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**Q.1 A Select the correct option and complete the following statements**

- i) KOH is a strong electrolyte.
- ii) pOH is defined as the negative logarithm to the base 10 of the hydroxyl ions concentration expressed in  $\text{mol/dm}^3$ .
- 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  $1.0 \times 10^{-14}$ . – False

**C) Match the following columns**

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

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Q.2 A i) At 298 K, Calculate the pH of a solution which contains  $0.2 \text{ mol/dm}^3$  of sodium acetate and  $0.1 \text{ mol/dm}^3$  of acetic acid  $[(K_a)_{\text{acetic acid}} = 1.8 \times 10^{-5}]$  ---- 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

$$pH = pK_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} = 4.744 + \log_{10} [0.2/0.1] = 4.744 + \log 2 = 4.744 + 0.3010 = 5.045$$

**pH = 5.045**

ii) 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.  $[(K_b)_{\text{ammonium hydroxide}} = 1.8 \times 10^{-5}]$

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

$$pOH = pK_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

$$3.75 = 4.744 + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\log_{10} \frac{[\text{Salt}]}{[\text{Base}]} = -0.994$$

$$\frac{[\text{Salt}]}{[\text{Base}]} = \text{Antilog}(-0.994) = 0.1014$$

Ans:  $[\text{Salt}] : [\text{base}] = 0.1014 : 1$

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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 dm<sup>3</sup> 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  $2.48 \times 10^{-19}$  J. Calculate wavelength, frequency and wave number of this scattered radiation. ( $h = 6.626 \times 10^{-34}$  J.s,  $c = 3 \times 10^8$  m/s)

**Solution :** Energy (E) =  $hc / \lambda$

$$\text{Wavelength} = hc / \text{energy} = (6.626 \times 10^{-34} \times 3 \times 10^8) / (2.48 \times 10^{-19}) = 8.015 \times 10^{-7} \text{ m}$$

$$\text{Wave number} = 1 / \lambda = 1 / 8.015 \times 10^{-7} = 1.248 \times 10^6 \text{ m}^{-1}$$

$$\text{Frequency } (\nu) = c / \lambda = (3 \times 10^8) / (8.015 \times 10^{-7}) = 3.743 \times 10^{14} \text{ Hz}$$

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<br>(a:b:c) | Reciprocals<br>(1/a:1/b:1/c) | Multiplied by<br>L.C.M. | Miller indices |
|--------------------------|------------------------------|-------------------------|----------------|
| 1/2: ∞: 2                | 2: 0: 1/2                    | (2: 0: 1/2) × 2         | 4 : 0 : 1      |
| 3 : 4: 2                 | 1/3:1/4: 1/2                 | (1/3:1/4: 1/2) × 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  $h \nu$  where  $h$  = Plank's constant =  $6.625 \times 10^{-34}$  J.s and  $\nu$  = 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  $\Delta E = h \nu$  where  $\Delta E$  = Difference in energy between two quantized state

$h$  = Plank's constant =  $6.625 \times 10^{-34}$  J.s and  $\nu$  = frequency of radiation in Hz.

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- 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.

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**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  $K_a$  of the acid is given by

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = K_a \frac{[A^-]}{[HA]} \quad \text{----- (I)}$$

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

$$[H^+] = K_a \frac{[Acid]}{[Salt]}$$

Taking log of both sides and multiplying both sides by -1,

$$-\log_{10} [H^+] = -\log_{10} K_a + \log_{10} \frac{[Salt]}{[Acid]}$$

$$pH = pK_a + \log_{10} \frac{[Salt]}{[Acid]}$$

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.

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**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.**