

LIFE ESSENTIAL ELEMENTS

In 1946, the World Health Organization defined Health as “a state of complete physical, mental well being and not merely the absence of disease or infirmity”. As we have known, at least 26 elements are necessary for man’s achievement of this state of health.

Of the 26 elements (Fig-1) H, C, N, O, P and S compose all of the body’s organic molecules, e.g., protein, carbohydrates, fats and energy transfer molecules ATP & ADP. These elements constitute by far the greatest proportion of the body’s atoms. e.g., 63% are H, 25.5% are O, 9.5% are C, 1.4% are N and the other is less than 0.7%.

The elements present in the animal body may be classified as principal elements (macronutrients) and trace elements.

Principal Mineral Elements (Macronutrients)

The essential elements are : Na, K, Ca, Mg, and Cl. They constitute 60-80% of all the inorganic material in the body.

Trace Elements

They may be subdivided into 2 groups:

- (1) Essential trace elements (micronutrient): Fe, Cu, Zn, S, P, Mn, Co, Se, F & I.
- (2) Non-essential trace elements: Hg, Pb, As, Cd, Al & B.

H ¹																			
													C ¹	N ¹	O ¹	F			
Na ¹	Mg ¹													P ¹	S ¹	Cl ¹			
K ¹	Ca ¹			V	Cr	Mn ¹	Fe ¹	Co	Ni	Cu ¹	Zn ¹				Se	Br			
	Sr										Cd					I			
	Ba																		

Fig .1- A periodic table for the biosphere. Superscripts 1, essential to all animals and plants.

PRINCIPAL MINERAL ELEMENTS

SODIUM

Sodium ions are the primary cations of the extracellular fluids. The principal functions of sodium ions are

- (1) To maintain the osmotic pressure of the extracellular fluid.
- (2) To control water retention in tissue spaces.
- (3) To help maintain blood pressure.
- (4) To regulate the irritability of the nerve and muscle tissue of the heart.

The average daily adult intake of sodium as NaCl, is 5 to 15 g. The body's sodium ion concentration is influenced by aldosterone, a hormone of the adrenal cortex. This hormone promotes the reabsorption of Na⁺ in the kidney.

POTASSIUM

Potassium ions are the principal cations of the intracellular fluid. The principal functions of potassium ions in the body are

- (1) To maintain the osmotic pressure of the cells.
- (2) To maintain the size of the cells.
- (3) To maintain proper contraction of the heart.
- (4) To maintain proper transmission of nerve impulses.

The normal intake of potassium in food is about 4g/dL. A high content of potassium is found in the following foods; chicken, beef, liver, pork, dried peaches, bananas, the juices of oranges and pineapples, potatoes and broccoli.

The symptoms of low serum potassium concentrations include muscle weakness, irritability, and paralysis and dilatation of the heart with gallop rhythm are also noted.

CALCIUM

Calcium is present in the body in larger amounts than any other mineral element. The body of an adult male weighing 70 kg contains approximately 1200 g of calcium. About 99 % of the body calcium is in the skeleton in the form of calcium carbonate and calcium phosphate, where it is maintained as deposits of calcium phosphate in a soft, fibrous matrix. The small amount of ionized calcium in the body fluids is of great importance in blood coagulation, in maintaining the normal excitability of the heart, muscles and nerves. Milk and milk products are the richest sources of calcium.

MAGNESIUM

Magnesium is one of the principal cation of soft tissue. The body contains about 21g of magnesium. 70 % is combined with calcium and phosphorous in the complex salts of bone; the remainder is in the soft tissue and body fluids. Magnesium is necessary for DNA replication and protein biosynthesis. A very important function of magnesium is in photosynthesis. Photosynthesis which is dependent upon one of the green pigments known as chlorophylls which contains Mg²⁺ as their central metal ion.

ESSENTIAL TRACE ELEMENTS

COPPER

Copper is an essential constituent of several proteins. It is essential for hemoglobin synthesis, normal bone formation and maintenance the nervous system. Copper is necessary for the release of Fe its storage proteins. The adult human body contains 100 - 150 mg of copper : about 64 mg are found in the muscles, 23 mg in the bones, and 18 mg in the liver.

Wilson's disease is due to the breakdown of copper metabolism causing deposition of the metal in the tissues including the liver and brain. The symptoms may resemble those of acute liver disease or of a brain disturbance causing a shaken and lack of control of the limbs.

IRON

Iron is involved almost exclusively cellular respiration. The best known function of iron in biological system is as an oxygen carrier in hemoglobin. Iron is part of hemoglobin, myoglobin, and cytochromes. The formation of hemoglobin requires the presence of traces of copper. The normal adult body contains 4.2 - 6.1 g of iron, 65 - 70 % of which is present as hemoglobin in the red blood cells.

A deficiency of iron (anaemia) may result from a low intake of iron because of a diet high in cereal and low in meat, and because of excessive loss of blood. The best dietary sources of iron are the 'organ meats', such as liver, heart, and kidneys. Other sources are beans, egg yolk and fish.

ZINC

Zinc is essential for normal growth and reproduction. It has a beneficial effect on wound healing and tissue repair. Zinc is an essential component of several enzyme, such as carbonic anhydrase. Zinc is necessary to maintain normal concentration of vitamin A in plasma.

Food sources of zinc include seafood (particularly oysters and clams) meat, liver, eggs, milk. The recommended daily allowance for zinc is 15 mg/ day for adults. For children, the recommended allowance is 6 to 10 mg/day.

SULFUR

Sulfur is present in all cell of the body, primarily in the cell protein in the form of the 2 sulfur containing amino acid, cysteine and methionine.

PHOSPHOROUS

Phosphorous is found in every cell of the body, but most of it (about 80% of the total) is combined with calcium in the bones and teeth. About 10% is combination with proteins, lipids and carbohydrates, and in other compounds in blood and muscle. The remaining 10% is widely distributed in various chemical compounds.

NONESSENTIAL TRACE ELEMENTS

The trace concentrations of the essential and beneficial elements are needed for human whereas other elements at similar concentrations are highly toxic. These elements include Hg, Pb, and As.

MERCURY

Mercury vapour can be absorbed in the lungs where, within an hour, it is oxidized and so appears as ionic mercury in the blood stream. These soluble inorganic mercury salts are extremely toxic mainly through corrosive action on the intestine, kidneys and brain. Another

danger is that the mercury alkyl will cross the placental barrier and so cause serious damage to the fetus.

LEAD

Inorganic lead exhibits its main effect as blood disorders caused by its combination with the sulphhydryl groups of enzyme in the biosynthesis of haem.

The pipes, solder, fittings and service connections of some household plumbing system contain lead and cause contamination of drinking-water supplies. Lead is hazardous to health. It accumulates in the body and its effects on the central nervous system can be particularly serious. The fetus, infants, children and pregnant women are most at risk.

Table : Some metal dependent conditions

Element	Disease arising from deficiency	Disease associated with an excess of the element
Na	Addison's disease, stocker's cramps.	-----
K	-----	Addison's disease Blind staggers in cattle
Ca	Bone deformities, tetany	Cataracts, gall stones, atherosclerosis
Cu	Anaemia, kinky hair syndrome	Wilson's disease
Fe	Anaemia	Haemochromatosis, siderosis
Zn	Dwarfism	Metal fume fever
Pb	-----	Anaemia, encephalitis, neuritis
Hg	-----	Encephalitis, neuritis



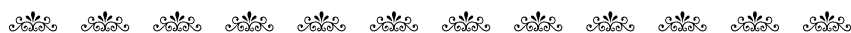
SOME INORGANIC COMPOUNDS USED IN TRADITIONAL MEDICINE

Local Name	-	Kant
Scientific/other name	-	Sulphur,S
Indication	-	Fever, scabies and ringworm
Uses	-	Orally use with warm water and betal decoction. Externally use on worms.

- Local Name - Kant-kuzan
Scientific/other name - Talc, magnesium silicate, $MgSiO_3$
Indication - Fever, urinary disorders, burns.
Uses - Orally use by making slurry and external use on burns by making slurry with water or coconut oil.
- Local Name - Kyauk chin
Scientific/other name - Alum, Aluminium potassium sulphate, $KAl(SO_4)_2 \cdot 12H_2O$
Indication - Haematemesis, bleeding per rectum, menorrhagia, injury, bleeding, gastric bleeding, scurvy, scanty micturition, conjunctivitis.
Uses - Orally use with drinking water sterilized by boiling or coconut water. Externally use by making ash for scurvy. Externally use by making slurry with tha-na-kha . (*Limonia acidissima*)
- Local Name - Sis hsat pya
Scientific/other name - Crude sodium carbonate, Na_2CO_3
Indication - Flatulence & colic, nausea & vomiting, urinary stone, sore on heel.
Uses - Orally use with drinking water sterilized by boiling or sesame oil.
- Local Name - Hsah- Kyat- khoe
Scientific/other name - Salty black soot
Indication - Fever, skin disorders due to cease perspiration, constipation, no flatus, gonorrhoea, leucorrhoea, scabies and itchy skin diseases.
Uses - Orally use with coconut water or drinking water sterilized by boiling. Externally use on scabies and itchy skin diseases.
- Local Name - Hsah-boke
Scientific/other name - Black salt, sodium chloride, $NaCl$
Indication - Indigestion, flatulence & colic, no flatus, bleeding, diarrhoea and gastritis.
Uses - Orally use as aqueous solution and together with jaggery or sugar for rehydration.
- Local Name - Hsa hlaw
Scientific/other name - Roasted sodium chloride, $NaCl$

- Indication - Indigestion, wind colic, no flatus, constipation
- Uses - Orally use with drinking water sterilized by boiling.
- Local Name - Hasy-dan
- Scientific/other name - Yellow arsenic orpiment, yellow arsenic sulphide, As_2S_3
- Indication - Hepatitis jaundice, malaria, skin disease, scabies and ringworm.
- Uses - Orally use with sugar drinking water sterilized by boiling for jaun dice and malaria. Externally use on scabies and ringworm by making slurry with tha-na-kha (*Limonia acidissima*)
- Local Name - Za-wet-tha
- Scientific/other name - Ammonium chloride, NH_4Cl
- Indication - Fever, infantile ailments.
- Uses - Orally use with tha-na-kha(*Limonia acidissima*) slurry. Externally use with onion expressed juice and inhalation.
- Local Name - Dok htar
- Scientific/other name - Copper sulphate, $CuSO_4 \cdot 5H_2O$, Cupper sulphate vitriol
- Indication - Leprosy, eczema, scabies, ringworm and poisonous animal bites.
- Uses - Externally use as aqueous solution.
(Remark- Vomiting, if it was taken orally)
- Local Name - Ma phuk htone
- Scientific/other name - Calcium oxide. CaO
- Indication - Diarrhoea, dysentery, typhiod, injuries, ringworm and scabies.
- Uses - Orally use as lime water obtained by dissolving calcium oxide in water.
Externally use on ringworm by making slurry with tha-na-kha (*Limonia acidissima*).
- Local Name - Myay-byu
- Scientific/other name - Chalk. calcium carbonate, $CaCO_3$
- Indication - Gastritis, sore and typhoid.
- Uses - Orally use with drinking water sterilized by boiling and externally use as powder on sore.
- Local Name - Myanmar hsa kha

- Scientific/other name - Sodium sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Glauber's salt
- Indication - Indigestion, wind colic, scanty micturition, constipation.
- Uses - Orally use with drinking water.
- Local Name - Yan zein
- Scientific/other name - Salt petre, potassium nitrate, KNO_3
- Indication - Scanty micturition, dysuria, flatulence, haematuria, menorrhagia.
- Uses - Orally use with water or cocount water
- Local Name - Letcha
- Scientific/other name - Borax, sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
- Indication - Fever, haematemesis and melaena, menorrhagia, food poisoning, scabies and ringworm, poisonous animal bite.
- Uses - Orally use with drinking water sterilized by boiling or coconut water. Externally use on poisonous animal bite. Externally use baked borax on scabies and ringworm.
- Local Name - Thein taw
- Scientific/other name - Natural sodium chloride, rock salt, NaCl
- Indication - Wind colic, constipation, flatulence, vomiting loss of appetite.
- Uses - Orally use with drinking water sterilized by boiling. Brush on tongue when loss appetite.
(Remark: Vomiting if it was orally taken with warm water.)
- Local Name - Hsa, Hsa yoe yoe
- Scientific/other name - Common salt, table salt, sodium chloride, NaCl
- Indication - Gastric disorders, flatulence, nausea & vomiting, constipation, no flauts
- Uses - Orally use as aqueous solution.



Electrolyte (Ionic Equilibria)

Metals are good conductors of electricity because they contain number of electrons which are free to move if an electric field is applied. If two ends of a piece of wire are connected to the terminals of a battery, the difference in potential causes electrons to flow towards the positive electrode.

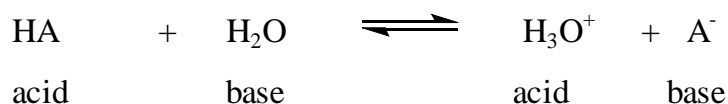
Certain liquids can also conduct electricity, for example, if battery is connected to two platinum electrodes immersed in a solution of copper sulphate, a current will flow. The mechanism by which electricity is conducted in copper sulphate solution is not the same as in case of a metal. This is because copper sulphate is an electrovalent material and is therefore ionic in nature, even in the solid state. In solution, copper and sulphate ions are free to move individually. When an electric field is applied the copper ions move towards the negative electrode (cathode) and the sulphate ions move towards the positive electrode (anode). The current is therefore carried across the solution by the movement of ions not by the electrons. This type of liquids are known as electrolytes. The decomposition of an electrolyte by means of the electric current is known as electrolysis.

Acids and Bases

Bronsted and Lowry Theory

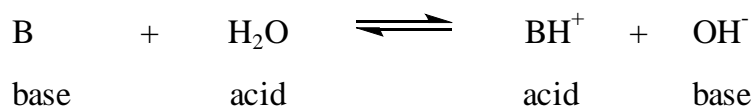
An acids is a substance with a tendency to lose a proton, and a base is a substances with a tendency to gain a proton.

Representing an acids as HA , a solution of the acid in water contains the following equilibrium.



The ionization of an acid or base always contains this equilibrium between two Pairs of acid and bases.

For a base (B) dissolved in water, the equilibrium is



It will be noticed that water has the property of being able to act either as an acid or a base.

In aqueous systems, acid (such as HCl, HNO₃, HClO₄) which undergo complete dissociation are called strong acids. Acid (like CH₃COOH, HCN) which are only partially ionized in solution are called weak acids. Similarly, completely ionized bases like NaOH, KOH, Ba (OH)₂ are termed strong bases, and a partially ionized base like ammonia is referred to as a weak base.

Solution of a weak acid

If HA is weak acid, the dissociation equilibrium of HA in water will be



The equilibrium constant for this reaction is

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \quad \text{or}$$

$$K_c \times [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The solution is dilute, the concentration of water remains constant. In that case K_c [H₂O] will be denoted by the constant K_a , we have

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

K_a is known as ionization constant or dissociation constant of weak acid, and it is depended only on the temperature.

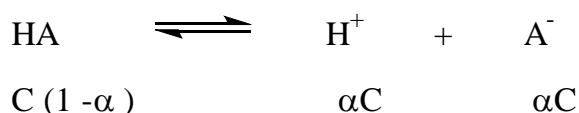
For convenience, the dissociation of HA is represented as



Then the ionization constant should be written as

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

The extent of ionization of a weak acid can be expressed in terms of degree of dissociation. For a weak acid HA, degree of dissociation is α , and C is the initial concentration, we have



The equilibrium concentrations will be

$$[H^+] = [A^-] = C\alpha$$

$$[HA] = C(1 - \alpha)$$

Therefore dissociation constant K_a becomes.

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K_a = \frac{C\alpha}{(1-\alpha)}$$

If α is very small compared to unity.

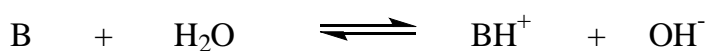
$$K_a = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}} \quad \text{or} \quad C\alpha = \sqrt{K_a C} = [H^+]$$

From this equation $[H^+]$ of a solution of weak acid can be calculated.

Solution of a weak base

If we represent the weak base by B, in solution the ionization equilibrium will be,

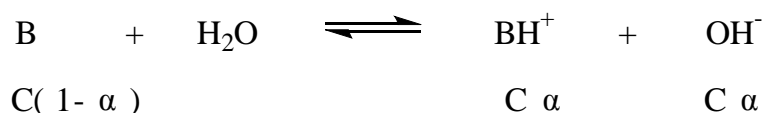


$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]} \quad \text{or} \quad K_c [H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

$K_c [H_2O]$ remains constant, which is represented by K_b

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

K_b is known as ionization constant of a weak base, which is also depended only on the temperature. If the degree of dissociation of weak base is α and C is the initial concentration.



At equilibrium

$$[BH^+] = [OH^-] = C\alpha$$

$$[B] = C(1 - \alpha)$$

$$K_b = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

If α is much smaller than unity.

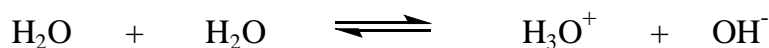
$$\alpha = \sqrt{\frac{K_b}{C}} = \quad \text{or}$$

$$C = \sqrt{K_b C} = [\text{OH}^-]$$

from this equation OH^- ion concentration can be calculated.

Ionization of water

We have seen that water can behave as an acid or a base. Since water has both proton donating and accepting properties, it is possible for two water molecules to exchange a proton, one molecules losing the proton (acid behavior) and the other gaining it (basic behavior).



This process is known as autoprotolysis. The equilibrium constant of the reaction is

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad \text{or} \quad K_c [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Since the extent of autoprotolysis is very low, the concentration of water remains almost constant. Hence

$$K_c [\text{H}_2\text{O}]^2 = K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

If the autoprotolysis of water is represented as the ionization of water.



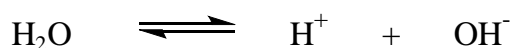
$$K_w = [\text{H}^+][\text{OH}^-]$$

K_w is known as ionic product of water. It is depends only on the temperature. At 25°C, K_w is found to be 1×10^{-14} at 25°C.

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \quad (\text{at } 25^\circ\text{C})$$

Hydrogen ion concentration and pH scale.

For the ionization of water, we have



$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \quad (\text{at } 25^\circ\text{C})$$

$$\text{but } [\text{H}^+] = [\text{OH}^-]$$

$$[\text{H}^+]^2 = [\text{OH}^-]^2 = 1 \times 10^{-14}$$

$$[H^+] = [OH^-] = 1 \times 10^{-7} \text{ M}$$

For pure water $[H^+]$ or $[OH^-]$ is equal to 1×10^{-7} M. In acidic solution $[H^+]$ becomes greater than 1×10^{-7} M and in basic solution $[H^+]$ becomes smaller than 1×10^{-7} M. Hydrogen ion concentration of solutions of acids and bases can vary within wide limits. It is more convenient to use a logarithmic scale defined as following way,

$$\text{pH} = -\log [H^+]$$

The neutral point will be

$$\text{pH} = -\log 1 \times 10^{-7} = 7$$

$$\text{pH} = 7$$

For acidic solution $\text{pH} < 7$ and in basic solutions $\text{pH} > 7$.

$$\text{Similarly } \text{pOH} = -\log [OH^-]$$

For aqueous solutions

$$K_w = [H^+] [OH^-]$$

Taking $-\log$ on both sides

$$-\log K_w = (-\log [H^+]) + (-\log [OH^-])$$

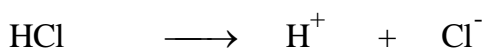
$$\text{p}K_w = \text{pH} + \text{pOH}$$

$$\text{At } 25^\circ\text{C } \text{p}K_w = -\log 1 \times 10^{-14} = 14$$

$$\text{p}K_w = \text{pH} + \text{pOH} = 14 \text{ (at } 25^\circ\text{C)}$$

Example - Calculate the pH 0.1 mol / dm³ solutions of the following (a) hydrochloric acid (b) acetic acid , (c) ammonia , (d) sodium hydroxide.

(a) Hydrochloric acid is a strong acid. It is completely ionized.



$$0.1\text{M} \qquad \qquad 0.1\text{M}$$

$$[H^+] = 0.1\text{M}$$

$$-\log [H^+] = -\log 0.1 = -\log 1 \times 10^{-1}$$

$$\text{pH} = 1$$

(b) Acetic acid is a weak acid. It is partially ionized. $K_a = 1.75 \times 10^{-5}$



$$[H^+] = \sqrt{K_a C} = \sqrt{1.75 \times 10^{-5} \times 0.1}$$

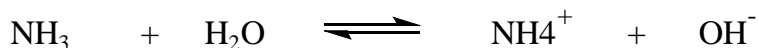
$$= 1.32 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log 1.32 \times 10^{-3} \text{ M}$$

$$= 3 - 0.12 = 2.88$$

(c) Ammonia is a weak base. It is partially ionized.

$$K_b = 1.8 \times 10^{-5}$$



$$[\text{OH}^-] = \sqrt{K_b C} = \sqrt{1.85 \times 10^{-5} \times 0.1}$$

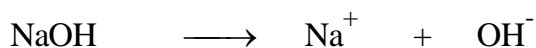
$$= 1.34 \times 10^{-3}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 1.34 \times 10^{-3}$$

$$= 3 - 0.13 = 2.87$$

$$\text{pH} = 14 - 2.87 = 11.13$$

(d) Sodium Hydroxide is a strong base. It is completely ionized.



$$[\text{OH}^-] = 0.1 \text{ M}$$

$$\text{pOH} = -\log 0.1 = 1$$

$$\text{pH} = 14 - 1 = 13$$

Hydrolysis of salts

The interaction between the particular ions of salts and water to produce an acidic or basic solution is called the hydrolysis of salts. There are four different kinds of salts.

1. Salts of strong acids and strong bases
2. Salts of weak acids and strong bases
3. Salts of strong acids and weak bases
4. Salts of weak acids and weak bases

Solutions of salts of strong acids and strong bases.

Let us consider the addition of a salts of a strong acids and strong bases, like NaCl, to a sample of pure water. NaCl is a strong electrolyte; it will completely ionized into ions.



The ionization of water is

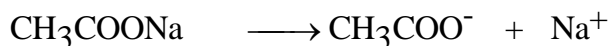


In solution there are four different ions of Na^+ , Cl^- , H^+ , and OH^- will present. HCl is a strong acid and NaOH is a strong base. Hence neither H^+ and Cl^- ions nor Na^+ and OH^- ions have tendency to combine of from either undissociated acid (HCl)

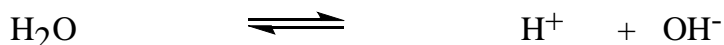
or base (NaOH).This means that the presence of NaCl in pure water does not affect the concentrations of hydrogen ions or hydroxide ions and the solution remains neutral . Therefore the pH of the solution may be 7.

Solutions of salts of weak acid and strong bases

In a solution containing a salt of weak acid and a strong base like CH₃COONa, the salt will ionized completely as follow.



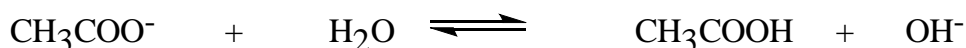
For water molecule



No interaction occur between Na⁺ and OH⁻ ions because NaOH is a strong base. However CH₃COO⁻ ion, is being an anion from the weak acid CH₃COOH, it will interact with H⁺ ions.



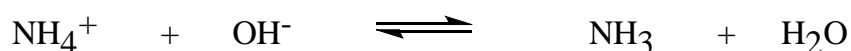
The net reaction is



OH⁻ ions are formed in this reaction. Therefore the salts of weak acid and strong base are dissolved in water, the anion will undergo hydrolysis and the solution will be basic and pH becomes greater than 7.

Solution of salts of strong acids and weak base

NH₄Cl is a salt of strong acid HCl and a weak base of NH₃. When it is dissolved in water the following equilibria are established in solution.



The net reaction is $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$

In this solution Cl⁻ will not combine with H⁺ions because HCl is a strong acid. The cation of the salt (NH₄⁺) undergo hydrolysis and produced H₃O⁺ or H⁺ was in the solution. The resulting solution become acidic and pH will be less than 7.

Solution of salts of weak acids and weak base

In the case of the solution containing a salt of weak acid and weak base, both the cation and anion can get hydrolysis .For example, in ammonium and cyanide ion can undergo hydrolysis simultaneously.





The solution can either acidic or basic or neutral. The property of the solution depends upon which equilibrium is displaced far to the right to a greater extent.

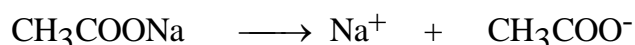
Buffer Solutions

Solutions which tend to resist the changes in $[\text{H}^+]$ or pH resulting upon addition of strong acids or strong bases or upon dilution are known as buffer solutions.

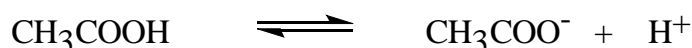
Buffer solutions can be prepared either by dissolving a weak acid and its salt in water or a weak base and its salt in water. The most common buffers are acetic acid and sodium acetate or ammonia and ammonium chloride.

Buffer Action

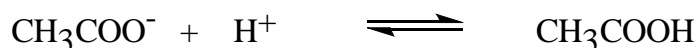
To understand how a buffer solution hinders the pH changes on addition of acids or bases, let us consider a solution containing acetic acid and sodium acetate buffer mixture. Sodium acetate being a strong electrolyte ionizes completely in solution.



Acetic acid is a weak acid, is only partially ionized in solution.



If a strong acid, such as HCl is added to the solution, H^+ ions formed from HCl will react with CH_3COO^- ions to form CH_3COOH .



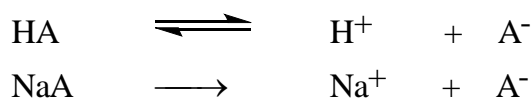
As a result of this reaction the added hydrogen ions are bound as undissociated CH_3COOH . Hence H^+ ions concentration or pH in the solution remains constant. If a strong base like NaOH is added, the OH^- ions react with H^+ ions from acetic acid to form water.



This reaction tends to lower the H^+ ions concentration in solution. But according to Le-Chatelier's principle, the ionization equilibrium of acetic acid must shift to the right to produce more H^+ ions. As a consequence the pH of the solution will not change to an appreciable extent.

pH of a buffer solution.(acid buffer)

pH of a buffer solution is governed by the dissociation equilibrium of weak acid. In a solution containing weak acid HA and its salt NaA, we have



The ionization constant of HA is

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

If C_a is the initial concentration of HA and C_s is the concentration of the salt NaA, at equilibrium, we have

$$[HA] = C_a - [H^+]$$

$$[A^-] = [A^-]_{\text{acid}} + [A^-]_{\text{salt}}$$

The salt NaA is completely ionized and thus we have

$$[A^-] = [A^-]_{\text{salt}} = [\text{Salt}]$$

Due to the presence of A^- ions from the ionization of NaA, the dissociation of HA is reduced.

$$[HA] = C_a = [\text{Acid}]$$

Inserting these values in the above equation $[H^+] = K_a = \frac{[\text{acid}]}{[\text{salt}]}$

Taking $-\log$ on both sides,

$$-\log [H^+] = -\log K_a - \log \frac{[\text{acid}]}{[\text{salt}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Note -

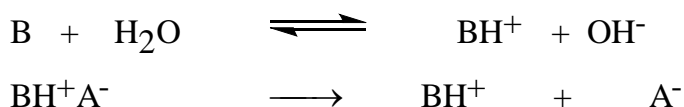
1. For the buffer action to be effective, the ratio of $\frac{[\text{salt}]}{[\text{acid}]}$ can only be varied within the limits of about 10/1 to 1/10. A useful range of pH is

$$\text{pH} = \text{p}K_a \pm 1$$

2. pH of the buffer solution depend upon the ratio of $\frac{[\text{salt}]}{[\text{acid}]}$. The ratio does not alter upon dilution. Thus pH of the solution remains constant though the solution is diluted.

pH of a buffer solution. (basic buffer)

pH of a basic buffer solution is governed by the dissociation equilibrium of weak base. In a solution containing weak base B and its salt BH^+A^- , we have



The ionization of weak base B is

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$[\text{OH}^-] = K_b \frac{[\text{B}]}{[\text{BH}^+]}$$

If C_b is initial concentration of weak base B and C_s is the initial concentration of the salt BH^+A^- , at equilibrium, we have

$$[\text{B}] = C_b - [\text{OH}^-]$$

$$[\text{BH}^+] = [\text{BH}^+]_{\text{base}} + [\text{BH}^+]_{\text{salt}}$$

The salt BH^+A^- is completely ionized and thus we have

$$[\text{BH}^+] = [\text{BH}^+]_{\text{salt}} = [\text{salt}]$$

Due to the presence of BH^+ ions from the ionization of BH^+A^- the dissociation of weak base B is reduced.

$$[\text{B}] = C_b = [\text{base}]$$

Inserting these values in the above equation.

$$[\text{OH}^-] = K_b \frac{[\text{base}]}{[\text{salt}]}$$

Taking - log on both sides,

$$-\log [\text{OH}^-] = -\log K_b - \log \frac{[\text{base}]}{[\text{salt}]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{pH} = \text{p}K_w - \text{pOH}$$

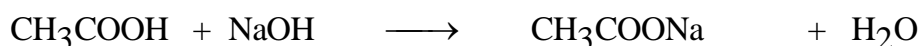
$$\text{pH} = \text{p}K_w - \text{p}K_b + \log \frac{[\text{base}]}{[\text{salt}]}$$

Example - 100cm^3 of 0.1 mol dm^{-3} acetic acid solution and 30cm^3 of 0.12 mol dm^{-3} NaOH solution are mixed at 25°C . Calculate the pH and pOH of the resulting solution. $K_a = 1.7 \times 10^{-5}$

$$100\text{cm}^3 \text{ of } 0.1 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH} = 100 \times 0.1 = 10 \text{ m mole of CH}_3\text{COOH}$$

$$30\text{cm}^3 \text{ of } 0.12 \text{ mol dm}^{-3} \text{ NaOH} = 30 \times 0.12 = 3.6 \text{ m mole of NaOH}$$

$$\text{Total volume} = 100 + 30 = 130 \text{ cm}^3$$



If the start	10m mole	3.6m mole	0	0
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Final state	6.4 m mole	0	3.6 m mole	
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The solution contains CH_3COOH and CH_3COONa so the final solution is a buffer solution.

$$[\text{acid}] = \frac{6.4}{130} \text{ mol dm}^{-3} \quad \text{and} \quad [\text{Salt}] = \frac{3.6}{130} \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{pH} &= \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= -\log 1.75 \times 10^{-5} + \log 5.6 \times 10^{-1} \\ &= 5 - 0.24 - 1 + 0.74 = 4.5 \\ \text{pOH} &= 14 - 4.5 = 9.5 \end{aligned}$$

Example - The concentration of NH_3 and NH_4Cl in 1.5 dm^{-3} of buffer solution are 0.1 mol dm^{-3} and 0.2 mol dm^{-3} respectively. Calculate the change in pH caused by the addition of 0.01 M of HCl to that solution. Assuming that no volume change on adding HCl . $K_b = 1.88 \times 10^{-5}$

$$\begin{aligned} \text{pOH} &= \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]} \\ \text{pOH} &= -\log K_b + \log \frac{[\text{salt}]}{[\text{base}]} \\ &= -\log 1.85 \times 10^{-5} + \log \frac{0.2}{0.1} \\ &= 5 - 0.26 + 0.30 \\ &= 5.04 \end{aligned}$$

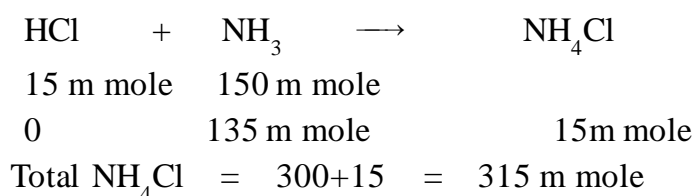
$$\text{pH} = 14 - 5.04 = 8.96$$

$$1.5 \text{ dm}^{-3} \text{ of } 0.1 \text{ M } \text{NH}_3 = 1500 \times 0.1 = 150 \text{ m mole of } \text{NH}_3$$

$$1.5 \text{ dm}^{-3} \text{ of } 0.2 \text{ M } \text{NH}_4\text{Cl} = 1500 \times 0.2 = 300 \text{ m mole of } \text{NH}_4\text{Cl}$$

$$1.5 \text{ dm}^{-3} \text{ of } 0.01 \text{ M } \text{HCl} = 1500 \times 0.01 = 15 \text{ m mole of } \text{HCl}$$

On addition of HCl following reaction will take place



$$[\text{base}] = \frac{135}{1500} \quad [\text{salt}] = \frac{315}{1500}$$

$$\frac{[\text{salt}]}{[\text{base}]} = \frac{315}{135} = 2.33$$

$$\begin{aligned} \text{pOH} &= \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]} \\ &= -\log K_b + \log \frac{[\text{salt}]}{[\text{base}]} \\ &= -\log 1.85 \times 10^{-5} + \log 2.33 \\ &= 5 - 0.26 + 0.37 \\ &= 5.11 \end{aligned}$$

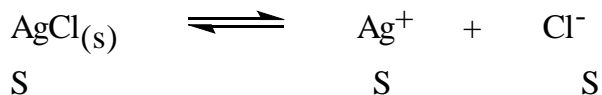
$$\text{pH} = 14 - 5.11 = 8.89$$

$$\text{Chang in pH} = 8.96 - 8.89 = 0.07$$

Sparingly soluble electrolyte

Many ionic salts are very sparingly soluble in water e.g AgCl, BaSO₄, CaCO₃.....For many purpose such substances are regarded as insoluble,

If a saturated solution of silver chloride is prepared by shaking the solid with water, the solution contains only silver and chloride ions in equilibrium with the solid.



The equilibrium constant will be

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

Taking the concentration of the solid, by the usual convention, a constant and equal to unity.

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

This constant is called the solubility product of the material. It is a constant under constant temperature. The solubility of the material, in mol dm⁻³ is related to the solubility product as follows.

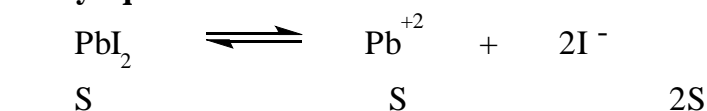
$$\text{Solubility of AgCl} = S = [\text{Ag}^+][\text{Cl}^-]$$

$$K_s = S^2$$

$$S = \sqrt{K_s}$$

Example - The solubility product of lead iodide at 25°C is 1.39 x 10⁻⁸. Calculate the molar solubility of lead iodide.

Solubility equilibrium



$$K_c = [\text{Pb}^{+2}][\text{I}^-]^2 = 1.39 \times 10^{-8}$$

$$S(2S)^2 = 1.39 \times 10^{-8}$$

$$4S^3 = 1.39 \times 10^{-8}$$

$$S^3 = 3.48 \times 10^{-9}$$

$$S = 1.51 \times 10^{-3} \text{ mol dm}^{-3}$$

The solubility product is considerable importance in analysis because it fixes the conditions under which a metal can be precipitated as a sparingly soluble salt. e.g AgCl solid is in equilibrium with a solution containing Ag⁺ and Cl⁻ ions when the product of concentration is equal to K_s. If the product [Ag⁺][Cl⁻] falls below this figure, silver chloride will dissolve conversely, when the concentration of the ions give a product greater than K_s, silver chloride will be precipitated.

Example - Will precipitate of AgCl be obtained when 3 mg of AgNO₃ 2mg of NaCl are mixed in a volume of 250 cm³ ? K_s = 1.82 x 10⁻¹⁰

$$3 \text{ mg of AgNO}_3 = 3 \times 10^{-3} \text{ g of AgNO}_3 = \frac{3 \times 10^{-3}}{169.88} = 1.77 \times 10^{-5} \text{ moles of AgNO}_3$$

$$2 \text{ mg of NaCl} = 2 \times 10^{-3} \text{ g of NaCl} = \frac{2 \times 10^{-3}}{58.46} = 3.42 \times 10^{-5} \text{ moles of NaCl}$$

$$\text{Concentration of AgNO}_3 = \frac{1.77 \times 10^{-5} \times 10^3}{250} = 7.08 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{Concentration of NaCl} = \frac{3.42 \times 10^{-5} \times 10^3}{250} = 1.37 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{Ag}^+] = 7.08 \times 10^{-5} \text{ mol dm}^{-3} ; [\text{Cl}^-] = 1.37 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{Ag}^+][\text{Cl}^-] = 7.08 \times 10^{-5} \times 1.37 \times 10^{-4} = 9.69 \times 10^{-9}$$

$$K_s = 1.82 \times 10^{-10}$$

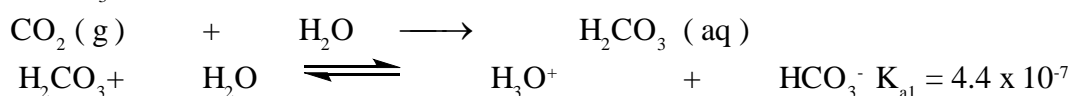
$$[\text{Ag}^+][\text{Cl}^-] > K_s$$

AgCl can get precipitated in the solution.

Buffers in Blood

One characteristic of blood that we rarely think about is its pH, yet maintaining the proper pH in blood and in intracellular fluids is crucial to human health and to life itself. This is primarily because the functioning of enzymes is sharply pH-dependent. The normal pH of blood is 7.4. Severe illness or death can result from sustained variations of just a few tenths of a pH unit. Among the factors that can lead to **acidosis**, a condition in which the pH of blood decrease below normal, are heart failure, kidney failure, diabetes, persistent diarrhea, and a long-term high-protein diet. Prolonged, extensive exercise also can produce a temporary condition of acidosis. **Alkalosis**, a condition of an increased pH of blood, may occur as a result of severe vomiting, hyperventilation, or exposure to high altitudes (altitude sickness).

Blood as a Buffer Solution : Human blood has a high buffer capacity. The addition of 0.01 mol HCl to one liter of blood lowers the pH only from 7.4 to 7.2. The same amount of HCl added to a saline (NaCl) solution isotonic with blood lowers the pH from 7.0 to 2.0. The saline solution has no buffer capacity. Several factors are involved in the control of blood pH. A particularly important one is the ratio of dissolved HCO₃⁻ (hydrogen carbonate ion) to H₂CO₃ (carbonic acid). Even though CO₂ (g) is only partially converted to H₂CO₃ when it dissolves in water, we generally treat the solution as if this conversion were complete. Moreover, although H₂CO₃ is a weak diprotic acid, we deal only with the first ionization step in the carbonic acid-hydrogen carbonate buffer system: H₂CO₃ is the weak acid and HCO₃⁻ is the conjugate base.



Carbon dioxide enters the blood stream from tissues as the byproduct of metabolic reactions. In the lungs CO₂ (g) is exchanged for O₂ (g), which is transported throughout the body by the blood.