Q.1 A Select the correct option and complete the following statements i) KOH is a <u>strong</u> electrolyte.

ii) pOH is defined as the negative logarithm to the base 10 of the <u>hydroxyl</u> ions concentration expressed in mol/dm³.

iii)The lowest energy and highest wavelength radiations are IR radiations.

iv) Two fold axes of symmetry is also called as diad.

B. State whether the following statements are true or false:

i) At 298 K, the value of ionic product of water is 14. – False

C) Match the following columns

Sr.	Column A	Sr. No.	Column B
No.			
i)	Unit cell	ii)	the smallest repeating unit in space lattice
ii)	SI unit of wavelength	iv)	meter

Q.2 A i) At 298 K, Calculate the pH of a solution which contains 0.2 mol/dm³ of sodium acetate and 0.1 mol/dm³ of acetic acid $[(K_a)_{acetic acid} = 1.8 \times 10^{-5}]$ ---- 5 Marks Solution : $pK_a = -log_{10} k_a = -log_{10} (1.8 \times 10^{-5}) = 4.744$ A solution containing sodium acetate and acetic acid is an acid buffer. By Henderson equation, pH of acid buffer is given by [Salt] $pH = pK_a + log_{10} - - - - = 4.744 + log [0.2/0.1] = 4.744 + log 2 = 4.744 + 0.3010 = 5.045$ [Acid] pH = 5.045ii)At 298 K, show that pH + pOH =14 ---- 3 marks Answer: Ionic product of water is given by $K_w = [H^+] [OH^-]$ At 298 K, $K_w = 10^{-14}$ $[H^+][OH^-] = 10^{-14}$ Taking logarithm of both sides and multiplying both sides by -1, we get $-\log_{10} [H^+] + - \log_{10} [OH^-] = - \log_{10} (10^{-14})$ pH + pOH = 14 at 298 K. OR A i) A buffer solution of pH 10.25 is to be prepared from ammonium chloride and ammonium hydroxide. In what ratio of molar concentration should ammonium chloride and ammonium hydroxide be mixed at 298 K. [(K_b) ammonium hydroxide = 1.8 x 10⁻⁵] Solution : $pK_b = -\log_{10} k_b = -\log_{10} (1.8 \times 10^{-5}) = 4.744$ At 298 K, pH + pOH =14 or pOH = 14 - 10.25 = 3.75 Its pOH is given by Henderson equation [Salt] pOH = pK_b + log₁₀ ------[Base] [Salt] 3.75= 4.744 + log₁₀ ------[Base] [Salt] log₁₀ ----- = - 0.994 [Base] [Salt] ------ = Antilog(-0.994) = 0.1014 [Base] Ans: [Salt] : [base] = 0.1014 : 1

DATE: 10/10/2017	F.Y.B.Sc.(Sem-II)	Chemistry P-II	QP CODE: 03736

ii. Write a short note on buffer capacity

Answer: Buffer capacity: It is a measure of the ability of the buffer solution to maintain its pH constant. It is defined as the amount of strong acid or base, in gram-equivalents, that must be added to 1 dm³ of the buffer solution to change its pH by one unit. The larger the amount of strong acid or base that should be added to change the pH of a buffer by one unit, the greater is the buffer capacity. For acid buffer, buffer capacity is maximum when concentration of acid is equal to concentration of salt i.e. [Acid]= [Salt]. Similarly for basic buffer, buffer capacity is maximum when concentration of base is equal to concentration of salt i.e. [Base]= [Salt].

B) i) The energy of a scattered radiation is 2.48 x 10 $^{-19}$ J. Calculate wavelength, frequency and wave number of this scattered radiation. (h = 6.626 x 10 $^{-34}$ J.s , C = 3 x 10 8 m/s)

Solution : Energy (E) = hc / λ

Wavelength = hc/ energy = $(6.626 \times 10^{-34} \times 3 \times 10^{8})/(2.48 \times 10^{-19}) = 8.015 \times 10^{-7} \text{ m}$ Wave number = $1/\lambda = 1/8.015 \times 10^{-7} = 1.248 \times 10^{6} \text{ m}^{-1}$ Frequency (v) = c/ λ = (3 × 10⁸)/(8.015 × 10⁻⁷) = 3.743 × 10¹⁴ Hz

Ii) Mention the properties of crystalline solids.

- Answer: 1. The constituent particles are arranged in a definite geometrical pattern throughout the three dimensional network of crystal.
 - 2. Crystalline solids have sharp melting point.
 - 3. Crystalline solids are anisotropic i.e. their physical properties are different along different direction.

OR

B) i) Find Miller indices of the planes whose intercepts on crystallographic axes are (a/2, ∞ b,2c) and (3a, 4b, 2c)

Solution:							
Weiss indices	Reciprocals	Multiplied by	Miller indices				
(a:b:c)	(1/a:1/b:1/c)	L.C.M.					
1/2: ∞:2	2: 0: 1/2	(2: 0: 1/2) x 2	4 :0 :1				
3 : 4: 2	1/3:1/4: 1/2	(1/3:1/4: ½) x 12	4:3: 6				

ii) Explain Plank's theory of radiation.

Answer:

According to Plank's theory, the emission and absorption of energy takes place not in a continuous manner but in discrete installments called quanta. Even the propagation of energy through space is discontinuous and takes place in quanta. Each quantum can be considered as a packet of energy equal to h v where h = Plank's constant = 6.625 x 10⁻³⁴ J.s and v = frequency of radiation in Hz.

A molecule can exist in number of energy levels. When it interacts with electromagnetic radiations, a transfer of energy from electromagnetic radiations to molecules occur only when $\Delta E = h v$ where $\Delta E = Difference$ in energy between two quantized state

h= Plank's constant = 6.625×10^{-34} J.s and v = frequency of radiation in Hz.

- C) i) Define a) Triprotic acids: The triprotic acids have three ionisable H⁺ atoms per molecule or The acids which are capable of donating three protons per molecule to a proton acceptor is called triprotic acids.
 - b) Buffer action : The mechanism by means of which a buffer solution tries to maintain its pH constant is known as buffer action.
- ii) Define a) Spectroscopy: The study of the interaction of electromagnetic radiation with matter is called as spectroscopy.

b) frequency of radiation: It the number of waves which cross a given point in one second.

OR

- C) i) Define a) Monoprotic acid: The monoprotic acids have one ionisable H⁺ atom per molecule or The acids which are capable of donating one proton per molecule to a proton acceptor is called monoprotic acids.
 - b) Buffer solutions: The solutions which have capacity to resist a change in pH on addition of a small quantity of dilute acid or base.
 - ii) Define a) Centre of symmetry: It is an imaginary point in the crystal such that any line drawn through it will intersect the surface of the crystal at equal distances in both directions.
 - b) Space lattice: The geometrical form consisting of a regular arrangement of a constituent particles of a crystalline solid in three dimensional space is called space lattice.

Q.5 A) Derive Henderson equation for the pH of acid buffer. Ans: Acid buffer is a mixture of weak acid HA and its salt BA Weak acid ionizes $HA \rightleftharpoons H^+ A^-$ The ionization constant Ka of the acid is given by

Due to common ion effect, the ionization of the weak acid HA is suppressed in presence of salt BA, the acid is assumed to be practically undissociated [HA] = [Acid]

The A⁻ ions in the solution are due to complete ionization of salt BA Hence [BA]= [Salt] Substituting in equation (I), we get

[Acid] [H⁺] = K_a ------[Salt] Taking log of both sides and multiplying both sides by -1,

pH = pK_a + log₁₀ ------[Acid]

This is Henderson equation for pH of acid buffer.

Henderson equation is used to calculate i) pH of a buffer solution ii) the ratio of the concentration of salt to concentration of acid that must be used to prepare an acid buffer of desired pH.

B) Explain the following phenomenon that occurs when electromagnetic radiation interact with matter i) Absorption ii)Emission

Answer: The study of the interaction of electromagnetic radiation with matter is called spectroscopy. Following four phenomenon occur when electromagnetic radiation interact with matter

- i) Absorption ii)Emission iii) Scattering iv) Fluorescence
- i) Absorption: It is a process by which energy of photons is transferred from an electromagnetic radiation to an atom or molecule and promotes it from lower energy level to higher energy level. According to quantum theory atoms or molecules possesses discrete energy levels. Absorption can occur when an atom or molecule absorbs a photon of radiation that has energy which exactly corresponds to the difference between two energy levels.

When electromagnetic radiations are incident on atoms or molecules, photons of certain frequencies may be selectively absorbed. A study of these absorbed radiation leads to the knowledge of constituents of that compound. This is absorption spectroscopy.

ii) Emission: It is reverse of absorption. Atom or molecule comes to lower energy state by giving up excess energy in the form of photons of radiations of certain frequencies. The energy of sample decreases during emission. The measurement of emitted radiations as a function of concentration of the emitting species is emission spectroscopy.

 $\int G_{x} x = \frac{1}{2} \int G_{x} = \frac{1}{2} \int G_{x}$ (2) fourd the oxidet can number of charmium on the following p-F equertion bond length, 2.04, 9.04, 2.19 Similar attans but with different bind length eg PE-, (b) The central atom of the malecule many be bonded cut -72 EOS (20N . 62 ef cpued for sally travelled for eg. NO2, 503 el-(3. The conded atom of the muleenle is bandled with symmetry à the central atom of the malecule is supported by both, bend dissimilar atom of the malecule is supported by both, bend Bind is supported by the malecule is supported by both, bend Q. The contract extrem of the malecule is bonded wills bet "the different kind of electron paris. The following va dustated germeter due ta segulaive intercetrons is distant of acomeday i A molecule will have rare vagedler part of same typed bonds eg. d-Be-d, 0=c=0 etz (1). The condrad schem is borded to other adam by single wrallend. (I) . HALThe band lengths should be the same. sasetals bound (1) The centrat atom of the mideente is susseended by band מאשי ביא מגר ו כרוא׳ בצי ברי U. The control eston of the milearle is bonded to all similar D. A mole cult will have a reguler geometry when it satisfies Has. 1:12 contar geometri. Des d'Explain the application of visions frains to predict-E = 1 17117 Prover 12120 2001 + Clarles mod

101

.

Out of these three possibilities gastingement Ghown in C in uning both the 2015 of the fargened bippyarmeded in velves equational possition of the fargened bippyarmeded in velves Three probable gennedy of citiz. (b) -J mentes these is minime reputsion anoraget cleation Themselves gavand the centrol adom in such a Atu to VSEP Rhund, 550 pairs 'Should assange Expected genneter = taigoned bipgaemi dad. ampender = No.9 enterne + 2 = 5-Centred ellem + Ne. of love prime Sterie number = No.9 enterne + Ne. of love prime THE SINKER -> TO CI-F [JURE ONE 3 POUGEG BOURS Lewis Stauture of CIF3 molecule con be waitten au 1=3 36=21 ... Total=28. electrons. Jotal no. y valence electron are F.g. - 152,255, 3076 & Them have seven valence El. CIF3 molecule. Chlorine being less électronic confige Hos. HB3 type molecule with two lone pairs of dectrons Q.3. C. Explain the explication of VSEPR theory by predicting () ILI LULH II-W 25 '95180=mm. La 'FILOIDI mod

(') Draw Lewis dot structure a) NO -. $\begin{bmatrix} 0 & \vdots & N & \vdots & 0 & \vdots \end{bmatrix}^{-1} \begin{bmatrix} 2 \mod y \end{bmatrix}$ $b) \quad 0_{3}.$ ii] Limitations of VSEPR Theory (4 marks)] Effect of Jonic character. Compounds with Jonie character do not follow VSEPR Rules Rx Lizo. 2] Deviation in Bond ongles. NM3 (107) PM3 (93.2) H2 S Can not explained by VSEPR 3) Pi bonding & Lone pair of electrons. NCCM3 or PCSIM3)3 have pyramidal shucture But planor shucture of NCSIM33 can not be

4) Stereo chemical activity & Inactivity of lone pair XeF6 has 6 bond pairs and one lone pair But does not follow USEPR theory XeF6 has dislorted of shucture. [Any Two limitations with explanation].

Q3 B] $f = \frac{1}{2} \frac{1}$ Evalues $\Delta G^{\circ} = - n F \varepsilon^{\circ}$ E1=+0.771V. -1 xf x (+0.771) = -0.771 $E_{2}^{\circ} = -0.440v$ Fe²⁺ + 2e⁻ > Fecs) -2xFx(-0.440) = 0.880 Fe^{3†} + 3e⁻ → Fe(aq) (aq) $E_3 = r$

$$E_{3} = \frac{n_{1}E_{1} + n_{2}E_{2}}{(n_{1} + n_{2})} \qquad (1 \text{ mark})$$

$$= [x \ 0.771 + (2 \times (-0.440)) = -0.036 \text{ V})$$

$$= \frac{2 + 1}{2 + 1}$$

 $\Delta G^{\circ} = - nF \varepsilon^{\circ} = -3F \times (0.036) = + 0.109F$ (1 mark) $Fe^{3t} \xrightarrow{\xi_1^0 = +0.771V} Fe^{2t} \underbrace{\xi_2^0 = -0.440V}_{f_2} \xrightarrow{\xi_1^0 = -0.440V}_{f_2} \xrightarrow{\xi_1^0 = -0.440V}_{f_2}$ $Fe^{3t} \xrightarrow{f_2^0 = -0.440V}_{f_2} \xrightarrow{\xi_1^0 = -0.440V}_{f_2}$

&3B

] Role of Jodine as redox agent with suitable examples. Iodine is mild oxidizing agent. I2/J redox own has relatively low potential and ph dependent : J2/J redox reversibility reaction allows it to be used as reducing as well as oxidizing agent-All oxidizing agents with electrode potential greater than 0.54V can oxidize J to J2 Imark Oxidation Reaction of J 2J J_J + 2e Reduction Reaction of J2 $2S_{2}O_{3}^{2} + J_{2} \longrightarrow S_{4}O_{6}^{2} + 9J^{-}$ Two types of Redox Tiliations of J2 Jodometric Zbret explanation Z I mark-

of OIMFECID VS OIM (CE(IV) on addn of (a) 5 cm³ (b) 10.0 cm³ (c) 11.0 cm³ OIM (ECIV)

$$E^{\circ} = 1 + 4 + \sqrt{2} \cdot 0.771$$

$$Pt / Fe(n) Fe(n)$$

$$E^{\circ} pt / ce^{4t}, ce^{3t} = 1.44$$

$$\int When 5 cm^{3} of 0.M (e(n)) soln in added$$

$$Concn of Fe^{3} = \frac{5 \times 6.1}{15} = 0.0333$$

$$Loncn of Fe^{2} = 5 \times 0.1 = 0.0333$$

$$E_{Fe^{3t}/Fe^{2t}} = E_{Pt/Fe^{3t}Fe^{2t}}^{6} - \frac{0.05916}{n} \log \left[\frac{Fe^{2t}}{Fe^{3t}} \right]$$

$$= 0.7771 - 0.05916 \log \left[\frac{0.033}{0.033} \right]$$

$$= 0.7771V$$

(1 mark).

At
$$\mathcal{E}_{q}$$
 point neither analyte nor
tabant $\mathcal{E}_{i} = \mathbf{e}$ in $\mathcal{E}_{0} \mathcal{E}_{0}^{3\dagger} \mathcal{F}_{0}^{2} \mathcal{I}_{0}^{4} \mathcal{E}_{0}^{3\dagger}$
 $= \mathcal{O} \mathcal{F}_{1}^{2} \mathcal{F}_{1}^{2} \mathcal{F}_{0}^{2} \mathcal{I}_{0}^{4} \mathcal{E}_{0}^{3\dagger}$
 $= \mathcal{O} \mathcal{F}_{1}^{2} \mathcal{F}_{0}^{2} \mathcal{I}_{0}^{4} \mathcal{E}_{0}^{3\dagger}$
 $\mathcal{I}_{0}^{2} \mathcal{I}_{0}^{4} \mathcal{I}_{0}^{4\dagger} \mathcal{E}_{0}^{4\dagger} \mathcal{E}_{0}^{4} \mathcal{E}_{0}^{4} \mathcal{E}_{0}^{$

I marke for correct formula.

Q (I) IN 842000 program of all (II) 71:-(II) . IN 8420000 program of adam - (II) 71:-(II) . IN 6420000 prince odour - (II) [I] C. Maddy the dollowing. B. II - False. repos en mel . p. ket is certed -Energy versus oxidection state of a chamical speared · p - rof · — avoy grow adauf vore front ·g· · full - Usiun un (1) The pollorizing power of a cation to polloria ·q·sut way no puso Let willont band i's called woodwarde P and 139. 200 - 131. 200 - 17 11 - 1 - 100

sepularion feaces between them became equal. generating author 5-F bonds are equivalent, the Thus all the band angles are goe. In this lype of and other s- s bond is below the plane maps underst de contra de la contra de la contra colorne moto might present subput a · poptarvog . pairs obtained themselver in such or new that there is minimum sepulsion bet n. them and maximum stability of molecule netaled in Octohed , Acc. to VSEPP. There a six deater persons aroand the central entries six decition Lewis strugsto File Steric No 2 6+0=6. 1. e thue are beleaton and has 7 valence es. . . Tatal No = 6+(6×2) =48 There are 6'es in the valence shell. F(g) Electronic config-15,2535 Ans. Steptist Hype of molecule. Scie) has electronic config-15,2555 of E-5-F band angles in 5F6. (At. No. 5E16) S. C) Explain the application of view of view of for productions NA 2 40 - 12 J - r. ts bends away to an lone parts Hend the malgade her Due to love pair separation, the axial d-p bood

(3)

1A ix – b)
1A x – b)
1A xi – a)
1A xii - a)
1Biii – False

1C v – vii (Minimum torsional strain)

4A **i**

(5)

Cyclopropane is highly unstable where as cyclohexane is highly stable.

In case of cyclopropane the 3 carbon ring should have the shape of an equilateral triangle and hence, the angle between the bonds which form the ring should be 60° .

$$d = \frac{1}{2}(109^{\circ}28^{\circ} - \alpha)$$
$$d = \frac{1}{2}(109^{\circ}28^{\circ} - 60^{\circ})$$
$$d = 24^{\circ}44^{\circ}$$

In case of cyclohexane, Internal angle (α) is 120°.

$$d = \frac{1}{2}(109^{\circ}28^{\prime} - \alpha)$$
$$d = \frac{1}{2}(109^{\circ}28^{\prime} - 120^{\circ})$$
$$d = -5^{\circ}16^{\prime}$$

Therefore cyclohexane is highly stable.

4A ii

4A i

Aromaticity of furan :-



It has 2 conjugated double bonds i.e. 4π electrons. These double bonds are conjugated with the lone pair of electrons (i.e. 2 electrons) on the heteroatom ie, O - atom. Thus, total 6π electrons are involved in resonance.

 $4 n + 2 = 4 (1) + 2 = 6 \pi$ electrons.

Therefore furan is aromatic.

OR Boat Twist boat

(5)

Half chair

Order of stability:-

Chair > boat > twist - boat > half - chair

4A ii (3)

Antiaromaticity :-

Chair

The compounds which are cyclic, unsaturated with planar ring structures and continuous conjugated double bonds but which do not obey Huckel's rule of aromaticity, they generally have $4n \pi$ electrons where,

(3)

 $n = 1, 2 \dots$ are called anti aromatic compounds and the phenomenon is antiaromaticity.

Example :- Cyclobutadiene

 $\Box_{4 \pi \text{ electrons, } n = 1}$

The π electron energy of cyclobutadiene is higher than its open chain counter part. It contains $4 n \pi = 4 x 1 = 4 \pi$ electrons.

Therefore, it is anti aromatic.

Any other example of anti aromatic compound can also be given.

Q.4 B i

(4)

Deactivated aromatic rings :-

If electron withdrawing groups are attached to the aromatic ring, then electrons are taken away from the ring due to resonance and inductive effect. Hence, the electron density on the ring is reduced and it gets deactivated.

Examples :- NO₂, -CO-R, -CN etc. (anyone with resonating structures)



Resonating structures

4B ii

(4)

Ethyl from benzene –

When benzene is mixed with is ethyl chloride and a small amount of anhydrous $AlCl_3$, a vigorous reaction takes place to form is ethyl benzene.



It is Friedel Crafts Alkylation reaction.

OR

(4)

4B i $i \mapsto conc.H_{2}SO_{4} \longrightarrow i \mapsto H_{2}O$ Benzene Benzene sulphonic acid $i \mapsto so_{3} \mapsto i \mapsto so_{3} \mapsto so_{4} \mapsto so_{4}$

4B ii

(4)

Early Transition state:- In an exothermic reaction the transition state resembles reactants more – than products.

Eg. SN^2 reaction



Time

Late transition state:- In an endothermic reaction the transition state resembles products more than reactants. Eg. SN^1 reaction.







OR

4C i

(2)

Acylation of benzene :-

Acylium ion is the electrophile.



5 E

(5)

Nitration :- It is introduction of nitro group (- NO₂) in an aromatic ring system is called nitration.

Mechanism :- Nitration of benzene

1) Formation of electrophile :-



2) Attack of electrophile :-



The nitronium ion is the electrophile in nitration; it reacts with benzene to form a resonance-stabilized arenium ion.

3) Loss of proton:



5 F

(5)

Ortho, para - directing effects :-

Certain substituents direct the second substituent to the ortho and para positions simultaneously. This is called ortho, para–director.

For eg., when phenol is nitrated, the only products obtained are onitrophenol (53%) and p-nitrophenol (47%) and nor a trace of meta isomer is formed.

The subittuent – OH is said to have directed the - NO_2 group to ortho and para positions on the ring . – OH is called as ortho, para – director.

Some common ortho, para – directing groups are –Cl, -Br, -NH₂, -OH, -CH₃ etc.

Example -

