \lambda_{25}^{0}\ [\alpha(t - 25)]$$

$$d\ln\Lambda^0 / dT = \alpha \qquad (5)$$

Combining equations 4 and 5,

$$\alpha = E/ RT^2$$

Activation energy $E = \alpha RT^2$

If α is approximately 0.02, then activation energy is about 3.6 kcal for conductance in water.

Influence of pressure on ion conductance

The activation energy for electrolytic conductance is almost identical with that for the viscous flow of water. Hence ion conductance is related to the viscosity of the medium. The product of the conductance of a given ion and the viscosity of water at a series of temperatures should be approximately constant.

The relationship between ionic mobility and viscosity can be shown from the effect of pressure on electrolytic conductance. The plot of the ratio of the equivalent conductance at a pressure p to that at unit pressure that is, λ_P/λ_1 against pressure is shown in the figure (figure)

The dotted lines indicate the variation of pressure with fluidity (reciprocal of viscosity) of water relative to that at unit pressure. The existence of a maximum in both the conductance and fluidity curves suggests that there is close agreement between these quantities at infinite dilution.

The relationship between viscosity and ion conductance has been proved by the application of Stokes law to ions in solution. According to this law, $f = 6\pi\eta r u$, where u is the steady velocity with which a particle of radius 'r' moves through a medium of viscosity η when a force f is applied. For a particular ion, r is a constant and the conductance is proportional to the speed of the ion under the influence of a definite applied potential. Then according to Stoke's law, $\lambda_0\eta_0$ should be constant. The ion in solution is so completely surrounded by solvent molecules that the movement of the ion through the medium is virtually the same as the movement of solvent molecules past one another in viscous flow of the solvent. It is experimentally found that the activation energies for ionic mobility and viscous flow are approximately equal. When an electric field is applied to a solution containing ions, the ions can move forward only if a solvent molecule standing in its path moves in the opposite direction. The actual rate of movement of an ion will depend on the effective size of the ion in the given solvent.

Transference numbers

The transport number (t) is defined as the fraction of total current carried by the particular ionic species in the solution. In a simple case of a single electrolyte yielding the ions designated by the suffixes (+) and (-), the corresponding transference numbers are given as follows:

$$t_+ = \frac{q_+}{Q}$$

Where +q is the quantity of electricity carried by the cation and Qis the total quantity of electricity carried by all the ions through the solution. Similarly, the anion transport number t_- is defined as:

$$t_- = \frac{q_-}{Q}$$

Where q_- is the quantity of electricity carried by the anion, equations can be expressed as

$$t_+ = \frac{c_+u_+}{c_+u_+ \ + \ c_-u_-}$$

$$t_- = \frac{c_- u_-}{c_+ u_+ + c_- u_-}$$

The quantities +c and −c which represent the concentrations of the ions, are equal and therefore for this type of the electrolyte.

$$t_+ = \frac{u_+}{u_+ + u_-}$$

$$t_- = \frac{u_-}{u_+ + u_-}$$

$$\text{and } t_+ + t_- = 1$$

u_+ and u_- are the mobilities of the ions in the same solution and we know that the speed of an ion in a solution at any concentration is proportional to the conductance of the ion at that concentration and therefore the transference number may be represented in the form;

$$t_+ = \frac{\wedge_+}{\wedge_m} \text{ and } t_- = \frac{\wedge_-}{\wedge_m}$$

Where the values of $\wedge_+$ and $\wedge_-$ (ion conductance) and Λ_m (molar conductance) of the solution, are at that particular concentration at which the transference numbers are applicable.

Determination of Transport Number

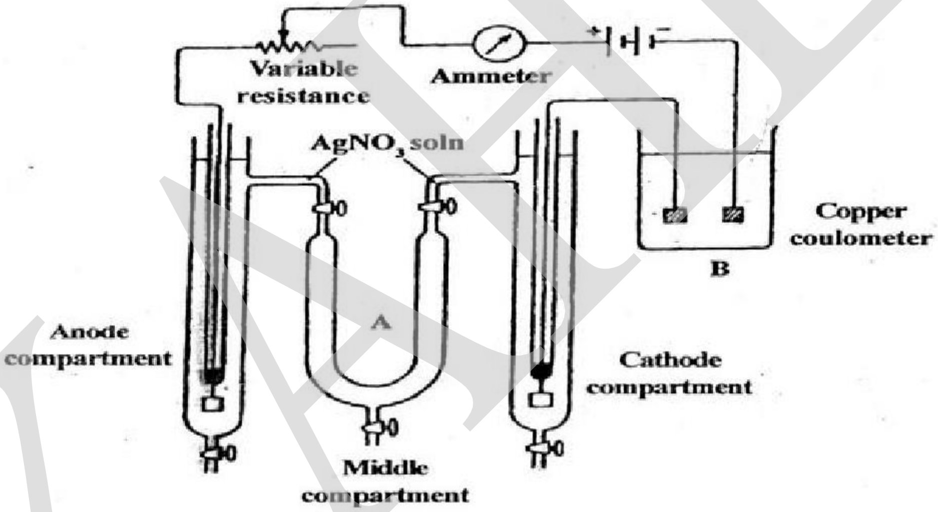
Three method have been generally employed for the experimental determination of transference numbers: the first, based on the procedure originally proposed by Hittorf, involves measurement of changes of concentration in the vicinity of the electrodes; in the second,known as the “ moving boundary” method, the rate of motion of the boundary between two solutions under the influence of current is studied; the third method, is based on electromotive force measurements of suitable cells.

Hittorf's Method

This method of determining transport numbers was described as long ago as 1901.

Apparatus

To understand the principle involved consider the overall description of the method given below. The apparatus consists of two separated compartments joined by a substantial middle compartment and may be of any of the shape as shown in figure. Let us take silver nitrate solution in a cell having silver electrodes. Before the experiment begins, the concentration of $AgNO_3$ is the same throughout the cell. The experiment involves passage of a direct electric current from a power source through the cell.



The apparatus consists of i) transport cell A, which consists of anode compartment, middle compartment and cathode compartment. ii) Copper coulometer, B.The transport cell is filled with AgNO3 solution. The electrolytes is carriedout using Ptelectrodes. A current of about 10 ampere is passed through the solution in the transport cell and Cu-coulometer for 2 to 3 hours. After electrolysis, the solution is drawn out from the anodic compartment and the change is concentration is determined

Calculation :

Before electrolysis:

1g of $AgNO_3$ solution contains 'a' g of $AgNO_3$ = a/170 gram equivalent of $AgNO_3$. Let it be 'x' gram equivalents

After electrolysis :

1g of $AgNO_3$ solution contains 'b' g of $AgNO_3$ = b/170 gram equivalent of $AgNO_3$. Let it be 'y' gram equivalents

Fall in concentration in the anode compartment = x – y gram equivalents of $AgNO_3$. Since copper- coulometer is connected, the weight of copper deposited in the same time is 'w' g = w/71.8 gram equivalent. Let it be 'z' gram equivalent.

$$\therefore \text{ Transport number of cation } = \frac{\text{Fall in concn. in anode compartment}}{\text{Amount of Cu deposited in the coulometer}}$$

$$t_{Ag+} = \frac{(x-y)}{z}$$

$$\therefore t_{NO_3^-} = 1 - \frac{x-y}{z}$$

where, t_{Ag+} and t_{NO3}^- tare the transport number of Ag^+ and $3NO_3^-$ ions respectively

Moving boundary method

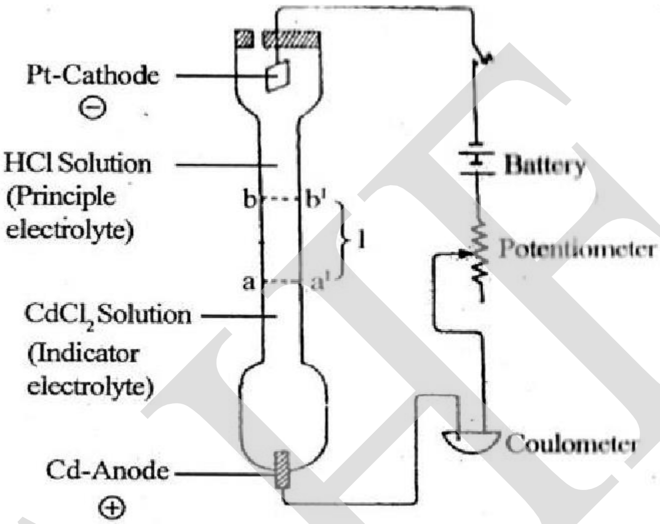
The moving boundary method is based on measuring the rate of migration ofone or both of the ionic species of the electrolyte, away from the similarly charged electrodes and by this method we can directly observe the migration of ions under the influence of an applied potential unlike the Hittrof's method in which concentration changes at the electrodes are observed. This method is very accurate and has been used in recent years for precision measurements.

Experiment:

To determine the transport number of H^+ ion, solution of Cl (principle electrolyte) is introduced above the solution of $CdCl_2$ (indicator electrolyte) in a tube as shown in the figures.

Since the number of coulombs passing can be determined, the transference number of the ion may be calculated from the rate of movement of one boundary.

The apparatus used for the determination of the transport number by this method, consist a long vertical tube of uniform bore fitted with two electrodes at the two ends as shown in figure.



The cathode is platinum (top) and the anode is cadmium metal (bottom). Before passing current, the mobility of Cd^{2+} ions is equal to that of H^+ ions. Thus at the junction of the two liquids, a sharp boundary is seen (aa1).

By passing current, H+ions move towards the cathode. The gap formed by the upward movement of the H^+ ions is filled by the Cd_2^+ ions. Thus the boundary moves up (bb1).

Conductometric titration

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located.

Graphically by plotting the change in conductance as a function of the volume of titrant added. In order to reduce the influence of errors in the conductometric titration to a minimum, the angle between the two branches of the titration. Curve should be as small as possible (see

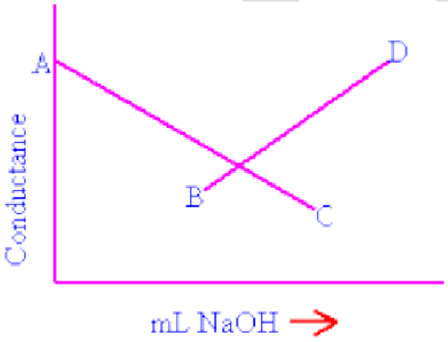
Figure).

Some Typical Conductometric Titration Curves are:

1. Strong Acid with a Strong Base, e.g. HCl with NaOH:

Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH^- ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl.

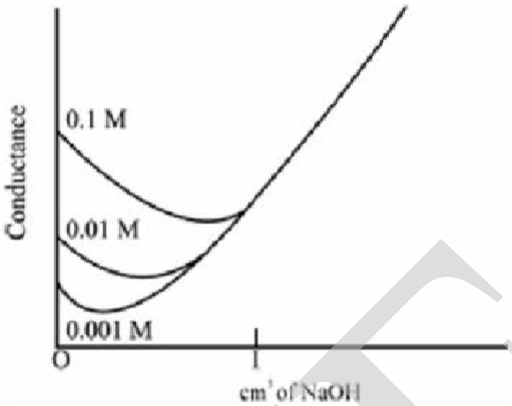
After the equivalence point, the conductance increases due to the large conductivity of OH^- ions



Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

2. Weak Acid with a Strong Base, e.g. acetic acid with NaOH:

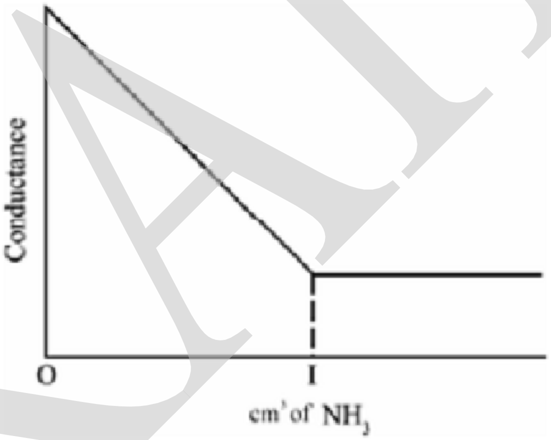
Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH_3COOH to CH_3COONa which is the strong electrolyte. This increase in conductance continue raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH3COONa. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions.



Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH)

3. Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia:

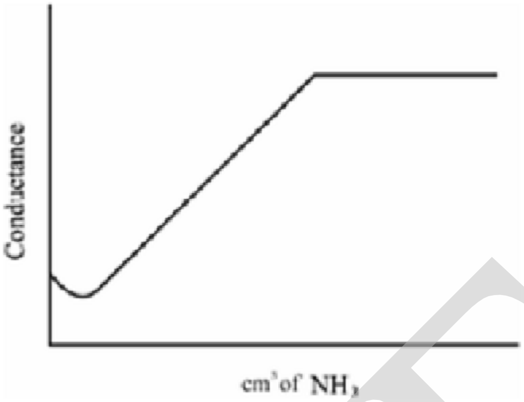
Initially the conductance is high and then it decreases due to the replacement of H^+. But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the Presence of ammonium sulphate.



Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)

4. Weak Acid with a Weak Base :

The nature of curve before the equivalence point is similar to the curve obtained by titratingweak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting.



Conductometric titration of a weak acid (acetic acid) vs. a weak base(NH_4OH)

UNIT II

POSSIBLE QUESTIONS

PART- B

(Each carries two marks)

1. What is meant by ionic velocities?
2. Define mobilities.
3. What are the transference numbers?
4. What is meant by degree of dissociation?
5. What is meant by hydrolysis constants?

PART C

(Each carries Six marks)

1. Explain the determination of transference numbers using Moving Boundary method.
2. What is meant by transport number? How is determined by Hittorf's method?
3. Write a note on (i) degree of dissociation of weak electrolytes, (ii) ionic product of water.
4. Discuss the conductometric titrations with suitable examples.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University under Section 3 of UGC Act 1956)
COIMBATORE-641 021
(For the candidates admitted from 2016 & onwards)
II B.Sc. Chemistry
PHYSICAL CHEMISTRY

UNIT II
Multiple choice questions

Question	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
Unit 2					
According to Lowry- bronsted theory, an acid is	donates proton	accepts proton	donates electron	accepts proton	donates proton
How residual part acid tends to behave, when acid loses a proton	acid	base	neutral	amphoteric	base
The H^+ ions present is largely found as	H_3O^+	H^+	OH^-	H_2O	H_3O^+
which among the following is hydronium ion	H^+	OH^-	H_3O^+	H_2O	H_3O^+
An acid according to lowry- bronsted theory	donates proton	accepts proton	donates electron	accepts proton	donates proton
When acid loses a proton, then its residual part tends to behave like	acid	base	neutral	amphoteric	base
When acetic acid is dissolved in water, the water behaves as	solvent	acid	amphoteric	neutral	solvent
The hydronium ion is	H^+	OH^-	H_3O^+	H_2O	H_3O^+
levelling point for acids can be obtained, when dissolving them in	water	glacial acetic acid	acedic solution	basic solution	water
An acid, according to lewis concept	accepts protons	accepts electron	donates electron	donates protons	accepts electron
Lewis concept tells, every species forms	ionic bond	covalent bond	metallic bond	coordinate bond	covalent bond
Reformation of HCl in aqueous solution is very slow why?	Cl^- is a weak base	Cl^- is a weak acid	Cl^- is a strong base	Cl^- is a strong acid	Cl^- is a weak base
In a conjugate acid-base pairs, if the acid is strong, then base is	strong	weak	neutral	moderate	weak
The extensive basic character of NaOH is due to	presence of anions and cations	presence of OH^- ions even in solid state	presence of water of hydration	presence of H^+ ions	presence of OH^- ions even in solid state

Acetic acid is a weak acid, because	it has very low tendency to donate OH^-	it has very low tendency to donate H^+	it has very high tendency to donate H^+	it has very high tendency to donate OH^-	it has very low tendency to donate H^+
The degree of dissociation of acids have coincidence with	strength of acid	solubility	polarity	strength of base	strength of acid
The 'levelling point' for acids can be obtained, when dissolving them in	water	glacial acetic acid	acedic solution	basic solution	water
Which one of the following is hydrated hydrogen ion	H^+	OH^-	H_3O^+	H_2O	H_3O^+
The conjugate pair of ammonia in aqueous solution is	CH_3COOH^+	NH_4OH	NH_4^+	H_3O^+	NH_4^+
HCl and CH_3COOH have same acedic strength when	dissolved in water	dissolved in CH_3COOH	dissolved in HCl	dissolved in liq. Ammonia	dissolved in liq. Ammonia
Nitric acid behaves as a base when	dissolved in HF	dissolved in water	dissolved in liq.ammonia	dissolved in CH_3COOH	dissolved in HF
According to Lewis concept, an acid	accepts protons	accepts electron	donates electron	donates protons	accepts electron
According to Lewis concept, every species forms	ionic bond	covalent bond	metallic bond	coordinate bond	covalent bond
$HClO_4$ is more acedic than $HClO_{3.}$ why?	$HClO_4$ has more number of oxygen atom	$HClO_4$ is soluble, where $HClO_3$ is insoluble	$HClO_4$ is covalent compound, where $HClO_3$ is ionic	$HClO_4$ has less number of oxygen atom	$HClO_4$ has more number of oxygen atom
In $[H_3O^+]$, the square bracket represent	concentration in moles per ml	concentration in moles per kg	concentration in moles per litre	concentration in moles per mg	concentration in moles per litre
Dissociation constant varies with	concentration	strength	stability	temperature	temperature
Degree of dissociation is a measure of its capacity to furnish	hydrogen atoms	hydrogen ions	hydroxyl ions	hydronium ion	hydrogen ions
The dissociation constant of 0.100M acetic acid, found to be dissociated to the extent 1.33% at room temperature is	1.77×10^{-6}	1.77×10^{-5}	17.7	0.177	1.77×10^{-5}
The dissociation constant of 0.2 M monobasic acid is 1.8×10^{-5}, then its degree of dissociation is	0.009486	9.486	0.9846	948.6	0.009486
Dissociation of phosphoric acid occurs in	three stages	two stages	one stages	ten stages	three stages
The square bracket $[H_3O^+]$ represent	concentration in moles per ml	concentration in moles per kg	concentration in moles per litre	concentration in moles per mg	concentration in moles per litre
Which of the following acid has Ka_3 value	H_2SO_4	H_3PO_4	HCLl	H_3PO_3	H_3PO_4

The dissociation constant of water is	ionic product of water	surface tension	viscosity	concentration	ionic product of water
Every aqueous solution contains	H^+	OH^-	H^+ and OH^-	H^+ or OH^-	H^+ and OH^-
The P^H value of HCl and NaOH are	1,14	1,1	14,14	3,4	1,14
Ions produced by water is	ionic product of water	surface tension	viscosity	concentration	ionic product of water
The P^H of 0.0001 M HCl is	3	4	1	14	4
The hydrogen ion concentration of a solution of P^H value 5.4 is	3.98×10^{-6}mol dm^{-3}	3.98×10^{-5}mol dm^{-3}	3.98×10^{-4}mol dm^{-3}	3.98×10^{-14}mol dm^{-3}	3.98×10^{-6}mol dm^{-3}
HCl solution of any concentration has P^H value	1	14	less than 7	3.14	less than 7
POH indicates	H^+ ions concentration	OH^- ions concentration	H_3O^+	H_2O	OH^- ions concentration
The sum of PH and POH of 0.03M aqueous solution of HCl at 25°C is	1.52	12.48	14	1	14
Addition of sodium acetate to acetic acid solution	increases the dissociation of acetic acid	decreases its acidity	suppresses the dissociation of acetic acid	increases its concentration	suppresses the dissociation of acetic acid
When Solubility product is constant	high concentration	particular room temperature	very low temperature	very high temperature	particular room temperature
What is meant byPOH	H^+ ions concentration	OH^- ions concentration	H_3O^+	H_2O	OH^- ions concentration
If the hydrogen ion concentration of a weak base decreases, then its acid-salt ratio	increases	decreases	remains unaltered	becomes zero	decreases
The hydrogen ion concentration of a solution obtained by mixing 500ml of 0.2 M acetic acid in 0.30 M sodium acetate is	1.17×10^{-5}mol dm^{-3}	1.17×10^{-6}mol dm^{-3}	1.17×10^{-3}mol dm^{-3}	1.17×10^{5}mol dm^{-3}	1.17×10^{-5}mol dm^{-3}
buffer mixture is a	strong acid & its salt	weak base & its salt	weak acid & its salt	strong base& its salt	weak acid & its salt
The PH of water	7	less than 7	more than 7	zero	7
Which of the following is not a buffer	sodium chloride solution	ammonium acetate solution	sodium acetate solution	potassium acetate solution	sodium chloride solution
The PH of aquous solution of ammonium acetate is	7	less than 7	more than 7	zero	7
Expression of POH	H^+ ions concentration	OH^- ions concentration	H_3O^+	H_2O	OH^- ions concentration

The capacity of a solution to resists alteration in its P^H is	buffer capacity	solubility	common ion effect	concentration	buffer capacity
The value of buffer index is always	positive	negative	zero	a constant	positive
A buffer mixture is a	strong acid & its salt	weak base & its salt	weak acid & its salt	strong base& its salt	weak acid & its salt
Henderson equation is used to calculate the P^H values for	buffer solution	buffer mixtures	acids	bases	buffer mixtures
Solubility product is constant at	high concentration	particular room temperature	very low temperature	very high temperature	particular room temperature
The solubility product of silver chloride, whose solubility in water at 25°C is 0.00179g per litre is	1.56 x 10^{10}mo^{2}l dm^{-6}	1.56 x 10^{-10}mo^{2}l dm^{-6}	1.56 x 10^5mo^{2}l dm^{-6}	1.56 x 10^{-15}mo^{2}l dm^{-6}	1.56 x 10^{-10}mo^{2}l dm^{-6}
Application of Henderson equation in the P^H calculation	buffer solution	buffer mixtures	acids	bases	buffer mixtures
If the ionic product of a compound exceeds the solubility product, then the compound	neutralises	precipitates	acidified	concentration becomes very high	precipitates
Which one of the following is buffer mixture	strong acid & its salt	weak base & its salt	weak acid & its salt	strong base& its salt	weak acid & its salt

UNIT-III

SYLLABUS

Chemical Kinetics: Order and molecularity of a reaction, rate laws in terms of the advancement of a reaction, differential and integrated form of rate expressions up to second order reactions, experimental methods of the determination of rate laws, kinetics of complex reactions (integrated rate expressions up to first order only): (i) Opposing reactions (ii) parallel reactions and (iii) consecutive reactions and their differential rate equations (steady-state approximation in reaction mechanisms) (iv) chain reactions

Chemical Kinetics:

Introduction

Chemical kinetics is concerned with the study and measurement of the rate of chemical reactions. There are many reactions which proceed at a very high speed that their rates cannot be measured. Such reactions are known as **fast reactions.** Familiar examples for fast reactions are- the neutralisation of a base by an acid, precipitation of silver chloride on mixing a solution of silver nitrate with sodium chloride.

There are also reactions which are very slow.

Ex: *rusting of iron.*

In between these two extremes, there are many reactions whose rates can be measured in the laboratory. The study of chemical kinetics helps us to know about the mechanism of chemical reactions i.e., the path followed by the reactants to form the products. This may also help us to know the various factors like temperature, pressure which affect the rate of chemical reactions.

The rate of a chemical reaction is the variation in the concentration of either reactants or the products with time.

i.e.,

$$\text{rate} = \frac{\text{change in concentration}}{\text{time taken}} = \frac{\text{moles/lit}}{\text{time}}$$

The unit for the rate is, mole $\text{lit}^{-1}\ \text{sec}^{-1}$ and is mathematically expressed as **dc/dt**.

According to Law of Mass Action, the speed or the velocity of a chemical reaction is directly proportional to the active mass of the reactants. For every reaction, rate equation connecting the rate of the reaction and the active mass of the reactants can be written. For example, consider the reaction -

$$A \rightarrow \text{Products} \qquad \text{-----------}\ (1)$$

The rate equation for this reaction is

$$\frac{-\,d[A]}{dt} = k\,[A]^1 \qquad \text{-----------}\ (2)$$

Here, the –ve sign indicates the decrease in the concentration of the reactants with time.

The order of reaction is defined as the sum of the powers of the concentration of the reactants in the rate equation.

OR

It is the number of molecules whose concentrations determine the rate of the reaction.

Evidently, in the above example, the rate is proportional to the first power of the concentration of A and the reaction is of first order.

Examples for first order reaction -

1) Radioactive decay.
2) Decomposition of hydrogen peroxide.
3) Thermal decomposition of nitrogen pentoxide.

For the reaction,

$$A + B \rightarrow \text{Products} \quad \ldots\ldots. (3)$$

The rate equation is

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k\,[A]^1\,[B]^1 \quad ----------- (4)$$

By our definition, the order of the reaction is 1+1 =2

Examples for second order reaction -

1) Base catalysed ester hydrolysis (**saponification)**.
2) Benzoin condensation.
3) Conversion of ammonium cyanate into urea.
4) Conversion of ozone into oxygen at 373 K.

In general, for the reaction

$$aA + bB + cC \ldots\ldots\ldots \rightarrow \text{Products} \quad \ldots\ldots\ldots\ldots\ldots (5)$$

The order is, a + b + c +… It must remembered here that the rate equation of a reaction is written on the basis of experimental results only. These are no necessary connection between the order and the balanced chemical equation of a reaction. This is exemplified by the following reaction,

$$2N_2O_5 \rightarrow 4\,NO_2 + O_2 \quad \ldots\ldots\ldots\ldots\ldots (6)$$

This may seem to be a second order reaction, but experimentally it is a first order reaction.

The order of a reaction need not be a whole number. It may be fraction or even zero. For example, the ortho-para hydrogen conversion is fractional with the order equal to 2/3. Many photochemical reactions are found to be of zero order. The order of a reaction is greatly influenced by factors like temperature, pressure, and concentration.

Theoretically speaking reactions of higher order are possible. But reactions of order more than three are very rare. This is because such reactions should involve simultaneous collisions of more than three molecules. The probability for such collisions is limited. Therefore our study is limited to reactions up to order three. The rate equations for the first, second and third order reactions are given in the table.

Order	Type of reaction	Rate equation
1	A → Products	$k_1 = \frac{2.303}{t} \log \frac{a}{(a-x)}$
2	2A → Products	$k_2 = \frac{1}{at} \frac{x}{(a-x)}$
3	3A → Products	$k_3 = \frac{1}{2t} \{\frac{1}{(a-x)} - \frac{1}{a^2}\}$

Note: The derivation of the above rate equations is beyond the scope of this book.

Order and molecularity of a reaction

Order of a reaction is defined as the sum of the power of the concentration terms that occurs in the rate equation and is purely experimental quantity. It may be a whole number, fraction or even zero.

The molecularity of a reaction is the number of species (atoms or molecules) of the reactants that participate in the step leading to the chemical reaction. In many cases the order and molecularity are equal. Molecularity is always a small whole number and cannot be zero or fraction.

Pseudo unimolecular reactions

For many reactions, the order and molecularity are often identical but in some cases, the order is not the same as that of molecularity of the reaction.

Consider the hydrolysis of ethyl acetate in presence of dilute hydrochloric acid. Here, hydrochloric acid acts as a catalyst.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{HCl} CH_3COOH + C_2H_5OH$$

Evidently, the molecularity of this reaction is two. The rate equation for this reaction will be,

$$\text{rate} = k\,[CH_3COOC_2H_5]\,[H_2O]$$

But the concentration of water does not alter the rate of reaction and the reaction rate is determined by ethyl acetate only. Hence, the reaction is of first order.

This type of first order, bimolecular reactions are called pseudo unimolecular reaction.

Other examples

1) Inversion of cane sugar

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

2) The oxidation of citric acid by perdisulphate ion.

Zero order reactions

These are the reactions in which the concentration of the reactants do not change with time i.e., the rate is unaffected by concentration. In other words, the rate remains constant throughout the reaction. For a reaction of this type, the rate of disappearance of reactant may be given by the relationship,

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

As the concentration remains constant throughout, the rate of zero order reaction is determined by some other limiting factors like intensity of the absorbed light in some photochemical reactions or the area of catalyst in certain surface reactions.

Examples for zero order reaction

i) Photochemical combination of H_2 and Cl_2 gas when exposed to sun light.

$$H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$$

ii) Iodination of acetone in presence of an acid.

iii) The decomposition of HI in which Au acts as catalyst.

$$2HI \xrightarrow{Au} H_2 + I_2$$

iv) The decomposition of NH_3 in presence of Mo or W

$$2NH_3 \xrightarrow[W]{Mo\ or} N_2 + 3H_2$$

v) All enzyme catalysed reactions.

Rate laws

The rate law is an expression relating the rate of a reaction to the concentrations of the chemical species present, which may include reactants, products, and catalysts. Many reactions follow a simple rate law, which takes the form

$$\nu = k\,[A]^a[B]^b[C]^c$$

i.e. the rate is proportional to the concentrations of the reactants each raised to some power. The constant of proportionality, k, is called the rate constant. The power a particular concentration is raised to is the order of the reaction with respect to that reactant. Note that the orders do not have to be integers. The sum of the powers is called the overall order. Even reactions that involve multiple elementary steps often obey rate laws of this kind, though in these cases the orders will not necessarily reflect the stoichiometry of the reaction equation. For example,

$$H_2 + I_2 \rightarrow 2HI \qquad \nu = k\,[H_2][I_2].$$

$$3ClO^- \rightarrow ClO_3^- + 2Cl^- \qquad \nu = k\,[ClO^-]^2$$

Other reactions follow complex rate laws. These often have a much more complicated dependence on the chemical species present, and may also contain more than one rate constant. Complex rate laws alwaysimply a multi-step reaction mechanism. An example of a reaction with a complex rate law is

$$H_2 + Br_2 \rightarrow 2HBr \qquad \nu = \frac{[H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}$$

In the above example, the reaction has order 1 with respect to [H2], but it is impossible to define orders with respect to Br2and HBr since there is no direct proportionality between their concentrations and the reaction rate. Consequently, it is also impossible to define an overall order for this reaction.

To give you some idea of the complexity that may underlie an overall reaction equation, a slightly simplified version of the sequence of elementary steps involved in the above reaction is shown below. We will return to this reaction later when we look at chain reactions

$$Br_2 \rightarrow Br + Br$$
$$Br + H_2 \rightarrow H + HBr$$
$$H + Br_2 \rightarrow Br + HBr$$
$$Br + Br \rightarrow Br_2$$

As well as having rate laws for overall reactions, we can of course also write down individual rate laws for elementary steps. Elementary processes always follow simple rate laws, in which the order with respect to each reactant reflects the molecularityof the process (how many molecules are involved). For example,

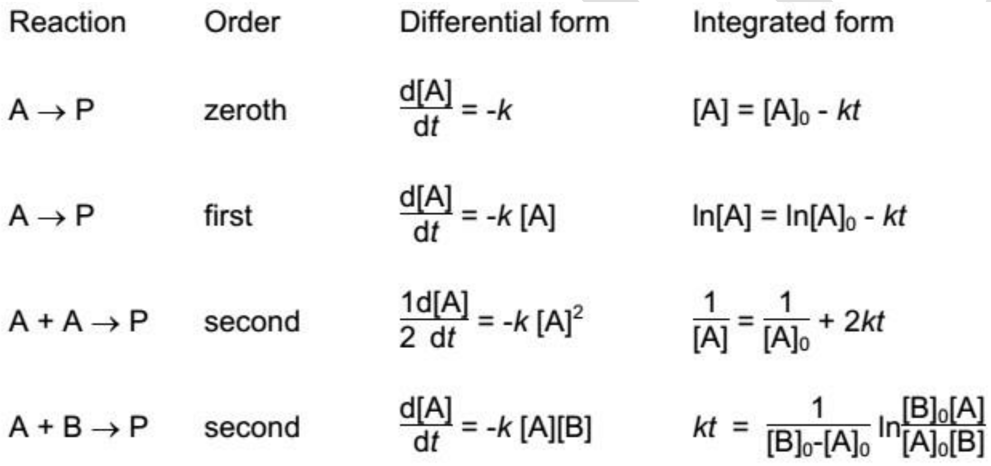
Unimolecular decomposition	$A \rightarrow B$	$\nu = k\,[A]$
Bimolecular reaction	$A + B \rightarrow P$	$\nu = k\,[A][B]$
	$A + A \rightarrow P$	$\nu = k\,[A][A] = k\,[A]^2$

Multi-step processes may follow simple or complex rate laws, and as the above examples have hopefully illustrated, the rate law generally does not follow from the overall reaction equation. This makes perfect sense, since the overall reaction equation for a multi-step process is simply the net result of all of the elementary reactions in the mechanism. The ‘reaction’ given in the overall reaction equation never actually takes place! However, even though the rate law for a multi-step reaction cannot immediately be written down from the reaction equation as it can in the case of an elementary reaction, the rate law isa direct result of the sequence of elementary steps that constitute the reaction mechanism. As such, it provides our best tool for determining an unknown mechanism. As we will find out later in the course, once we know the sequence of elementary steps that constitute the reaction mechanism, we can quite quickly deduce the rate law. Conversely, if we do not know the reaction mechanism, we can carry out experiments to determine the orders with respect to each reactant (see Sections 7 and 8) and then try out various ‘trial’ reaction mechanisms to see which one fits best with the experimental data. At this point it should be emphasised again that for multi-step reactions, the rate law, rate constant, and order are determined by experiment, and the orders are not generally the same as the stoichiometric coefficients in the reaction equation.

A final important point about rate laws is that overallrate laws for a reaction may contain reactant, product and catalyst concentrations, but must not contain concentrations of reactive intermediates (these will of course appear in rate laws for individual elementary steps).

Integrated rate laws:

A rate law is a differential equation that describes the rate of change of a reactant (or product) concentration with time. If we integrate the rate law then we obtain an expression for the concentration as a function of time, which is generally the type of data obtained in an experiment. In many simple cases, the rate law may be integrated analytically. Otherwise, numerical (computer-based) techniques may be used. Four of the simplest rate laws are given below in both their differential and integrated form.



Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k\,[A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \rightarrow P$	second	$\frac{1}{2}\frac{d[A]}{dt} = -k\,[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
$A + B \rightarrow P$	second	$\frac{d[A]}{dt} = -k\,[A][B]$	$kt = \frac{1}{[B]_0-[A]_0} \ln\frac{[B]_0[A]}{[A]_0[B]}$

In the above $[A]_0$ and $[B]_0$ represent the initial concentrations of A and B i.e. their concentrations at the start of the reaction.

Half lives:

The half life, $t_{1/2}$, of a substance is defined as the time it takes for the concentration of the substance to fall to half of its initial value. Note that it only makes sense to define a half life for a substance not present in excess at the start of the reaction. We can obtain equations for the half lives for reactions of various orders by substituting the values $t= t_{1/2}$ and $[A] = ½ [A]_0$ into the integrated rate laws. We obtain

Determining the rate law from experimental data

A kinetics experiment consists of measuring the concentrations of one or more reactants or products at a number of different times during the reaction. We will review some of the experimental techniques used to make these measurements. In the present section, we will look at the methods that allow us to use the experimental data to determine the reaction orders with respect to each reactant, and therefore the rate law.

(i) Isolation method

The isolation method is a technique for simplifying the rate law in order to determine its dependence on the concentration of a single reactant. Once the rate law has been simplified, the differential or integral methods discussed in the following subsections may be used to determine the reaction orders.

The dependence of the reaction rate on the chosen reactant concentration is isolated by having all other reactants present in a large excess, so that their concentration remains essentially constant throughout the course of the reaction. As an example, consider a reaction A + B →P, in which B is present at a concentration 1000 times greater than A. When all of species A has been used up, the concentration of B will only have changed by 1/1000, or 0.1%, and so 99.9% of the original B will still be present. It is therefore a good approximation to treat its concentration as constant throughout the reaction.

This greatly simplifies the rate law since the (constant) concentrations of all reactants present in large excess may be combined with the rate constant to yield a single effective rate constant. For example, the rate law for the reaction considered above will become:

$$\nu = k\,[A]^a[B]^b \approx k\,[A]^a[B]_0{}^b = k_{\mathrm{eff}}[A]^a \quad \text{with} \quad k_{\mathrm{eff}} = k[B]_0{}^b$$

When the rate law contains contributions from a number of reactants, a series of experiments may be carried out in which each reactant is isolated in turn.

***(ii)* Differential methods**

When we have a rate law that depends only on the concentration of one species, either because there is only a single species reacting, or because we have used the isolation method to manipulate the rate law, then the rate law may be written

$$\nu = k[A]^a$$

$$\log \nu = \log k + a \log[A]$$

A plot of logvagainst log[A] will then be a straight line with a slope equal to the reaction order, *a*, and an intercept equal to log *k*. There are two ways in which to obtain data to plot in this way.

1. We can measure the concentration of the reactant [A] as a function of time and use this data to calculate the rate, $\nu = -d[A]/dt$, as a function of [A]. A plot of logν vs log[A] then yields the reaction order with respect to A.

2. We can make a series of measurements of the initial rate ν_0 of the reaction with different initial concentrations $[A]_0$. These may then be plotted as above to determine the order, *a*. This is a commonly used technique known as the initial rates method.

(iii) Integral methods

If we have measured concentrations as a function of time, we may compare their time dependence with the appropriate integrated rate laws. Again, this is most straightforward if we have simplified the rate law so that it depends on only one reactant concentration. The differential rate law given in Equation, will give rise to different integrated rate laws depending on the value of a, some of which were given. The most commonly encountered ones are:

Zeroth order integrated rate law:	$[A] = [A]_0 - kt$ A plot of [A] vs *t* will be linear, with a slope of -*k*.
First order integrated rate law:	$\ln[A] = \ln[A]_0 - kt$ A plot of ln[A] vs *t* will be linear with a slope of -*k*.
Second order integrated rate law:	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$ A plot of $\frac{1}{[A]}$ vs *t* will be linear with a slope of 2*k*.

If none of these plots result in a straight line, then more complicated integrated rate laws must be tried.

Consecutive reactions

The simplest complex reaction consists of two consecutive, irreversible elementary steps e.g.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

An example of such a process is radioactive decay. This is one of the few kinetic schemes in which it is fairly straightforward to solve the rate equations analytically, so we will look at this example in some detail. We can see immediately that the following initial conditions hold.

$$\text{at } t = 0, \qquad [\mathrm{A}] = [\mathrm{A}]_0,\quad [\mathrm{B}] = 0,\quad [\mathrm{C}] = 0$$

$$\text{with at all times} \qquad [\mathrm{A}]+[\mathrm{B}]+[\mathrm{C}] = [\mathrm{A}]_0.$$

Using this information, we can set up the rate equations for the process and solve them to determine the concentrations of [A], [B], and [C] as a function of time. The rate equations for the concentrations of A, B, and C are:

$$(1) \qquad \frac{d[\mathrm{A}]}{dt} = -\,k_1[\mathrm{A}]$$

$$(2) \qquad \frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}]$$

$$(3) \qquad \frac{d[\mathrm{C}]}{dt} = -\,k_2[\mathrm{B}]$$

Integrating (1) gives

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t).$$

Substituting this into (2) gives

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] = k_1[\mathrm{A}]_0 \exp(-k_1 t)$$

a differential equation with the solution,

$$[\mathrm{B}] = \frac{k_1}{k_2-k_1}\{\exp(-k_1 t) - \exp(-k_2 t)\}\,[\mathrm{A}]_0$$

Finally, since $[C] = [A]_0 – [B] – [A]$, we find

$$[C] = \left(1 + \frac{k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)}{k_2 - k_1}\right)[A]_0$$

We will consider two special cases for a pair of sequential reactions:

Case 1: $k_1 >> k_2$

In this case, all of the A initially present is rapidly converted into B, which is then slowly used up to form C. Since k_2 becomes negligible in comparison with k_1, the equation for [C] becomes

$$[C] = \{1 - \exp(-k_2 t)\}[A]_0$$

i.e. the rate of production of C (and therefore the overall rate of the two-step reaction) becomes independent of k_1(apart from at the very beginning of the reaction). In other words, the second step is the rate determining step.

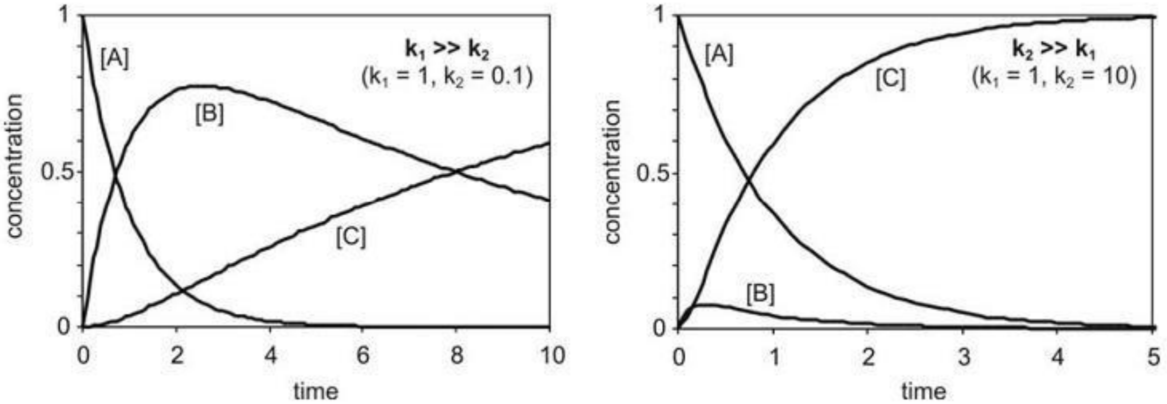
Case 2: $k_2 >> k_1$

In this case, B is consumed as soon as it is produced, and since k_1 becomes negligible in comparison with k_2, the equation for [C] simplifies to

$$[C] = \{1 - \exp(-k_1 t)\}[A]_0$$

i.e. the overall rate now depends only on k1, and the first step is rate determining.

The way in which the concentrations of A, B and C vary with time for each of the two cases considered above is shown in the figures below.



Parallel Reactions

Definition:

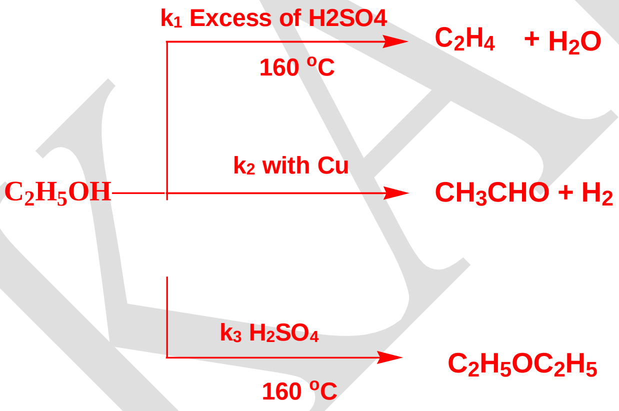
When a reactant (A) undergoes two (or) more independent reactions at the same time, it is a case of side reaction (or) parallel reaction.

Each independent reaction gives rise to its own set of products.

Consider a reaction

------------------> B (90%)
A---------------------->
------------------> C (10%)

Where A is the reactant which undergoes two reactions I and II to form the products B and C. The reaction I is known as the main reaction and II is known as side reaction. An example of side reaction is that when ethyl alcohol is made to react under different conditions the following side reaction along the small reaction may occur.



Mathematical Treatment of Side reactions:

Suppose a is the initial concentration of A. Let x of A decompose in time‘t’ to form partly as B and partly as C.

If y and z are the amounts of B and C formed in time ‘t’ then we can write

Rate of disappearance of A = -dx/dt

Rate of formation of B and C together = dx/dt -----------(1)

Rate of formation of B = dy/dt -----------(ii)

Rate of formation of C = dz/dt -----------(iii)

As both B and C are formed from A one can write,

dx/dt = dy/dt + dz/dt ------------(2)

If both the reactions I and II are of first order velocity for the formation of B from A is given by

$dy/dt = k_1 (a-x)$ ------------(3)

And the velocity for the formation of C from A is given by

$dz/dt = k_2 (a-x)$ -------------(4)

Where, k_2 is the first order velocity constant for the formation of C from A.

Substituting the Eqn (3) and (4) in Eqn (2) We get

$dx/dt = k_1 (a-x) + k_2 (a-x)$

$dx/dt = (a-x) (k_1 + k_2)$

$dx/(a-x) = (k_1 + k_2) dt$

(or) dx/(a-x) = k dt ----------------(5)

Where $k = k_1 + k_2$

Integrating Eqn (5) We get

$k_{(say)} = 1/t \log a/(a-x)$ ------(6)

The value of k can be obtained by nothing the concentration changes in A with time. But the separate evaluations of k_1 and k_2 require some relationship between them. The amounts of B and C formed at any time will depend upon the rate of two reactions. Therefore one can write. The value of k can be obtained by nothing the concentration changes in A with time. But the separate evaluations of k_1 and k_2 require some relationship between them. The amounts of B and C formed at any time will depend upon the rate of two reactions. Therefore one can write.

$$\frac{\text{Amount of B at any stage}}{\text{Amount of C at the same stage}} = \frac{\text{Rate of formation of B}}{\text{Rate of formation of C}}$$

$$= \frac{dy/dt}{dz/dt} = \frac{k_1\,(a-x)\ \text{(first order reaction)}}{k_2\,(a-x)}$$

$$= k_1 / k_2 = k' \text{ ------------------------}(7)$$

Thus

$$k' = k_1 / k_2 \text{ ------------------------}(8)$$

Thus the estimations of B and C at the end of the reaction would give the value of k'. Hence the values of k_1 and k_2 can be evaluated separately by using eqns (6) and (8) in terms k and k' which can be measured experimentally.

Chain reactions

Chain reactions are complex reactions that involve chain carriers, reactive intermediates which react to produce further reactive intermediates. The elementary steps in a chain reaction may be classified into initiation, propagation, inhibition, and termination steps. As an example, consider the infamous reaction by which chlorofluorocarbons (CFCs) destroy ozone:

$C_nF_mCl + h\nu \rightarrow \cdot C_nF_m + \cdot Cl$	Initiation
$\cdot Cl + O_3 \rightarrow \cdot ClO + O_2$	Propagation
$\cdot ClO + O \rightarrow \cdot Cl + O_2$	Propagation
$\cdot Cl + CH_4 \rightarrow \cdot CH_3 + HCl$	Termination

Initiation step

Reaction is initiated either thermally or photochemically. The first reactive intermediates/chain carriers (in this case a $^{\cdot}$Cl radical) are produced.

Propagation step

Reaction of a radical leads to formation of another radical – another reactive intermediate. In the

first propagation step above, $^{\cdot}$Cl reacts to form $^{\cdot}$ClO; in the second step $^{\cdot}$ClO reacts to form $^{\cdot}$Cl.

Termination step

Chain carriers are deactivated. Often this occurs through radical-radical recombination, reaction with walls, or reaction with another molecule to create an inactive product.

Some chain reactions involve inhibition steps, in which product molecules are destroyed. Inhibition steps are also sometimes referred to as retardationor de-propagationsteps.

The chain length in a chain reaction is defined as the number of propagation steps per initiation step, or alternatively as the rate of propagation divided by the rate of initiation. Chain lengths can be very long – in the above example a single ˚Cl radical can destroy around 10^6 molecules of ozone.

$$\text{chain length, } n = \frac{\nu(\text{propagation})}{\nu(\text{initiation})} = \frac{\nu(\text{propagation})}{\nu(\text{termination})}$$

The above reaction is an example of a cyclic chain reaction. The ½Cl essentially acts as a catalyst and is continuously regenerated until it is removed by a termination step. It is also possible to have non-cyclic chain reactions, involving many reactive species and elementary steps. Non-cyclic chain reactions can have extremely complicated kinetic mechanisms.

Chain reactions in which each propagation step produces only one reactive intermediate are called linear chain reactions (as opposed to branched chain reactions, which we will cover in. We will look at some examples of linear chain reactions in the following section.

UNIT III

POSSIBLE QUESTIONS

PART- B

(Each carries two marks)

1. What are the difference between order and molecularity of a reaction?
2. Write some examples of first order reaction.
3. Define fast reaction.
4. Define rate of the reaction.
5. Define order of a reaction. Write any two examples for first order reaction.
6. What is meant by zero order reactions?
7. Define molecularity of a reaction.
8. Write some examples of zero order reaction.
9. Define fast chain reactions.
10. What is meant by parallel reactions?

PART C

(Each carries Six marks)

1. Explain (i) first order (ii) second order (iii) zero order reaction.
2. Explain the kinetics of complex reactions.
3. Write a note on following terms (i) Opposing reactions (ii) parallel reactions
4. Discuss the consecutive reactions with examples.

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II B.Sc. Chemistry
PHYSICAL CHEMISTRY

UNIT III

Multiple choice questions

Question	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
Which of the following statements about molecularity of any reaction is correct?	a. It is experimentally determined	b. It is meant for the reaction and not for its individual steps	c. It may or may not be whole number	d. It can never me zero	d. It can never me zero
Rate of a reaction depends on	a. slow step	b. fast step	c. overall reaction	d. both slow and fast step	a. slow step
Molecularity of the reaction $2HI \rightarrow H_2 + I_2$ is?	a.1	b. 2	c.1/2	d.3/2	b. 2
Decomposition of nitrogen pentoxide in CCl_4 is an example for	a) second order reaction	b) third order reaction	c) zero order reaction	d) first order reaction.	d) first order reaction.
Hydrolysis of an ester by dilute HCl is an example for	a) zero order reaction	b) first order reaction	c) second order reaction	d) pseudo first order reaction	d) pseudo first order reaction
Reactions in which the reacting molecules react in more than one way yielding different set of products are called	a) consecutive reactions	b) parallel reactions	c) opposing reactions	d) chain reactions	b) parallel reactions
The sum of the powers of the concentration terms that occur in the rate equation is called	a) molecularity	b) order	c) rate	d) rate constant	b) order
Half life of first order reaction is	a) greater	b) lesser	c) high	d) constant	d) constant
Time required for concentration of reactant to fall down to its half value from original value is	a) reaction life	b) half life	c) half reactant	d) ideal life	b) half life
As the chemical reaction proceeds, the concentration of	a. reactants increases	b. prducts increases	c. reactant remains constan	d. products decreases	b. prducts increases
Rate of reaction is rate of change of concentration with	a. pressure	b. temperature	b. volume	d. time	b. volume
When the concentration of reactant molecules is increased, the rate of reaction increases. The best explanation is: As the reactant concentration increases,	(a) the average kinetic energy of molecules increases.	(b) the frequency of molecular collisions increases.	(c) the rate constant increases.	(d) the order of reaction increases.	(b) the frequency of molecular collisions increases.
To increase the rate of a reaction, there must be	a) a decrease in the frequency of collisions.	b) an increase in the frequency of collisions.	c). a decrease in the frequency of successful collisions.	d) an increase in the frequency of successful collisions.	d) an increase in the frequency of successful collisions.
An increase in temperature increases the rate of a chemical reaction because	a) the activation energy is lower	b) exothermic reactions are always favoured	c) a greater fraction of particles have sufficient kinetic energy	d) the particles are more likely to have favourable collision geometry	c) a greater fraction of particles have sufficient kinetic energy
As reactant molecules approach each other	a) heat is released.	b) a reaction intermediate forms.	c) kinetic energy changes to potential energy	d) potential energy changes to kinetic energy	c) kinetic energy changes to potential energy
As reactant particles approach one another, their	a) kinetic energy increases and their potential energy increases.	b) kinetic energy increases and their potential energy decreases	c) kinetic energy decreases and their potential energy increases	d) kinetic energy decreases and their potential energy decreases	c) kinetic energy decreases and their potential energy increases
The units of "reaction rate" are	a) L mol–1 s–1	b) L2 mol–2 s–1	c) s–1	d) mol L–1 s–1	d) mol L–1 s–1
Appropriate units for a first-order rate constant are	a) M/s	b) 1/M·s	c) C. 1/s	d) 1/M2·s	c) C. 1/s
Appropriate units for a second-order rate constant are	a) M/s	b) 1/M·s	c) C. 1/s	d) 1/M2·s	b) 1/M·s
Which one of the following changes would alter the rate constant (k) for the reaction $2A + B \rightarrow$ products?	a) increasing the concentration of A	b) increasing the concentration of B	c) increasing the temperature	d) measuring k again after the reaction has run for a while	c) increasing the temperature
The minimum amount of energy required to overcome the energy barrier in a chemical reaction is the	a) heat of reaction.	b) activation energy	c) KE of the reactants	d) enthalpy of the products	b) activation energy
Decomposition of nitrogen pentoxide in CCl_4 is an example for	a) second order reaction	b) third order reaction	c) zero order reaction	d) first order reaction	d) first order reaction

50% of a first order reaction is completed in 20 minutes. The time required for 75% completion is	a) 60 minutes	b) 10 minutes	c) 40 minutes	d) 80 minutes.	c) 40 minutes
For a reaction: aA → bB, the rate of reaction is doubled when the concentration of A is increased by four times. The rate of reaction is equal to	a) k [A]a	b) k $[A]^{½}$	c) k $[A]^{1/a}$	d) k [A]	b) k $[A]^{½}$
If the activation energy is high then the rate of the reaction is	a) high	b) moderate	c) low	d) cannot be predicted	c) low
In a first order reaction the concentration of the reactant is increased by 2 times. The rate of the reaction is increased by	a) 2 times	b) 4 times	c) 10 times	d) 6 times.	b) 4 times
Parallel reactions take place in	a. more than one way	b. more than one step	c. in one way but more than one step	d. in one step but more than one way	a. more than one way
Which one of the following statements is correct?	a. parallel reactions are also known as consecutive reactions	b. Competingreactions have more than one step	c. Sequential reactions are also called consecutive reactions	d. Consecutive reactions do not have intermediates	c. Sequential reactions are also called consecutive reactions
Decomposition of ethylene oxide is	a. parallel reaction	b. competing reaction	c.both parallel as well as competing reaction	d. sequential reaction	d. sequential reaction
Sequential reactions have	a. more than one way to proceed toward product	b. more than one step	c. no intermediate	d. catalyst	b. more than one step
For first and second order of reactions graph will be	a) straight line	b) falling	c) rising	d) curve	d). curve
Units of concentration is	a) $moldm^{-3}$	b) $moldm^{-3}s^{-1}$	c) dm3mol-1	d) dm3mol-1s-1	a) $moldm^{-3}$
Rate-determining step containing single specie (atom, ion or molecule) will make reaction	a) molecular	b) unimolecular	c) polymolecular	d). multimolecular	b) unimolecular
Effect of concentration of reagent on rate of reaction is determines	a) order of reaction	b) concentration of products	c) concentration of reactants	d). energy of activation	a) order of reaction
Over all representation of a reaction rate in terms of equation is known as	a) rate of reaction	b) rate equation	c) reaction equation	d) balanced equation	b) rate equation
Order of reaction can be identified by plotting graphs of	a) reaction	b) concentration	A. pH value	d) A. both A and B	A. both A and B
Slowest step on which overall reaction depends is	a) rate of reaction	b) rate equation	c) rate determining step	A. all of them	c) rate determining step
Half-life period of a second order reaction is	a) independent of the concentration	b) directly proportional to the initial concentration	c) inversely proportional to concentration	d) directly proportional to the concentration	b) directly proportional to the initial concentration
What is the order of a chemical reaction whose rate is determined by the variation of one concentration term only?	a) Second	b) Four	c) First	d) Zero	c) First
The rate of chemical reaction depends on the nature of chemical reactants because	a) energy of activation differs from one reaction to another	b) some are solid at room temperature	c) some are coloured	d) all the above	a) energy of activation differs from one reaction to another
All the radioactive changes are of	a) Third order	b) Second order	c) First order	d) Zero order	c) First order
Rate of reation is defined as	(a) decrease in the concentration of a reactant	(b) increase in the concentration of a product	(c) change in the concentration of any one of the reactants or products per unit time	(d) all the above three are correct	(c) change in the concentration of any one of the reactants or products per unit time
______ does not affect the rate of reaction	(a) size of the vessel	(b) amount of the reactants	(c) physical state of reactants	(d) DH of reaction	(d) DH of reaction
The rate constant of a reaction changes when ...	(a) pressure is changed	(b) concentration of reactants changed	(c) temperature is changed	(d) a catalyst is added	(c) temperature is changed
A reaction involving two different reactants can never be a ….	(a) bimolecular reaction	(b) Unimolecular reaction	(c) first order reaction	(d) second order reaction	(b) Unimolecular reaction
The rate constant of a reaction has same units as the rate of reaction. The reaction is of ...	(a) third order	(b) second order	(c) first order	(d) zero order	(d) zero order
Which of the following statements is incorrect about the molecularity of a reaction ?	(a) Molecularity of a reaction is the number of molecules in the slowest step.	(b) Molecularity of a reaction is the number of molecules of the reaction present in the balanced equation	(c) There is no difference between order and molecularity of a reaction	(d) Molecularity is always a positive whole number	(c) There is no difference between order and molecularity of a reaction
For a single step reaction A + 2B → Products , the molecularity is	(a) zero	(b) 1	(c) 2	(d) 3	(d) 3
Many reactions which proceed at a very high speed that their rates cannot be measured such reactions are known as	complex reaction	fast reaction	slow reaction	elementary reaction	fast reaction
The rate of chemical reaction is the variation in the concentration of either reactants or the products with	time	mass	temperature	pressure	time

UNIT-IV

SYLLABUS

Temperature dependence of reaction rates; Arrhenius equation; activation energy. Collision theory of reaction rates, Lindemann mechanism, qualitative treatment of the theory of absolute reaction rates.
Catalysis: Types of catalyst, specificity and selectivity, mechanisms of catalyzed reactions at solid surfaces. Enzyme catalysis, Michaelis-Menten mechanism, acid-base catalysis.

Temperature dependence of reaction rates

Activation energy:

The particles collide with a certain minimum amount of energy called the **activation energy**.

It is found experimentally that the rate constants for many chemical reactions follow the Arrhenius equation.

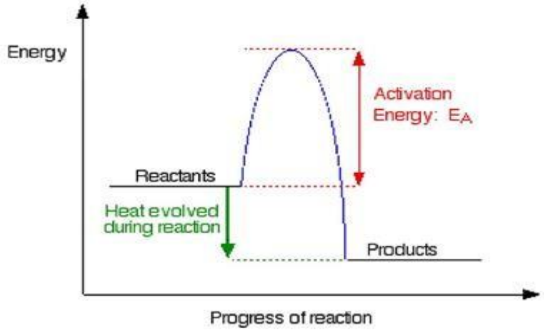
$$k = A exp\,(-E_a/RT) \text{ ……………………… } (1)$$

or equivalently

$$\ln k = \ln A - E_a/RT$$

where A is the pre-exponential factor and E_a is the activation energy. These parameters may be determined from experimental rate data by plotting ln$k$ against $1/T$. This is known as an Arrhenius plot, and has an intercept of ln$A$ and a slope of $-E_a/R$. For most reactions, the Arrhenius equation works fairly well over at least a limited temperature range. However, there are often deviations. These are generally due to the temperature dependence of the pre-exponential factor[2] (which you will cover in detail in statistical mechanics next year), but may also be due to more exotic effects, such as the influence of quantum mechanical tunnelling mechanisms on the reaction rate at low temperatures.

For an elementary reaction, both E_a and A have definite physical meanings; in particular, the activation energy may be interpreted as the energy difference between the reactants and the transition state involved in the collision and associated chemical rearrangement (see figure).



When the Arrhenius equation is applied to the overall kinetics of a multi-step reaction, Easimply becomes an experimental parameter describing the temperature dependence of the overall reaction rate. Eamay vary with temperature, and may take positive or negative values. In this context, we may define the activation energy as:

$$E_a = RT^2\, d\ln k/dT \text{ ……………………… } (2)$$

This is a more general definition of the activation energy than the Arrhenius equation, and the two definitions become equivalent in the case when E_a is independent of temperature (all you need to do to prove this is to integrate the above equation, treating E_a as a constant). With the above definition, we can determine E_a at a given temperature from the slope (at the temperature of interest) of a plot of ln*k* against *T*, even if the Arrhenius plot is not a straight line. There are a few observations that follow from Equation (2).

1. The higher the activation energy, the stronger the temperature dependence of the rate constant.
2. A reaction with no temperature dependence has an activation energy of zero (this is common in ion-molecule reactions and radical-radical recombinations)
3. A negative activation energy implies that the rate decreases as the temperature increases, and always indicates a complex reaction mechanism. An example of a reaction with negative activation energy was the oxidation of NO to form NO_2, which has the mechanism.

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NO)_2$$

$$(NO)_2 + O_2 \xrightarrow{k_2} 2NO_2$$

At higher temperatures, the intermediate complex $(NO)_2$ becomes more unstable and has a shorter lifetime. There is therefore less time for the O_2 to react with it to form the NO_2 products, and the reaction rate therefore decreases. Another way of thinking about this is that formation of the complex is exothermic, and increasing the temperature will therefore shift the pre-equilibrium to the left (by Le Chatelier's principle), again reducing the overall rate of reaction.

Overall activation energies for complex reactions

When dealing with complex reactions, the Arrhenius equation can often be used to estimate the overall activation energy from knowledge of the activation energies of individual steps. For example, in the above reaction, the overall rate law is

$$\nu = \frac{k_1 k_2}{k_{-1}}[NO]^2[O_2] = k[NO]^2[O_2]$$

where *k* is the observed third order rate constant. The temperature dependence of *k* is

$$k = \frac{k_1 k_2}{k_{-1}} = \frac{A_1 \exp\left(\frac{-E_a^{(1)}}{RT}\right) A_2 \exp\left(\frac{-E_a^{(2)}}{RT}\right)}{A_{-1}\exp\left(\frac{-E_a^{(-1)}}{RT}\right)} = \frac{A_1 A_2}{A_{-1}} \exp\left(\frac{-E_a^{(1)} - E_a^{(2)} + E_a^{(-1)}}{RT}\right)$$

We can therefore identify that for the overall reaction,

$$A = \frac{A_1 A_2}{A_{-1}} \quad \text{and} \quad E_a = E_a^{(1)} + E_a^{(2)} - E_a^{(-1)}$$

Theory of reaction rate:

Rate of a reaction is defined as the rate of change concentration of reactant or product per unit time.

Collision theory of reaction rates:

According to collision theory,

i). Molecule must collide with react.

ii). The rate of the reaction is proportional to the number of reacting molecules.
i.e., the number of colliding molecules.

- The collision theory account for the dependence of the rate on the product of concentration terms.
- Let us consider that molecule A combines directly with a molecule B to form AB.

$$A + B \longrightarrow AB$$

Visualize four molecules each of A and B in a box.

How many ways can be collision between A and B occur?

- Molecule A can be collide with any of four B molecules; hence it has four opportunities for collision.
- The same is true each of the four A molecules making 16 possible collisions in all.

Rate of the reaction α [AB]

Let us consider the reaction,

$$A + B \longleftrightarrow C + D$$

- In collision, certain molecule exceeds the minimum activation energy which results in the formation of product.

Rate of reaction = Number of colliding molecules per litre per cc × fraction of the effective collision.

Rate of reaction.,

$$-dn/dt = Z_{AB}\, e^{-E/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where , Z_{AB} = Number of collisions per unit time

E = Energy of activation

CATALYSIS

- Catalyst is any substance which can change the rate of the reaction without being used up in that reaction and the phenomenon is known as catalysis.
- In many reactions one of the product acts as a catalyst and this phenomenon is called autocatalysis.

Types of catalysis:

This can be divied into the classes

Homogeneous catalysis:

Here the catalyst and the reactants are in same phase.

Eg:

$2SO_{2(g)} + O_{2(g)} \quad 2SO_3$

$CH_3COOCH_{3(l)} + H_2O \quad CH_3COOH + CH_3OH$

These are the examples of homogeneous catalysis.

Heterogeneous catalysis:

In heterogeneous catalysis, the catalyst is present in a different phase then that of reactants.

Eg:

$2KCl_{3(S)} \quad 2\,KCl + 3O_2$

$2H_2O_{2(l)} \quad 2H_2O + O_2$

$SO_{2(g)} + O_{2(g)} \quad 2SO_3$

Enzyme Catalysts

- ‘Enzymes’ are biological catalysts. There may be as many as 30,000 enzymes in the human body. (Ex: Lactase)
- Most enzymes are protein molecules with large molecular masses (10,000 to 10^6 amu).
- Enzymes have very specific shapes.
- Most enzymes catalyze very specific reactions.
- The substances that undergo reaction at the active site on enzymes are called ‘substrates’.
- A substrate locks into an enzyme and a fast reaction occurs. The products then move away from the enzyme.

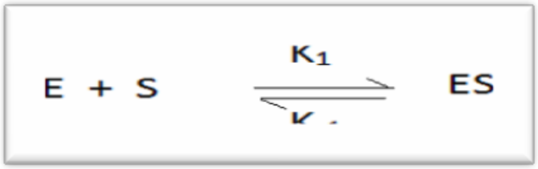
- Catalysis by enzymes are the biological catalysis, is much more specific than that by acids and bases. Some enzyme show absolute specificity; an example is urease, which only catalysis the hydrolysis of urea,

$$\mathbf{CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3}$$

- Many enzymes exhibit *stereochemical specificity*, in that they catalysis the reactions of one stereochemical from and not the other, the *proteolytic enzymes.*
- The enzymes are proteins, but they may be associated with *non-protein* substances (known as coenzymes) that are essential to the action of the enzymes. Some enzymes are catalytically inactive in the absence of certain metal ions. For a number of enzymes the evidence is that the catalytic activity is due to a relatively small region of the protein molecule; this region is usually referred to as the '***active center'.***
- The present treatment of enzyme kinetic is confined to the influence of concentration pH and temperature and to some brief comments about enzyme mechanisms.

SINGLE SUBSTRATE REACTION

- The simplest case is that of an enzyme catalysis reaction where there is a single substrate. An example is the hydrolysis of an ester.
- The rate varies linearly with the substrate concentration at low concentration (First order kinetics) and becomes independent of substrate concentration (zero order kinetics) at high concentration.
- This type of reaction is unimolecular surface reaction was first explained by 'Michaelis and Menten' in terms of the mechanism.



$$\boxed{ES \xrightarrow{K_2} E + P}$$

- Here E and S are the enzyme and substrate, P is the product and ES is an addition complex. The steady-state treatment was first applied to this mechanism by *Briggs and Haldane*. The steady- state equation is

$$K_1 [E][S] - K_{-1} [ES] - K_2 [ES] = 0 \qquad \text{.........(1)}$$

- In studies of enzyme reactions the molar concentration of substrate is usually very much greater than that of the enzymes only a small proportion of the substrate therefore is bound to the enzymes.

- The total concentration of enzyme, [E] and the concentration of complex,[ES]

$$[E]_0 = [E] + [ES]$$

- Elimination of [E] between these two equations gives

$$K_1([E]_0 - [ES]) [S] - (K_{-1} + K_2) [ES] = 0$$

And therefore

$$[ES] = \frac{K_1([E]_0 [S]}{K_{-1} + K_2 + K_1[S]} \qquad \text{...........(4)}$$

- The rate of reaction is

$$v = K_2 \; [ES] = \frac{K_1K_2[E]_0[S]}{K_{-1}+K_2+K_1[S]} \text{........(5)}$$

$$= \frac{K_2[E]_0[S]}{(K_{-1} + K_2) / K_1 + [S]} \text{..........(6)}$$

$$= \frac{K_2[E]_0[S]}{K_m + [S]} \text{............(7)}$$

- In this equation K_m, equal to $(K_{-1} + K_2) / K_1$ is known as the ***Michaelis constant.*** And an equation of the form of Eq.(7) is referred to as a ***Michaelis-menten*** equation. it is referred ***single substrate reaction***.

$$\boxed{V = \frac{K_2}{K_m} [E]_0[S] \text{.............(8)}}$$

Michaels-Menton equation:

- The rate of the reaction is approximately proportional to the concentration of enzyme.

  Step 1: Formation of complex

$$E + S \underset{k_{-1}}{\overset{K_1}{\rightleftarrows}} ES \text{ (fast)}$$

  Step 2: Decomposition of complex to give products

$$ES \xleftrightarrow{K_2} E + P \text{(slow)}$$

  Where, P is the product. By using steady state approximation,

$$K_1 [E] [S] – K_{-1} [ES] – K_2 [ES] = 0$$

$$K_1 [E] [S] – [ES] [K_{-1} + K_2] = 0\text{.......(1)}$$

  Total enzyme concentration,

$$[E]_0 = [E] + [ES]$$

  Where [E] is the free enzyme concentration.

$$[E] = [E]_0 – [ES]$$

  Substitute the above equation in (1)

$$K_1 [[[E]_0 – [ES]] – [ES] [K_{-1} + K_2] = 0$$

$$K_1 [[E]_0 [S]] – K_1 [[ES] [S]] = [ES] [K_{-1} + K_2]$$

$$K_1 [[E]_0 [S]] = K_1 [[ES] [S]] = [ES] [K_{-1} + K_2]$$

$$K_1 [[E]_0[S]] = [K_1 [S] + K_{-1} + K_2] [ES]$$

$$[ES] = \frac{[K_1 [E]_0 [S]}{K_1[S] + K_{-1} + K_2}$$

We know that, rate = k_2 [ES]

$$\text{Rate} = \frac{K_2 [E]_0 [S]}{Km + [S]}$$

- The above equation is called as Michael's-Menton equation. Here k_m is called as Michael's constant.

UNIT IV
POSSIBLE QUESTIONS
PART- B
(Each carries two marks)

1. Define activation energy.
2. Define collision number.
3. What is meant by catalyst? Give an example.
4. Define enzyme catalysis.
5. What are the activated complexes?
6. What is meant by acid catalysis? With one example.

PART C

(Each carries Six marks)

1. Describe the Arrhenius equation.

2. Write a note on collision theory of reaction rates.

3. Explain the absolute reaction rate theory.

4. Discuss the enzyme catalysis with example.

5. Write a note on (i) Michaelis-Menten mechanism (ii) Lindemann mechanism.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University under Section 3 of UGC Act 1956)
COIMBATORE-641 021
(For the candidates admitted from 2016 & onwards)
II B.Sc. Chemistry
PHYSICAL CHEMISTRY

UNIT IV
Multiple choice questions

Question	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
The temperature coefficient of a reaction is	a)the rate constant at a fixed rate constant	b)the ratio of rate constants at two temperatures	c)The ratio of rate constants differing by 10° C preferably 25° C and 35° C	d)the ratio of rate constant at ordinary temperature	c)The ratio of rate constants differing by 10° C preferably 25° C and 35° C
A large increase in the rate of reaction for a rise in temperature is due to	a)Increase in the number of collisions	b)Increase in the number of activated molecules	c)Lowering of activation energy	d)Shortening of activation energy	b)Increase in the number of activated molecules
Rate of which reaction increases with temperature	a)of any	b)of endothermic reaction	c)of exothermic reaction	d)No reaction	of any
For a reaction, the rate of reaction was found to increase about 1.8 times when the temperature was increased by 10° C, the increase in rate is due to	a)increase in the number of active molecules	b)increase in activation energy of reactants	c)Decrease in activation energy of reactants	d)Increase in the number of collisions between reacting molecules	a)increase in the number of active molecules
On increasing the temperature by 10 k in the case of slow reactions	a)No of collisions get doubled	b)value of rate constant increases	c)Energy of activation increases	d)value of rate constant decreases	b)value of rate constant increases
An increase in the rate of a reaction for a rise in temperature is due to	a)Increase in collision frequency	b)Shortening of mean free path	c)Increase in number activated molecules	d)All	d)All
If the rate of reaction becomes 2 times for every 10° C rise in temperature, by what factor the rate of reaction increases when temperature is increased from 30° C to 80° C	a)16	b)32	c)64	d)128	b)32
As the temperature of a gaseous system increases, the number of molecules with a higher kinetic energy	a)Increases	b)decreases	c)Remains same	d)varies irregularly	a)Increases
For a slow reaction, the ratio of rate constants at 35° C and 25° C is generally	a)2	b)3	c)1	d)4	a)2
In a reaction, the threshold energy is equal to	a)Activation energy + normal energy of reactants	b)Activation energy - normal energy of reactants	c)Activation energy	d)Normal energy of reactants	c)Activation energy
Minimum energy required by molecules to enter into chemical reaction is called	a)Kinetic energy	b)Potential energy	c)Threshold energy	d)Activation energy	c)Threshold energy
The enzyme catalysed reactions are faster than metal catalysed reactions because their activation energy is	a)Greater	b)smaller	c)same	d)Zero	b)Smaller
For a reactionfor which the activation energies of forward and backward reactions are equal	a)$\Delta H = 0$	b)$\Delta S = 0$	c)The order is zero	d)There is no need of catalyst	a)$\Delta H = 0$
Activation energy of a reaction is	a)The energy released during the reaction	b)energy involved when activation complex is formed	c)Minimum amount of energy required to overcome the potential barrier	d)The enrgy needed to form 1 mole of the product	c)Minimum amount of energy required to overcome the potential barrier

Combustion of carbon is exothermic but coal stored in coal depots does not burnt automatically because of	a)High threshold barrier	b)Kinetic stability of coal	c)Higher activation energy required for burning	d)All	d)All
The threshold energy of a chemical reaction depends on	a)Nature of reacting species	b)Temperature	c)Concentration of species	d)No of collisions per unit time or collision frequency	a)Nature of reacting species
The minimum energy necessary to permit a reaction to take place is	a)Threshold energy	b)Activation energy	c)Free energy	d)Kinetic energy	b)Activation energy
The value of activation energy of a chemical reaction is primarily determined by	a)Nature of reacting species	b)Temperature	c)concentration of species	d)No of collisions per unit time or collision frequency	a)Nature of reacting species
As more molecules reach the activation energy of the molecules	a)Increases	b)Decreases	c)Remains the same	d)varies irregularly	a)Increases
The minimum amount of energy required by the reacting molecules at the time of collisions inorder to produce effective collisions is called	a)Activation energy	b)Threshold energy	c)Internal energy	d)Potential energy	b)Threshold energy
The chemical reactions in which reactants need high amount of activation energy are generally	a)Fast	b)slow	c)very fast	d)spontaneous	b)Slow
According to Arrhenius equation a straight line is obtained by ploting the log of the rate constant of a chemical reaction (log k) against	a)T	b)Log T	c)1/T	d)Log 1/T	c)1 / T
Which of the following is used to determine the rate of fast reactions	a)Ostwald's isolation method	b)Nuclear magnetic resonance method	c)Graphical method	d)Half change method	b)Nuclear magnetic resonance method
According to collision theory of reaction rates	a)Every collision between reactant molecules leads to chemical reaction	b)Rate of reaction is proportional to velocity of molecules	c)All reactions which occur in gaseous phase are zero order reactions	d)Rate of reaction is directly proportional to collision frequency	d)Rate of reaction is directly proportional to collision frequency
Kinetic theory of collision is putforward by	a)Max Trautz	b)Arrhenius	c)Lewis	d)Draper	b)Arrhenius
In homogeneous catalytic reactions,the rate of reaction	a)Depends upon the concentration of catalyst	b)Independent upon the concentration of catalyst	c)Depends upon the free energy change	d)Depends upon the physical state of the catalyst	a)Depends upon the concentration of catalyst
V_2O_5 has replaced Pt as catalyst in the contact process because	a)It is cheap	b)It is not easily poisoned	c)Both are correct	d)None is correct	c)Both are correct
When a catalyst increases the rate of a chemical reaction,the rate constant	a)Increases	b)Decreases	c)Remains constant	d)Becomes infinite	a)Increases
A substance which promotes the activity of a catalyst is known as	a)Initiator	b)Catalyst	c)Promotor	d)Autocatalyst	c)Promotor
Which is the following is an example of autocatalysis	a)Decomposition of $KCIO_3$ + MnO_2 mixt.	b)The decomposition of nitroglycerine	c)Breakdown of ${}_6C^{14}$	d)Hydrogenation of vegetable oil using Ni catalyst	b)The decomposition of nitroglycerine
An auto catalyst is	a)Catalyst for catalyst	b)One which starts a reaction	c)One of the products of the reaction which acts as a catalyst	d)Which retards a chemical reaction	c)One of the products of the reaction which acts as a catalyst
Catalytic poison acts by	a)Chemically combining with catalyst	b)Coagualting the catalyst	c)Getting adsorbed on the active centres on the surfaces	d)Chemical combination with anyone of the reactants	c)Getting adsorbed on the active centres on the surfaces
In temporary poisoning,catalytic poison acts by	a)Coagualting the catalyst	b)Chemical combination with anyone of the reactants	c)Chemically combining with catalyst	d)Getting adsorbed on the active centres on the catalyst	d)Getting adsorbed on the active centres on the catalyst
A substance like CO,As_2O_3,HCN etc,which paralyses the catalytic activity of a catalyst is called	a)A negative catalyst	b)Auto catalyst	c)A Promotor	d)Poison	d)Poison
Catalytic poisoners are usually the same as	a)Poison for human body	b)Enzyme for human body	c)Vitamins for human body	d)proteins for human body	a)Poison for human body

Negative catalyt is that	a)Which retards the rate of reaction	b)Takes the reaction in the backward direction	c)Promotes the side reaction	d)Coagualting the catalyst	a)Which retards the rate of reaction
Which of the following acts as negative catalyst	a)Lead tetraethyl as antiknock compound	b)Glycerol in decomposition of H_2O_2	c)Ethanol in oxidation of chloroform	d)All are correct	d)All are correct
The efficiency of an enzyme in catalysing a reaction is due to its capacity	a)To form a strong enzyme substrate molecule	b)To change the shape of the substrate molecule	c)To lower the activation energy of the rection	d)To decrease the bond energy of all substrate molecules	c)To lower the activation energy of the rection
enzymes are	a)substance made by chemist to activate washing powder	b)very active vegetable catalysts	c)catalysts found in organisms	d)synthetic catalysts	c)catalysts found in organisms
The efficiency of an enzyme in catalysing a reaction is due to its capacity	a)To form a strong enzyme substrate molecule	b)To decrease the bond energies of the substrate molecule	c)To change the shape of the substrate molecule	d)To lower the activation energy of the reaction	d)To lower the activation energy of the reaction
enzymes take part in reaction and	a)Decreases the rate of reaction	b)Increases the rate of reaction	c)Both (a) and (b)	d)None	b)Increases the rate of reaction
When a catalyst is introduced into a reversible reaction	a)Equilibrium reaction rate increases	b)Backward reaction rate increases	c)Equilibrium is not changed	d)Equilibrium is attained quickly	d)Equilibrium is attained quickly
A biological catalyst is essentially	a)An amino acid	b)An enzyme	c)A carbohydrate	d)A nitrogen molecule	b)An enzyme
Which of the following is not correct in case of heterogenous catalyst	a)The catalyst decrease the energy of activation	b)The surface of catalyst plays an important role	c)The catalyst actually forms a compound with reactants	d)There is no change in the energy of activation	d)There is no change in the energy of activation
Which is true in case of catalyst	a)The catalyst altered during the reaction is regenerated	b)It does not alter the equilibrium	c)It lowers the energy of activation	d)All the above	d)All the above
A catalyst in a chemical reaction	a)Does not initiate a reaction	b)Increases the activation energy of the reaction	c)Changes the equilibrium constant of a reaction	d)Does not change the rate of reaction	a)Does not initiate a reaction
The enzyme which can catalyze the conversion of glucose to ethanol is	a)Zymase	b)Invertase	c)Maltase	d)Diastate	a)Zymase
A catalyst is used	a)Only for increasing the velocity of the reaction	b)For altering the velocity of the reaction	c)Only for decreasing the velocity of the reaction	d)All are correct	b)For altering the velocity of the reaction
A catalyst increases the rate of reaction by	a)Decreasing activation energy	b)Decreasing internal energy	c)Decreasing enthalpy	d)increasing activation energy	a)Decreasing activation energy
The ability of catalyst to accelerate the chemical reaction is known as	a)Selectivity	b)Activity	c)Negative catalyst	d)None of these	b)Activity
The process which is catalysed one of the product is called	a)Acid-base catalysis	b)Auto catalysis	c)Negative catalyst	d)Positive catalysis	b)Auto catalysis
When the catalyst is added to the reversible reaction in equlibrium state,the value of equlibrium constant	a)Increases	b)Decreases	c)Becomes zero	d)Does not change	d)Does not change
In the case of auto catalysis	a)Solvent catalysis	b)Product catalyses	c)Reactant catalyses	d)Heat produced in the reaction catalyses	b)Product catalyses
which of the following is true about the catalyst	a)It initiates reaction	b)It changes equlibrium point	c)It alters the rate of reaction	d)It increase average kinetic energy	c)It alters the rate of reaction
Which of the following statements about the active site of an enzyme is correct?	a)The active site of an enzyme binds the substrate of the reaction it catalyses more tightly than it does the transition state intermediate.	b)The active site of an enzyme binds the substrate of the reaction it catalyses less tightly than it does the transition state intermediate.	c)The active site of an enzyme binds the product of the reaction it catalyses more tightly than it does the transition state intermediate.	d)The active site of an enzyme is complementary to the substrate of the reaction it catalyses.	b)The active site of an enzyme binds the substrate of the reaction it catalyses less tightly than it does the transition state intermediate.

Which of the following statements about the nature of enzyme catalysis is correct?	a)An enzyme can change the equilibrium position of the reaction it catalyses by lowering the energy of activation of that reaction.	b)An enzyme can lower the energy of activation of the reaction it catalyses by increasing the molecular collisions between the molecules.	c)An enzyme lowers the free energy difference between substrate(s) and product(s) but it cannot change the equilibrium position of the reaction it catalyses.	d)An enzyme cannot change the equilibrium position of the reaction it catalyses but it lowers the energy of activation of that reaction.	d)An enzyme cannot change the equilibrium position of the reaction it catalyses but it lowers the energy of activation of that reaction.
Which of the following statements about Michaelis-Menten kinetics is correct?	a)K_m, the Michaelis constant, is defined as the concentration of substrate required for the reaction to reach maximum velocity.	b)K_m, the Michaelis constant, is defined as the dissociation constant of the enzyme-substrate complex.	c)K_m, the Michaelis constant, is expressed in terms of the reaction velocity.	d)K_m, the Michaelis constant, is a measure of the affinity the enzyme has for its substrate.	d)K_m, the Michaelis constant, is a measure of the affinity the enzyme has for its substrate.
Which of the following statements about the competitive inhibition of an enzyme-catalyzed reaction is correct?	a)A competitive inhibitor and substrate can bind simultaneously to the enzyme.	b)The V_{max} and K_m (Michaelis constant) for a reaction are unchanged in the presence of a competitive inhibitor.	c)The V_{max} for a reaction remains unchanged in the presence of a competitive inhibitor.	d)The K_m for a reaction remains unchanged in the presence of a competitive inhibitor.	c)The V_{max} for a reaction remains unchanged in the presence of a competitive inhibitor.
The Michaelis-Menton equation relates the rate of an enzyme-catalysed reaction to which of the following?	a)Substrate concentration	b)Product concentration	Activation Energy	d)Inhibitor concentration	Substrate concentration
Which of the following statements about Michaelis-Menten kinetics are correct? Please select all that apply.	**a)** A high Michaelis constant (K_m) indicates a high affinity of an enzyme for its substrate.	**b)** A low Michaelis constant (K_m) indicates a high affinity of an enzyme for its substrate.	**c)** The Michaelis constant (K_m) of an enzyme increases when the enzyme concentration is increased.	**d)** The Michaelis constant (K_m) of an enzyme is unchanged when the enzyme concentration is increased.	**d)** The Michaelis constant (K_m) of an enzyme is unchanged when the enzyme concentration is increased.

UNIT-V

SYLLABUS

Photochemistry: Characteristics of electromagnetic radiation, Lambert-Beer's law and its limitations, physical significance of absorption coefficients. Laws, of photochemistry, quantum yield, actinometry, examples of low and high quantum yields, photochemical equilibrium and the differential rate of photochemical reactions, photosensitised reactions, quenching. Role of photochemical 34 reactions in biochemical processes, photostationary states, chemiluminescence.

Characteristics of electromagnetic radiation

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. The electric and magnetic fields come at right angles to each other and combined wave moves perpendicular to both magnetic and electric oscillating fields thus the disturbance. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum. These electric and magnetic waves travel perpendicular to each other and have certain characteristics, including amplitude, wavelength, and frequency.

General Properties of all electromagnetic radiation:

1. Electromagnetic radiation can travel through empty space. Most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through in order to be heard.
2. The speed of light is always a constant. (Speed of light : 2.99792458×10^8 m s^{-1})
3. Wavelengths are measured between the distances of either crests or troughs. It is usually characterized by the Greek symbol λλ.

Waves and their Characteristics

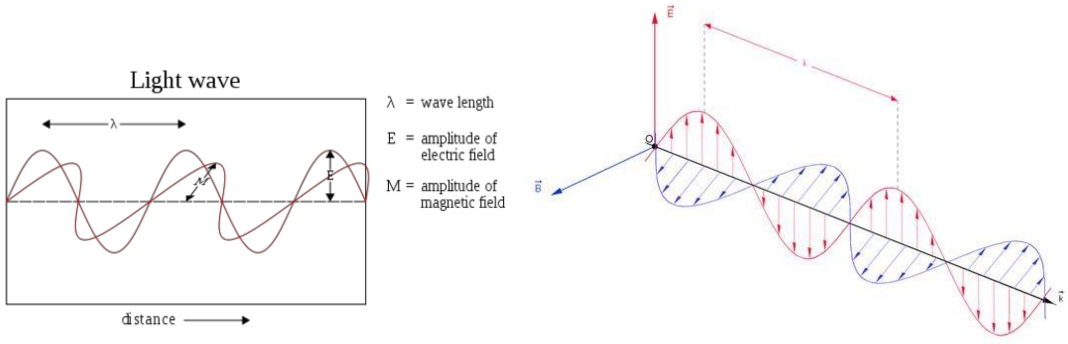


Fig. 1 & 2: Electromagnetic Waves

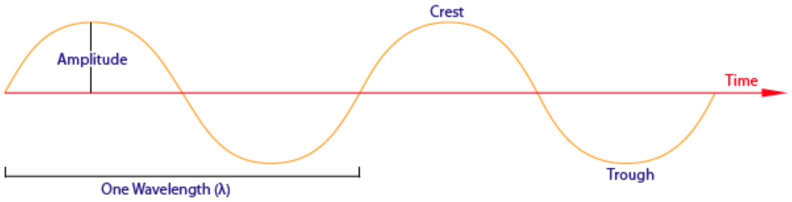


Fig. 3: An EM Wave

Amplitude

Amplitude is the distance from the maximum vertical displacement of the wave to the middle of the wave. This measures the magnitude of oscillation of a particular wave. In short, the amplitude is basically the height of the wave. Larger amplitude means higher energy and lower amplitude means lower energy. Amplitude is important because it tells you the intensity or brightness of a wave in comparison with other waves.

Wavelength

Wavelength (λλ) is the distance of one full cycle of the oscillation. Longer wavelength waves such as radio waves carry low energy; this is why we can listen to the radio without any harmful consequences. Shorter wavelength waves such as x-rays carry higher energy that can be hazardous to our health. Consequently lead aprons are worn to protect our bodies from harmful radiation when we undergo x-rays. This wavelength frequently relationship is characterized by:

$$c=\lambda\nu c=\lambda\nu$$

where

- c is the speed of light,
- λλ is wavelength, and
- νν is frequency.

Shorter wavelength means greater frequency, and greater frequency means higher energy. Wavelengths are important in that they tell one what type of wave one is dealing with.

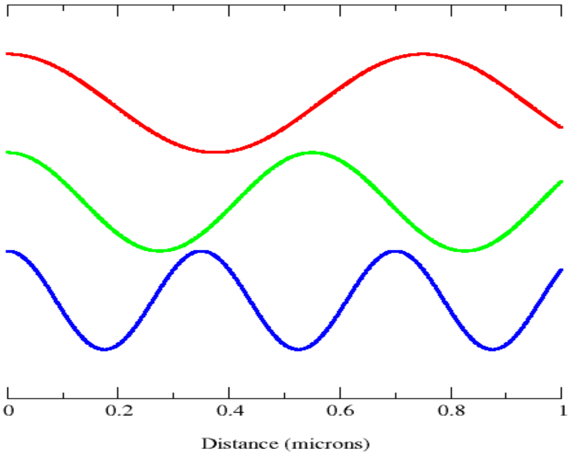


Fig. 4: Different Wavelengths and Frequencies

Frequency

Frequency is defined as the number of cycles per second, and is expressed as sec^{-1} or Hertz (Hz). Frequency is directly proportional to energy and can be express as:

$$E=h\nu E=h\nu$$

where

- E is energy,
- h is Planck's constant, ($h= 6.62607 \times 10^{-34}$ J), and
- νν is frequency.

Electromagnetic spectrum

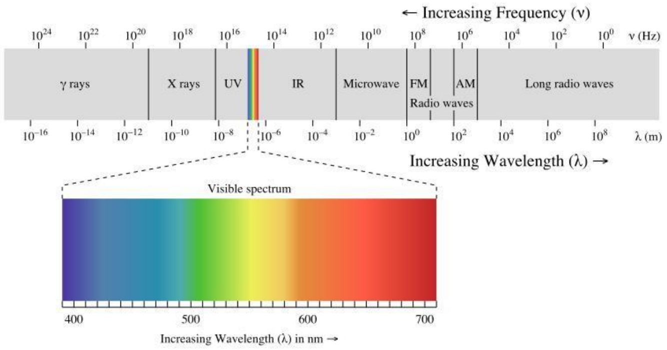


***Figure 5**: Electromagnetic spectrum with light highlighted. Image used with permission from Wikipedia.*

As a wave's wavelength increases, the frequency decreases, and as wave's wavelength decreases, the frequency increases. When electromagnetic energy is released as the energy level increases, the wavelength decreases and frequency decreases. Thus, electromagnetic radiation is then grouped into categories based on its wavelength or frequency into the electromagnetic spectrum. The different types of electromagnetic radiation shown in the electromagnetic spectrum consists of radio waves, microwaves, infrared waves, visible light, ultraviolet radiation, X-rays, and gamma rays. The part of the electromagnetic spectrum that we are able to see is the visible light spectrum.

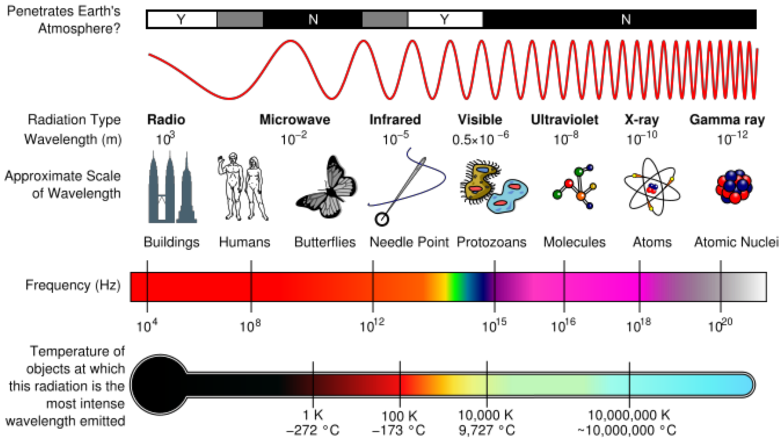


Fig. 6: Electromagnetic Spectrum with Radiation Types

Radiation Types

Radio Waves are approximately 10^3 m in wavelength. As the name implies, radio waves are transmitted by radio broadcasts, TV broadcasts, and even cell phones. Radio waves have the lowest energy levels. Radio waves are used in remote sensing, where hydrogen gas in space releases radio energy with a low frequency and is collected as radio waves. They are also used in radar systems, where they release radio energy and collect the bounced energy back. Especially useful in weather, radar systems are used to can illustrate maps of the surface of the Earth and predict weather patterns since radio energy easily breaks through the atmosphere.

Microwaves can be used to broadcast information through space, as well as warm food. They are also used in remote sensing in which microwaves are released and bounced back to collect information on their reflections.

Microwaves can be measured in centimeters. They are good for transmitting information because the energy can go through substances such as clouds and light rain. Short microwaves are sometimes used in Doppler radars to predict weather forecasts.

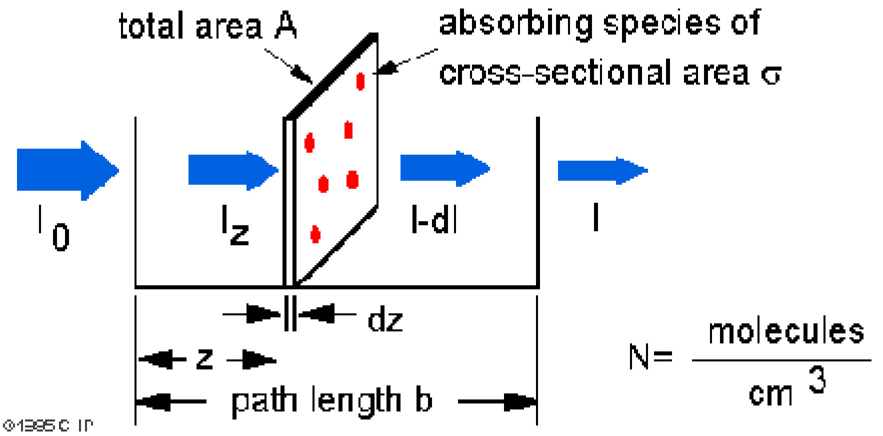
Infrared radiation can be released as heat or thermal energy. It can also be bounced back, which is called near infrared because of its similarities with visible light energy. Infrared Radiation is most commonly used in remote sensing as infrared sensors collect thermal energy, providing us with weather conditions.

Visible Light is the only part of the electromagnetic spectrum that humans can see with an unaided eye. This part of the spectrum includes a range of different colors that all represent a particular wavelength. Rainbows are formed in this way; light passes through matter in which it is absorbed or reflected based on its wavelength. Thus, some colors are reflected more than other, leading to the creation of a rainbow.

Color Region	Wavelength (nm)
Violet	380-435
Blue	435-500
Cyan	500-520
Green	520-565
Yellow	565-590
Orange	590-625
Red	625-740

Lambert-Beer's law and its limitations

The Beer-Lambert law can be derived from an approximation for the absorption coefficient for a molecule by approximating the molecule by an opaque disk whose cross-sectional area, σ, represents the effective area seen by a photon of frequency *w*. If the frequency of the light is far from resonance, the area is approximately 0, and if *w* is close to resonance the area is a maximum. Taking an infinitesimal slab, dz, of sample:



I_o is the intensity entering the sample at z=0, I_z is the intensity entering the infinitesimal slab at z, dI is the intensity absorbed in the slab, and I is the intensity of light leaving the sample. Then, the total opaque area on the slab due to the absorbers is $\sigma * N * A * dz$. Then, the fraction of photons absorbed will be $\sigma * N * A * dz / A$ so,

$$dI / I_z = - \sigma * N * dz$$

Integrating this equation from z = 0 to z = b gives:

$$\ln(I) - \ln(I_o) = - \sigma * N * b$$

$$\text{or } - \ln(I / I_o) = \sigma * N * b.$$

Since N (molecules/cm^3) * (1 mole / $6.023x10^{23}$ molecules) * 1000 cm^3 / liter = c (moles/liter) and * log(x) = ln(x) then

$$- \log(I / I_o) = \sigma * (6.023x10^{20} / 2.303) * c * b$$

$$- \log(I / I_o) = A = \varepsilon * b * c$$

$$\text{where } \varepsilon = \sigma * (6.023x10^{20} / 2.303) = \sigma * 2.61x10^{20}$$

Typical cross-sections and molar absorptivities are:

	σ (cm^2)	ε ($M^{-1}\ cm^{-1}$)
absorption - atoms	10^{-12}	$3x10^8$
molecules	10^{-16}	$3x10^4$
infrared	10^{-19}	3x10
Raman scattering	10^{-29}	$3x10^{-9}$

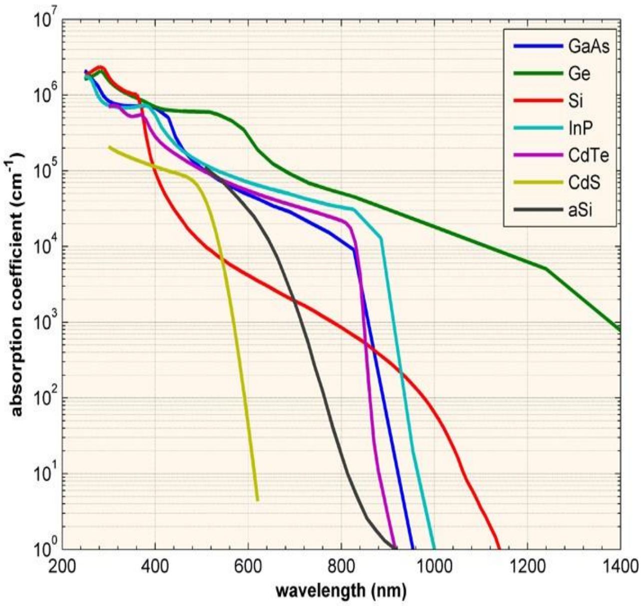
Limitations of the Beer-Lambert law

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

- deviations in absorptivity coefficients at ***high concentrations (>0.01M)*** due to electrostatic interactions between molecules in close proximity
- **scattering of light due to particulates** in the sample
- **fluoresecence or phosphorescence** of the sample
- changes in refractive index at high analyte concentration
- shifts in chemical equilibria as a function of concentration
- non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
- stray light

Physical significance of absorption coefficients

The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. In a material with a low absorption coefficient, light is only poorly absorbed, and if the material is thin enough, it will appear transparent to that wavelength. The absorption coefficient depends on the material and also on the wavelength of light which is being absorbed. Semiconductor materials have a sharp edge in their absorption coefficient, since light which has energy below the band gap does not have sufficient energy to excite an electron into the conduction band from the valence band. Consequently this light is not absorbed. The absorption coefficient for several semiconductor materials is shown below.



The absorption coefficient, α, in a variety of semiconductor materials at 300K as function of the vacuum wavelength of light.

The above graph shows that even for those photons which have energy above the band gap, the absorption coefficient is not constant, but still depends strongly on wavelength. The probability of absorbing a photon depends on the likelihood of having a photon and an electron interact in such a way as to move from one energy band to another. For photons which have energy very close to that of the band gap, the absorption is relatively low since only those electrons directly at the valence band edge can interact with the photon to cause absorption. As the photon energy increases, not just the electrons already having energy close to that of the band gap can interact with the photon. Therefore, a larger number of electrons can interact with the photon and result in the photon being absorbed.

The absorption coefficient, α, is related to the extinction coefficient, k, by the following formula:

$$\alpha = \frac{4\pi k}{\lambda}$$

where λ is the wavlength. If λ is in nm, multiply by 10^7 to get the absorption coefficient in the the units of cm^{-1}.

Laws of photochemistry

Grotthus-Draper Law (or) The Principle of Photochemical Activation:

Grotthus-Draper law states that only the light which is absorbed by a substance can bring about a photochemical change.

However, the absorbed radiation does not necessarily cause a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy may be re- emitted as heat or light or it remains unused.

Stark-Einstein Law of Photochemical Equivalence (or) Principle of Quantum Activation:

It states that in a primary photochemical process (first step) each molecule is activated by the absorption of one quantum of radiation (one photon).

When a molecule absorbs a photon, it is not necessary that only one molecule should react. The absorption of one photon by a molecule is only the first step resulting in the formation of an activated molecule. This further may or may not react or may cause the reaction of many molecules through a chain mechanism.

Some important relations:

Photons	≡	quanta
One molecule absorbs photon	≡	one
One mole of a substance (or) Containing 6.023 x 1023 quanta of (Avogadro number)	≡	one mole of quanta 6.023 x 1023 light (or) one

LAMBERT's LAW: When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of the light.

Mathematically, it may be stated as follows

$$- dI/dl \propto I \quad \text{(or)} \quad -dI/dl = kI \quad \text{----------} \ (1)$$

Where I = the intensity if incident light of wavelength

l = the thickness of the

medium k = the

proportionality factor

on integrating equation 1 and putting $I = I_0$ when $l = 0$, we get

$$\ln I_0/I = kl \quad \text{(or)} \quad I = I_0e^{-kl} \quad \text{----------} \ (2)$$

BEER's LAW : The intensity of a beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically.

$$I = I_0e^{-kc} \quad \text{----------} \ (3)$$

On combining both laws, we get $\log I_0/I = cl$ ---------- (4)

The equation 4 is termed as mathematical statement of Beer-Lambert"s law. In the above equation = the molar absorption coefficient

$$A = \log I_0/I \text{ is the absorbance (or) optical density (OD)}$$

Limitations of Beer-Lambert's law : The law is not valid i) when non-monochromatic radiation is used, ii) if temperature changes during measurements, iii) the law is applicable only to dilute solutions.

Quantum Yield (or) Quantum Efficiency (ϕ):

To express the relationship between the number of molecules reacting with the number of photons absorbed, the concept of quantum yield or quantum efficiency 'ϕ' is introduced.

Quantum yield is defined as "the number of molecules of the substance undergoing photochemical change per quantum of radiation absorbed. Thus,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

In certain photochemical reaction, λ = wavelength of light in Å; q = amount of radiation absorbed in certain interval of t s. & n = number of moles of substance reacted in the same time interval (t), then

Number of einsteins absorbed = $q/(Nhc/\lambda) = q\lambda/Nhc$

Quantum yield $\phi = n/(q\lambda/Nhc) = nNhc/q\lambda$

In CGS units, $\phi = n/q \times [1.196 \times 10^{16}/\lambda \text{ (in Å)}]$

High (or) Low Quantum Yield:

The quantum efficiency varies from zero to 10^6. If a reaction obeys the Einstein law, one molecule is decomposed per photon, the quantum yield = 1.

High Quantum Yield: When two or more molecules are decomposed per photon, the quantum yield > 1 and the reaction has a high quantum yield.

Low Quantum Yield: When the number of molecules decomposed is less than one per photon, the quantum yield < 1 and the reaction has a low quantum yield.

Conditions for high and low quantum yield: The reacting molecules should fulfil the following conditions:

1. All the reactant molecules should be initially in the same energy state and hence equally reactive.
2. The reactivity of the molecules should be temperature independent.
3. The molecules in the activated state should be largely unstable and decompose to form the products.

***Causes (or) Reasons for low quantum yield*:**

1. Excited molecules may get deactivated before they form products.
2. Excited molecules may lose their energy by collisions with non-excited molecules.
3. Molecules may not receive sufficient energy to anable them to react.
4. The primary photochemical reaction may be reversed.
5. Recombination of dissociated fragments will give low quantum yield.

Example: Dimerization of anthracene to dianthracene

$$2C_{14}H_{10} + h\gamma \rightarrow C_{28}H_{20}$$

The quantum yield = 2, but actually it is found to be = 0.5 ; the reason is the above reaction is reversible.

$$2C_{14}H_{10} \rightarrow C_{28}H_{20}$$

Measurement of Absorbed Intensity: A photochemical reaction takes place by the absorption of photons of light by the reacting molecules. Therefore, it is essential to determine the intensity of light absorbed by the reacting molecules.

Radiation emitted from a source of light, L (sun light, tungsten filament, and mercury vapour lamp) is passed through the lens, which produces parallel beams. The parallel beams are then passed through a monochromator, B, which yields a beam of the desired wavelength only. This monochromatic light is allowed to enter into the reaction cell, C, immersed in a thermostat, containing the reaction mixture. The part of the light that is not absorbed fall on a detector, X, which measures the intensity of radiation.

The most frequently used detector is the chemical actinometer. A chemical actinometer is a device used to measure the amount of radiation absorbed by the system in a photochemical reaction. Using chemical actinometer, the rate of a chemical reaction can be measured easily.

Uranyl oxalate actinometer is a commonly used chemical actinometer. It consists of 0.05 M oxalic acid and 0.01 M uranyl sulphate in water. When it is exposed to radiation, oxalic acid undergoes decomposition to give CO_2, CO and H_2O.

The residual concentration of oxalic acid can be found out by titrating with standard KMnO4. The amount of oxalic acid consumed is a measure of the intensity of radiation.

Calculation of the amount of radiation absorbed:

The empty cell (or) the cell filled with solvent is exposed to radiation and reading is noted = Total incident energy

The cell is filled with the reactants and again The reading is noted = Residual energy

Total energy absorbed by the reacting mixture transmitted = Total incident energy – Residual energy

Classification of photochemical reaction based on quantum yield: Based on quantum yield, the various photochemical reactions can be divided into three categories.

1. The reaction in which the quantum yield is a small integer like 1, 2.
   Examples: a) Dissociation of HI & HBr; b) Combination of SO_2 + Cl_2 and c) Ozonisation of O_2.
2. The reaction in which the quantum yield is less than 1.
   Eaxmples: a) Dissociation of NH_3, CH_3COCH_3& NO_2; b) Transformation of maleic acid into fumaric acid.
3. The reaction in which the quantum yield is extremely high.
   Examples: a) Combination of CO + Cl_2; b) Combination of H_2 + Cl_2.

Processes of photochemical reactions: The overall photochemical reaction consists of

i) *Primary reaction* and ii) *Secondary reaction*.

- In the primary reaction, the quantum of light is absorbed by a molecule „A‟ resulting in the formation of an excited molecule „A*‟.$A + h\upsilon \rightarrow A^*$
- In the secondary reaction, the excited molecules react further to give the product of higher quantum yield. $A^* \rightarrow B$

Photochemical Decomposition of HI: It takes place in the radiation of wave length between 2070 Ǻ - 2820 Ǻ. The quantum yield of the reaction is foun to be closer to 2.0.

ENERGY TRANSFER IN PHOTOCHEMICAL REACTIONS:

Photosensitizations and Quenching: In some photochemical reactions, the reactant molecules do not absorb radiation and no chemical reaction occurs. However, if a suitable foreign substance (called sensitizer), which absorbs radiation, is added to the reactant, the reaction takes place. The sensitizer gets excited during absorption of radiation and transfers its energy to the reactants and initiates the reaction.

1. ***Photosensitization***: The foreign substance absorbs the radiation and transfers the absorbed energy to the reactants is called a photosensitizer. This process is called photosensitized reaction (or) photosensitization. Examples,

   i) Atomic photosensitizers : mercury, cadmium, zinc and
   ii) Molecular photosensitizers: benzophenone, sulphur dioxide.

2. ***Quenching***: When the excited foreign substance collides with another substance it gets converted into some other product due to the transfer of its energy to the colliding substance. This process is known as quenching.

Mechanism of Photosensitization and Quenching can be explained by considering a general donor (D) and acceptor (A) system. In a donor-acceptor system, the donor D (sensitizer) absorbs the incident photon and gets excited from ground state (S_0) to singlet state (S_1). Then the donor attains the triplet excited state (T_1 or ^3D). The triplet state of the donor is higher than the triplet state of the acceptor (A). This triplet excited state of the donor collides with the acceptor produces the triplet excited state of the acceptor (^3A) and returns to the ground state (S_0). If the triplet excited state of the acceptor (^3A) gives the desired products, the mechanism is called photosensitization. If the products are resulted directly from the excited state of the donor (^3D), then A is called quencher and the process is called quenching.

The sequence of photosensitization and quenching may be represented as follows:

$$^3D + A \rightarrow D + {}^3A$$

$$^3A \rightarrow \text{Products (photosensitization)}$$

$$^3D \rightarrow \text{Products (quenching)}$$

It is necessary that the energy of the triplet excited state of the donor (sensitizer) must be higher than the triplet excited state of the acceptor (reactant). Thus the energy available is enough to excite the reactant molecule to its excited state. The dotted line indicates the transfer of energy from the sensitizer to reactant.

<u>Examples for photosensitized reactions</u>:

1. ***Dissociation of hydrogen molecule***: UV light does not dissociate H_2 molecule, because the molecule is unable to absorb the radiation. But, if a small amount of mercury vapour is added, dissociation of hydrogen takes place. Here Hg acts as photosensitizer.
2. ***Photosynthesis in plants***: During photosynthesis of carbohydrates in plants from CO_2 and H_2O, chlorophyll of plants acts as a photosensitizer. The energy of the light absorbed by the chlorophyll (due to the presence of conjugation in chlorophyll) is transformed to CO_2 and H_2O molecules, which then react to form glucose.

   In the presence of light and chlorophyll ΔG^o becomes negative; thereby the reaction proceeds and produces glucose. But in the absence of chlorophyll, the ΔG^o for this reaction is +2875 kJ. Since ΔG^o is positive, the above reaction is not possible.

The **photostationary state** of a reversible photochemical reaction is the equilibrium chemical composition under a specific kind of electromagneticirradiation (usually a single wavelength of visible or UV radiation). It is a property of particular importance in photochromic compounds, often used as a measure of their practical efficiency and usually quoted as a ratio or percentage. The position of the photostationary state is primarily a function of the irradiation parameters, the absorbance spectra of the chemical species, and the quantum yields of the reactions.

Absorption of radiation by reactants of a reaction at equilibrium increases the rate of forward reaction without directly affecting the rate of the reverse reaction.

The rate of a photochemical reaction is proportional to the absorption cross section of the reactant with respect to the excitation source (σ), the quantum yield of reaction (Φ), and the intensity of the irradiation. In a reversible photochemical reaction between compounds A and B, there will therefore be a "forwards" reaction of A→B at a rate proportional to $\sigma_a \times \Phi_{A\rightarrow B}$ and a "backwards" reaction of B→A at a rate proportional to $\sigma_b \times \Phi_{B\rightarrow A}$. The ratio of the rates of the forward and backwards reactions determines where the equilibrium lies, and thus the photostationary state is found at:

$$\sigma_a \times \Phi_{A\rightarrow B} / \sigma_b \times \Phi_{B\rightarrow A}$$

If (as is always the case to some extent) the compounds A and B have different absorption spectra, then there may exist wavelengths of light where σ_a is high and σ_b is low. Irradiation at these wavelengths will provide photostationary states that contain mostly B. Likewise, wavelengths that give photostationary states of predominantly A may exist. This is particularly likely in compounds such as some photochromics, where A and B have entirely different absorption bands. Compounds that may be readily switched in this way find utility in devices such as molecular switches and optical data storage.

Practical considerations

- Quantum yields of reaction (and to a lesser extent, absorption cross sections) are usually temperature and environment-dependent to some extent, and the photostationary state may therefore depend slightly on temperature and solvent as well as on the excitation.
- If thermodynamic interconversion of A and B can take place on a similar timescale to the photochemical reaction, it can complicate experimental measurements. This phenomenon can be important, for example in photochromatic eyeglasses.

Chemiluminescence (also **chemoluminescence**) is the emission of light (luminescence), as the result of a chemical reaction. There may also be limited emission of heat. Given reactants **A** and **B**, with an excited intermediate ,

$$[\mathbf{A}] + [\mathbf{B}] \rightarrow [\Diamond] \rightarrow [\mathit{Products}] + \text{light}$$

For example, if [A] is luminol and [B] is hydrogen peroxide in the presence of a suitable catalyst where:

- 3-APA is 3-aminophthalate
- 3-APA is the vibronic excited state fluorescing as it decays to a lower energy level.

The decay of this excited state to a lower energy level causes light emission. In theory, one photon of light should be given off for each molecule of reactant. This is equivalent to Avogadro's number of photons per mole of reactant. In actual practice, non-enzymatic reactions seldom exceed 1% Q_C, quantum efficiency.

In a chemical reaction, reactants collide to form a transition state, the enthalpic maximum in a reaction coordinate diagram, which proceeds to the product. Normally, reactants form products of lesser chemical energy. The difference in energy between reactants and products, represented as, is turned into heat, physically realized as excitations in the vibrational state of the normal modes of the product. Since vibrational energy is generally much greater than the thermal agitation, it rapidly disperses in the solvent through molecular rotation. This is how exothermic reactions make their solutions hotter. In a chemiluminescent reaction, the direct product of the reaction is an excited electronic state. This state then decays into an electronic ground state and emits light through either an allowed transition (analogous to fluorescence) or a forbidden transition (analogous to phosphorescence), depending partly on the spin state of the electronic excited state formed.

Chemiluminescence differs from fluorescence or phosphorescence in that the electronic excited state is the product of a chemical reaction rather than of the absorption of a photon. It is the antithesis of a photochemical reaction, in which light is used to drive an endothermic chemical reaction. Here, light is *generated* from a chemically exothermic reaction. The chemiluminescence might be also induced by an electrochemical stimulus, in this case is called electrochemiluminescence.

A standard example of chemiluminescence in the laboratory setting is the luminol test. Here, blood is indicated by luminescence upon contact with iron in hemoglobin. When chemiluminescence takes place in living organisms, the phenomenon is called bioluminescence. A light stick emits light by chemiluminescence.

Infrared chemiluminescence

In chemical kinetics, *infrared chemiluminiscence* (IRCL) refers to the emission of infrared photons from vibrationally excited product molecules immediately after their format ion. The intensities of infrared emission lines from vibrationally excited molecules are used to measure the populations of vibrational states of product molecules.

The observation of IRCL was developed as a kinetic technique by John Polanyi, who used it to study the attractive or repulsive nature of the potential energy surface for gas-phase reactions. In general the IRCL is much more intense for reactions with an attractive surface, indicating that this type of surface leads to energy deposition in vibrational excitation. In contrast reactions with a repulsive potential energy surface lead to little IRCL, indicating that the energy is primarily deposited as translational energy.

Enhanced chemiluminescence

Enhanced chemiluminescence is a common technique for a variety of detection assays in biology. A horseradish peroxidase enzyme (HRP) is tethered to an antibody that specifically recognizes the molecule of interest. This enzyme complex then catalyzes the conversion of the enhanced chemiluminescent substrate into a sensitized reagent in the vicinity of the molecule of interest, which on further oxidation by hydrogen peroxide, produces a triplet (excited) carbonyl, which emits light when it decays to the singlet carbonyl. Enhanced chemiluminescence allows detection of minute quantities of a biomolecule. Proteins can be detected down to femtomole quantities well below the detection limit for most assay systems.

Applications

- Gas analysis: for determining small amounts of impurities or poisons in air. Other compounds can also be determined by this method (ozone, N-oxides, S-compounds). A typical example is NO determination with detection limits down to 1 ppb. Highly specialised chemiluminescence detectors have been used recently to determine concentrations as well as fluxes of NOx with detection limits as low as 5 ppt
- Analysis of inorganic species in liquid phase
- Analysis of organic species: useful with enzymes, where the substrate is not directly involved in the chemiluminescence reaction, but the product is
- Detection and assay of biomolecules in systems such as ELISA and Western blots
- DNA sequencing using pyrosequencing
- Lighting objects. Chemiluminescence kites, emergency lighting, glow sticks(party decorations).
- Combustion analysis: Certain radical species (such as CH* and OH*) give off radiation at specific wavelengths. The heat release rate is calculated by measuring the amount of light radiated from a flame at those wavelengths.

Biological applications

Chemiluminescence has been applied by forensic scientists to solve crimes. In this case, they use luminol and hydrogen peroxide. The iron from the blood acts as a catalyst and reacts with the luminol and hydrogen peroxide to produce blue light for about 30 seconds. Because only a small amount of iron is required for chemiluminescence, trace amounts of blood are sufficient.

In biomedical research, the protein that gives fireflies their glow and its co-factor, luciferin, are used to produce red light through the consumption of ATP. This reaction is used in many applications, including the effectiveness of cancer drugs that choke off a tumor's blood supply. This form of bioluminescence imaging allows scientists to test drugs in the pre-clinical stages cheaply. Another protein, aequorin, found in certain jellyfish, produces blue light in the presence of calcium. It can be used in molecular biology to assess calcium levels in cells. What these biological reactions have in common is their use of adenosine triphosphate (ATP) as an energy source. Though the structure of the molecules that produce luminescence is different for each species, they are given the generic name of luciferin. Firefly luciferin can be oxidized to produce an excited complex. Once it falls back down to a ground state a photon is released. It is very similar to the reaction with luminol.

Many organisms have evolved to produce light in a range of colors. At the molecular level, the difference in color arises from the degree of conjugation of the molecule, when an electron drops down from the excited state to the ground state. Deep sea organisms have evolved to produce light to lure and catch prey, as camouflage, or to attract others. Some bacteria even use bioluminescence to communicate. The common colors for the light emitted by these animals are blue and green because they have shorter wavelength than red and can transmit more easily in water.

UNIT V

POSSIBLE QUESTIONS

PART- B

(Each carries two marks)

1. What is meant by electromagnetic radiation?
2. State Lambert-Beer’s law.
3. What is absorption coefficient?
4. Define quenching.
5. What is meant by photochemical reactions?
6. Give any two Lambert-Beer’s law limitations.
7. Write any three characteristics of electromagnetic radiation.

PART C

(Each carries Six marks)

1. Explain the Lambert-Beer’s law and its limitations.
2. Write a note on laws of photochemistry.
3. Describe the photosensitized reactions with suitable reactions.
4. Explain the following terms

    (a) photostationary states (b) chemiluminescence

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COIMBATORE-641 021
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II B.Sc. Chemistry

PHYSICAL CHEMISTRY

UNIT V
Multiple choice questions

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
Unit V						
1	Photochemistry deals with the study of chemical reactions which are caused by absorption of	a)electrons	b)photons	c)protons	d)neutrons	b)photons
2	In ordinary thermal reactions, the activation energy results from the random	a)intermolecular collisions	b)intramolecular collisions	c)collisions	d)vibrations of atoms	a)intermolecular collisions
3	Formation of vitamin D is an important example of -------------- reactions	a)chemical reactions	b)nuclear reactions	c)photochemical reactions	d)dark reactions	c)photochemical reactions
4	-------------------deals with photochemistry of biological reactions and has helped a great deal in partly understamding the mechanism of photosynthesis	a)photobiology	b)biology	c)chemistry	d)photophysics	a)photobiology
5	-----------synthesised through photochemistry	a)caprolactum	b)cholestral	c)proteins	d)peptides	a)caprolactum
6	The development of -----------------technology is a recent marvellous application of photophysics	a)laser	b)photo	c)nano	d)radiation	a)laser
7	Grotthus -Draper law is also called the principle of ----------------- activation	a)photochemical	b)physical	c)chemical	d)photphysical	a)photochemical
8	The light absorbed may be re-emitted almost instantaneously is known as----------	a)phosphorescence	b)fluorescence	c)metastable state	d)excited state	b)fluorescence
9	The light absorbed is given out slowly and even long after the removal of the source of light is known as	a)phosphorescence	b)fluorescence	c)metastable state	d)excited state	a)phosphorescence
10	The phenomena of fluorescence and phosphorescence are best explained by------------diagram	a)phase	b)fluorescence	c)jablonski	d)phosphorescence	c)jablonski
11	In jablonski diagram most molecules have an even number of electrons and thus in the -------- state all the electrons are spin paired	a)excited	b)metastable	c)activated	d)ground	d)ground
12	S is known as-------------	a)spin	b)spin multiplicity	c)multiplicity	d)singlet	b)spin multiplicity
13	The transition from the higher excited state to the first excited state is known as	a)radiative transition	b)non-radiative transition	c)d-d	d)charge transfer	b)non-radiative transition
14	The transition involve the return of the activated molecule from the singlet excited state and triplet excited state to the ground state are known as	a)radiative transition	b)non-radiative transition	c)d-d	d)charge transfer	a)radiative transition
15	The transition from the triplet excited state to the ground state is slow and it is a	a)d-d	b)charge transfer	c)allowed	d)forbidden	d)forbidden
16	The life time of ---------------are much longer	a)fluorescence	b)phosphorescence	c)fluorescence and phosphorecence	d)excited state	b)phosphorescence

17	The absorption of light in the visible and near ultraviolet regions by a solution is governed by a photophysical law, known as-----------	a)lambert law	b)charles law	c)Boyles law	d)Lambert-Beer law	d)Lambert-Beer law
18	The Beer-Lambert law is not obeyed if the radiation is not --------------	a)monochromatic	b)dichromatic	c)polychromatic	d)same frequency	a)monochromatic
19	The Beer-Lambert law governs the absorption behaviour of -------------solutions only	a)concentrated	b)dilute	c)two-phase	d)one-phase	b)dilute
20	The increase in temperature has a --------------------effect on ions in solution	a)hypsochromic	b)hypochromic	c)bathochromic	d)chromic	c)bathochromic
21	Stark-Einstein law was enunciated by Stark in ---------	a)1907	b)1906	c)1908	d)1910	c)1908
22	One molecule is activated by the absorption of one quantum of radiation in the primary step of a photchemical reaction-----------------	a)Stark-Einstein law	b)Grotthus-Draper law	c)Boyles law	d)charles law	a)Stark-Einstein law
23	In the determination of number of moles reacting--------------are used as light source	a)tungsten lamp	b)hydrogen lamp	c)deuterium lamp	d)hydrogen and deuterium lamp	a)tungsten lamp
24	The energy of radiation is measured by	a)actinometer	b)calorimeter	c)photometer	d)potentiometer	a)actinometer
25	Excited molecules may be deactivated before they form products, because of	a)high quantum yield	b)low quantun yield	c)high and low quantum yield	d)average quantum yield	b)low quantun yield
26	The primary photochemical process may be reversed in	a)high quantum yield	b)low quantun yield	c)high and low quantum yield	d)average quantum yield	b)low quantun yield
27	The dissociated fragements may recombine to form the original molecule	a)high quantum yield	b)low quantun yield	c)high and low quantum yield	d)average quantum yield	b)low quantun yield
28	Collisions of excited molecules with non-excited molecules may cause the former to lose their energy	a)high quantum yield	b)low quantun yield	c)high and low quantum yield	d)average quantum yield	b)low quantun yield
29	The-----------------process which absorbes llight may be dissociated yielding atoms	a)primary process	b)secondary process	c)tertiary process	d)photobiological	a)primary process
30	--------------------process in which the excited atoms, molecules or free radicals produced in the primary stage react further giving rise to higher quantum yields	a)primary process	b)secondary process	c)tertiary process	d)photobiological	b)secondary process
31	Dimerization of anthracene in benzene solution in the absence of oxygen is an example for	a)chemical reactions	b)photochemical reactions	c)photophysical reactions	d)dark reactions	b)photochemical reactions
32	Isomerization of maleic acid to fumaric acid can be achieved by	a)chemical reactions	b)photochemical reactions	c)photophysical reactions	d)dark reactions	b)photochemical reactions
33	Combination of hydrogen and halogens to form hydrogen halides can be achieved by	a)chemical reactions	b)photochemical reactions	c)photophysical reactions	d)dark reactions	b)photochemical reactions
34	Deceomposition of hydrogen halides can be achieved by	a)chemical reactions	b)photochemical reactions	c)photophysical reactions	d)dark reactions	b)photochemical reactions
35	Example for atomic sensitizer	a)mercury	b)hydrogen	c)deuterium	d)nitrogen	a)mercury
36	Example for molecular sensitizer	a)oxygen	b)hydrogen	c)acetophenone	d)benzophenone	d)benzophenone
37	Example for molecular sensitizer	a)hydrogen	b)sulphur dioxide	c)acetophenone	d)oxygen	b)sulphur dioxide
38	D→Products ia an example for	a)photosensitization	b)sensitization	c)quenching	d)photosenstization and sensitization	c)quenching

39	A→Products ia an example for	a)photosensitization	b)sensitization	c)quenching	d)photosenstization and sensitization	a)photosensitization
40	Photosensitization was discovered by	a)Franck	b)cario	c)Franck and cario	d)Boyles	c)Franck and cario
41	Photosensitization was discovered in	a)1922	b01950	c)1960	d)1925	a)1922
42	The most important photochemical reaction and the most outstanding example of photosensitization is the	a)photosynthesis of carbohydrates in plants	b)photolysis	c)chemicluminescence	d)bioluminescence	a)photosynthesis of carbohydrates in plants
43	In the absence of light, the ΔG for photosynthesis of carbohydrates is-------kJ	a)+200	b)+4500	c)+2878	d)+2780	c)+2878
44	In the presence of light absorbed by chlorophyll, ΔG becomes--------------	a)positive	b)negative	c)fraction	d)positive and negative	b)negative
45	photosynthesis requires -----------photons per molecule of carbondioxide	a)9	b)10	c)8	d)11	c)8
46	-------------------------according to M.Calvin, proceeds through two mian stages-light and dark reactions	a)photolysis	b)photosynthesis	c)chemiluminescence	d)bioluminescence	b)photosynthesis
47	Fluorescence may be quenched when the excited state specieds undergoes--------------with a normal molecule before it has the chance to fluoresce	a)collision	b)photophysical process	c)photolysis	d)photochemical process	a)collision
48	Internal Quenching occur then the molecule changes from the singlet excited state to the ------------excited state	a)doublet	b)triplet	c)quatret	d)doublet and triplet	b)triplet
49	External quenching result from the presence of an externally added species which takes up energy from the --------------state molecule	a)ground	b)metastable	c)ground and metastable	d)excited	d)excited
50	$A^*\rightarrow A$ is an example for ------------------quenching	a)internal	b)external	c)external and internal	d)triplet	a)internal
51	$A^*+Q\rightarrow A+Q$	a)internal	b)external	c)external and internal	d)triplet	b)external
52	K sv is called --------------constant	a)stern-volmer	b)stern	c)volmer	d)singlet	a)stern-volmer
53	---------------------------is defined as the production of light by a chemical reaction and is thus the reverse of a photochemical reaction	a)photolysis	b)photosynthesis	c)chemiluminescence	d)bioluminescence	c)chemiluminescence
54	The glow of phosphorus and its oxide is an example for	a)photolysis	b)photosynthesis	c)chemiluminescence	d)bioluminescence	c)chemiluminescence
55	Oxidation-reduction reactions of hydrazine is an example for	a)photolysis	b)photosynthesis	c)chemiluminescence	d)bioluminescence	c)chemiluminescence
56	Cold light emission by glow worms is an example for	a)photolysis	b)photosynthesis	c)chemiluminescence	d)bioluminescence	d)bioluminescence
57	Interaction between the aromatic anions and cations generated during electrolysis of large -----------------------hydrocarbons	a)polycyclic	b)monocyclic	c)dicyclic	c)tricyclic	a)polycyclic
58	The luminescence observed at night in the ocean is probably due to the decay of the luminous----------------	a)star fish	b)jelly-fish	c)fish	d)whale	b)jelly-fish

59	The phenomena of fluorescence and phosphorescence fid useful applications in the development of ----------	a)X-ray	b)gamma ray	c)beta ray	d)gamma and beta ray	a)X-ray
60	The light radiations of the visible and ultraviolet regions lie between--------	a)800 and 200 nm	b)600 and 400 nm	c)800 and 600 nm	d)1000 and 800 nm	a)800 and 200 nm

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to beUniversity Established Under Section 3 of UGC Act 1956)
UG DEGREE EXAMINATION, JANUARY 2018
(For the candidates admitted from 2016 onwards)

DEPARTMENT OF CHEMISTRY
EVEN SEMESTER

II B.Sc., CHEMISTRY
INTERNAL EXAM-I
PHYSICAL CHEMISTRY-IV (Electrochemistry)

ANSWER KEY
PART- A

1.b)concentrations

2.a)(specific/observed)conductance

3.a)increases

4.b)HCl

5.b)high

6.d)is the site of reduction

7.a)ohm cm^{-1} mol^{-1}

8.b)specific conductance

9.a)molar conductance

10.d)increases with dilution

11.d)equivalent weight of the anion

12.c)electrochemical equivalent

13.c) a liquid

14.c)hydrogen

15.d)ammonia solution

16.c)hydrogen

17.a)transport number

18.b)ionic mobility

19.c)principle

20.a)smaller

PART B

21. According to this law, the chemical deposition due to flow of current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it. *i.e.* mass of chemical deposition, $m \propto Quantity\ of\ electricity,\ Q \Rightarrow m = Z.Q$ Where, Z is a constant of proportionality and is known as electro-chemical equivalent of the substance.

22.Electrolyte which completely ionizes atmost at all dilutions is known as strong electrolytes

Eg., HCl, NaOH

23. An empirical rule suggested by P. Walden (1863–1957) concerning ions in solutions, stating that the product of the molar conductivity, Λ_m, and the viscosity, η, is approximately constant for the same ions in different solvents. Some justification for Walden's rule is provided by the proportional relationship between Λ_m and the diffusion coefficient, *D*; as *D* is inversely proportional to the viscosity, Λ_m is inversely proportional to η, which is in accordance with Walden's rule. However, different solvents hydrate the same ions differently, so that both the radius and the viscosity change when the solvent is changed. It is this fact that limits the validity of the rule.

PART C

24.a) (i) **Debye –Falkenhagen effect**

Debye and Falkenhagen examined the conductance behavior of a solution of a strong electrolyte by applying alternating currents of different frequencies. They predicted that if the frequency of alternating current is high so that the time of oscillation is small in comparison with the relaxation time of the ionic atmosphere, the asymmetry effect will be virtually absent. In other words, the ionic atmosphere around the central ion will remain symmetric. The retarding effect due to asymmetry may, therefore be entirely absent and the conductance may be higher. The conductance of a solution, therefore should vary with the frequency of the alternating current used. The higher the frequency, the higher the conductance, evidently. This effect also known as dispersion of conductance, has been verified experimentally.

(ii) **Wien effect**

Speed of an ion in an electric field varies with the applied potential gradient. Thus, under a potential gradient of about 20,000 volt per cm, an ion may have a speed of about 100 cm per sec. the ion, therefore should pass several times through the thickness of the ionic atmosphere during the time of relazation. The moving ion, therefore, will be moving so fast that there will be no time for the ionic atmosphere to be built up. The asymmetry and electrophoretic effects, under these circumstances, may be negligibly small or even absent. Thus, the conductance of a strong electrolyte in aqueous solution increases to a certain limiting value with increase in potential gradient applied.

b) Kohlrausch law of independent migration of ions states that the dissociation of an electrolyte is complete in the infinite dilution and thus the the ions that constitute the electrolyte contributes definitely. Thus the limiting equivalent conductivity of an electrolyte is the algebraic sum of the limiting equivalent conductivity of it's constituent ions. The molar equivalent conductivity can also be calculated using the Kohlrausch law. Here the Λ^o or Λ^o_{eq} resembles equivalent molar conductivity and the Λ^o_m resembles molar conductivity.

Each ionic species makes a contribution to the conductivity of the solution that depends only on the nature of that particular ion, and is independent of the other ions present.

Kohlrausch's law can be expressed as

$$\Lambda_0 = \Sigma\, \lambda_0+ + \Sigma\, \lambda_0^-$$

Just as a compact table of thermodynamic data enables us to predict the chemical properties of a very large number of compounds, this compilation of equivalent conductivities of twenty different species yields reliable estimates of the of Λ_0 values for five times that number of salts.

We can now estimate weak electrolyte limiting conductivities

One useful application of Kohlrausch's law is to estimate the limiting equivalent conductivities of weak electrolytes which, as we observed above, cannot be found by extrapolation. Thus for acetic acid CH3COOH ("HAc"), we combine the λ0 values for H3O+ and CH3COO– given in the above table:

$$\Lambda_0\text{HAc} = \lambda_0\text{H+} + \lambda_0\text{Ac–}$$

Movement of a migrating ion through the solution is brought about by a force exerted by the applied electric field. This force is proportional to the field strength and to the ionic charge.

Calculations of the frictional drag are based on the premise that the ions are spherical (not always true) and the medium is continuous (never true) as opposed to being composed of discrete molecules. Nevertheless, the results generally seem to be realistic enough to be useful.

25.a)

Transference numbers are often referred to as transport numbers; either term is acceptable in the context of electrochemistry.

The fraction of charge carried by a given kind of ion is known as the transference number t±. For a solution of a simple binary salt,

$$t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \qquad t_- = \frac{\lambda_-}{\lambda_- + \lambda_+}$$

By definition, t+ + t– = 1.

To help you visualize the effects of non-identical transference numbers, consider a solution of M+ X– in which t+ = 0.75 and t– = 0.25. Let the cell be divided into three [imaginary] sections as we examine the distribution of cations and anions at three different stages of current flow. Transference numbers can be determined experimentally by observing the movement of the boundary between electrolyte solutions having an ion in common, such as LiCl and KCl

b) **Molar conductivity** is defined as the conductivity of an electrolyte solution divided by the molar concentration of the electrolyte, and so measures the efficiency with which a given electrolyte conducts electricity in solution. It is the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution. Its units are siemens per meter per molarity, or siemens meter-squared per mole. The usual symbol is a capital lambda, Λ, or Λ_m. It can also be defined as follows: Molar conductivity of a solution at a given concentration is the conductance of the volume (V) of the solution containing one mole of electrolyte kept between two electrodes with area of cross section (A) and at a distance of unit length.

Variation of molar conductivity with dilution

There are two types of electrolytes: strong and weak. Strong electrolytes will undergo complete ionization, and therefore they have higher conductivity than weak electrolytes which undergo only partial ionization. For strong electrolytes, such as salts, strong acids and strong bases, the molar conductivity depends only *weakly* on concentration. On dilution there is a regular increase in the molar conductivity of strong electrolyte, due to the decrease in solute-solute interaction. Based on experimental data Friedrich Kohlrausch (around the year 1900) proposed the non-linear law for strong electrolytes:

$$\wedge_m=\wedge^0_m-\sqrt{C}$$

where

- $\wedge^0_m$ is the molar conductivity at infinite dilution (or *limiting molar conductivity*), which can be determined by extrapolation of $\wedge_m$ as a function of $\sqrt{C}$
- *K* is the Kohlrausch coefficient, which depends mainly on the stoichiometry of the specific salt in solution.

This law is valid for low electrolyte concentrations only; it fits into the Debye-Hückel-Onsager equation :

For weak electrolytes (i.e. incompletely dissociated electrolytes), however, the molar conductivity *strongly* depends on concentration: The more dilute a solution, the greater its *molar* conductivity, due to increased ionic dissociation. For example, acetic acid has a higher molar conductivity in dilute aqueous acetic acid than in concentrated acetic acid.

26.a)(i) Conductance is an expression of the ease with which electric current flows through a substance. In equations, conductance is symbolized by the uppercase letter *G*. The standard unit of conductance is the *siemens* (abbreviated S), formerly known as the *mho*.

(ii) It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

It is expressed as Λ_e and is related to specific conductance as

$$\Lambda_e = \frac{\kappa \times 1000}{C} = \kappa \times \frac{1000}{M}$$ (M is Molarity of the solution)

where C is the concentration in gram equivalent per litre (or Normality). This term has earlier been quite frequently used. Now it is replaced by molar conductance. The units of equivalent conductance are $Ohm^{-1}\ cm^{2}(gm\ equiv)^{-1}$.

(iii) Molar conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.

It is denoted by Λ (lambda). Molar conductance is related to specific conductance (κ) as,

$$\Lambda = \frac{\kappa}{M}$$

where, M is the molar concentration.

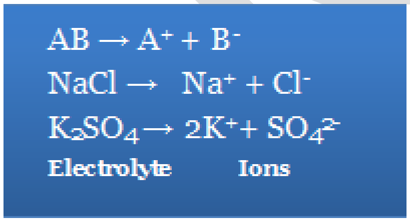
If M is in the units of molarity i.e., moles per litre $(mol\ L^{-1})$, the Λ may be expressed as,

$$\Lambda = \frac{\kappa \times 1000}{M}$$

For the solution containing 1 gm mole of electrolyte placed between two parallel electrodes of 1 sq. cm area of cross-section and one cm apart,

(iv) The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. It is generally defined as the reciprocal of resistance of that material. SI unit of conductance is S (Siemens). Specific conductivity (better known as conductivity) is the measure of the ability of that material to conduct electricity. It is represented by the symbol “Κ”.

b) An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed cations and negatively charged as anions.



$AB \rightarrow A^+ + B^-$

$NaCl \rightarrow Na^+ + Cl^-$

$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$

Electrolyte **Ions**

In its modern form, the theory assumes that solid electrolytes are composed of ions which are held together by electrostatic forces of attraction. When an electrolyte is dissolved in a solvent, these forces are weakened and the electrolyte undergoes dissociation into ions. The ions are solvated.

The process of splitting of the molecules into ions of an electrolyte is called ionization. The fraction of the total number of molecules present in solution as ions is known as degree of ionization or degree of dissociation. It is denoted by

$$\alpha = \frac{Number\ of\ molecuiles\ dissociated\ into\ ions}{Total\ number\ of\ molecules}$$

It has been observed that all electrolytes do not ionize to the same extent. Some are almost completely ionized while others are feebly ionized. The degree of ionization depends on a number of factors.

Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionized the ionized and non-ionised molecules, i.e., $\mathbf{AB \rightleftharpoons A^+ + B^-}$

Applying the law of mass action to above equilibrium $\mathbf{[A^+][B^-]\ /[AB]\ =K}$
K is known as ionization constant. The electrolytes having high value of K are termed strong electrolytes and those having low value of K as weak electrolytes.

When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged. i.e The ions are discharged always in equivalent amounts, no matter what their relative speeds are.

The electrolytic solutions is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.

The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^- ions and OH^- ions respectively.

The ions act like molecules towards depressing the freezing point, elevating the boiling point, lowering the vapour pressure and establishing the osmotic pressure.

The conductively of the electrolytic solution depends on the nature and number of ions as the current is carried through solution by the movement of ions.