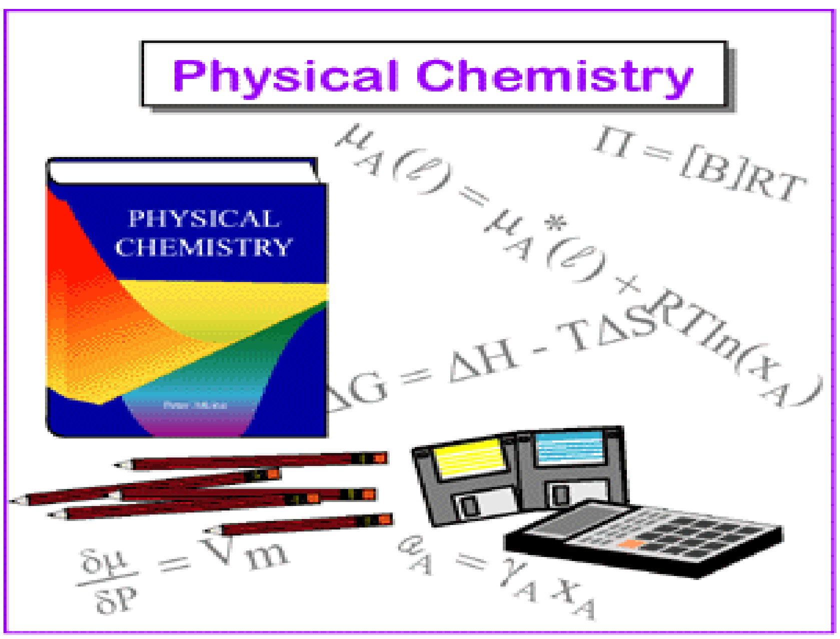
SHRIMATI INDIRA GANDHI COLLEGE

(Nationally Re-accredited at "A" Grade by NAAC)

Tiruchirappalli – 620 002

DEPARTMENT OF CHEMISTRY



PHYSICAL CHEMISTRY-II

STUDY MATERIAL FOR SLOW LEARNERS

PHYSICAL CHEMISTRY-II

Subject Code: RCCSCH9

Core Course XIII: PHYSICAL CHEMISTRY II

UNIT 1: ELECTRICAL CONDUCTANCE:

Electrical transport and conducatnce in metal and in electrolytic solution.-specific conductance and equivalent conductance. Measurement ofequivalent conductance. using Kohlraush's bridge. Arrhenius theory ofelectrolytic dissociation and its limitation. Weak and strong electrolyteaccording to Arrhenius theory. Ostwald's dilution law - applications andlimitation. variation of equivalent conductance with concentrationmigrationof ion- ionic mobility. Kohlrausch's law and its applications. Theelementary treatment of the Debye – Huckel- Onsager equation for strongelectrolytes. evidence for ionic atmosphere. The conductance at high fields(Wein effect) and high frequencies (Debye - Falkenhagen effect). Transport number & Hittorfs rule. determination by Hittorf's method and movingboundary method application of conductance measurements -determination of strong electrolytes and acids. Determination of Ka of acids.Determination of solubility product of a sparingly soluble salt. common ioneffect. conductometric titrations.

UNIT 2: ELECTROCHEMICAL CELLS

Electrolytic & galvanic cells - reversible and irreversible cells. Conventionalrepresentation of electrochemical cells. Electromotive force of a cell and itsMeasurement- computation of E.M.F- calculation of thermodynamicquantities of cell reactions (□G. □H, □S and K)- application of Gibbs Helmholtzequation. concentration and E.M.F- Nernst equation,Types of reversible electrodes - gas/metal ion - metal/metal ion;metal/insoluble salt/ anion and redox electrodes. electrode reactions -Nernst equation – derivation of cell.

E.M.F and single electrode potentialstandardhydrogen electrode - reference electrodes - standard electrodepotentials - sign convention - electrochemical series and its significance.

concentration cell with and without transport- liquid junction potential.application of EMF of concentration cells. Valency of ion- solubility productand activity co-efficient. Potentiometric titrations. Determination of pHusing hydrogen and quinhydrone electrodes- determination of pKa of acidsby potentiometric method. Corrosion - general and electrochemical theory -passivity - prevention of corrosion.

UNIT 3: PHOTO CHEMISTRY AND GROUP THEORY

Consequences of light absorption - Jablonski diagram- radiative and non -radiative transitions. laws of photo chemistry - Lambert – Beer, Grothus -Draper and Stark - Einstein. quantum efficiency. photo chemical reactions- rate law - kinetics ofH_2-Cl_2, H_2-Br_2 and H_2-I_2 reactions. comparison between thermal andphotochemical reactions. photo sensitization and quenching. Fluorescence,phosphorescence and chemiluminescence. Laser and uses of lasers -population inversion and optical pumping.Group theory: symmetry elements and symmetry operation-group postulatesand types of groups-Abelian and non Abelian- symmetry operation of H_2Omolecule-illustration of group postulates using symmetry operations of H_2Omolecule-construction of multiplication table for the operation of H_2Omolecule-point group-definition –elements (symmetry operations) of thefollowing point groups: Cn (C2, C3)Sn (S1, S2) , C1V (C2V, C3V) and C2R . group theory and optical activity

UNIT 4: SPECTROSCOPY I

Electromagnetic spectrum - The regions of various types of spectra.Microwave spectroscopy: Rotational spectra of diatomic molecules treated asrigid rotator, condition for a molecule to be active in microwave region,rotational constants (B), and selection rules for rotational transition.

Frequency of spectral lines, calculation of inter - nuclear distance indiatomic molecules.

Infrared spectroscopy : Vibrations of diatomic molecules - harmonic andanharmonic oscillators, zero point energy, dissociation energy and forceconstant, condition for molecule to be active in the IR region, selection rulesfor vibrational transition, fundamental bands, overtones and hot bands,diatomic vibrating rotator - P,Q,R branches. Determination of forceconstant.

UV visible spectroscopy : conditions - theory of electronicspectroscopy - types of electronic transitions - Franck - Condon principle –pre dissociation - applications.

UNIT 5: SPECTROSCOPY II

Raman spectroscopy : Rayleigh scattering and Raman scattering. Stokesand antistokes lines in Raman spectra, Raman frequency, quantum theoryof Raman effect, condition for a molecule to be Raman active. comparison ofRaman and IR spectra- structural determination from Raman and IRspectroscopy, rule of mutual exclusion.

NMR spectroscopy : Nuclear spin and conditions for a molecule to give riseto NMR spectrum- theory of NMR spectra, number of NMR signals,equivalent and non - equivalent protons, position of NMR signals, shielding,de-shielding, chemical shift, □□ □□ and□ □ □□ scales. Peak area and number ofprotons. Splitting of NMR signals - spin - spin coupling.

Books for Reference :

1. Maron S.H. and Lando J.B., Fundamentals of Physical Chemistry, Macmillan.

2. Puri B.R., Sharma L.R., and Pathania B.K., Principles of Physical Chemistry, Vishal publishing company.

3. Glasstone S. and Lewis D. Elements of physical Chemistry, macmillan

4. Rajaram and Keeriacose, Thermodynamics for students of chemistry.

5. Khterpal S.C. Pradeeps, Physical Chemistry, Volume I & II, Pradeep publications Jalandhur, (2004).

6. Jain D.V.S and Jainhar S.P., Physical chemistry, Principles and problems, Tata Mc Graw Hill, New Delhi, (1988)

TWO MARKS QUESTION

1.**Define Raman scattering?**

The scattering of radiations with certain discrete frequencies above and below that of the incident beam is called Raman scattering.

2.State stokes lines?

When the scattering of radiation produce lines with lower frequency compared to that of the incident beam then these are called stokes lines.

3. What is meant by Raman spectroscopy?

Raman spectroscopy involves the study of vibrational-rotational energy changes in molecules by means of scattering of light.

4. What is spin-spin coupling?

It is the interaction of the magnetic fields of two or more nuclei, both through their connecting bonds and space. Spin-spin splitting causes the PMR signals to split and thus appear as multiplets,i.e.doublets, triplets etc.

5.Define coupling constant (J).

The distance between the centers of the two adjacent peaks in a multiplet is usually constant and is called the coupling constant.

6. What is meant by induced magnetic field?

The magnetic field that is set up by the motion of electrons in a molecule in response to the application of an external field is termed induced magnetic field

7.Define the term “Chemical shift”.

The chemical shift i.e. δ –value in ppm is the position of an absorption peak relative to that of a reference compound which is usually TMS

(Tetra methyl silane).

8.What is meant by (n+1)rule in spin-spin coupling?

The protons on adjacent carbon atoms with different electronic environments cause spin-spin coupling. The signal that is being split by n equivalent protons appear as multiple with(n+1)peaks. It is called the (n+1) rule.

9.State Hittorfs rule?

The volume of the solution from the cathode and anode compartment does not matter as long as the s/n has been drawn off to a point up to which any detectable change in concentration might have take place.

10.Define Growth’s Drapers law.

This law states that only that light which is observed by a system can cause chemical charge; this means that all the incident light would not be effective in bringing about a chemical change.

11.What is meant by electromagnetic radiation?

Electromagnetic radiation is a form of energy which is transmitted through the space at a constant velocity of 3* 10 meter second. This radiation is considered to have a dual character both as a particle and as a wave.

12. What is Zero point energy?

The energy contained by the atoms and molecules of a substance at absolute zero (ok)

13. What is Dissociation energy?

When a crystal is a subjected to heat orany othersource of energy the ions dissociate and the crystal collapses. The amount of energy thus absorbed is termed as dissociation energy.

14.What is Hooke's law?

Hooke's law helps to calculate approximately the values of stretching vibration frequency of bond.

1**5. Mention the various modes of vibrations in carbon di oxide molecule.**

Co2 is a linear molecule. It contains 3 atoms. It has four fundamental vibrations given below.

16.How will you show that the compound under investigation is notaromatic? Use Infrared technique.

The absence of bands due to C- C str at 1600 cm. 1500 cm and 1450 shows that the given compound is not aromatic.

17**. Which of the following atomic molecules do not absorbs in the Infrared region?**

HCl,ClBr,N_2,H_2,O_2.

N_2,H_2 and O_2 are homodiatomic molecules. Their molecular vibrations are not accompanied by any change in dipole moment and hence they do not absorb in IR region.

18. Why is methanol a good solvent for UV but not for IR spectroscopy?

The reason is that methanol does not absorbs in UV, i.e. it is transparent above 200 microns but is absorbs strongly in the infrared region (4000 cm to 667 cm).

19. State Kohlraush`s law

It`s state that equivalent conductivity of an any electrolyte at infinitesdilution solution is the sum of the equal conductivity of cata ions and anions.

Molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivity of the cations and anions each multiplied by the number of ions present in one formula unit of the electrolyte.

20. Define photochemical reaction.

A reaction which takes place by absorption of the visible and UV radiation is called photochemical reaction.

21. What is Quantum yield?

The number of molecules reacted or formed per photon of light absorbed is termed Quantum yield. It is denoted by φ

22. Define photochemistry.

The branch of chemistry which deals with study of photochemical reaction is called photochemistry

23. State phosphorescence.

When a substance absorbs radiation of high frequency and emits light even after the incident radiation is cut off the process is called phosphorescence.

24. Give one examples Of Chemiluminescene.

The oxidation of 5-aminophthalic cyclic hydrazine (luminal) by hydrogen peroxide in alkaline solution. Producing bright green light.

25. State Growth's-Drapers law.

This law states that only that light which is absorbed by a system can cause chemical change. This means that the entire incident light would not be effective in bringing about a chemical change.

26. State stark-Einstein law.

This law states that each molecule taking part in photochemical reactions absorbs one quantum of a radiation. The energy absorbed by each reacting molecule in $h\gamma$ and that absorbed by one mole of molecules will be equal to $Nh\gamma$ and is known as one Einstein of energy

27. Define Abelian.

A group in which all the elements commute it is called Abelian group if A and B are two elements.

$AB = BA$.

The two elements commute therefore A and B belongs to Abeliangroup .

A set numbers between - &+ from abelian group and a multiplication process

Example: symmetry operation of water molecules.

28. Define symmetry elements:

A symmetry element is a geometrical entity such as line or plane or point .such as operation of rotation or reflection or inversion.

29. IdentifyH_2O, C_6H_6, NH_3point group?

H_2O – C_2 point group

C_6H_6 – C_3 point group

NH_3 – C_4 point group

30. Give any two uses of LASER:

1. The light is cogrunt with waves all exactly in phase with one another.

2. The light is very nearly monochromatic .

3. A laser beam diverges hardly at all.

31. Define Plane of Symmetry.

An imaginary plane with in the molecule which divides in to two parts. Which are mirror images of each other. That is if a reflection of any atom of the molecule is carried out on the plane of symmetry.

32. Write the determination of transport no.

Ew.t = t-(RT/F)ln(a2/a1) --------- (1)

Ew.ot = (RT/Fln(a2/a1)) --------- (2)

Dividing (i) by (ii) we have

t- = Ew.t / Ew.ot

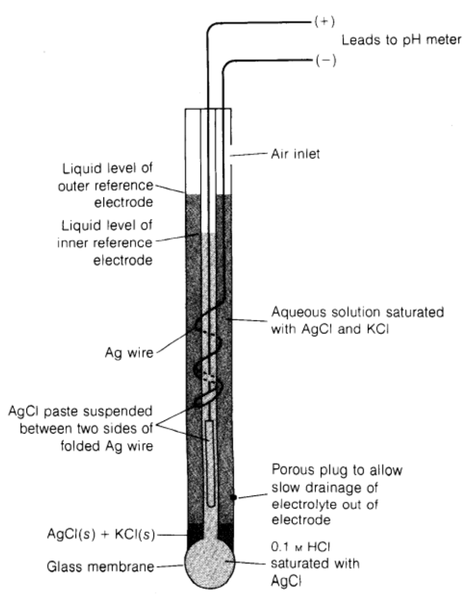
If the end electrodes are reversible with respect to the anion then the ratio of the two EMFs will give the transference no. of electrolyte.

33. Write about the limitation of quinhydrone electrode.

i) It iscannot be used for solution of pHmore than 8

ii) In more alkaline solutions hydroquinone ionizes appreciably as an acid also gets oxidized partly by atmospheric $O_{2.}$

34. Write the potentiometric curve obtained in acid base titration.



35. What is Corrosion?

It is the slow and continuous deterioration of metals and alloys by chemical (or) electrochemical actions of environments e, g.rusting of iron.

FIVE MARKS QUESTION

1. Distinguish between photochemical and thermal reaction.

Photochemical reaction	Thermal reaction
1. These involve absorption of light radiations.	These reactions involve absorption or evolution of Heat.
2.The presence of light is the primary requirement for reactions to take place	These reactions can take place in dark as well as in light.
3. Temperature has a very little effect on the rate of Photochemical reactions.	Temperature has a significant effect on the rate of a thermo chemical reaction.
4. G for photochemical spontaneous reactions may be (+)ve or(-)ve	G for a thermo chemical reaction is always (-)ve
5. Photochemical activation is highly selective. The absorbed photon excites a particular atom or group of atoms which become site for the reaction.	Thermo chemical activation is not selective in nature.

2. Write short note on Chemiluminescense.

Chemical reactions are accompanied by the emission of visible light at ordinary temperature. The emission of light as result of chemical action is called Chemiluminescense.

Example:

The glow of fireflies due to the aerial oxidation of luciferin (a protein) in the presence of enzyme luciferase.

The oxidation of 5-aminophthalic cyclic hydrazide (luminol) by hydrogen peroxide in alkaline solution. Producing bright green light.

Explanation:

In a Chemiluminescent reaction. The energy released in the reaction makes the product molecule electronically excited. The excited molecule then gives up its excess energy as visible light while reverting to ground state.

3. Derive lamberts-beer law.

When a beam of monochromatic light travels a homogeneous absorbing medium the intensity of the incident light decreases exponentially with thickness of the medium as well as the concentration of the solution

In other words this law can be stated as the rate of decrease of incident light intensity with thickness of the absorbing medium is proportional to the intensity of incident light as well as the concentration of the solution.

$$\frac{-dI}{dl} = \frac{k'}{C}$$

I −Intensity of the incident light .

dl −Thickness

c −Concentration of the solution

k' −Constant or the molar absorption coefficient

On rearranging and integrating we get,

$ln\frac{I}{I_0} = -k'cl$ or I=$I_0 e^{-kct}$

Changing the equation to logarithm to the base of 10 we get '

A=£cl

Where

A - Called absorbents

£ - molar extinction coefficient

4. Explain phosphorescence.

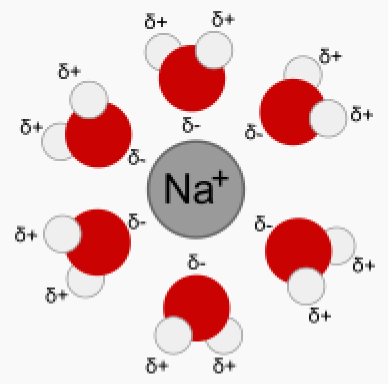
When a substance absorbs radiation of high frequency and emits light even after the incident radiation is cut off the process is called phosphorescence.

Ex. Sulphates of Ca, Ba, Sr exhibit phosphorescence

Explanation:

As in fluorescence a molecule absorbs light radiation and gets excited while returning to the ground state it emits light energy of longer wavelength the excited molecule passes from one series of electronic state to another and gets trapped. This shows the emission of light which persists even after the removal of light sources thus phosphorescence could be designated as delayed fluorescence.

5. Explain the Limitations and extension of Debye Heckle theory.



The first solvation shell of a sodium ion dissolved in water. The oxygen atoms are arranged at the vertices of an octahedron with the sodium ion at its centre

The equation for log $\gamma_\pm$ gives satisfactory agreement with experimental measurements for low electrolyte concentrations, typically less than 10^{-3} mol dm^{-3}. Deviations from the theory occur at higher concentrations and with electrolytes that produce ions of higher charges, particularly unsymmetrical electrolytes. Essentially these deviations occur because the model is hopelessly oversimplified, so there is little to be gained making small adjustments to the model. The individual assumptions can be challenged in turn.

Complete dissociation. Ion-association may take place, particularly with ions of higher charge. This was followed up in detail by Niles Bjerrum. The Bjerrum length is the separation at which the electrostatic interaction between two ions is comparable in magnitude to kT.Weak electrolytes. A weak electrolyte is one that is not fully dissociated. As such it has a dissociation constant. The dissociation constant can be used to calculate the extent of dissociation and hence, make the necessary correction needed to calculate activity coefficientsIons are spherical and are not polarized. Many ions such as the nitrate ion, NO_3^-, are manifestly not spherical. Polyatomic ions are also polarizable.

Role of the solvent. The solvent is not a structure less medium but is made up of molecules. The water molecules in aqueous solution are both dipolar and polarizable. Both cations and anions have a strong primary solvation shell and a weaker secondary solvation shell. Ion-solvent interactions are ignored in Debye–Heckle theory.

Moreover, we assume that the ionic radius is negligible, but at higher concentrations, the ionic radius becomes comparable to the radius of the ionic cloud. Most extensions to Debye– Hackle theory are empirical in nature. They usually allow the Debye–Hückel equation to be followed at low concentration and add further terms in some power of the ionic strength to fit experimental observations. The main extensions are the Davies equation, Pitzer equations and Specific ion interaction theory.

6. Write a short note on common ion effect?

The suppression of dissociation of a week acid (or) base of the addition of own ion. It's called common ion effect.

e.g., Ionic water of the product

The product of concentration of H_3O+OH- ions is constant at constant temperature. This is known as the ionic product of water.

The value of kw at 298 kelvin 1*10-14mol 2dm-6(unit).

The disassociationsa reaction is endothermic reaction kw value increase with increasing with temperature.

7. Define stokes and antistokes radiations.

Radiation scattered with a frequency lower than that of the incident beam is called stokes radiation and that with higher frequency is called antistokes radiation. Stokes radiation is generallymore intense than antistokes radiation.

8. Explain the Phosphorescence's.

A substance absorbs radiation of higher frequency and emit light even after the incident radiation is cut off the process is called phosphorescence.

The substance which phosphorescence's is called Phosphorescent substance.

EXAMPLE: Sulphates of calcium, barium exhibit phosphorescence's.

Fluorescence in blue region at 5700A wave length.

EXPLANATION:

A molecule absorb light variations and gets excited while returning to the ground state it emits light energy on longer wave length. The excited molecules passes from one series to another series of electronic state and gets trapped. The emission of light which persist even afterthe removal of light source.

9. Explain the C_2vPoint group.

C2v point group there are four operation .There are four irreducible representation r1, r2, r3, r4.Thesome of the square of the dimension of irreducible representation should be equal to four.

Example: H_2O

Hence each dimension must be uni dimension.

1+1+1+1=4;

Since the dimension of the representation is equal to character of the identity element (or) operation of the irreducible representation E must be equal to 1 in all the terms.

The some of the square of characters of irreducible representation must be equal to four.

So for one of irreducible representation (r1) all the characters must be 1.

C2v	E	C2	v	v’
r1	1	1	1	1
r2	1			
r3	1			
r4	1			

In case of other irreducible representation the some of the square of character must be equal to four. The character must be orthogonal two (or) one. The character must include two +1, two-1.

C2v	E	C2	v	v’
r	1	1	1	1
r2	1	1	-1	-1
r3	1	-1	1	-1
r4	1	-1	-1	1

Uni dimensional – A, B

Two dimensional –E

Three dimensional-T

Are called difference symbol.

On the basis of above points symbols can be assign to the irreducible representation of C2v point group.r1 is one dimensional symmetrical to the principal axes and the vertical plane v(xz).Hence the symbol is A. r2 is irreducible representation symmetrical to principal axis but unsymmetrical v(xz),hence the symbol is A2.r3 –one dimensional unsymmetrical to principle axis but symmetrical with respect to v(xz) .Hence the symbol is B1.r4 is one dimensional unsymmetrical to the principle axis .symbol is B2. V (xz)

C2v		E	C2	v	v’		
A1	r1	1	1	1	1	Z	$x_2y_2z_2$
A2	r2	1	1	-1	-1	Rzxy	
B1	r3	1	-1	1	-1	x,Ryxz	
B2	r4	1	-1	-1	1	y,Rxzy	

10. The EMF of standard Weston cell written $CdSo_4$(sat),Hg_2So_4(s),Hg in which cell reaction is

Cd(Hg), $CdSo_4$(sat). 8/3H2O(s)//, CdSo4(sat)., Hg_2So_4(s), Hg in which cell reaction isCd(Hg) +Hg_2So_4(s)+8/3H_2O (l) $CdSo_4$. 8/3H_2O(s)+2Hg(l)

Is 1.0185v at 25^0c calculate ΔG^0,ΔS^0 , &ΔH^0 for the all reaction if ($\partial E^0/\partial T$)p for the cell is 5.00 10^{-5}VK$^{-\cdot}$ F=9685Cmol^{-1}

Solution:

1. Standard free energy change ΔG^0,

$\Delta G^0 = -nFE^0$

$= -2(96485 Cmol^{-1})m(1.0813V)$

$= -196501.3$ J =-196.501KJ

2. Standard entropy change ΔS^0

$\Delta S^0 = nF (\partial E^0/\partial T)$

$= 2(96485C \times (5.00\times10^{-}5VK^{-1})$

$= 9.65JK^{-1}$

3. Standard enthalpy change ΔH^0

$\Delta H^0 = \Delta G^0 + T\Delta S^0$

$= -196501J\times(298K)(9.65JK^{-1})$

$= -193625J=-193.6KJ.$

11. What is the function of salt bridge cell?

The salt bridge serves three important functions in a galvanic cell;

(i) It prevents any net chare accumulation in other beaker by permitting the excess of ions to diffuse from one half cells to other through the salt bridge. Thus, it maintains electrical neutrality in the two half cells.

(ii) It physically separates the two electrodes, but completes the electrical circuit with electrons flowing from one electron to another externally and the ions flow in between the two compartments through salt bridge.

(iii) It minimizes the liquid functions potential between the two solutions connected through salt bridge.

12**.Derive on Nernst equation from reversible reaction**

From the reaction isotherm, the free energy (ΔG) for the cell reaction

$$\Delta G = - RT \ln Kc + RT\Delta v \ln a$$

Where Kc is the equilibrium constant and 'a' terms denote activities

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

$$\Delta G = - \Delta G^0 + RT\Delta v \ln a$$

If E is the emf of the cell in the given state and E^0 is the standard emf of the cell, then

$$\Delta G = -nFE \text{ and } \Delta G^0 = -nFE^0$$

$$-nfe = -nFE^0 + RT\Delta v \ln a \text{ (or)}$$

$$E = E^0 - RT/nF\, \Sigma v \ln a = E^0 - 2.303RT/nF \log \frac{[\text{activities of product}]}{[\text{activities of reactant}]}$$

This equation is called the Nernst equation. E^0 is the EMFof the cell at standard conditions, n is the number of electrons involved, F is the Faraday equal to 96500 coulombs, T is temperature in Kelvin, and R is the gas constant in joules, 8.314. At 25^0C, 2.303RT/F=0.059 and the equation becomes

1. $E = E^0 - 0.0591/n \log$ [activities of product]

   ____

[activities of reactant]

If the cell reaction is $aA+bB \rightleftharpoons lL+mM$, the above equation can be written in terms of single electrode potentials as

$E = [E_1^0 - RT/nF\Delta \ln a_1^{v1}] - [E_2^0 - RT/nF\Delta \ln a_2^{v2}]$

E_1^0 and E_2^0 are the standard single electrode potentials,

a_1&a_2 are the activity terms and

v_1& v_2 are the no. of molecules or ions involved in the corresponding electrode reaction.

13. What is meant by standard electrode potential?

If in an electrode set up, all active constituents or reactants are at unit activity, it is said to be normal or standard electrode. This can be achieved, when the concentration of the electrolyte taken is one molar and the electrode is a pure solid or gas at a pressure of one atmosphere. The electrode is set up at a temperature of 298K. The electrode potential. It is denoted by E^O, such an electrode is called standard or normal electrode. For example, a standard zinc electrode is set up by dipping a zinc metal rod into one molar zinc sulphate solution kept at 298K and one atmosphere pressure. It can be represented ad $Zn(s)/Zn^{+2}$(1M).

The electrode potential developed in a standard electrode due to oxidation reaction taking place on the electrode in a galvanic cell is called standard oxidation electrode potential and is denoted by E^o oxidation,. Similarly, the electrode potential developed in a standard electrode due t reduction reaction taint place on the electrode in a galvanic cell is called standard reduction electrode potential and is denoted by E^o reduction. Since the reduction half reaction is just the reverse of oxidation half reaction, therefore reduction potential is obtained from oxidation potential by simply changing the sin for any electrode as these are equal in magnitude but opposite in direction. So $E^o_{red} = - E^o_{oxi}$

It is important to mention here that is a convention tom express all electrode potential as per the recommendations of IUPAC .Therefore, E_{red} may be expressed as E only and stand

and free energy cE^o_{red} as E^o.

14. Explain the WienEffect?

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 c, per sec.

The ion therefore should pass several times through the thickness of the ionic atmosphere during the time of relaxation.

The moving ion therefore, will be almost free from the effect of the oppositely charged ionic atmosphere.

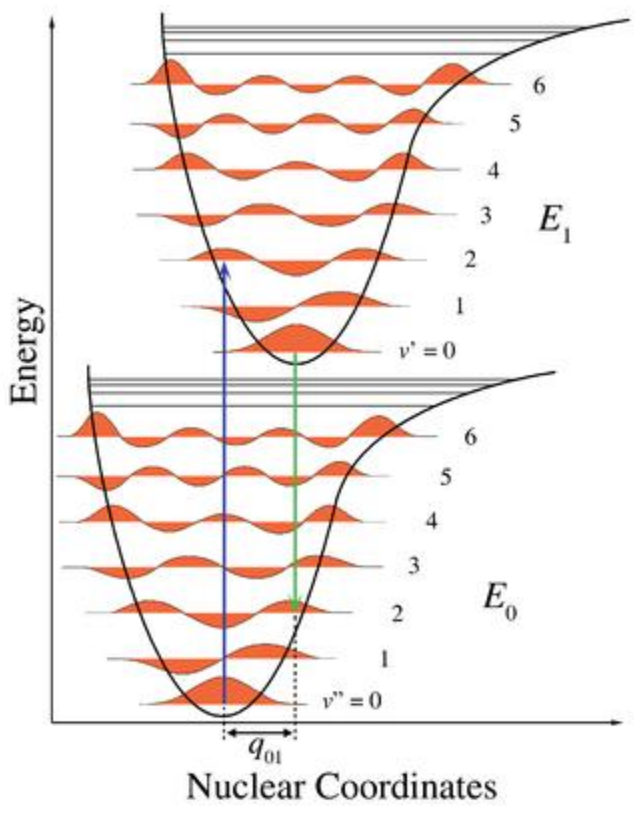
The ion will be moving so fast that there will be no time for the ionic atmosphere to be brittle up.

The asymmetry and electrophoretic effects under these circumstances may be negligibly small (or) even absent.

Thus the conductance of a strong electrolyte inaqueous solution increase in potential gradient applied. This observation has been verified experimentally by wein much before the development of the theory of strong electrolyte and is known as wein effect.

TEN MARKS

1. Explain briefly about frankCondon principle?



Using the Franck-Condon principle, we are able to calculate the intensities of transitions between vibrational states of the electronic energy levels. Due to their low mass, electron movement is fast compare with the nuclear movement and we can consider these two movements separately. Particularly, the position of nucleus can be considered as fixed during the electron transition. This means that the electron transition can be drawn as a vertical line on the potential curve diagram. However, after the electron transition took place, the nuclear vibrations move the nucleus toward the position of a new equilibrium distance with respect to the new potential energy curve.In terms of quantum mechanics, the probability of an electron transition is proportional to the squire of the overlap integral between the vibrational wave function $\Psi_{v''}(R)$ and $\Psi_{v'}(R$ before and after the electronic transition.

To treat the problem quantitatively, the complete molecular wave function of the initial and the final state are needed. Fortunately, it is often possible to present this wave function as a product of the electronic wave function Ψ_{el} with depends on the coordinates of all electrons $\mathbf{r}_i$ and the vibrational wave function $\Psi_v(R)$ which is a solution of the Schrödinger equation for nuclei and depend on the inter nuclear distance R. This approach is based on the Born-Oppenheimer approximation which argues with large difference in mass for nuclei and electrons. In the Born-Oppenheimer approximation the probability of a radiative transition is written as

$$W_{k\leftarrow 0} \propto |\langle k|\,\mu_Z|0\rangle|^2\, E_z^2,$$

Where $\langle k|\,\mu_Z|0\rangle$ is the matrix element of the **transition dipole moment**:

$$\langle k|\mu_Z|0\rangle \quad = \quad q_{v''v'}\int \Psi_{el_k}{}^{*}(\mathbf{r}_i)\mu_z\Psi_{el_0}(\mathbf{r}_i)d\mathbf{r}_i$$

$$q_{v''v'} = \int \Psi^*_{v''}(R)\Psi_{v'}(R)dR$$

The integral over the electron coordinates r_i does not dependent on the vibration of nuclei and it is identical for all pairs of v', v''. The integral over R represents overlap of the vibrational wave functions.

The quantities $|q_{v''v'}|^2$ are called **Franck-Condon factors**. No selection rules exist for changes of the vibrational quantum number v. This is because the vibrational wave functions of the initial and final states are in general not orthogonal to each other being the subject of Scrödinger equation with two different potentials $V'(R)$ and $V''(R)$. Apart from that, the **Franck-Condon-principle** allows to calculate the probability of a transition from some vibrational level v' of the initial state to another vibrational level v'' of the final state.

2. **Describe Debye huckel theory?**

A description of Debye–Hückel theory includes a very detailed discussion of the assumptions and their limitations as well as the mathematical development and applications.

A snapshot of a 2-dimensional section of an idealized electrolyte solution is shown in the adjacent picture. The ions are shown as spheres with unit electrical charge. The solvent (pale blue) is shown as a uniform medium, without structure. On average, each ion is surrounded more closely by ions of opposite charge than by ions of like charge. These concepts were developed into a quantitative theory involving ions of charge z_1e^+ and z_2e^-, where z can be any integer. The principal assumption is that departure from ideality is due to electrostatic interactions between ions, mediated by Coulomb's law: the force of interaction between two electric charges, separated by a distance, *r* in a medium of relative permittivity ε_r is given by

$$\text{force} = \frac{z_1 z_2 e^2}{4\pi \epsilon_0 \epsilon_r r^2}$$

It is also assumed that

- The solute is completely dissociated; it is a strong electrolyte.
- Ions are spherical and are not polarized by the surrounding electric field. Solvation of ions is ignored except insofar as it determines the effective sizes of the ions.
- The solvent plays no role other than providing a medium of constant relative permittivity (dielectric constant).
- There is no electrostriction.
- Individual ions surrounding a "central" ion can be represented by a statistically averaged cloud of continuous charge density, with a minimum distance of closest approach.

The last assumption means that each cation is surrounded by a spherically symmetric cloud of other ions. The cloud has a net negative charge. Similarly each anion is surrounded by a cloud with net positive charge.

Debye–Huckel equation:

The deviation from ideality is taken to be a function of the potential energy resulting from the electrostatic interactions between ions and their surrounding clouds. To calculate this energy two steps are needed.

The first step is to specify the electrostatic potential for ion *j* by means of

Poisson's equation

$$\nabla^2 \psi_j(r) = -\frac{1}{\epsilon_0 \epsilon_r} \rho_j(r)$$

$\psi(r)$ is the total potential at a distance, r, from the central ion and $\rho(r)$ is the averaged charge density of the surrounding cloud at that distance. To apply this formula it is essential that the cloud has spherical symmetry, that is, the charge density is a function only of distance from the central ion as this allows the Poisson equation to be cast in terms ofspherical coordinates with no angular dependence.[

The second step is to calculate the charge density by means of a

Maxwell–Boltzmann distribution.

$$n_i' = n_i \exp\left(\frac{-z_i e \psi_j(r)}{kT}\right)$$

This distribution also depends on the potential $\psi(r)$ and this introduces a serious difficulty in terms of the superposition principle. Nevertheless, the two equations can be combined to produce the

Poisson–Boltzmann equation.

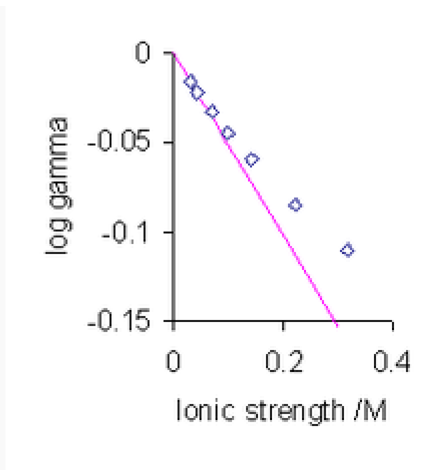
$$\nabla^2 \psi_j(r) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_i \left\{ n_i (z_i e) \exp\left(\frac{-z_i e \psi_j(r)}{kT}\right) \right\}$$

Solution of this equation is far from straightforward. It can be solved by successive approximations using modern electronic computers, but these were not available to Debye and Hückel. Instead they expanded the exponential as a truncated Taylor series. This results in the truncated Poisson–Boltzmann equation,

$$\nabla^2\psi_j(r) = \frac{d^2}{dr^2}\psi_j(r) = \kappa^2\psi_j(r)$$

Which is a type of differential equation which has an analyticalsolution. This equation applies to 1:1, 2:2 and 3:3 electrolytes; for unsymmetrical electrolytes another term in ψ^2must be included. Incidentally, the truncated expansion may also remove the difficulty with the superposition principle.

The solution for a symmetrical electrolyte, in terms of the mean activity coefficient is given as



Experimental log $\gamma_\pm$ values for KBr at 25°C (points)and Debye–Hückel limiting law (coloured line)

$$\log_{10}\gamma_\pm = -Az_i^2\frac{\sqrt{I}}{1+Ba_0\sqrt{I}}$$

$$A = \frac{e^2 B}{2.303 \times 8\pi\epsilon_0\epsilon_r kT}$$

$$B = \left(\frac{2e^2 N}{\epsilon_0\epsilon_r kT}\right)^{1/2}$$

I is the ionic strength and a_0 is a parameter which represent the distance of closest approach of ions. For aqueous solutions at 25 °C A = 0.51 $mol^{-1/2}dm^{3/2}$ and B = 3.29 $nm^{-1}mol^{-1/2}dm^{3/2}$The most significant aspect of these algebraic manipulations is the prediction that the mean activity coefficient is a function of ionic strength. Of course the ionic strength of a 1:1 electrolyte is equal to its concentration, but that is not true for other types of electrolyte. Generally, activity coefficients are discussed in terms of ionic strength rather than the electrolyte concentration. For very low values of the ionic strength the value of the denominator in the expression above becomes nearly equal to one. In this situation the mean activity coefficient is proportional to the square root of the ionic strength. This is known as the Debye–Hückel limiting law.

3. Write a short note on moving boundary method?

In this method the motion [moment] under the inclusion of an applied electric field is directly observed. A solution of HCL called the principle electrolyte. HCL in the space is gently introduced above the solution of cdcl2. So the selected that the anion is common to both the electrolytes.

And the Cd is less mobile the HCL. The density of HCL should be less than CdCl2 and HCL solution is filled in. Such a weight that this is definite boundary visible at the junction of two solutions

[a-a']. The cathode is a platinum wire. The anode is the strick of Cd metal current I is passed. The Cd dissolved at the anode direct reaction.

At the cathode take place. The ions migrate towards the cathode through the cell their place being take by the ion. The current amplier(s) is passed for t seconds. The ion move down wards the towards the anode move acquards towards the cathodes. The consequently the boundary b/w the two solution moves acquards.If the charge on cations is z+.

The amount of cations transported =t+ [It/Sift].

Where,

[It/F]--->don’ts the equivalent of electricity passed.

If the solution concentration is Ceq dm-3 the volume swept out.

$$v= (1000/c)\ It/Z+F\ t+cm3$$

$$It/Z+t=Q$$

$$t=V*c/1000Q$$

Q====>Faradays

V====>Volume incm3

Swept out by the boundary in moving from aa'to bb'. Q is the faradays of electrocity passed and C====>the concentration of the acid is eq dm-3.

It S ----->this area of cross secction of the tube.

X ------>the distance moved[bb'-aa']

V ------>XS cm3

Hence,

$t+=Sxc/1000Q$.

4. Discuss the Selection rule for Vibrational transition.

Infrared light is absorbed only when a change in dipole character of the molecule takes place complete symmetry about a bond eliminates some absorption bands. Clearly, some of the fundamental vibrations are infrared active and some are not. It is governed by the selection rules.

(i) If a molecule has a centre of symmetry then the vibrations are centrosymmetric and are inactive in the infrared but are active in the raman.

(ii) The vibrations which are not centre of symmetric are active in infrared but inactive in Raman.

Since in most of the organic compounds the functional groups are not conrosymmetric. Infrared spectroscopy is most informative. Consider various vibrations incase of co2

The above vibrations are all fundamental vibrations of CO_2. Since

(i) Does not give rise toany change in dipole moment, It is infrared in active.

(ii) An asymmetric stretching cause, a net change in dipole moment and thus are infrared active and absorbs at 2350 cm vibrations and are said to be degenerate.

(iii) The bending of bonds in the molecule are identical but occur in perpendicular Planes and thus appear in the same position in the spectrum.

(iv) The spectrum of co2 consist of two bands

a. 2350cm due to asymmetric stretching

b. 667 cm due to bending vibrations.

5. Explain the Debye Falkenhagen effect?

Debye and falkenhagen examined the conductance behavior of a solution of a strong electrolyte by applying alternating current of different frequencies. The predicted that of 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 rotating 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.

The conductance remains independent of the frequency of alternating current up to 10 cycles per second. But with further increase in frequency the conductance starts increase towards a certain limiting value indicating effect.

Thus the conductance of a strong electrolyteinaqueoussolution increasein potential gradient applied . This observation has been verified experimentally by wein much before the development of the theory of strong electrolyte and is known as wein effect.

6 .Explain the radiative& non radiative transition of Jablonski diagram

Non-radiative transition:

This transition involve the return of the activated molecule from the higher excited state.[S2-S3]or[T3-T2].To the first excited state [S1-T1].This transition do not involve the emission of radiation and thus term as non-radiative transition .the energy of the molecule is dissipated in the form of heat through molecular collision. The process is called internal conversion[IC].The transition are also non-radiative spin-forbidden.

An accurse in less the above 10-11 sec.The molecules may also less energy by another process is called inter system crossing[ISC].Which involve transition between states of different spin.S2-T2,S1-T1,S2-S1,T2-T1.This transition are also non-radiative transition.

Radiative transition:

The transition involve return of the activated molecule from this singlet excited state.S1&T2.

Such transition are accompanied of emission of radiationThese transition from S1-S0.is a allowed transition and accursin above 10-8 sec .The emission of radiation in this transition is called fluorescence.

The transition from triplet excited state T1to the ground state soT1-S0.It is spin forbidden .The emission of radiation in this transition is called phosphorescence. The life time of phosphorescence’s is much longer then the order of 10-3 sec and 10-7 sec.

7**. Explain the construction of C3v C3haracter table.**

There are three classes of operation there should be three equal irreducible representation r1, r2, and r3.

The sum of the square to t .Therefore should be two one dimensional and one two dimensional representation .So that,

1+1+2 =6

1+1+4 =6

The irreducible representation with the character of identity operation.

C3v	E	2C3	3v
r1	1	1	1
r2	1	x	y
r3	2	a	b

For any point group there should be one irreducible representation which is symmetrical to all the operations. That is the character corresponding to all the operation is +1.

C3v	E	2C3	3 v
r1	1	1	1

1+2(1) +3(1) =6

The sum of the square of the character of the operation is equal to 6.

1+2(1) +3(1) =6

The character of the two irreducible representation are orthogonal to each other .Let x &y represent the character of the C3 & v operation in the irreducible representation r2.

C3v	E	2C3	3v
r1	1	1	1
r2	1	x	y
r3	1		

If r1&r2 are orthogonal.

1.1.1+2.1.x+3.1.y=0

The above equations can be correct only when the values of x=1,

Y=-1, thus the character of r2 represents,

C3v	E	2C3	3v
r1	1	1	1
r2	1	1	-1
r3	1	a	b

The character of r3 should be orthogonal to r1&r2 and the character of identity operation is 2.Let a&b represent the character of C3&v operation in the reducible representation are 3 if r1&r2 orthogonal.

r1&r3

1(1) (2) +2(1) (a) +3(1) (b) =0

2+2(a) +3(b) =0

2a+3b=-2 (1)

r2&r3

1(1) (2) +2(1) (a) +3(-1) b=0

2+2a-3b=0

2a-3b=-2 (2)

From equation (1) & (2) we get

a=-1, b=0

2(-1)-3(0) =-2

-2-0=-2 =1

C3v	E	2C3	3v	
R1	1	1	1	(x2, y2)
R2	1	1	-1	Rxy
R32	-1	0	(xy) (yx)	

R1 irreducible representation of one dimensional symmetrical to the principle axis and to the vertical plane .it is denoted A1.

R2 is also one dimensional but it is asymmetrical with respect to the vertical plane hence the symbol is A2.

R3-is two dimensional and the symbol is E.

8. Derive the Photo chemical reaction between H_2 &Br_2.

$H_2 + Br_2 \rightarrow \quad 2HBr$

$d[HBr]/dt = K'[H_2][I_2]/ 1+ [HBr]/m'[Br_2]$

$Br_2 \rightarrow 2Br$ (1)

$Br+H_2 \rightarrow HBr+H$ (2)

$H+Br_2 \rightarrow HBr + Br$(3)

$H+HBr \rightarrow H_2+Br$ (4)

$Br + Br \rightarrow Br_2$ (5)

The photochemical reaction between H_2 and Br_2 proceeds according to the empirical equation . Where K' and m' are constant I is intensity of the radiation or light absorbed .Only different between the thermal and photochemical process.

The photochemical process the Br_2 radicals are produced by absorption of photons by bromine molecule.

$d[Br]/dt=2I-K2[I2][Br]+K3[H][Br_2]+K4[H][H Br]-K5[Br]2 =0$ (1)

$d[H]/dt =K2[H_2][Br]-K3[H][Br_2]-K4[H][H Br] =0$ (2)

Adding equation (1) & (2)

$2I =K5[Br]2$

$[Br] = [k5/2I]1/2$ (3)

Rearranging equation (2) we get,

$K2 [H_2][BR] = [H]\{K3[Br_2]+K4[H Br]\}$

$[H] = k2\ [H_2]\ [Br]/K3\ [Br_2] + K4\ [H\ Br]$ (4)

The rate of formation of H Br can be written as,

$D[HBr]/dt = k2[H_2][Br]+k3[H][Br_2]-k4[H][H\ Br]$ (5)

$K2\ [H2][Br]+[H]\{K3[Br2]-K4[H\ Br]\}$ (6)

Substituting the value [H] from equation (4) in equation (6) we get,

$d\ [H\ Br]/dt= K2[H_2][Br]+K2[H_2][Br]/K3[Br_2]+K2[H\ Br]\{k3[Br2]-$

$k4\ [H\ Br]\}$

$d\ [H\ Br]/dt =2k2[H_2][Br]k3[Br2]/k3[Br_2]+k4[HBr]$

$d\ [HBr]=2k2[H_2][Br]k3[Br_2]/1+K4[HBr]/k3[Br_2]$

$d\ [HBr]/dt=2(2I/K5)1/2\ K2\ [H_2]/1+K4\ [HBr]/k5[Br_2]$

$k'=2k2(k5)1/2$ and $m'=k3/k4$

The rate of photochemical reaction is 300 times that of the thermal reaction at the same temperature.

9. Derive on expression for Liquid junction potential and Thermodynamics of reversible reaction.

a) **Liquid junction potential.**

Liquid junction potential occurs when two solutions of different concentrations are in contact with each other. The more concentrated solution will have a tendency to diffuse into the comparatively less concentrated one. The rate of diffusion of each ion will be roughly proportional to its speed in an electric field. If the anions diffuse more rapidly than the cations, they will diffuse ahead into the dilute solution, leaving the latter negatively charged and the concentrated solution positively charged. This will result in an electrical double layer of positive and negative charges at the junction of the two solutions. Thus at the point of junction, a potential difference will develop because of the ionic transfer. This potential is called liquid junction potential or diffusion potential. The magnitude of the potential depends on the relative speeds of the ions' movement.

The liquid junction potential cannot be measured directly but calculated. The Electromotive force (EMF) of a concentration cell with transference includes the liquid junction potential.

Calculation

$$E_{\text{without transference}} = RT/F \, . \ln(a_2/a_1)$$

where a_1 and a_2 are activities of HCl in the two solutions, R is the Universal Gas Constant, T is the temperature and F is Faraday's Constant.

$$E_{\text{with transference}} = t_M \, RT/F \, . \ln(a_2/a_1)$$

Where a_2 and a_1 are activities of HCl solutions of right and left hand electrodes respectively and t_M be transport number of Cl^-

Liquid Junction potential = $E_{\text{with transference}} - E_{\text{without transference}}$ =

$$(t_M - 1) \, RT/F \, . \ln(a_2/a_1)$$

b) Thermodynamics of reversible cells

From Gibb's –Helmholtz equation,

$\Delta G = \Delta H + T[\partial(\Delta G/\Delta H)]p$ -------(1)

The relation between and ΔG, $\Delta G = -nFE$ ----(2)

On diffrentiation with respect to temperature,

$[\partial(\Delta G/\Delta H)]p = -nf[\partial E/\partial T]p$ ------(3)

Substitting eq.(3) and (2) in eq.(1) ,

$-nFE= -nFT[\partial E/\partial T]p$

.. $\Delta H = -nFE+nFT\ [\partial E/\partial T]p == nF\{T[[\partial E/\partial T]p-E\}$-------(4)

$[\partial E/\partial T]p$ is known as the temperature coefficient of EMF.

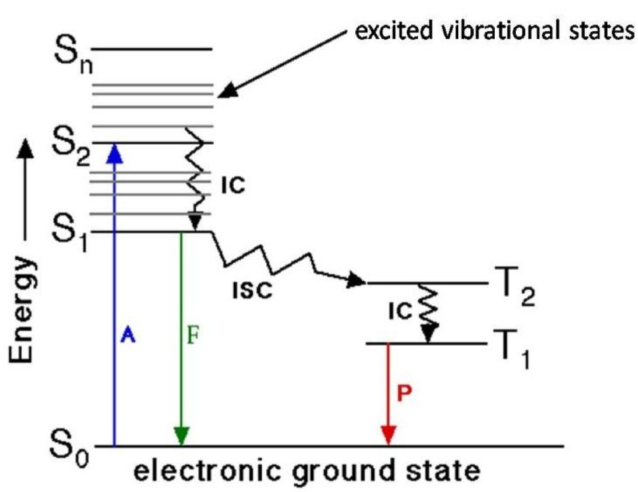
We know that $\Delta H = \Delta G+T\Delta S$ --------(5)

Comparision of eqs.(5) and (4) gives

$T\Delta S = nFT\ [\partial E/\partial T]p$ and hence $\Delta S = nF[\partial E/\partial T]p$--------(6)

The entropy change of a reaction can be calculated from the temperature co-efficient

10) Explain the JablonskiDiagram.



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The transition involve returns of the activated molecule from this singlet excited state.S1&T2.

Such transition are accumbine by emision of radiation.This transition from S1->S0,is an spin allowed transition and accurs in above 10-8 sec.Theemision of radiation in this transition is called fluorescence.

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PHOSPHORESCENES:

A substance absorbs radiation of higher frequency and emit light even ofter the incident radiation is cut off the process is called phosphorescene.

The substance which phosphorescenes is called phosphorescent substance.

EXAMPLE: sulphates of calcium,barium exhibit phosphoresscenes.

Flurescenes in blue region at 5700A wave length.

EXPLANATION:

A molecule absorb light variations and gets excited while returning to the ground state it emits light energy on longer wave length.The excited molecules passes from one series to another series of electronic state and gets trapped.The emission of light which persist even ofterthe removal of light source.

11. Discuss about the Factors influencing chemical shift.

Follwing are the factors which influence the chemical shift:

(a) Inductive effect
(b) Vander waalsdeshielding
(c) Anisotropic effects
(d) Hydrogen bonding

(a) Inductive effect: A proton is said to be deshielded if it is attached to an electronegative atom or group. Greater the electronegativity of the atom,greater is the deshielding caused to the proton.If the deshielding is more for a proton,then its ∂ value will also be more.

(b) Consider the following compounds:

(1) CH_3CH_2F (2) CH_3CH_2-Cl

b a b a

Two signals are expected for each of the two compounds. Deshielding for protons ‘a’ in compound (1) is more than that for similar protons in compound (2)

As the distance from the electronegative atom increases,thedeshielding effect due to it diminishes. Protons ‘b‘ are comparatively less deshielded and hence will resonate at comparatively lower value of ∂.

Tau value for CH_3-protons

Compound	Value
CH_3F	5.75
CH_3Cl	6.90
CH_3Br	7.36

(c) Van der waal’sdeshielding: In overcrowded molecules, it is possible that some proton may be occupying sterically hindered position. Clearly,electron cloud of a bulky group (hindering group) will tend to repel the electron cloud surrounding the proton.Thus, such a proton will be deshielded and will resonate at slightly higher value of ∂ than expected in the absence of this effect.

(d) Anisotropic effects(space effect): The deshielding effect on protons attached to C=C is higher than that can be accounted for by the inductive effect alone. Aldehydic and aromatic protons are much more deshielded. Alkyne protons appear at relatively low value of ∂. The values of ∂ (chemical shift) in each case can be justified by explaining the manner in which the ∏ electrons circulate under the influence of the applied field. Consider an alkene. It is so oriented that the plane of the double bond is at right angles to the applied field. Induced circulation of ∏ electrons generates induced magnetic field which is diamagnetic around carbon and paramagnetic in the region of the alkene protons. Thus the protons will feel greater field strength and hence resonance occurs at lower applied field.

(e) Hydrogen bonding: It has been found that a hydrogen atom exhibiting property of hydrogen bonding in a compound absorbs at a low field in comparison to the one which does not. The hydrogen bonded proton being attached to a highly electronegative atom will have smaller electron density around it.Being less shielded,the field felt by such a proton will be more and hence resonance will occur downfield.The downfield shift depends upon the strength of hydrogen bonding.Intermolecular and intra-molecular hydrogen bonding can be easily distinguished as the latter does not show any shift in absorption due to the change in concentration.In case of phenols,absorption occurs between-2 to 6Ʈ.But if the concentration is decreased,i.e.,if the volume of the solvent,say,carbon tetrachloride is increased,then the a absorption for OH proton occurs upfield.In case the OH group on benzene is intramolecularly bonded with some other group in the orthoposition,the absorption for OH proton may occur even at the negative tau value.Forexample,the OH proton in salicylic acid absorbs at-0.6Ʈ.Enols show strong intra-molecular hydrogen bonding which is further stablised by resonance.Due to this,a great deshielding effect is caused and absorption for such a proton occurs at the negative tau value(10.5-12∂).It is due to the fact that acids exist as a result of hydrogen bonding.A signal for carboxylic acid proton in ethoxy acetic acid appears at -0.95Ʈ(10.95∂).

In the enolicform,the compound is found to show absorptions at

(1) a=8.02 1.98∂

(2) b=-4.9 14.9∂

(3) c=4.5 5.5∂

(4) d=8.02 1.98∂

Similarly,amines show hydrogen bonding and thus,absorptions in them occur downfield.Since intermolecular hydrogen bonding is concentration dependent,the concerned proton absorption shifts upfield by decreasing the concentration.With decreasing concentration, the extent of hydrogen bonding falls and thus,the paramagnetic effect is also diminished.

12.Explain the Spin-Spin Coupling of Ethyl bromide.

To understand it properly,consider a molecule of ethyl bromide(CH_3CH_2Br).The spin of two protons($-CH_2-$)can couple with the adjacent methyl group($-CH_3$) in three different ways relative to the external field.

The three different ways of alignment are:

↑↑ (Reinforcing)

↑↓ ↓↑ (Not effecting)

↓↓ (Opposing)

(1)Thus, a triplet of peaks results with the intensity ratio of 1:2:1 which corresponds to the distribution ratio of alignment.

Similarly,the spin of three protons (CH_3-) can couple with the adjacent methylene group($-CH_2-$) in four different ways relative to the external field.

Thus,quartet of peaks results with an intensity ratio of 1:3:3:1 which corresponds to the distribution ratio of all the alignments.The relative intensities of the individual lines of a multiplet correspond to the numerical coefficient of the binomial expression: (1+x)= 1+x if n=1, If n=2,then(1+x)=1+2x+x.Thus the lines of the triplet have relative intensities 1:2:1.If n=3, then (1+x)=1+3x+3x+x.Thus the lines of the quartet formed due to the influence of three equivalent protons will have relative intensities 1:3:3:1. Similarly,the lines of the pentet(quitet) formed will have relative intensities 1:4:6:4:1. Hence, the splitting of a signal is due to the different environment of the absorbing proton not with respect to electrons but with respect to the nearby protons(protons attached to the adjacent carbon atom). Let us consider the case of 1:1:2 trichloro-ethane $ClCH_2$-$CHCl_2$. This compound has two types of protons in it. The mutual magnetic influence between the protons 'a' and 'b' is not transmitted through the electrons in the intervening bonds.The nuclear spin of protons 'a' first couples with the electron spin of C-H_a bonding electrons and these in turn couple with C-C bonding electrons and then with C-H bonding electrons.thus the coupling is eventually transmitted to the spin of H nucleus.The magnetic field that the proton 'a' feels at a particular instant is slightly increased or decreased by the spin of the neighbouring proton 'b'.The field felt by proton 'a' is increased if the proton 'b' happens to be aligned at that instant with the applied field.If the proton 'b' is aligned against the applied field,then at that instant,the field felt by the proton 'a' will be slightly decreased.Thus,absorption by protons 'a' is shifted slightly downfield for half the molecules and slightly upfield for other half of the molecules.Thus,the signal for 'a' kind of protons is split into two peaks,i.e.,into doublet with equal peak intensities.Splitting by proton 'b'

Thus,coupling with proton 'b'(one proton) gives 1:1 doublet. Splitting by proton 'a' Now let us see,how the signal from 'b' proton is effected by 'a' kind of proton(two protons).These two protons can be aligned with the applied field in three different ways and will consequently influence the proton 'b'. Thus,a signal for 'b' proton will be split up into three peaks (Triplet) Which are equally spaced with peak intensities 1:2:1.It is called one proton triplet.Thus,in the above compound,we observe 1:1 doublet which corresponds to ‘a’ protons(-CH_2-) and 1:2:1 triplet which represents ‘b’ proton.($CHCl_2$).The total area under the doublet is twice as large as the total area under the triplet which shows that the number of protons representing doublet is twice as many as the number of protons which represent a triplet.Fromthis,we see that a single proton ‘b’ is split into a triplet(group of three peaks) under the influence of two equivalent protons ‘a’.Similarly,a signal for two equivalent protons ‘a’ is split into a doublet under the influence of the neighbouring proton ‘b’.Thus ,in general,we say that a set of n equivalent protons splits up a signal(due to neighbouring protons)into a group of (n+1) peaks (multiplet).

13. Explain the C2v Point Group of water molecule.

C2v point group there are four operation .There are four irreducible representation r1,r2,r3,r4.Thesome of the square of the dimension of irreducible representation should be equal to four.

Example:H2O

Hence each dimension must be uni dimension.

1+1+1+1=4;

Since the dimension of the representation is equal to character of the identity element (or)operation of the irreducible representation E must be equal to 1 in all the terms.

The some of the square of characters of irreducible representation must be equal to four

So for one of irreducible representation (r1)all the characters must be 1.

C2v	E	C2	v	v’
r1	1	1	1	1
r2	1			
r3	1			
r4	1			

In case of other irreducible representation the some of the square of character must be equal to four. The character must be orthogonal two (or)one.The character must include two +1,two-1.

C2v	E	C2	v	v’
r1	1	1	1	1
r2	1	1	-1	-1
r3	1	-1	1	-1
r4	1	-1	-1	1

Uni dimensional – A,B

Two dimensional –E

Three dimensional-T

are called difference symbol.

On the basis of above points symbols can be assign to the irreducible representation of C2v point group.r1 is one dimensional symmetrical to the principal axes and the vertical plane v(xz).Hence the symbol is A. r2 is irreducible representation symmetrical to principal axis but unsymmetrical v(xz),hence the symbol is A2.r3 –one dimensional unsymmetrical to principle axis but symmetrical with respect to v(xz) .Hence the symbol is B1.r4 is one dimensional unsymmetrical to the principle axis .symbol is B2. V(xz).

C2v		E	C2	v	v'		
A1	r1	1	1	1	1	Z	x2y2z2
A2	r2	1	1	-1	-1	Rzxy	
B1	r3	1	-1	1	-1	x,Ryxz	
B2	r4	1	-1	-1	1	y,Rxzy	