

IONIC EQUILIBRIA 2



Salts of weak acid and weak base:

I. If, $K_a > K_b$, the solution will be acidic. Ex NH_4F

II. If, $K_a < K_b$, the solution will be basic. Ex NH_4CN

III. If, $K_a = K_b$, the solution will be neutral. Ex $\text{CH}_3\text{COONH}_4$

Salts formed by the neutralization of weak acid HA and weak base BOH are acidic, basic or neutral depending on the nature of acids and bases involved.

It can be explain with the help of relation between dissociation constant.

I. Salt of weak acid and weak base for which $K_a > K_b$

NH_4F is a salt of weak acid HF ($K_a = 7.2 \times 10^{-4}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$).

The salt hydrolyses as



HF is slightly stronger than base NH_4OH . The two ions react with water as



In the solution NH_4^+ ions are hydrolyse to a slightly greater extent than the F^- ions.

That means reaction produces more H_3O^+ ions than the OH^- ions.

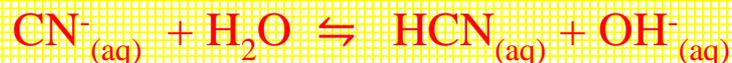
Therefore the solution of NH_4F is slightly acidic in nature and turns blue litmus red.

II. Salt of weak acid and weak base for which $K_a < K_b$

NH_4CN is a salt of weak acid HCN ($K_a = 4 \times 10^{-10}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$). The salt hydrolyses as



NH_4OH is slightly stronger than acid HCN . The two ions react with water as



In the solution CN^- ions hydrolyses to a greater extent than NH_4^+ ions i.e. reaction produces more OH^- ions than the H_3O^+ ions.

Therefore the solution of NH_4CN is slightly basic in nature and turns red litmus blue.

III. Salt of weak acid and weak base for which $K_a = K_b$

For example: $\text{CH}_3\text{COONH}_4$ is a salt of weak acid CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$).

The salt hydrolyses as



The two ions react with water as



As $K_a = K_b$ the relative strength of acid and base produced in hydrolysis is the same. **Therefore solution is neutral.**

Or

Degree of hydrolysis in such cases is independent of the concentration of solution .

SUMMARY OF HYDROLYSIS OF DIFFERENT TYPES OF SALTS (BA)

Type of salt	General hydrolysis reaction	Nature of aqueous soln.	Examples
Salt of strong acid and weak base	$B^+ + H_2O \rightleftharpoons BOH + H^+$	Acidic	$NH_4Cl, CuSO_4$ $FeCl_3, AlCl_3$
Salt of weak acid and strong base	$A^- + H_2O \rightleftharpoons HA + OH^-$	Basic	$CH_3COONa,$ $NaCN, KCN$
Salt of weak acid and weak base	$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$	Uncertain, may be Acidic, Basic or Neutral	$CH_3COONH_4,$ $NH_4CN,$ $C_6H_5NH_2$
Salt of strong acid and strong base	No reaction	Neutral	$NaCl, KCl$

Test yourself

GIVE REASON-

1. 'Salt of strong acid and strong base does not undergo hydrolysis.'

ANS.

*Neither the cation nor anion of the salt react with water or there is no hydrolysis.
Ionization of water is not disturbed and solution is neutral.*

2. 'Aqueous FeCl_3 solution becomes turbid'.

Due to formation of sparingly soluble $\text{Fe}(\text{OH})_3$ weak electrolyte, which remains unionised.

BUFFER SOLUTIONS-

Buffer solution is defined as a solution which resists drastic change in pH when a small amount of strong acid or strong base or water is added to it.

There are three types of buffer solutions.

- 1. Acidic buffer-** A solution containing a weak acid (CH_3COOH) and its salt of strong base (CH_3COONa) is called an acidic buffer.
- 2. Basic buffer -** A solution containing a weak base (NH_4OH) and its salt of strong acid (NH_4Cl) is called a basic buffer.
- 3. Neutral buffer-** A solution containing a salt of weak acid and weak base ($\text{CH}_3\text{COONH}_4$).

Mechanism of buffer solution

Acidic buffer- Acidic buffer is solution of strong electrolyte (CH_3COONa) and weak acid (CH_3COOH).

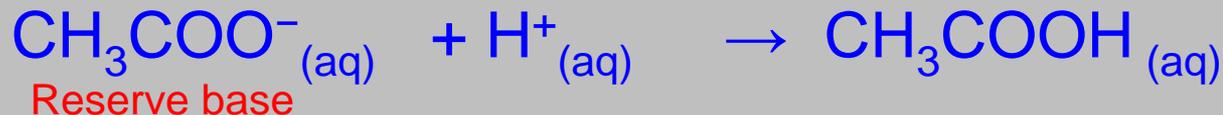
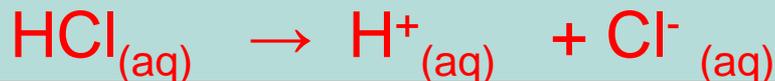
CH_3COONa dissociate completely and produces large concentration of acetate ion (CH_3COO^-)



CH_3COOH dissociate slightly and attain equilibrium

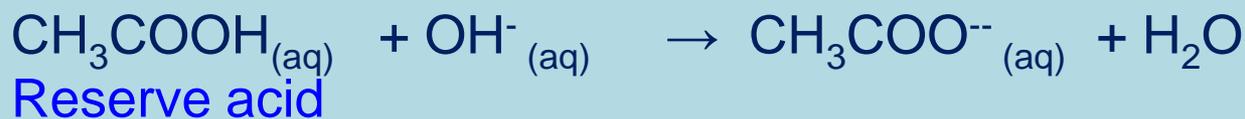


If small amount of strong acid (HCl) added to the solution then H^+ ions produced by dissociation of strong acid neutralizes by CH_3COO^- ions.



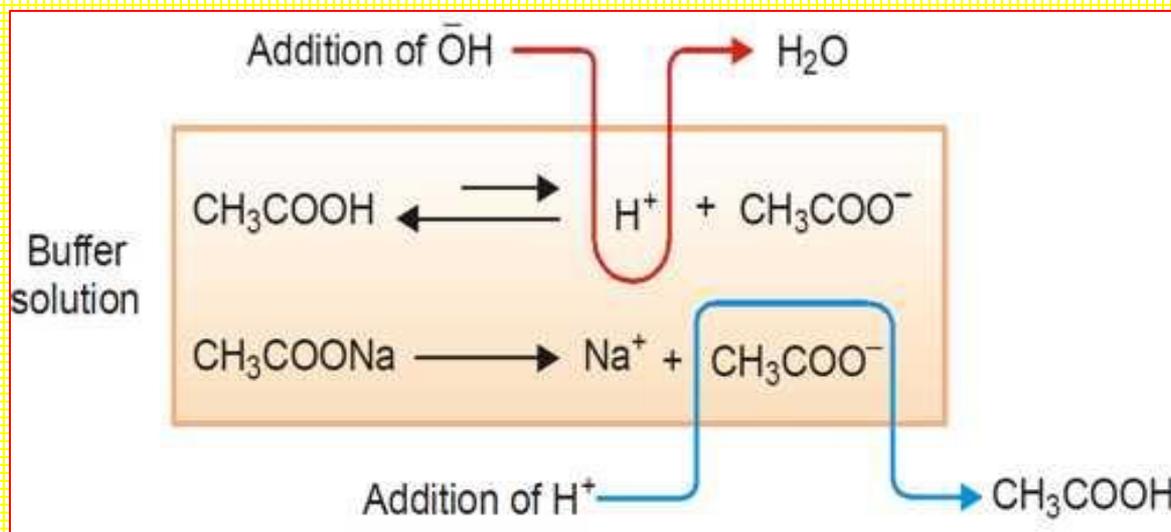
Since CH_3COOH present in solution, there is no change in pH

If small amount of **strong base (NaOH)** added to solution then **OH⁻** ions produced by dissociation of strong base neutralizes by **CH₃COOH**.



Since both products are present in solution, there is no change in pH.

Dilution does not change pH. Therefore pH of buffer solution remains same.



How to calculate pH of a buffer solution?.

We can calculate pH and pOH of buffer solutions using **Henderson Hasselbalch** equation.

For acidic buffer $\text{pH} = \text{pK}_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}$

$$\text{pK}_a = -\log_{10} K_a$$

For basic buffer $\text{pOH} = \text{pK}_b + \log_{10} \frac{[\text{salt}]}{[\text{base}]}$

$$\text{pK}_b = -\log_{10} K_b$$

K_a is dissociation constant of weak acid and

K_b is dissociation constant of weak base.

Henderson–Hasselbalch Equation: Derivation



Taking log of both side

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

$$\log K_a = \log\left(\frac{[H^+][A^-]}{[HA]}\right) = \log[H^+] + \log\frac{[A^-]}{[HA]}$$

$$pH \equiv -\log[H^+] \quad pK_a \equiv -\log[K_a]$$

$$-pK_a = -pH + \log\frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Q1. A buffer is prepared containing 1.00 M acetic acid and 1.00 M sodium acetate. What is its pH? The K_a of acetic acid is 1.77×10^{-5}

Solution: **Given:** $K_a(\text{CH}_3\text{COOH}) = 1.77 \times 10^{-5}$

Conc. of $\text{CH}_3\text{COOH} = 1.0 \text{ M}$, Conc. of $\text{CH}_3\text{COONa} = 1.0 \text{ M}$
pH of buffer = ?

Calculate the $\text{p}K_a$:

$$\begin{aligned}\text{p}K_a &= -\log K_a \\ &= -\log (1.77 \times 10^{-5}) = -\log 1.77 - \log 10^{-5} \\ &= 5 - 0.2480 \\ &= 4.752\end{aligned}$$

$$\text{pH} = \text{p}K_a + \log [\text{Salt}] / [\text{Acid}]$$

$$= 4.752 + \log 1/1$$

Since the log of 1 is zero,

$$\text{pH} = 4.752$$

Q2: Calculate the pH of a 0.500 L buffer solution composed of 0.700 M formic acid (HCOOH , $K_a = 1.77 \times 10^{-4}$) and 0.500 M sodium formate (HCOONa).

Solution:

Given: **Conc. of $\text{HCOOH} = 0.7 \text{ M}$**

Conc. of $\text{HCOONa} = 0.5 \text{ M}$

$K_a (\text{HCOOH}) = 1.77 \times 10^{-4}$

We can use the given molarities in the Henderson-Hasselbalch Equation:

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log [\text{salt} / \text{acid}] \\ &= -\log (1.77 \times 10^{-4}) + \log [0.5 / 0.7] \\ &= -\log 1.77 - \log 10^{-4} + [\log 5 - \log 7] \\ &= 4 - 0.2480 + [0.6990 - 0.8451]\end{aligned}$$

$$\text{pH} = 3.7520 + (-0.1461)$$

$$\text{pH} = 3.6059$$

Q1. Determine the pH of a buffer solution comprised of 1.41 M HF and 0.583 M NaF. The K_a of HF = 7.20×10^{-4} .

Test yourself

Q1: Which of the following statement/s is false about buffer solutions?

1. The pH of a buffer solution does not change on dilution.
2. Buffer solutions do not have a definite pH.
3. The pH of a buffer solution changes slightly on the addition of a small amount of acid or base.
4. The pH of buffer solution does not change on standing for long.

Solution: The option '2' is false. Buffer solutions have a definite pH.

Q2. Ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl), gives rise to ____

A. acidic buffer



B. basic buffer

C. neutral buffer

D. single salt buffer

Q3. An acidic buffer solution can be prepared by mixing a ___.

- A. strong acid and its salt
B. strong acid and its salt with a weak base
C. weak acid and its salt with a strong base
D. weak acid and its salt with a weak base

Q4. What happens to the pH value of an acidic buffer when a small amount of strong acid is added?

- A. decreases
B. increases
C. practically remains constant
D. first increases then decreases

Q5. In a basic buffer, if a small amount of strong acid is added, its H^+ ions are neutralized and the pH value does not change due to _____

- A. reserve acidity
B. reserve basicity
C. reserve solubility
D. both A and C

Applications of Buffer solution-

Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical **applications**. In nature, there are many systems that use **buffering** for pH regulation. For example, the bicarbonate **buffering** system is used to regulate the pH of blood.

- The most common of three major chemical buffer systems in the body
- First line of defense for control of body pH....can act within a fraction of a second
- Formula:



cellular respiration carbonic acid bicarbonate ion

In food industry

Sodium citrate is a versatile food additive used as a buffer principally in jams and jellies.



Calcium citrate is an important acidity regulator that is often used in carbonated drinks.



Potassium tartrate is obtained from grapes during the wine-making process. In addition to its buffering action, potassium tartrate also helps bread to rise consistently. It is used as a buffer in wine and bread production.



IN PHARMACEUTICAL INDUSTRY

Most pharmaceutically acceptable buffering systems are based on carbonates, citrates, gluconates, lactates, phosphates or tartrates.

Borates can be used for external application, but not to mucous membranes or to abraded skin.

Faculty of Pharmacy, Omar Al-Mukhtar University



Buffered aspirin has a buffering agent, such as magnesium oxide, that will maintain the pH of the aspirin as it passes through the patient's stomach.



In analytical chemistry-

In qualitative analysis, a pH of 8 to 10 is required for precipitation of cations of III A group. It is maintained with the use of ($\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$) buffer.

Solubility and Solubility product:

The maximum amount of solute that can dissolve in a known quantity of solvent at a certain temperature is its solubility.

SATURATED SOLUTION-

It is the maximum amount of solute that can be dissolved in a solvent at equilibrium, which produces a saturated solution.

When certain conditions are met, additional solute can be dissolved beyond the equilibrium solubility point, which produces a **supersaturated solution**.

Applicable for sparingly soluble salts.

Suppose some powdered sparingly soluble salt **AgCl** is dissolve in water.

A very small amount of salt dissolves in water and form saturated solution at given temperature.

A dynamic equilibrium exist between undissolved AgCl and its ions

Ag⁺ and **Cl⁻** in the saturated solution.





The expression for equilibrium constant is:

$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

The concentration of undissolved AgCl is constant.

Therefore $[\text{AgCl}] = K'$

$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{K'}$$

OR $K \times K' = [\text{Ag}^+][\text{Cl}^-]$

$$\mathbf{K_{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

Where **K_{sp}** is another constant is called as **solubility product** i.e. product of concentration of ions in a saturated solution.



(aq)

$$K_{sp} = [\text{B}^{Y+}]^x [\text{A}^{X-}]^y$$

Solubility Product:

The term solubility product is generally applicable for sparingly soluble salts.

It is the product of the molar concentration of the ions at equilibrium, raised to the power equal to their coefficients in the balanced equation at a given temperature.

At a given temperature the solubility product is constant.

Lesser the value of solubility product indicates lower solubility and higher value of solubility product indicates greater solubility.

Consider following examples.



$$K_{sp} = [\text{Ba}^{2\oplus}][\text{SO}_4^{2\ominus}]$$



$$K_{sp} = [\text{Ca}^{2\oplus}][\text{F}^{\ominus}]^2$$



$$K_{sp} = [\text{Bi}^{3\oplus}]^2[\text{S}^{2\ominus}]^3$$



$$K_{sp} = [\text{Ca}^{2\oplus}]^3[\text{PO}_4^{3\ominus}]^2$$

Relationship between Solubility(S) and Solubility product (Ksp):

The solubility of a compound is the amount in grams that dissolves per unit volume.
The number of moles of a compound that dissolve to give one litre of saturated solution is called its molar solubility.

$$\text{Molar solubility(S)} = \frac{\text{Number of moles of compound}}{\text{Volume of solution in L}}$$

General expression for a compound (salt)-



$$K_{sp} = [B^{y+}]^x [A^{x-}]^y$$

If 'S' is the molar solubility of the salt, then

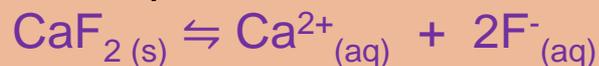
$$[B^{y+}]^x = xS \text{ mol/L} \quad [A^{x-}]^y = yS \text{ mol/L}$$

Therefore,

$$K_{sp} = [xS]^x [yS]^y$$

$$K_{sp} = x^x y^y S^{(x+y)}$$

For examples:



$$x=1 \quad y=2$$

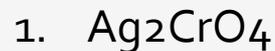
$$\begin{aligned} \therefore K_{sp} &= x^x y^y S^{(x+y)} \\ &= 1^1 \times 2^2 \times S^{(1+2)} \\ &= 4 S^3 \end{aligned}$$



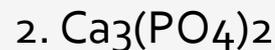
$$x=1 \quad y=3$$

$$\begin{aligned} \therefore K_{sp} &= x^x y^y S^{(x+y)} \\ &= 1^1 \times 3^3 \times S^{(1+3)} \\ &= 27 S^4 \end{aligned}$$

Use your brain power- What is relationship between 'S' and 'Ksp' for salts given.



$$K_{sp} = 4 S^3$$



$$K_{sp} = 108 S^5$$



$$K_{sp} = 27 S^4$$

Condition of precipitation of a salt(electrolyte):

The ionic product and solubility product of a salt compared to give condition of precipitation. **It is very useful in qualitative analysis of salts.**

- I. If, $IP = K_{sp}$; the solution is saturated and solubility equilibrium exists.
- II. If, $IP > K_{sp}$; the solution is super saturated and hence precipitation of the salt will occur.
- III. If, $IP < K_{sp}$; the solution is unsaturated and precipitation of the salt will not occur.

NUMERICALS

A solution is prepared by mixing equal volumes of 0.1 M MgCl_2 and 0.3 M $\text{Na}_2\text{C}_2\text{O}_4$ at 293 K. Would MgC_2O_4 precipitate out?. K_{sp} of MgC_2O_4 at 293 K is 8.56×10^{-5} .

Soln. Suppose 1 volume of 0.1 M MgCl_2 and 1 volume of 0.3 M $\text{Na}_2\text{C}_2\text{O}_4$ mixed to prepare soln.

Therefore, Total volume of soln = twice of the volume of each soln.

Therefore, effective conc. of each salt soln will be half of the given concentration.



If, $IP > K_{sp}$, Then precipitation will take place. Let's check condition of precipitation.

$$[\text{Mg}^{2+}] = 0.1 / 2 = 0.05 \text{ M}, \quad [\text{C}_2\text{O}_4^{2-}] = 0.3 / 2 = 0.15 \text{ M} \qquad (C = 1/V)$$

$$I.P. = [\text{Mg}^{2+}] \times [\text{C}_2\text{O}_4^{2-}] = 0.05 \times 0.15 = 0.0075 = 7.5 \times 10^{-3}$$

$IP > K_{sp}$ i.e. 7.5×10^{-3} is greater than 8.56×10^{-5} ,
Therefore precipitation will take place.

Q2. Solubility product of BaCO_3 is 2.6×10^{-9} . Estimate its molar solubility.
($5.09 \times 10^{-5} \text{ mol / dm}^3$)

Q3. Solubility product of AgCl is 1.8×10^{-10} . Calculate its molar solubility and solubility in g/dm^3 . Molar mass of AgCl is 143.5 g/mol .

($1.342 \times 10^{-5} \text{ mol/dm}^3$, $1.925 \times 10^{-3} \text{ g/ dm}^3$)

TEST YOURSELF

Q1. Incorrect statement among the following is__

- A. K_{sp} varies with temperature.
- B. From the K_{sp} of a compound, it is possible to calculate its solubility.
- C. If the product of the concentration of the ions of a compound exceeds its K_{sp} , the compound precipitate out.
- D. The solubility product concept is applicable to all compounds.

ANS. D

Q2. What is the solubility of A_2B ($K_{sp} = 4 \times 10^{-9}$)

A. 10^{-3} mol/dm^3

B. $4^{1/3} \times 10^{-3} \text{ mol/dm}^3$

C. 10^{-3} mol/cm^3

D. $2 \times 10^{-5} \text{ mol/dm}^3$

ANS. A

Q3. The expression for K_{sp} for $Ca_3(PO_4)_2$ is _____

A. $[Ca^{2+}]^2 [PO_4^{3-}]^3$

B. $[Ca^{2+}]^3 [PO_4^{3-}]^2$

C. $[Ca^{2+}]^2 [PO_4^{3-}]^2$

D. $[Ca^{2+}] [PO_4^{3-}]^2$

ANS. B

Q4. The solubility product of a salt AB is 1×10^{-8} . Concentration of A^+ is 10^{-3} M . What will be concentration of B^- such that AB will precipitate?

A. 10^{-4} M

B. 10^{-5} M

C. 10^{-6} M

D. 10^{-7} M

ANS. A

Q5. Solubility of calcium hydroxide, if its solubility product is $12\sqrt{3}$, is _____

A. $\sqrt{3}$

B. 432

C. 108

D. $\sqrt{108}$

ANS. A

Q6. Solubility of CaF_2 is $4 \times 10^{-3} \text{ mol/cm}^3$, its solubility product is _

A. 2.56×10^{-7}

B. 3.2×10^{-4}

C. 6.4×10^{-8}

D. 3.2×10^{-11}

ANS. A

Common ion effect- *The common ion effect states that the ionization of weak electrolyte is suppressed by addition of strong electrolyte containing an ion common to the weak electrolyte.*

Consider a weak electrolyte CH_3COOH dissolve in water, dissociated slightly as



A strong electrolyte CH_3COONa added to this solution. CH_3COONa being a strong electrolyte dissociate completely as



Both acid and salt contain a common ion $\text{CH}_3\text{COO}^{-}$.

Therefore concentration of $\text{CH}_3\text{COO}^{-}$ increases in the solution and equilibrium shifted from right to left (*Le-chatelier's principle*).

Thus reverse reaction is favoured in $\text{CH}_3\text{COO}^{-}$ combine with H^{+} ion and produces more unionised CH_3COOH .

Hence dissociation of CH_3COOH is suppressed due to presence of CH_3COONa containing a common ion.

Common ion effect and Solubility:

The presence of common ion also affects solubility of sparingly soluble salt.

For ex solubility of AgCl is suppressed by addition of AgNO₃



$$K_{sp} = [\text{Ag}^{+}] [\text{Cl}^{-}]$$



The dissociation of AgCl is suppressed due to common ion Ag⁺, produced by AgNO₃.

According to Le-chatelier's principle the reverse reaction is favoured and AgCl precipitates.

The solubility of AgCl decreases due to presence of common ion.

1. Choose the most correct answer :

- i. The pH of 10^{-8} M of HCl is
- a. 8 b. 7
c. less than 7 d. greater than 7

Ans. c. less than 7

- ii. Which of the following solution will have pH value equal to 1.0 ?
- a. 50 mL of 0.1M HCl + 50mL of 0.1M NaOH
b. 60 mL of 0.1M HCl + 40mL of 0.1M NaOH
c. 20 mL of 0.1M HCl + 80mL of 0.1M NaOH
d. 75 mL of 0.2M HCl + 25mL of 0.2M NaOH

Ans. d. 75mL 0.2 M HCl +
25mL 0.2 M NaOH

- iii. Which of the following is a buffer solution ?
- a. $CH_3COONa + NaCl$ in water
b. $CH_3COOH + HCl$ in water
c. $CH_3COOH + CH_3COONa$ in water
d. $HCl + NH_4Cl$ in water

Ans. c. $CH_3COOH +$
 CH_3COONa

iv. The solubility product of a sparingly soluble salt AX is 5.2×10^{-13} . Its solubility in mol dm^{-3} is

- a. 7.2×10^{-7} b. 1.35×10^{-4}
c. 7.2×10^{-8} d. 13.5×10^{-8}

Ans. a. 7.2×10^{-7}

v. Blood in human body is highly buffered at *pH* of

- a. 7.4 b. 7.0
c. 6.9 d. 8.1

Ans. a. 7.4

vi. The conjugate base of $[\text{Zn}(\text{H}_2\text{O})_4]^{2\oplus}$ is

- a. $[\text{Zn}(\text{H}_2\text{O})_4]^{2\ominus}\text{NH}_3$
b. $[\text{Zn}(\text{H}_2\text{O})_3]^{2\ominus}$
c. $[\text{Zn}(\text{H}_2\text{O})_3\text{OH}]^{\oplus}$
d. $[\text{Zn}(\text{H}_2\text{O})\text{H}]^{3\oplus}$

Ans. c.

vii. For *pH* > 7 the hydronium ion concentration would be

- a. 10^{-7}M b. $< 10^{-7}\text{M}$
c. $> 10^{-7}\text{M}$ d. $\geq 10^{-7}\text{M}$

Ans. b. $< 10^{-7}\text{M}$

THANK YOU