विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचितः मानव धर्म प्रणेता

सद्गुरु श्री रणछोड़दासजी महाराज

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THE KEY

Fundamentals of Acids, Bases & Ionic Equilibrium

Acids & Bases

When dissolved in water, acids release H^+ ions, base release OH^- ions.

Arrhenius Theory

When dissolved in water, the substances which release

(i) H^+ ions are called acids (ii) OH^- ions are called bases

Bronsted & Lowry Concept

Acids are proton donors, bases are proton acceptors

Note that as per this definition, water is not necessarily the solvent.

When a substance is dissolved in water, it is said to react with water e.g.

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$; HCl donates H^+ to water, hence acid.

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$; NH_3 takes H^+ from water, hence base.

For the backward reaction, NH_4^+ donates H^+, hence it is an acid; OH^- accepts H^+, hence it is base.

NH_3 (base) & NH_4^+ (acid) from conjugate acid base pair.

Conjugate acid and bases

To get *conjugate acid* of a given species add H^+ to it. e.g. conjugate acid of N_2H_4 is $N_2H_5^+$.

To get *conjugate base* of any species subtract H^+ from it. e.g. Conjugate base of NH_3 is NH_2^-.

Note: Although Cl^- is conjugate base of HCl, it is not a base as an independent species. In fact, anions of all strong acid like Cl^-, NO_3^-, ClO_4^- etc. are neutral anions. Same is true for cations of strong bases like K^+, Na^+, Ba^{++} etc. When they are dissolved in water, they do not react with water (i.e. they do not undergo hydrolysis) and *these ions* do not cause any change in pH of water (others like CN^- do).

Some examples of :

<u>Basic Anions</u> : CH_3COO^-, OH^-, CN^- (Conjugate bases of weak acids)

<u>Acid Anions:</u> HSO_3^-, HS^- etc. Note that these ions are *amphoteric*, i.e. they can behave both as an acid and as a base. e.g. for $H_2PO_4^-$:

$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+$ (functioning as an acid)

$HS^- + H_2O \rightleftharpoons H_2S + OH^-$ (functioning as a base)

<u>Acid Cations</u> : NH_4^+, H_3O^+ etc.(Conjugate acids of weak bases)

Note : Acid anions are rare.

Lewis Concept : Acids are substances which accept a pair of electrons to form a coordinate bond and bases are the substances which donate a pair of electrons to form a coordinate bond.

e.g.

$$\begin{array}{c} H \\ | \\ H - N: \\ | \\ H \end{array} \quad + \quad \begin{array}{c} F \\ | \\ B - F \\ | \\ F \end{array} \quad \longrightarrow \quad \begin{array}{c} H \quad\;\; F \\ | \qquad\; | \\ H - N \rightarrow B - F \\ | \qquad\; | \\ H \quad\;\; F \end{array}$$

(Lewis base) (Lewis acid)

Important : $Ca + S \rightarrow Ca^{2+} + S^{2-}$ is not a Lewis acid–base reaction since dative bond is not formed.

Lewis Acids : As per Lewis concept, following species can acts as Lewis Acids :

(i) Molecules in which central atom has *incomplete octet.* (e.g. BF_3, $AlCl_3$ etc.)

(ii) Molecules which have a central atom with empty d– orbitals (e.g. SiX_4, GeX_4, PX_3, $TiCl_4$ etc.)

(iii) *Simple Cations:* Though all cations can be expected to be Lewis acids, Na^+, Ca^{++}, K^+ etc. show no tendency to accept electrons. However H^+, Ag^+ etc. act as Lewis acids.

(iv) Molecules having multiple bond between atoms of dissimilar electronegativity.

e.g. $CO_2, SO_2, SO_3 \longrightarrow \left(\underset{\text{Lewis acid}}{O=C=O} + \underset{\text{Lewis base}}{OH^-} \longrightarrow {}^{-}O-\underset{\underset{OH}{|}}{C}=O \text{ or } HCO_3^-\right)$

Lewis bases are typically :

(i) Neutral species having at least one lone pair of electrons.

e.g. $\ddot{N}H_2-\ddot{N}H_2,\ R-\ddot{\underset{\cdot\cdot}{O}}-H$

(ii) Negatively charged species (anions). e.g. CN^-, OH^-, Cl^- etc.

pH and pOH $\quad pH = -\log_{10}[H_3O^+]$, $\quad pOH = -\log_{10}[OH^-]$

Note : * pH of very dilute (~ 10^{-8}M or Lower) acids (or bases) is nearly 7 (not simply –log[acid] etc. due to ionization of water.

* pH of strong acids with concentration > 1M is never negative. It is zero only.
* At 25°C, if pH = 7, then solution is neutral, pH > 7 than solution is basic.

Autoprotolysis of water (or any solvent)

Autoprotolysis (or self–ionization) constant $(K_w) = [H_3O^+][OH^-]$

Hence, $pH + pOH = pK_w$ at all temperatures

Condition of neutrality $[H_3O^+] = [OH^-]$ (for water as solvent)

At 25°C, $K_W = 10^{-14}$. K_W increases with increase in temperature. Accordingly, the neutral point of water (pH = 7 at 25°C) also shifts to a value lower than 7 with increase in temperature.

Important: $K_W = 10^{-14}$ is a value at (i) 25°C (ii) for water only. If the temperature changes or if some other solvent is used, autoprotolysis constant will not be same.

Ionisation Constant

* For dissociation of weak acids (eg. HCN), $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$ the equilibrium constant expression is written as $K_a = \dfrac{[H_3O^+][CN^-]}{[HCN]}$

* For the Polyprotic acids (e.g. H_3PO_4), sucessive ionisation constants are denoted by K_1, K_2, K_3 etc. For H_3PO_4,

$$K_1 = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} \qquad K_2 = \frac{[H_3O^+][HPO_4^{2-}]}{[H_3PO_4^-]} \qquad K_3 = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

Similarly, K_b denotes basic dissociation constant for a base.

Also, $pK_a = -\log_{10}K_a$, $pK_b = -\log_{10}K_b$

Some Important Results: $[H^+]$ concentration of

<u>Case (i)</u> A weak acid in water

(a) if $\alpha = \sqrt{\dfrac{K_a}{C}}$ is < 0.1, then $[H^+] \approx \sqrt{K_a c_0}$.

(b) **General Expression :** $[H^+] = 0.5(-K_a + \sqrt{K_a^2 + 4K_a c_o})$

Similarly for a weak base, substitute $[OH^-]$ and K_b instead of $[H^+]$ and K_a respectively in these expressions.

<u>Case (ii)</u>(a) **A weak acid and a strong acid** $\quad [H^+]$ is entirely due to dissociation of strong acid

(b) **A weak base and a strong base** $[H^+]$ is entirely due to dissociation of strong base
Neglect the contribution of weak acid/base usually.
Condition for neglecting : If c_0 = concentration of strong acid, c_1 = concentration of weak acid then neglect the contribution of weak acid if $K_a \le 0.01\, c_0^2 / c_1$

Case (iii) Two (or more) weak acids

Proceed by the general method of applying two conditions
(i) of electroneutrality (ii) of equilibria.
The accurate treatement yields a cubic equation. Assuming that acids dissociate to a negligible extent [i.e. $c_0 - x \approx c_0$] $[H^+] = (K_1c_1 + K_2c_2 + ...+ K_w)^{1/2}$

Case (iv) When dissociation of water becomes significant:

Dissociation of water contributes significantly to $[H^+]$ or $[OH^-]$ only when for
(i) strong acids (or bases) : $10^{-8}M < c_0 < 10^{-6}M$. Neglecting ionisation of water at $10^{-6}M$ causes 1% error (approvable). Below $10^{-8}M$, contribution of acid (or base) can be neglected and pH can be taken to be practically 7.
Weak acids (or bases) : When $K_ac_0 < 10^{-12}$, then consider dissociation of water as well.

HYDROLYSIS

* ***Salts of strong acids and strong bases*** do not undergo hydrolysis.
* ***Salts of a strong acids and weak bases*** give an acidic solution. e.g. NH_4Cl when dissolved, it dissociates to give NH_4^+ ions and $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$.
$K_h = [NH_3][H_3O^+] / [NH_4^+] = K_w/K_b$ of conjugate base of NH_4^+
Important! In general : K_a(of an acid)xK_b(of its conjugate base) = K_w
If the degree of hydrolysis(h) is small (<<1), $h = \sqrt{K_hc_0}$.

Otherwise $h = \dfrac{-K_h + \sqrt{K_h^2 + 4K_hc_0}}{2c_0}$, $[H^+] = c_0h$

* ***Salts of strong base and weak acid*** give a basic solution (pH>7) when dissolved in water, e.g. NaCN, $CN^- + H_2O \rightleftharpoons HCN + OH^-$ $[OH^-] = c_0h$, $h = \sqrt{K_hc_0}$

* ***Salts of weak base and weak acid***
Assuming degree of hydrolysis to be same for the both the ions,
$K_h = K_w / (K_a.K_b)$, $[H^+] = [K_a\, K_w/K_b]^{1/2}$
Note: Exact treatment of this case is difficult to solve. So use this assumption in general cases.
Also, degree of anion or cation will be much higher in the case of a salt of weak acid and weak base. This is because each of them gets hydrolysed, producing H^+ and OH^- ions. These ions combine to form water and the hydrolysis equilibrium is shifted in the forward direaction.
Buffer Solutions are the solutions whose pH does not change significantly on adding a small quantity of strong base or on little dilution.

These are typically made by mixing a weak acid (or base) with its conjugate base (or acid). e.g. CH_3COOH with
CH_3COONa, NH_3(aq) with NH_4Cl etc.

If K_a for acid (or K_b for base) is not too high, we may write :
Henderson's Equation
$pH = pK_a + \log \{[salt] / [acid]\}$ for weak acid with its conjugate base.
or $pOH = pK_b + \log \{[salt] / [base]\}$ for weak base with its conjugate acid.

Important : For good buffer capacity, [salt] : [acid ratios should be as close to one as possible. In such a case, $pH = pK_a$. (This also is the case at midpoint of titration)
Buffer capacity = (no. of moles of acid (or base) added to 1L) / (change in pH)

Indicators. Indicator is a substance which indicates the point of equivalence in a titration by undergoing a change in its colour. They are weak acids or weak bases.

Theory of Indicators. The ionized and unionized forms of indicators have different colours. If 90 % or more of a particular form (ionised or unionised) is present, then its colour can be distinclty seen.In general, for an indicator which is weak acid, $HIn \rightleftharpoons H^+ + In^-$, the ratio of ionized to unionized form can be determined from

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

So, for detectable colour change, $pH = pK_a \pm 1$

This roughly gives the range of indicators. Ranges for some popular indicators are

Table 1 : Indicators

Indicators	pH range	Colour	
		acid medium	basic medium
Methyl Orange	3.1-4.4	pink	yellow
Methyl red	4.2-6.3	red	yellow
Litmus	5.5-7.5	red	blue
Phenol red	6.8-8.4	yellow	red
Phenolphathlene	8.3-10	colourless	pink
Thymol blue	1.2-2.8	red	yello

Equivalence point. The point at which exactly equivalent amounts of acid and base have been mixed.

Acid Base Titration. For choosing a suitable indicator titration curves are of great help. In a titration curve, change in pH is plotted against the volume of alkali to a given acid. Four cases arise.

(a) **Strong acid vs strong base.** The curve is almost vertical over the pH range 3.5-10. This abrupt change corresponds to equivalence point. Any indicator suitable.

(b) **Weak acid vs strong base.** Final solution is basic 9 at equivalence point. Vertical region (not so sharp) lies in pH range 6.5-10. So, phenolphathlene is suitable.

(c) **Strong acid vs weak base.** Final solution acidic. Vertical point in pH range 3.8-7.2. Methyl red or methyl orange suitable.

(d) **Weak acid vs weak base.** No sharp change in pH. No suitable indicator.

Note : at midpoint of titration, $pH = pK_a$, thus by pH measurements, K_a for weak acids (or K_b for weak bases) can be determined.

Polyprotic acids and bases. Usually K_2, K_3 etc. can be safely neglected and only K_1 plays a significant role.

Solubility product (K_{sp}). For sparingly soluble salts (eg. $Ag_2C_2O_4$) an equilibrium which exists is

$$Ag_2C_2O_4 \rightleftharpoons 2Ag^+ (aq.)\ C_2O_4^{2-} (aq.)$$

$$\text{Then } K_{sp} = [Ag^+]^2[C_2O_4^{2-}]$$

Precipitation. Whenever the product of concentrations (raised to appropriate power) exceeds the solubility product, precipitation occurs.

Common ion effects. Suppression of dissociation by adding an ion common with dissociation products. e.g. Ag^+ or $C_2O_4^{2-}$ in the above example.

Simultaneous solubility. While solving these problems, go as per general method i.e.

(i) First apply condition of electroneutrality and

(ii) Apply the equilibria conditions.

THE ATLAS

The concept of ionic equilibria as equilibria involving ions in solution

(i) Arrhenius theory of electrolytes.
(ii) Ostwards dilution law for weak electrolyte $K_a = \left(\frac{\alpha^2}{1-\alpha}\right)\left(\frac{1}{V}\right)$
(iii) Acid & Bases
(a) Arrhenius H^+/OH^- theory.
(b) Bronsted lowery - protonic concept.
(c) Lewis concept - electronic concept of acids and bases.

Some basic concept

pH scale : $pH = -\log[H^+]$.
(i) Water as amphiprotic solvent.
(ii) Autoionization of water : $K_w = [H^+][OH^-]$.
(iii) $K_a[H_2O] = K_w/[H_2O]$
(iv) Change in pH of neutral H_2O with temperature.

Homogenons Ionic equilibria

(i) Acid/ base equilibrium.
(a) Strong acid/ base-$[H]^+ = \frac{c}{2} + \sqrt{\frac{c^2 + K_w}{4}}$;c=conc. of (acid)
(b) pH due to polyprotic weak acids
(c) Weak monobasic acid/base $[H]^+ = \sqrt{K_a.c}$ (if $\alpha < 0.1$)
(d) Mixture of S.A./W.A.
(e) Mixture of W.A./ W.A. $H^+ = \sqrt{K_1c_1 + K_2c_2}$
(f) Buffer solutions : $pH = pK_a + \log\left(\frac{\text{salt}}{\text{acid}}\right)$

$pOH = pK_b + \log\left(\frac{\text{salt}}{\text{base}}\right)$

(g) Salt hydrolysis – (W.A./S.B) $pH = \frac{1}{2}(pK_w + pK_a + \log c)$

(W.B/S.A.) $pH = \frac{1}{2}(pK_w - pK_b - \log c)$

(W.A./W.B.) $pH = \frac{1}{2}(pK_w + pK_a - pK_b)$

Heterogenons equilibria

Solubility of sparingly soluble salt's
$(AB, AB_2, A_xB_y) K_{sp} = (S^{x+y})X^xY^y$
(i) Effect of pH on solubility.
(ii) Simultaneous solubility.

Application of both heterogenous and homogenous equilibrium

(i) Extent of hydrolysis in buffer solution.
(ii) Change in solubility due to complex formation.
(iii) Solubility and hydrolysis.

GLOSSARY

Amphoteric substance. A molecule which can act both as an acid and as a base.

Autoprotolysis constant. The equilibrium constant for the reaction in which one solvent molecule loses a proton to another, as $2H_2O \rightleftharpoons H_3O^+ + OH^-$.

Amphiprotic solvent. A solvent which possesses both acidic and basic properties.

Aprotic solvent. A solvent which is neither appreciably acidic or basic.

Bronsted acid. A substance which furnishes a proton.

Bronsted base. A substance which accepts a proton.

Buffer capacity. A measure of the effectiveness of a buffer in resisting changes in pH; the capacity is greater the concentrations of the conjugate acid-base pair.

Buffer solution. A solution which contains a conjugated acid-base pair. Such a solution resists large changes in pH when H_3O^+ or OH^- ions are added and when the solution is diluted.

Charge-balance equation. The equation expressing the electroneutrality principle; i.e., the total concentration of positive charge must equal the total concentration of negative charge.

Common-ion effect. The effect produced by an ion, say from a salt, which is the same ion produced by the dissociation of a weak electrolyte. The "common" ion shifts the dissociation equilibrium in accordance with LeChatelier's principle.

Central metal atom. A cation which accepts electrons from a ligand to form a complex ion.

Conjugate acid-base pair. An acid-base pair which differ only by a proton, as HCl and Cl^-.

Diprotic acid. An acid which furnishes two protons.

Electrolyte. A compound which produces positive and negative ions in solution. Strong electrolytes are completely dissociated, whereas weak electrolytes are only partially dissociated.

Hydrolysis. An acid-base reaction of a cation or anion with water.

Isoelectric point. The pH at which there is an exact balance of positive and negative charge on an amino acid.

Indicator. A visual acid-base indicator is a weak organic acid or base which shows different colors in the molecular and ionic forms.

Ligand. An anion or neutral molecule which forms a complex ion with a cation by donating one or more pairs of electrons.

Nonelectrolyte. A substance which does not dissociate into ions in solution.

pH. The negative logarithm of the hydrogen ion concentration.

pK. The negative logarithm of an equilibrium constant.

Polyprotic acid. An acid which furnishes two or more protons.

Range of an indicator. That portion of the pH scale over which an indicator changes color, roughly the pK of the indicator ± 1 unit.

Salt. The product other than water which is formed when an acid reacts with a base; usually an ion solid.

Simultaneous equilibria. Equilibria established in the same solution in which one molecule or ions is a participant in more than one of the equilibria.

Solubility product constant, K_{sp}. The constant for the equilibrium established between a slightly soluble salt and its ions in solution.

Stability constant. The equilibrium constant for a reaction in which a complex is formed. Also called a formation constant.

EXERCISE I

IONIZATION CONSTANTS AND pH

Q.1.1 Calculate

(i) K_a for H_2O ($K_w = 10^{-14}$)

(ii) K_b for $B(OH)_4^-$, K_a $(B(OH)_3) = 6 \times 10^{-10}$

(iii) K_a for HCN, K_b $(CN^-) = 2.5 \times 10^{-5}$

Q.1.2 Calculate the ratio of degree of dissociation (α_2/α_1) when 1 M acetic acid solution is diluted to $\frac{1}{100}$ times. [Given K_a=1.8×10^{-5}]

Q.1.3 Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids.[Given $K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$; $K_{a(HCN)} = 6.2 \times 10^{-10}$]

Q.1.4 Calculate :

(a) K_a for a monobasic acid whose 0.10 M solution has pH of 4.50.

(b) K_b for a monoacidic base whose 0.10 M solution has a pH of 10.50.

Q.1.5 Calculate pH of following solutions :

(a) 0.1 M HCl

(b) 0.1 M H_2SO_4 (50 ml) + 0.4 M HCl 50 (ml)

(c) 0.1 M CH_3COOH (K_a= 1.8×10^{-5})

(d) 0.1 M NH_4OH (K_b= 1.8×10^{-5})

(e) 10^{-8} M HCl

(f) 10^{-10} M NaOH

(g) 10^{-6} M CH_3COOH

(h) 10^{-8} M CH_3COOH

(i) 0.1 M HA + 0.1 M HB [K_a (HA) = 2×10^{-5} ; K_a (HB) = 4×10^{-5}]

(j) Decimolar solution of Baryta ($Ba(OH)_2$), diluted 100 times.

(k) 10^{-3} mole of KOH dissolved in 100 L of water.

(l) 0.5 M HCl (25 ml) + 0.5 M NaOH (10 ml) + 40 ml H_2O

(m) equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution

Q.1.6 The value of K_w at the physiological temperature (37°C) is 2.56×10^{-14}. What is the pH at the neutral point of water at this temperature, where there are equal number of H^+ and OH^-?

Q.1.7 Calculate the number of H^+ present in one ml of solution whose pH is 13.

Q.1.8 Calculate change in concentration of H^+ ion in one litre of water, when temperature changes from 298 K to 310 K. Given $K_w(298) = 10^{-14}$ K_w $(310) = 2.56 \times 10^{-14}$.

Q.1.9

(i) K_w for H_2O is 9.62×10^{-14} at 60°C. What is pH of water at 60°C.

(ii) What is the nature of solution at 60°C whose

(a) pH = 6.7 (b) pH = 6.35

Q.1.10 pH of a dilute solution of HCl is 6.95. Calculate molarity of HCl solution.

Q.1.11 The pH of aqueous solution of ammonia is 11.5. Find molarity of solution. K_b $(NH_4OH) = 1.8 \times 10^{-5}$.

Q.1.12 The solution of weak monoprotic acid which is 0.01 M has pH = 3. Calculate K_a of weak acid.

Q.1.13 Boric acid is a weak monobasic acid. It ionizes in water as

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ : K_a = 5.9 \times 10^{-10}$$

Calculate pH of 0.3 M boric acid.

Q.1.14 Calculate $[H^+]$ and $[CHCl_2COO^-]$ in a solution that is 0.01 M in HCl and 0.01 M in $CHCl_2COOH$. Take ($K_a = 2.55 \times 10^{-2}$).

Q.1.15 Calculate the percent error in the $[H_3O^+]$ concentration made by neglecting the ionization of water in a 10^{-6}M NaOH solution.

Q.1.16 Calculate $[H^+]$, $[CH_3COO^-]$ and $[C_7H_5O_2^-]$ in a solution that is 0.02 M in acetic acid and 0.01M in benzoic acid. K_a(acetic) = 1.8×10^{-5}, K_a (benzoic) = 6.4×10^{-5}.

Q.1.17 At 25°C, the dissociation constant of HCN and HF are 4×10^{-10} and 6.7×10^{-4}. Calculate the pH of a mixture of 0.1 M HF and 0.1 M HCN.

POLYPROTIC ACIDS & BASES

Q.2.1 Determine the $[S^{2-}]$ in a saturated (0.1M) H_2S solution to which enough HCl has been added to produce a $[H^+]$ of 2×10^{-4}. $K_1 = 10^{-7}$, $K_2 = 10^{-14}$.

Q.2.2 Calculate $[H^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ in a 0.01M solution of H_3PO_4.
Take $K_1 = 7.225 \times 10^{-3}$, $K_2 = 6.8 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

Q.2.3 Calculate the pH of a 0.1M solution of $H_2NCH_2CH_2NH_2$; ethylenediamine (en). Determine the en H_2^{2+}. Concentration in the solution. K_{b_1} and K_{b_2} values of ethylenediamine are 8.5×10^{-5} and 7.1×10^{-8} respectively.

Q.2.4 What are the concentrations of H^+, HSO_4^-, SO_4^{2-} and H_2SO_4 in a 0.20 M solution of sulphuric acid ?

Given : $H_2SO_4 \longrightarrow H^+ + HSO_4^-$; strong

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$; $K_2 = 1.3 \times 10^{-2}$ M

Q.2.5 What are the concentration of H^+, $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$ in a 0.1 M solution of oxalic acid ? [$K_1 = 5.9 \times 10^{-2}$ M and $K_2 = 6.4 \times 10^{-5}$ M]

Q.2.6 Nicotine, $C_{10}H_{14}N_2$, has two basic nitrogen atoms and both can react with water to give a basic solution

$Nic\ (aq) + H_2O\ (l) \rightleftharpoons NicH^+\ (aq) + OH^-\ (aq)$

$NicH^+\ (aq) + H_2O\ (l) \rightleftharpoons NicH_2^{2+}\ (aq) + OH^-\ (aq)$

K_{b1} is 7×10^{-7} and K_{b2} is 1.1×10^{-10}. Calculate the approximate pH of a 0.020 M solution.

Q.2.7 Ethylenediamine, $H_2N{-}C_2H_4{-}NH_2$, can interact with water in two steps, giving OH^- in each step. Calculate the concentration of OH^- and $[H_3N{-}C_2H_4{-}NH_3]^{2+}$ in a 0.15 M aqueous solution of the amine. $K_1 = 8.5 \times 10^{-5}$, $K_2 = 2.7 \times 10^{-8}$ for the base.

BUFFER SOLUTION

Q.3.1 Determine $[OH^-]$ of a 0.050 M solution of ammonia to which has been added sufficient NH_4Cl to make the total $[NH_4^+]$ equal to 0.100.[$K_{b(NH_3)} = 1.8 \times 10^{-5}$]

Q.3.2 Calculate the pH of a solution prepared by mixing 50.0 mL of 0.200 M $HC_2H_3O_2$ and 50.0 mL of 0.100 M NaOH.[$K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$]

Q.3.3 A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x.

Q.3.4 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, calculate pH.

Q.3.5
(a) Determine the pH of a 0.2 M solution of pyridine C_5H_5N . $K_b = 1.5 \times 10^{-9}$
(b) Predict the effect of addition of pyridinium ion $C_5H_5NH^+$ on the position of the equilibrium. Will the pH be raised or lowered ?
(c) Calculate the pH of 1.0 L of 0.10 M pyridine solution to which 0.3 mol of pyridinium chloride $C_5H_5NH^+Cl$, has been added, assuming no change in volume.

Q.3.6 Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M NH_3 . [K_b $(NH_3) = 1.8 \times 10^{-5}$]

Q.3.7 Calculate the pH of a solution made by mixing 50.0 ml of 0.2M NH_4Cl & 75.0 ml of 0.1 M NaOH. [K_b $(NH_3) = 1.8 \times 10^{-5}$]

Q.3.8 A buffer solution was prepared by dissolving 0.02 mol propionic acid & 0.015 mol sodium propionate in enough water to make 1.00 L of solution .(K_a for propionic acid is 1.34×10^{-5})
(a) What is the pH of the buffer?
(b) What would be the pH if 1.0×10^{-5} mol HCl were added to 10 ml of the buffer ?
(c) What would be the pH if 1.0×10^{-5} mol NaOH were added to 10 ml of the buffer.
(d) Also report the percent change in pH of original buffer in cases (b) and (c).

Q.3.9 A solution was made up to be 0.01 M in chloroacetic acid, $ClCH_2COOH$ and also 0.002 M in sodium chloroacetate $ClCH_2COONa$. What is [H^+] in the solution ? $K_a = 1.5 \times 10^{-3}$.

INDICATORS

Q.4.1 A certain solution has a hydrogen ion concentration 4×10^{-3} M. For the indicator thymol blue, pH is 2.0 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with $[H^+] = 4 \times 10^{-3}$ M.

Q.4.2 At what pH does an indicator change colour if the indicator is a weak acid with $K_{ind} = 4 \times 10^{-4}$. For which one(s) of the following neutralizations would the indicator be useful ? Explain.
(a) NaOH + CH_3COOH (b) HCl + NH_3 (c) HCl + NaOH

Q.4.3 What indicator should be used for the titration of 0.10 M KH_2BO_3 with 0.10 M HCl ? K_a $(H_3BO_3) = 7.2 \times 10^{-10}$.

Q.4.4 Bromophenol blue is an indicator with a K_a value of 6×10^{-5} . What % of this indicator is in its basic form at a pH of 5 ?

Q.4.5 An acid base indicator has a K_a of 3×10^{-5}. The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75 % blue?

HYDROLYSIS

Q.5.1 What is the OH^- concentration of a 0.08 M solution of CH_3COONa. [$K_a(CH_3COOH)=1.8 \times 10^{-5}$]

Q.5.2 Calculate the pH of a 2.0 M solution of NH_4Cl. [K_b $(NH_3) = 1.8 \times 10^{-5}$]

Q.5.3 0.25 M solution of pyridinium chloride $C_5H_6N^+Cl^-$ was found to have a pH of 2.699. What is K_b for pyridine, C_5H_5N ?

Q.5.4 Calculate the extent of hydrolysis & the pH of 0.02 M CH_3COONH_4.
[K_b $(NH_3)= 1.8 \times 10^{-5}$, $K_a(CH_3COOH)=1.8 \times 10^{-5}$]

Q.5.5 Calculate the percent hydrolysis in a 0.06 M solution of KCN. [$K_a(HCN) = 6 \times 10^{-10}$]

Q.5.6 Calculate the extent of hydrolysis of 0.005 M K_2CrO_4. [$K_2 = 3.1 \times 10^{-7}$ for H_2CrO_4]
(It is essentially strong for first ionization).

Q.5.7 Calculate the percent hydrolysis in a 0.0100 M solution of KCN.($K_a = 6.2 \times 10^{-10}$)

Q.5.8 A 0.010 M solution of $PuO_2(NO_3)_2$ was found to have a pH of 4.0. What is the hydrolysis constant, K_h, for PuO_2^{2+} ,and what is K_b for PuO_2OH^+ ?

Q.5.9 Calculate the pH of 1.0×10^{-3} M sodium phenolate, $NaOC_6H_5$. K_a for HOC_6H_5 is 1.05×10^{-10}.

Q.5.10 What is the pH of 0.1M $NaHCO_3$? $K_1 = 4.5 \times 10^{-7}$, $K_2 = 4.5 \times 10^{-11}$ for carbonic acids.

Q.5.11 Calculate pH of 0.05M potassium hydrogen phthalate, $KHC_8H_4O_4$.

$$H_2C_8H_4O_4 + H_2O \rightleftharpoons H_3O^+ + HC_8H_4O_4^- \qquad pK_1 = 2.94$$

$$HC_8H_4O_4^- + H_2O \rightleftharpoons H_3O^+ + C_8H_4O_4^{2-} \qquad pK_2 = 5.44$$

Q.5.12 Calculate OH^- concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for the acid = 1.9×10^{-5}.

Q.5.13 The acid ionization (hydrolysis) constant of Zn^{2+} is 1.0×10^{-9}
(a) Calculate the pH of a 0.001 M solution of $ZnCl_2$
(b) What is the basic dissociation constant of $Zn(OH)^+$?

ACID BASE REACTIONS & TITRATIONS

Q.6.1 Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10M acetic acid, CH_3COOH, with 22.0 mL of 0.10 M NaOH.

Q.6.2 Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH_3 with 0.40M HCl.

Q.6.3 In the titration of a solution of a weak acid HX with NaOH, the pH is 5.8 after 10.0 mL of NaOH solution has been added and 6.402 after 20.0 mL of NaOH has been added. What is the ionization constant of HX?

Q.6.4 The equivalent point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10M NaOH solution has been added. The pH of the solution is 5.75 after the addition of 20.0 mL of NaOH solution. What is the dissociation constant of the acid?

Q.6.5 Phenol, C_6H_5OH, is a weak organic acid that has many uses, and more than 3 million ton are produced annually around the world. Assume you dissolve 0.515 g of the compound in exactly 100mL of water and then titrate the resulting solution with 0.123M NaOH.
$C_6H_5OH\,(aq) + OH^-\,(aq) \rightarrow C_6H_5O^-\,(aq) + H_2O(l)$
What are the concentrations of all of the following ions at the equivalence point: Na^+, H_3O^+, OH^- and $C_6H_5O^-$? What is the pH of the solution ? [K_a (phenol) = 1.3×10^{-10}]

Q.6.6 A weak base (50.0mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point.

Q.6.7 A weak acid (50.0mL) was titrated with 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate K_a of the acid and pH at the equivalence point.

Q.6.8 CH_3COOH (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml 20 ml, 25 ml, 40 ml, 50 ml of NaOH. K_a of CH_3COOH is 2×10^{-5}.

SOLUBILITY & SOLUBILITY PRODUCT'S

Q.7.1 The values of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18}. Which salt is more soluble? Explain your answer fully.

Q.7.2 The solubility of $PbSO_4$ water is 0.038 g/L. Calculate the solubility product constant of $PbSO_4$.

Q.7.3 Calculate the solubility of $Mg(OH)_2$ in water. $K_{sp} = 1.2 \times 10^{-11}$.

Q.7.4 How many mol CuI ($K_{sp} = 5 \times 10^{-12}$) will dissolve in 1.0 L of 0.10 M NaI solution ?

Q.7.5 A solution of saturated CaF_2 is found to contain 4.1×10^{-4} M fluoride ion. Calculate the K_{sp} of CaF_2. Neglect hydrolysis.

Q.7.6 The solubility of ML_2 (formula weight, 60 g/mol) in water is 2.4×10^{-5} g/100 mL solution. Calculate the solubility product constant for ML_2.

Q.7.7 What is the solubility (in mol/L) of $Fe(OH)_3$ in a solution of pH = 8.0 ? [K_{sp} for $Fe(OH)_3 = 1.0 \times 10^{-36}$]

Q.7.8 The solubility of Ag_2CrO_4 in water is 0.044 g/L. Determine the solubility product constant.

Q.7.9 Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. For A_2X_3, [$K_{sp} = 1.1 \times 10^{-23}$]

Q.7.10 Determine the solubility of AgCl in 0.1 M $BaCl_2$. [K_{sp} for AgCl = 1×10^{-10}]

Q.7.11 What mass of Pb^{2+} ion is left in solution when 50.0 mL of 0.20M $Pb(NO_3)_2$ is added to 50.0 mL of 1.5 M NaCl ?[Given K_{sp} for $PbCl_2 = 1.7 \times 10^{-4}$]

Q.7.12 A solution has a Mg^{2+} concentration of 0.0010 mol/L. Will $Mg(OH)_2$ precipitate if the OH^- concentration of the solution is [$K_{sp} = 1.2 \times 10^{-11}$]

(a) 10^{-5} mol/L (b) 10^{-3} mol/L ?

Q.7.13 Calculate solubility of PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) in water at 25°, which is 90% dissociated.

Q.7.14 Calculate solubility of AgCN ($K_{sp} = 4 \times 10^{-16}$) in a buffer solution of PH = 3.

SIMULTANEOUS SOLUBILITY

Q.8.1 Calculate the Simultaneous solubility of AgSCN and AgBr. K_{sp} (AgSCN) = 1.1×10^{-12}, K_{sp}(AgBr) = 5×10^{-13}.

Q.8.2 Calculate F^- in a solution saturated with respect of both MgF_2 and SrF_2. $K_{sp}(MgF_2) = 9.5 \times 10^{-9}$, $K_{sp}(SrF_2) = 4 \times 10^{-9}$.

Q.8.3 Equal volumes of 0.02M $AgNO_3$ and 0.02M HCN were mixed. Calculate [Ag^+] at equilibrium . Take K_a(HCN) = 9×10^{-10}, K_{sp} (AgCN) = 4×10^{-16}.

COMPLEXATION EQUILIBRIA

Q.9.1 Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.010 mol AgCl in 100 L solution. [$K_f(AgCl_2^-) = 3 \times 10^5$, K_{sp} = (AgCl) = 1×10^{-10}]

Q.9.2 A recent investigation of the complexation of SCN^- with Fe^{3+} led of 130, 16, and 1.0 for K_1, K_2, and K_3, respectively. What is the overall formation constant of $Fe(SCN)_3$ from its component ions, and what is the dissociation constant of $Fe(SCN)_3$ into its simplest ions on the basis of these data ?

Q.9.3 How much AgBr could dissolve in 1.0 L of 0.40 M NH_3 ? Assume that $Ag(NH_3)_2^+$ is the only complex formed. [$K_f(Ag(NH_3)_2^+) = 1 \times 10^8$; K_{sp} (AgBr) = 5×10^{-13}]

PROFICIENCY TEST

Q.1 True / False. When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralization point, $pH = \frac{1}{2} pK_a$.

Q.2 True / False. A solution of sodium acetate and ammonium acetate can act as a buffer.

Q.3 True / False. If the solubility of the salt $Li_3Na_3(AlF_6)_2$ is x, then its solubility product would be 2916 x^8.

Q.4 True / False. A buffer has maximum buffer capacity when the ratio of salt to acid is 10.

Q.5 True / False. In the presence of a common ion (incapable of froming complex ion), the solubility of salt decreases.

Q.6 In a mixture of waek acid and its salt, the ratio of concentration of salt to acid is increased ten fold. The pH of the solution would __________ by __________ unit.

Q.7 The solubilty of CH_3COOAg in water considering hydrolysis of CH_3COO^- ions would be ________ than that ignoring the hydrolysis.

Q.8 From an equimolar solution of Cl^- and Br^- ions, the addition of Ag^+ will selectively precipitates _____ (K_{sp} of AgCl & AgBr are 1×10^{-10} & 1×10^{-13} respectively).

Q.9 The solubility of AgCl in NH_3 is ______ than the solubility in pure water because of complex ion, $[Ag(NH_3)_2]^+$ formation.

Q.10 The hydrolytic constant K_h for the hydrolytic equilibrium

$$H_2PO_4^- + H_2O \longrightarrow H_3PO_4 + OH^- \text{ is } 1.4 \times 10^{-12}$$

What is the value of ionization constant for the $H_3PO_4 + H_2O \longrightarrow H_2PO_4^- + H_3O^+$?

Q.11 Given the equilibrium constants

$$HgCl^+ + Cl^- \rightleftharpoons HgCl_2 \qquad ; K_1 = 3 \times 10^6$$

$$HgCl_2 + Cl^- \rightleftharpoons HgCl_3^- \qquad ; K_2 = 8.9$$

The equilibrium constant for the dispropotionation equilibrium.

$$2HgCl_2 \rightleftharpoons HgCl^+ + HgCl_3^- \text{ is}$$

Q.12 Under which set of conditions is the ionic product of water, K_w, constant at a given temperature in aqueous system?

Q.13 If the salts M_2X, QY_2 and PZ_3 have same solubilities (<<<1), their K_{sp} values are related as _____.

Q.14 K_a for an acid HA is 1×10^{-6}. K_b for A^- would be ___________.

Q.15 An aqueous solution of K_2SO_4 has pH nearly equal to ________.

Q.16 The pH of a solution which is 0.1 M in sodium acetate and 0.01 M in acetic acid (pK_a = 4.74) would be _______.

Q.17 The conjugate acid of sulphate (SO_4^{2-}) is ____________.

Q.18 The value of K_w _______ with increase in temperature.

Q.19 AgCl is _______ soluble in aqueous sodium chloride solution than in pure water.

Q.20 The buffer HCOOH / HCOONa will have pH _________ than 7.

Q.21 In the reaction $I_2 + I^- \longrightarrow I_3^-$, I_2 acts as __________.

Q.22 An equimolar solution of $NaNO_2$ and HNO_2 can act as a ________ solution.

Q.23 Larger the value of pK_a, _________ is the acid.

Q.24 An aqueous solution of potash alum is ______ in nature.

Q.25 Salts of strong acids and weak bases undergo __________ hydrolysis.

Q.26 For salts of weak acid with weak bases, degree of hydrolysis is _______ of concentration of the salt in solution.

BEWARE OF SNAKES

1. ***General Mistake :*** pH of a neutral water solution is always equal to 7.

Explanation : pH of neutral water depend on temperature. Since pH (neutral point) = $\frac{pK_w}{2}$; pK_w decreases with temperature hence pH of neutral solution.

2. ***General Mistake :*** If a solution is diluted half times pH of solution becomes double.
Explanation : Infact pH increases by 0.3010 unit. If it is diluted x times pH increases by log x.
e.g. If solution is diluted 10 times pH increases by $\log_{10}10 = 1$ unit.

3. ***General Mistake :*** For calculation of pH of 10^{-6} M CH_3COOH the formula $(H^+) = \sqrt{K_a c}$ will give

$$pH = -\log\left(\sqrt{1.8\times10^{-5}\times10^{-6}}\right) = 5.37.$$

Explanation : 5.37 is incorrect answer. pH should be calculated by taking $\alpha = \frac{-K_a + \sqrt{K_a^2 + 4K_a c}}{2c}$

4. ***General Mistake :*** If 10^3 mole CH_3COONa and 1 mole CH_3COOH is added in 10^4 litres water the pH of resulting solution is equal to $pH = pK_a + \log\frac{10^3}{1} = 7.74$.

Explanation : 7.74 is incorrect answer. The CH_3COOH concentration is too low to be taken as constituent of buffer solution. Use salt hydrolysis formula instead to calculate the pH.

5. ***General Mistake :*** The equilibrium concentration of anion and cation of a sparingly soluble salt (A_2C_3) are a and c moles lit^{-1} respectively. The solubility product is $(2a)^2(3c)^3 = K_{sp}$
Explanation : $K_{sp} = a^2c^3$.

6. ***General Mistake :*** pH of 10^{-8} M HCl is equal to 8.
Explaination **:** pH = 8 means basic solution. Contribution of water can not be neglected in this case.

7. ***General Mistake :*** If NaOH is added to NH_4Cl so that NaOH is limiting, the resulting solution is containing some remaining conc. of NH_4Cl. Now use salt hydrolysis condition to calculate pH of solution.
Explanation : The addition of NaOH in NH_4Cl results in a basic buffer solution.

8. ***General Mistake :*** Do not use the K_1K_2 form of equation unless you have an independent method of calculating $[H^+]$ or $[S^{2-}]$
Explanation : Determine the $[S^{2-}]$ in a saturated H_2S solution to which enough HCl has been added to produce a $[H^+]$ of 2×10^{-4}.

Sol. : $K_1K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{(2\times10^{-4})^2[S^{2-}]}{0.10} = 1.0 \times 10^{-21}$ or

$$[S^{2-}] = \frac{1.0\times10^{-22}}{4\times10^{-8}} = 2.5 \times 10^{-15}.$$

EXERCISE II

Q.1 At 25°C, the degree of dissociation of water was found to be 1.8×10^{-9}. Calculate the ionization constant and ionic product of water at this temperature.

Q.2 A solution contains HCl, Cl_2HC COOH & CH_3 COOH at concentrations 0.09 M in HCl, 0.09 M in Cl_2HC COOH & 0.1 M in CH_3 COOH. pH for the solution is 1. Ionization constant of CH_3 COOH = 10^{-5}. What is the magnitude of K for dichloroacetic acid ?

Q.3 A solution of chloroacetic acid, $ClCH_2COOH$ containing 9.45 grams in 500 ml of the solution has a pH of 2.0. What is the degree of ionization of the acid.

Q.4 A solution of ammonia bought for cleaning the windows was found to be 10% ammonia by mass, having a density of 0.935 g . ml^{-1}. What is the pH of the solution. Take K_b for protonation of ammonia = 5.5×10^{-6}.

Q.5 The K_w of water at two different temperatures is :

T	25°C	50°C
K_w	1.08×10^{-14}	5.474×10^{-14}

Assuming that ΔH of any reaction is independent of temperature, calculate the enthalpy of neutralization of a strong acid and strong base.

Q.6 What is the pH of a 1.0 M solution of acetic acid ? To what volume must 1 litre of the solution be diluted so that the pH of the resulting solution will be twice the original value. Given $K_a = 1.8 \times 10^{-5}$.

Q.7 A handbook states that the solubility of methylamine $CH_3NH_2(g)$ in water at 1 atm pressure at 25°C is 959 volumes of $CH_3NH_2(g)$ per volume of water (pk_b =3.39)

(a) Estimate the max. pH that can be attained by dissolving methylamine in water.

(b) What molarity NaOH (aq.) would be required to yield the same pH ?

Q.8 The equilibrium constant of the reaction

$$2Ag(s) + 2I^- + 2H_2O \rightleftharpoons 2AgI(s) + H_2(g) + 2OH^-$$

is 1.2×10^{-23} at 25°C. Calculate the pH of a solution at equilibrium with the iodine ion concentration = 0.10 and the pressure of H_2 gas = 0.60 atm.

Q.9 For the reaction

$$A + B \rightleftharpoons C + D$$

(all reactants in solution) calculate the value of the equilibrium constant for the following percentages of conversion of A and B into products. (Assume the initial concentrations of A and B are each 1.0 M)
(a) 67%; (b) 95%; (c) 99%.

Q.10 Mixtures of soutions. Calculate the pH of the following solutions. (Use data of Q.14)

(a) 50 ml of 0.12 M H_3PO_4 + 20 ml of 0.15 M NaOH;

(b) 50 ml of 0.12 M H_3PO_4 + 40 ml of 0.15 M NaOH;

(c) 40 ml of 0.12 M H_3PO_4 + 40 ml of 0.18 M NaOH;

(d) 40 ml of 0.10 M H_3PO_4 + 40 ml of 0.25 M NaOH.

Q.11 Mixtures of solution. Calculate the pH of the following solution.(Use data of Q.14)

(a) 40 ml of 0.050 M Na_2CO_3 + 50 ml of 0.040 M HCl;

(b) 40 ml of 0.020 M Na_3PO_4 + 40 ml of 0.040 M HCl;

(c) 50 ml of 0.10 M Na_3PO_4 + 50 ml of 0.10 M NaH_2PO_4 ;

(d) 40 ml of 0.10 M H_3PO_4 + 40 ml of 0.10 M Na_3PO_4.

Q.12 The electrolytic reduction of an organic nitro compound was carried out in a solution buffered by acetic acid and sodium acetate. The reaction was

$$RNO_2 + 4H_3O^+ + 4e \longrightarrow RNHOH + 5H_2O$$

300 ml of a 0.0100 M solution of RNO_2 buffered initially at pH 5.00 was reduced, with the reaction above going to completion. The total acetate concentration, [HOAc] + [OAc^-], was 0.50 M.Calculate the pH of the solution after the reduction is complete.

Q.13(a) It is desired to prepare 100 ml of a buffer of pH 5.00.Acetic, benzoic and formic acids and their salts are available for use. Which acid should be used for maximum effectiveness against increase in pH? What acid-salt ratio should be used ?pK_a values of these acids are : acetic 4.74; benzoic 4.18 and formic 3.68.

(b) If it is desired that the change in pH of the buffer be no more than 0.10 unit for the addition of 1 m mol of either acid or base, what minimum concentrations of the acid and salt should be used ?

Q.14 Calculate the pH of 0.1 M solution of (i) $NaHCO_3$, (ii) Na_2HPO_4 and (iii) NaH_2PO_4. Given that:

$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$; $K_1 = 4.2 \times 10^{-7}$ M

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$; $K_2 = 4.8 \times 10^{-11}$ M

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_1 = 7.5 \times 10^{-3}$ M

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; $K_2 = 6.2 \times 10^{-8}$ M

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; $K_3 = 1.0 \times 10^{-12}$ M

Q.15 When a 40 mL of a 0.1 M weak base is titrated with 0.16M HCl, the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution.

Q.16 A buffer solution was prepared by dissolving 0.05 mol formic acid & 0.06 mol sodium formate in enough water to make 1.0 L of solution. K_a for formic acid is 1.80×10^{-4}.

(a) Calculate the pH of the solution .

(b) If this solution were diluted to 10 times its volume, what would be the pH ?

(c) If the solution in (b) were diluted to 10 times its volume,what would be the pH?

Q.17 How many moles of sodium hydroxide can be added to 1.00 L of a solution 0.1 M in NH_3 & 0.1 M in NH_4Cl without changing the pOH by more than 1.00 unit ? Assume no change in volume. $K_b(NH_3) = 1.8 \times 10^{-5}$.

Q.18 20 ml of a solution of 0.1 M CH_3COOH solution is being titrated against 0.1 M NaOH solution. The pH values after the addition of 1 ml & 19 ml of NaOH are $(pH)_1$ & $(pH)_2$, what is ΔpH ?

Q.19 Calculate the OH^- concentration and the H_3PO_4 concentration of a solution prepared by dissolving 0.1 mol of Na_3PO_4 in sufficient water to make 1L of solution. $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

Q.20 Find the pH of 0.068M Na_2HPO_4 solution. Use K values from the above problem if required.

Q.21 Calculate the values of the equilibrium constants for the reactions with water of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} as bases. Comparing the relative values of the two equilibrium constants of $H_2PO_4^-$ with water, deduce whether solutions of this ion in water are acidic or basic. Deduce whether solutions of HPO_4^{2-} are acidic or basic. Take $K_1 = 5 \times 10^{-3}$, $K_2 = 5 \times 10^{-8}$, $K_3 = 5 \times 10^{-13}$.

Q.22 Determine the equilibrium carbonate ion concentration after equal volumes of 1.0M sodium carbonate and 1.0M HCl are mixed. $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-11}$.

Q.23 K_1 and K_2 for oxalic acid, $H_2C_2O_4$, are 5.6×10^{-2} and 5.0×10^{-5}. What is $[OH^-]$ in a 0.4mM solution of $Na_2C_2O_4$?

Q.24 If 0.00050 mol $NaHCO_3$ is added to 1 litre of a buffered solution at pH 8.00, how much material will exist in each of the three forms H_2CO_3, HCO_3^- and CO_3^{2-}? For H_2CO_3, $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-13}$.

Q.25 Equilibrium constant for the acid ionization of Fe^{3+} to $Fe(OH)^{+2}$ and H^+ is 6.5×10^{-3}. What is the max.pH, which could be used so that at least 95% of the total Fe^{3+} in a dilute solution. exists as Fe^{3+}.

Q.26 Hydrazine, N_2H_4, can interact with water in two stages.

$$N_2H_4\,(aq) + H_2O\,(l) \rightleftharpoons N_2H_5^+\,(aq) + OH^-\,(aq.) \qquad K_{b1} = 8.5 \times 10^{-7}$$
$$N_2H_5^+\,(aq) + H_2O\,(l) \rightleftharpoons N_2H_6^{2+}\,(aq) + OH^-\,(aq.) \qquad K_{b2} = 8.9 \times 10^{-16}$$

(i) What are the concentration of OH^-, $N_2H_5^+$ and $N_2H_6^{2+}$ in a 0.010 M aqueous solution of hydrazine?
(ii) What is pH of the 0.010 M solution of hydrazine?

Q.27 How much Na_2HPO_4 must be added to one litre of 0.005M solution of NaH_2PO_4 in order to make a 1L of the solution of pH 6.7? $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$ for H_3PO_4.

Q.28 A solution of volume V contains n_1 moles of QCl and n_2 moles of RCl where QOH and ROH are two weak bases of dissociation constants K_1 and K_2 respectively. Show that the pH of the solution is given by $pH = \frac{1}{2}\log\left[\left(\frac{K_1K_2}{K_W}\right)\frac{V}{(n_1K_2 + K_1n_2)}\right]$

State assumptions, if any.

Q.29 The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50 % of the new indicator is in ionic form.

Q.30 A buffer solution, 0.080 M in Na_2HPO_4 and 0.020 M in Na_3PO_4, is prepared. The electrolytic oxidation of 1.00 mmol of the organic compound RNHOH is carried out in 100 ml of the buffer. The reaction is

$$RNHOH + H_2O \longrightarrow RNO_2 + 4H^+ + 4e$$

Calculate the approximate pH of the solution after the oxidation is complete.

Q.31 A solution of weak acid HA was titrated with base NaOH. The equivalence point was reached when 36.12 ml of 0.1 M NaOH has been added. Now 18.06 ml of 0.1 M HCl were added to titrated solution, the pH was found to be 4.92. What will be the pH of the solution obtained by mixing 10 ml of 0.2 M NaOH and 10 ml of 0.2 M HA.

Q.32 A weak base BOH was titrated against a strong acid . The pH at 1/4th equivalence point was 9.24. Enough strong base was now added (6m.eq.) to completely convert the salt. The total volume was 50ml. Find the pH at this point.

Q.33 An organic monoprotic acid [0.1M] is titrated against 0.1M NaOH. By how much does the pH change between one fourth and three fourth stages of neutralization? If at one third stage of neutralization, the pH is 4.45 what is the dissociation constant of the acid? Between what stages of neutralisation may the pH change by 2 units?

Q.34 50 ml of a solution which is 0.050 M in the acid HA, $pK_a = 3.80$ and 0.10 M in HB, $pK_a = 8.20$, is titrated with 0.2 M NaOH. Calculate the pH

(a) at the first equivalence point and

(b) at the second equivalence point.

Q.35 Calculate the solubility of solid zinc hydroxide at a pH of 5, 9 and 13. Given

$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq)$	$K_1 = 10^{-6}$ M	(1)
$Zn(OH)_2(aq) \rightleftharpoons Zn(OH)^+ + OH^-$	$K_2 = 10^{-7}$ M	(2)
$Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^-$	$K_3 = 10^{-4}$ M	(3)
$Zn(OH)_2\,(aq) + OH^- \rightleftharpoons Zn(OH)_3^-$	$K_4 = 10^3\ M^{-1}$	(4)
$Zn(OH)_3^- + OH^- \rightleftharpoons Zn(OH)_4^{2-}$	$K_5 = 10\ M^{-1}$	(5)

Q.36 The salt $Zn(OH)_2$ is involved in the following two equilibria,

$Zn(OH)_2\,(s) \rightleftharpoons Zn^{2+}\,(aq) + 2OH^-\,(aq)$; $K_{sp} = 1.2 \times 10^{-17}$

$Zn(OH)_2\,(s) + 2OH^-\,(aq) \rightleftharpoons [Zn(OH)_4]^{2-}\,(aq.)$; $K_c = 0.13$

Calculate the pH of solution at which solubility is minimum.

Q.37 What is the solubility of AgCl in 0.20 M NH_3?

Given : $K_{sp}(AgCl) = 1.7 \times 10^{-10}\ M^2$, $K_1 = [Ag(NH_3)^+] / [Ag^+][NH_3] = 2.33 \times 10^3\ M^{-1}$ and $K_2 = [\,Ag(NH_3)_2^+\,] / [Ag(NH_3)^+]\,[NH_3] = 7.14 \times 10^3\ M^{-1}$.

Q.38 H_2S is bubbled into a 0.2 M NaCN solution which is 0.02 M in each $Ag(CN)_2^-$ and $Cd(CN)_4^{2-}$. Determine which sulphide precipitates first.

Given : $K_{sp}(Ag_2S) = 1.0 \times 10^{-50}\ M^3$

$K_{sp}(CdS) = 7.1 \times 10^{-28}\ M^2$

$K_{inst}(\,Ag(CN)_2^-\,) = 1.0 \times 10^{-20}\ M^2$

$K_{inst}(\,Cd(CN)_4^{2-}\,) = 7.8 \times 10^{-18}\ M^4$

Q.39 Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in $KAg(CN)_2$. Given $K_{inst}(\,Ag(CN)_2^-\,) = 4.0 \times 10^{-19}\ M^2$ and $K_{sp}(AgCl) = 2.8 \times 10^{-10}\ M^2$.

Q.40 Show that solubility of a sparingly soluble salt $M^{2+}A^{2-}$ in which A^{2-} ions undergoes hydrolysis is given by

$$: S = \sqrt{K_{sp}\left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}\right)}.$$

where K_1 and K_2 are the dissociation constant of acid H_2A. K_{sp} is solubility product of MA.

EXERCISE III

Q.1 The conjugate acid of NH_2^- is

(A) NH_3 (B) NH_2OH (C) NH_4^+ (D) N_2H_4

Q.2 pH of an aqeous solution of NaCl at 85°C should be

(A) 7 (B) > 7 (C) < 7 (D) 0

Q.3 1 CC of 0.1 N HCl is added to 99 CC solution of NaCl. The pH of the resulting solution will be

(A) 7 (B) 3 (C) 4 (D) 1

Q.4 10 ml of $\frac{M}{200}$ H_2SO_4 is mixed with 40 ml of $\frac{M}{200}$ H_2SO_4. The pH of the resulting solution is

(A) 1 (B) 2 (C) 2.3 (D) none of these

Q.5 The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is

(A) 1 (B) 2 (C) 3 (D) 11

Q.6 If K_1 & K_2 be first and second ionisation constant of H_3PO_4 and $K_1 >> K_2$ which is incorrect.

(A) $[H^+] = [H_2PO_4^-]$ (B) $[H^+] = \sqrt{K_1[H_3PO_4]}$

(C) $K_2 = [HPO_4^{--}]$ (D) $[H^+] = 3[PO_4^{3-}]$

Q.7 The degree of hydrolysis of a salt of weak acid and weak base in it's 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be

(A) 100% (B) 50% (C) 25% (D) none of these

Q.8 What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$

(A) 2.48 (B) 5.26 (C) 8.2 (D) 9.6

Q.9 The compound whose 0.1 M solution is basic is

(A) Ammonium acetate (B) Ammonium chloride

(C) Ammonium sulphate (D) Sodium acetate

Q.10 Which of the following solution will have pH close to 1.0?

(A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH

(B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH

(C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH

(D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH

Q.11 The ≈ pH of the neutralisation point of 0.1 N ammonium hydroxide with 0.1 N HCl is

(A) 1 (B) 6 (C) 7 (D) 9

Q.12 If equilibrium constant of

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^-$

Is 1.8×10^{-5}, equilibrium constant for

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$ is

(A) 1.8×10^{-9} (B) 1.8×10^9 (C) 5.55×10^{-9} (D) 5.55×10^{10}

Q.13 If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [$K_a = 2\times10^{-4}$], the pOH of the resulting solution is

(A) 3.4 (B) 3.7 (C) 7 (D) 10.3

Q.14 The range of most suitable indicator which should be used for titration of $X^- Na^+$ (0.1 M, 10 ml) with 0.1 M HCl should be (Given: $k_{b(X^-)} = 10^{-6}$)

(A) 2–3 (B) 3–5 (C) 6–8 (D) 8–10

Q.15 When NO_2 is bubbled into water, it disproportionates completely into HNO_2 and HNO_3.

$$2NO_2 + H_2O\ (l) \longrightarrow NHO_2\ (aq.) + HNO_3\ (aq.)$$

The concentration of NO_2^- in a solution prepared by dissolving 0.05 mole of NO_2 gas in 1 litre H_2O is $\{K_a\ (HNO_2) = 5 \times 10^{-4}\}$ is

(A) $\sim 5 \times 10^{-4}$ (B) $\sim 4.8 \times 10^{-5}$ (C) $\sim 4.8 \times 10^{-3}$ (D) $\sim 2.55 \times 10^{-2}$

Q.16 Which of the following is most soluble in water?

(A) MnS ($K_{sp}= 8\times10^{-37}$) (B) ZnS ($K_{sp}= 7\times10^{-16}$)
(C) Bi_2S_3 ($K_{sp}= 1\times10^{-72}$) (D) $Ag_3(PO_4)$ ($K_{sp}= 1.8\times10^{-18}$)

Q.17 The precipitate of CaF_2($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed

(A) 10^{-4} M Ca^{3+} + 10^{-4} M F^- (B) 10^{-2} M Ca^{2+} + 10^{-3} M F^-
(C) 10^{-5} M Ca^{2+} + 10^{-3} M F^- (D) 10^{-3} M Ca^{2+} + 10^{-5} M F^-

Q.18 The solubility of AgCl in water, 0.01 M $CaCl_2$, 0.02 M NaCl and 0.05 M $AgNO_3$ are denoted by S_1, S_2, S_3 and S_4 respectively. Which of the following relationship is correct?

(A) $S_1 > S_2 > S_3 > S_4$ (B) $S_1 = S_2 = S_3 = S_4$
(C) $S_1 > S_3 > S_2 > S_1$ (D) $S_1 > S_2 = S_3 > S_4$

Q.19 How many moles NH_3 must be added to 2.0 litre of 0.80 M $AgNO_3$ in order to reduce the Ag^+ concentration to 5×10^{-8} M. K_f of $[Ag(NH_3)_2^+] = 10^8$

(A) 0.4 (B) 2 (C) 3.52 (D) 4

Q.20 The solubility of metal sulphides in saturated solution of H_2S **{[H_2S]= 0.1 M}** can be represented by

$$MS + 2H^+ \rightleftharpoons M^{2+} + H_2S\ ;\ K_{eq} = \frac{[M^{2+}][H_2S]}{[H^+]^2}$$

The value of K_{eq} is given for few metal sulphide. If conc. of each metal ion in solution is **0.01 M**, which metal sulphides are selectively ppt at total **[H^+]= 1M** in saturated H_2S solution.

Metal sulphides	MnS	ZnS	CoS	PbS
$\mathbf{K_{eq}} = \frac{[M^{2+}][H_2S]}{[H^+]^2}$	3×10^{10}	3×10^{-2}	3	3×10^{-7}

(A) MnS, ZnS, CoS (B) PbS, ZnS, CoS (C) PbS, ZnS (D) PbS

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EXERCISE IV

Q.1 In the reaction $I^- + I_2 \longrightarrow I_3^-$, the Lewis acid is ______ . **[JEE '97, 1]**

Q.2 Between Na^+ & Ag^+ which is a stronger Lewis acid & why ? **[JEE '97, 2]**

Q.3 Select the correct alternative . **[JEE'97,1+1]**
If pK_b for fluoride ion at 25° C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is :
(A) 1.74×10^{-5} (B) 3.52×10^{-3} (C) 6.75×10^{-4} (D) 5.38×10^{-2}

Q.4 The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is **[JEE 97]**
(A) $6\ y^2$ (B) $64\ y^4$ (C) $36\ y^5$ (D) $108\ y^5$

Q.5 Which of the following statement(s) is/are correct ? **[JEE '98, 2]**
(A) the pH of 1.0×10^{-8} M solution of HCl is 8
(B) the conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(C) autoprotolysis constant of water increases with temperature
(D) when a solution of a weak monoprotic acid is titrated again a strong base, at half–neutralization point pH = (1/2) pKa .

Q.6 A buffer solution can be prepared from a mixture of **[JEE 99]**
(A) sodium acetate and acetic acid in water
(B) sodium acetate and hydrochloric acid in water
(C) ammonia and ammonium chloride in water
(D) ammonia and sodium hydroxide in water.

Q.7 The pH of 0.1 M solution of the following salts increases in the order **[JEE 99]**
(A) $NaCl < NH_4Cl < NaCN < HCl$ (B) $HCl < NH_4Cl < NaCl < NaCN$
(C) $NaCN < NH_4Cl < NaCl < HCl$ (D) $HCl < NaCl < NaCN < NH_4Cl$

Q.8 An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is **[JEE 2001]**
(A) 40 mL (B) 20 mL (C) 10 mL (D) 4 mL

Q.9 For sparingly soluble salt ApBq, the relationship of its solubility product (Ls) with its solubility (S) is
(A) $Ls = S^{p+q}, p^p. q^q$ (B) $Ls = S^{p+q}, p^p. q^p$ (C) $Ls = S^{pq}, p^p. q^q$ (D) $Ls = S^{pq}, (p.q)^{p+q}$
[JEE 2001]

Q.10 A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16}M sulphide ion. If K_{sp}, MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first ?
(A) FeS (B) MnS (C) HgS (D) ZnS
[JEE 2003]

Q.11 HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is
(A) 0.01% (B) 0.0001% (C) 0.1% (D) 0.5% **[JEE 2004]**

Q.12 CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is
(A) 1.6×10^{-11} (B) 8×10^{-11} (C) 5×10^{-5} (D) 2×10^{-2} **[JEE 2005]**

SUBJECTIVES

Q.13 An acid type indicator, HIn differs in colour from its conjugate base (In^-) . The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1 . What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a = 1.0 \times 10^{-5}$) ? **[JEE '97, 2]**

Q.14 A sample of AgCl was treated with 5.00 ml of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre . Calculate the solubility product of AgCl.
(K_{sp} $Ag_2CO_3 = 8.2 \times 10^{-12}$) **[JEE '97, 5]**

Q.15 Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2\,NH_3$, $K_c = 6.2 \times 10^{-8}$ & K_{sp} of AgCl = 1.8×10^{-10} at 298 K . Calculate the concentration of the complex in 1.0 M aqueous ammonia . **[JEE '98, 5]**

Q.16 What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0) ? **[JEE '98, 2]**

Q.17 The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6}M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8. **[JEE '99, 4]**

Q.18 The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 moles litre^{-1} and the pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **[JEE 2000]**

Q.19 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.
(a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.
(b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. K_a of acetic acid is 1.75×10^{-5} M. **[JEE 2002]**

Q.20 Will the pH of water be same at 4°C and 25°C ? Explain. **[JEE 2003]**

Q.21 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given Ka(HA) = 5×10^{-6} and $\alpha << 1$. **[JEE 2004]**

ANSWER KEY
EXERCISE I

IONIZATION CONSTANTS AND pH

Q.1.1 (i) 1.8×10^{-16}, (ii) 1.66×10^{-5}, (iii) 4×10^{-10} Q.1.2 10 Q.1.3 170.4
Q.1.4 (a) $K_a = 10^{-8}$, (b) $K_b = 10^{-6}$
Q.1.5 (a) +1, (b) 0.522, (c) 2.87, (d) 11.13 (e) 6.97, (f) 7, (g) 6.01, (h) 6.97, (i) 2.61, (j) 11.30 (k) 9 (l) 1 , (m) 3
Q.1.6 6.81 Q.1.7 6.022×10^{7} Q.1.8 0.6×10^{-7}
Q.1.9 (i) 6.51 ; (ii) (a) Basic , (b) Acidic Q.1.10 2.31×10^{-8} M Q.1.11 0.556 M
Q.1.12 1.11×10^{-4} Q.1.13 4.87 Q.1.14 $[H^+] = 1.612 \times 10^{-2}$M, $[CHCl_2COO^-] = 6.126 \times 10^{-3}$M
Q.1.15 error = 1% Q.1.16 $[H^+] = 10^{-3}$M, $[CH_3COO^-] = 3.6 \times 10^{-4}$M, $[C_7H_5O_2^-] = 6.4 \times 10^{-4}$M
Q.1.17 2.08

POLYPROTIC ACIDS & BASES

Q.2.1 $[S^{2-}] = 2.5 \times 10^{-15}$
Q.2.2 $[H^+] = [H_2PO_4^-] = 5.623 \times 10^{-3}$, $[HPO_4^{2-}] = 6.8 \times 10^{-8}$, $[PO_4^{3-}] = 5.441 \times 10^{-18}$
Q.2.3 pH = 11.46, $[enH_2^{2+}] = 7.1 \times 10^{-8}$ M Q.2.4 0.2116 M, 0.1884 M, 0.0116 M, 0
Q.2.5 0.0528 M, 0.0472 M, 0.0528 M, 0.000064 M Q.2.6 10.07
Q.2.7 $[OH^-] = 3.57 \times 10^{-3}$ M, $[H_2en]^{2+} = 2.7 \times 10^{-8}$ M

BUFFER SOLUTION

Q.3.1 $[OH^-] = 9.0 \times 10^{-6}$ Q.3.2 4.74 Q.3.3 0.05 mol
Q.3.4 9.56 Q.3.5 (a) pH = 9.239 (b) lowered (c) pH = 4.699
Q.3.6 8.7782 Q.3.7 9.7324
Q.3.8 (a) 4.7525 (b) 4.697, (c) 4.798 (d) 1.134% on acid addition 0.96% on base addition.
Q.3.9 $[H^+] = 2.5 \times 10^{-3}$

INDICATORS

Q.4.1 $[HI_n] = 28.57\%$ Q.4.2 (b), (c)
Q.4.3 (methyl red), one with pH = 5.22 as midpoint of colour range
Q.4.4 85.71% Q.4.5 ΔpH = 0.954

HYDROLYSIS

Q.5.1 $[OH^-] = 6.664 \times 10^{-6}$ Q.5.2 pH = 4.477 Q.5.3 $K_b = 6.25 \times 10^{-10}$
Q.5.4 0.56%, pH = 7 Q.5.5 1.667% Q.5.6 0.26%
Q.5.7 4.0% Q.5.8 10^{-6} ; 10^{-8} Q.5.9 pH = 10.43
Q.5.10 8.34 Q.5.11 4.19 Q.5.12 5.12×10^{-6} M
Q.5.13 (a) 6, (b) 1×10^{-5}

ACID BASE REACTIONS & TITRATIONS

Q.6.1 8.71 Q.6.2 4.98 Q.6.3 6.1
Q.6.4 2.37×10^{-6} Q.6.5 pH = 8.73, $[Na^+] = 0.0379$, $[C_6H_5O^-] = 0.0373$
Q.6.6 $K_b = 1.8 \times 10^{-5}$, 5.27 Q.6.7 8.73
Q.6.8 (i) 2.85, (ii) 4.0969, (iii) 4.5229, (iv) 4.699, (v) 5.301, (vi) 8.699

SOLUBILITY & SOLUBILITY PRODUCT'S

Q.7.1 QX_2 is more soluble Q.7.2 1.6×10^{-8} Q.7.3 1.4×10^{-4}
Q.7.4 $[Cu^+] = 5 \times 10^{-11}$ M Q.7.5 3.4×10^{-11} Q.7.6 2.6×10^{-16}
Q.7.7 1.0×10^{-18} M Q.7.8 8.8×10^{-12} Q.7.9 1.0×10^{-5} mol/lit
Q.7.10 5×10^{-10} M Q.7.11 12 mg
Q.7.12 (a) no precipitation will occur, (b) a precipitate will form Q.7.13 1.6×10^{-3}
Q.7.14 2.1×10^{-5}

SIMULTANEOUS SOLUBILITY

Q.8.1 4×10^{-7} mol/L AgBr, 9×10^{-7} mol/L AgSCN Q.8.2 $[F^-] = 3 \times 10^{-3}$M
Q.8.3 $[Ag^+] = 6.667 \times 10^{-5}$M

COMPLEXATION EQUILIBRIA

Q.9.1 19.3 kg Q.9.2 $K_d = 1/K_f = 4.8 \times 10^{-4}$ Q.9.3 2.8×10^{-3} M

PROFICIENCY TEST

Q.1	False	Q.2	False	Q.3	True	Q.4	False	Q.5	True
Q.6	Increase, one	Q.7	Greater	Q.8	Br^- ion	Q.9	Greater		
Q.10	7.14×10^{-3}	Q.11	3×10^{-6}	Q.12	in both dil acidic and alkaline solution				
Q.13	$M_2X = QY_2 > PZ_3$								
Q.14	10^{-8}	Q.15	7	Q.16	5.74	Q.17	HSO_4^-		
Q.18	increases	Q.19	less	Q.20	less	Q.21	Lewis acid		
Q.22	Buffer	Q.23	Weaker	Q.24	acidic	Q.25	cationic	Q.26	independent

EXERCISE II

Q.1 1.8×10^{-16}, 10^{-14} Q.2 $K_a = 1.25 \times 10^{-2}$ Q.3 $\alpha = 0.05$
Q.4 11.74 Q.5 $\Delta H_{neut} = -51.963$ kJ mol^{-1}
Q.6 $V = 2.77 \times 10^4$ litre Q.7 (a) 13.1, (b) 0.13 M Q.8 1.650
Q.9 (a) 4.1, (b) 3.6×10^2, (c) 9.8×10^3 Q.10 (a) 2.12 (b) 4.66 (c) 7.2 (d) 12
Q.11 (a) 8.34 (b) 4.66 (c) 9.6 (d) 7.20 Q.12 5.158
Q.13 (a) acetic acid, salt-acid molar ratio 1.8 :1 ;
(b) [HOAc] = 0.066 mmol/ml and $[OAc^-] = 0.119$ mmol/ml
Q.14 8.35, 9.60, 4.66 Q.15 9.168 Q.16 (a) pH = 3.83 (b) pH = 3.85 , (c) = 3.99
Q.17 0.0818 moles Q.18 2.558 Q.19 $[OH^-] = 3.73 \times 10^{-2}$M, $[H_3PO_4] = 6 \times 10^{-18}$M
Q.20 9.7736
Q.21 $K_h(H_2PO_4^-) = 2 \times 10^{-12}$; $K_h(HPO_4^{2-}) = 2 \times 10^{-7}$, $K_h(PO_4^{3-}) = 2 \times 10^{-2}$; acidic, basic
Q.22 $[CO_3^{2-}] = 4.9 \times 10^{-3}$M Q.23 $[OH^-] = 3 \times 10^{-7}$M
Q.24 $[H_2CO_3] = 9.85 \times 10^{-6}$M ; $[HCO_3^-] = 4.9 \times 10^{-4}$ $[CO_3^{2-}] = 2.45 \times 10^{-8}$
Q.25 0.908 Q.26 (a) 9.21×10^{-5} M, 9.21×10^{-5} , 8.9×10^{-16} (b) 9.96
Q.27 1.6 mmol Q.29 pH = 7.3 Q.30 7.81 Q.31 8.96
Q.32 11.22 Q.33 0.9542, $pK_a = 4.751$, $\frac{1}{11}$th & $\frac{10}{11}$th stages of neutralisation
Q.34 (a) 5.85 (b) 10.48 Q.35 10 M, 1.12×10^{-6} M, 2×10^{-4} M
Q.36 9.99, $s = 2.5 \times 10^{-5}$ M Q.37 9.66×10^{-3} Q.38 $[Cd^{2+}]$
Q.39 Precipitation will occur

EXERCISE III

Q.1	A	Q.2	C	Q.3	B	Q.4	B	Q.5	C	Q.6	D	Q.7	B
Q.8	A	Q.9	D	Q.10	D	Q.11	B	Q.12	B	Q.13	D	Q.14	B
Q.15	A	Q.16	D	Q.17	B	Q.18	D	Q.19	D	Q.20	D		

EXERCISE IV

Q.1 I_2 Q.2 Ag^+, Na^+ has no tendency to accept e^- Q.3 C Q.4 D
Q.5 B, C Q.6 A, B, C Q.7 B Q.8 A Q.9 A
Q.10 C Q.11 A Q.12 B

SUBJECTIVES

Q.13 $\Delta pH = 2$ Q.14 $K_{sp} = 1.71 \times 10^{-10}$ Q.15 $[Ag(NH_3)_2^+] = 0.0539$
Q.16 pH = 11.3010 Q.17 $s = 1.203 \times 10^{-3}$M Q.18 think ?
Q.19 (a) 0.0175% , (b) 4.757 Q.20 No it will be > 7 Q.21 pH = 9