CHAPTER # 8

ACIDS, BASES AND SALTS

Introduction:

Acids:

Acids were first recognized as substances that taste sour.

Vinegar tastes sour because it is a dilute solution of acetic acid. Citric acid is responsible for the sour taste of a lemon

Bases:

Bases sometimes called alkalis are characterized by their bitter taste and slippery feel.

Commercial preparations for unclogging drains are highly basic

Salt:

A salt is an ionic substance that results from the neutralization of an acid and a base.

Importance:

Acid-base chemistry is important in a wide variety of everyday applications.

The influence of acids on living things has assumed special importance in recent years due to the phenomenon of acid rain.

Q1. What do you know about the terms?

i. mineral acids

ii. organic acids

Ans: Acids:

Acids were first recognized as substances that taste sour

The acids classified into

(i) Mineral acids   (ii) organic acids.

Organic acids:

The organic acids are much weaker and less convenient mineral acids. The organic acids are mostly found in vegetables, fruit and other stuffs. Some common

organic acids and their appearance in different categories are as follows:

Organic acids	Where it is found
Lactic acid	Sour Milk
Citric acid	Citrus fruits like lemons, oranges
Formic acid	Insect bites
Tartaric acid	Grape juice
Maleic acid	Apples and pears

Mineral acids:

The mineral acids are much stronger acids. e.g. HCl, H_2SO_4 , HNO,

## Q2. Explain acid and bases in terms of their reaction with water.

Ans: Acid in aqueous solution:

The presence of water is essential for the formation of H^+ Acid produce H^+ ion in water which is the indication of their acidic nature

Example:

HCl is covalent in nature and does not form H^{+1} ions. However it forms H_3O^+ ions (which is hydrated proton) in the presence of H_2O
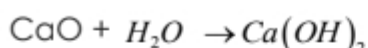
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
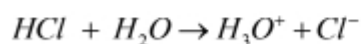
Base in aqueous solution:

Bases form a class of chemical substances including metal oxides and hydroxides. A soluble base is called an alkali and forms OH^{-1} ions when

dissolved in H_2O. In general the bases on hydrolysis produce alkali.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Here CaO is a base where as $Ca(OH)_2$ is an alkali.

Importance:

Alkalies are important in soap and detergent manufacture. Caustic soda (NaOH) is used for this purpose.

Q3. Write different properties of acids and bases.

Ans: **Properties of acids:**

Following are the different properties of acids.

i. Acids turn blue litmus red

ii. They react with carbonates to evolve carbon dioxide

iii. They have sour taste.

iv. Examples: HCl, H_2SO_4. HNO_3

Properties of bases:

i. Bases turn red litmus blue

li. They have slippery touch.

iii. They have bitter taste,

iv. Examples: sodium hydroxide (NaOH), calcium hydroxide $Ca(OH)_2$

**Q4. Define basic oxides and acidic oxides. Explain them with the help of examples.**

Ans: **Basic oxides:**

The oxides which dissolve in water to form bases are called basic oxides.

Example:

There are certain oxides of metals, like sodium oxide Na_2O and calcium

oxide (CaO) which react with water to furnish bases sodium hydroxide (NaOH) and

calcium hydroxide $Ca(OH)_2$.

$$Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2NaOH_{(aq)}$$

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)}$$
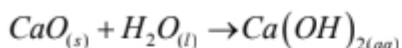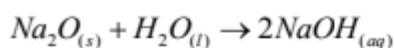
Thus, these oxides are basic in nature.
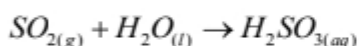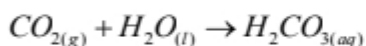
Acidic oxides:

The oxides which dissolve in water to form acids are called acidic oxides.

Example:

Non-metal oxides like carbon dioxide (CO_2) sulphur dioxide (SO_2) and nitrogen

pentoxide (Na_2O_5) when react with water yield carbonic acid (H_2CO_3)

sulphurous

acid (H_2SO_3) and nitric acid (HNO_3). Such oxides are thus acidic in nature.

$$CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)}$$

$$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$$

Note:

In addition to oxides, certain salts are also acidic and basic in nature eg

ammonium chloride (NH_4Cl) is acidic because when dissolved in water it

furnishes

an acidic solution: potassium carbonate (K_2CO_3) is basic since it yields a basic

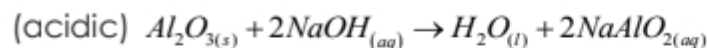solution in water. $NH_4Cl + HOH \rightarrow NH_4OH + HCl$

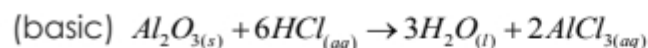$$N_2O_{5(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(aq)}$$
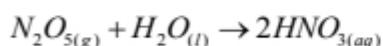
Q5. Define amphoteric oxides and give its examples.

Ans: There are certain oxides which are on the border line of being acidic or basic. These oxides which tend to be insoluble in water, are soluble in both acids and bases are called amphoteric oxides. In character that is both acidic and basic

Example:

Aluminium oxide (Al_2O_3) is amphoteric and it reacts with both acidic and basic solutions

(basic) $Al_2O_{3(s)} + 6HCl_{(aq)} \rightarrow 3H_2O_{(l)} + 2AlCl_{3(aq)}$

(acidic) $Al_2O_{3(s)} + 2NaOH_{(aq)} \rightarrow H_2O_{(l)} + 2NaAlO_{2(aq)}$

Also, chromium trioxide is amphoteric since it reacts with both acids and bases

(basic) $Cr_2O_{3(s)} + 6HNO_{3(aq)} \rightarrow 2Cr(NO_3)_{3(aq)} + 3H_2O_{(l)}$

(acidic) $Cr_2O_{3(s)} + 6KOH_{(aq)} \rightarrow 2K_3CrO_{3(aq)} + 3H_2O_{(l)}$

Q6. Define Salt, and also explain its types.

Ans:

The substance obtained as a result of neutralization of acids and bases are called salts

A salt is of three types (1) Neutral salt (2) Acidic salt (3) Basic salt.
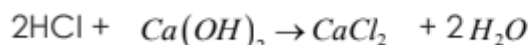
1. Neutral Salt:

It is obtained by the neutralization of a strong acid and a strong base

e.g. HCl + NaOH _NaCl + H_2O

  Strong   Strong Neutral

   acid   base

2. Acid salt:

It is obtained by the neutralization of a strong acid with a weak base.

2HCl + $Ca(OH)_2 \rightarrow CaCl_2$ + $2H_2O$

Strong Weak   Neutral

acid   base

3. Basic salt:

It is obtained by the neutralization of a strong base with a weak acid

e.g. 2NaOH + H_2CO_3 $\rightarrow Na_2CO_3 + 2H_2O$
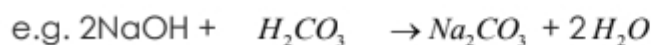
Strong base Weak acid   Neutral

Q7. 'Write a detailed note on the relative strength of acids and bases

Ans: Strength of Acids:

Different Bronsted acids donate proton to different extents

The ability of an acid to donate proton is called 'strength of acid' or the 'acid strength'.

An acid which can donate proton to a higher degree than another acid is said to be relatively strong acid.

Example:

Hydrochloric acid is a relatively stronger acid than acetic acid. Also, acetic acid is relatively stronger than water.

Strength of bases:

The bases also differ in their ability to accept proton.

A base which can accept proton to higher degree than another base is a relatively stronger base.

Example:

Thus ammonia is a relatively stronger base than water because ammonia can accept a proton to a higher degree than water

Q8. Define pH and explain different types of solutions on the bases of pH.

Ans: pH:

Since the concentration of $[H^+]$ and $[OH^-]$ are usually very small numbers and inconvenient to work with, a more practical measure called pH was proposed and defined as:

It means that pH of a solution is given by the negative logarithm of the $[H^+]$ concentration (in mol/dm^3).

pH = -log $[H^+]$

No units:

However it must be kept in mind that pH being a logarithmic value, does not have any units

The pH concept implies that at 25°C, the different types of solutions will show the following behaviour:

Acid solution: $[H^+] > 1.0 \times 10^{-7}$ M, pH < 7.00

Basic solution: $[H^+] < 1.0 \times 10^{-7}$ M, pH > 7.00

Neutral solution: $[H^+] = 1.0 \times 10^{-7}$ M, pH = 7.00

A scale analogous to the pH can be devised using the negative logarithm of the H^+ concentration.

29. Define pOH and prove that: pH + POH = 14

Ans: POH:

The negative logarithm of OH" ions concentration (in mol dm) is called POH

pH + pOH = 14

as $K_w = (H^+)(OH^-)$

$1.0 \times 10^{-14} = (H^+)[OH^-]$

Taking log of both sides

$\log(1.0 \times 10^{-14}) = \log \times (H^+) + \log(OH^-)$

$-14 = \log[H^+] + \log(OH^-)$

$14 = -\log[H^+] - \log[OH^-]$

$14 = (-\log[H^+]) + (-\log OH^-)$

$14 = PH + POH$

This equation provides another way to express the relationship between the (H^+) and $[OH^-]$ concentrations.

Q10. The concentration of $[OH^-]$ ion in a household ammonia solution is 0.005M. Calculate the concentration of (H^+) in it.

Solution: $[OH^-]$ = 0.005 M

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

$1.0 \times 10^{-14} = [H^+] \times 0.005$
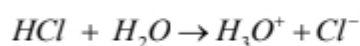
$[H^+] = \dfrac{1.0 \times 10^{-14}}{0.005}$

$= 2.0 \times 10^{-12}$ M

Q11. Calculate the pH of 0.001 M aqueous hydrochloric acid solution.

Solution:

Hydrochloric acid ionizes in water completely therefore,

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

0.001 M   0.001 M

$[H_3O^+]$ is in fact the same as $[H^+]$

Therefore $[H^+]$ = 0.001 M
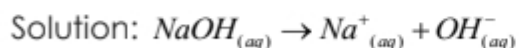
pH = -log(0.001)

= -log 10^{-3}

= 3.00

Therefore, the pH of 0.001 M aqueous hydrochloric acid is 3.00

Q12. Calculate the pH of 0.062 M NaOH solution.

Solution: $NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

0.062M   0.062 M   0.062 M

POH = -log(OH^-)

= -log (0.062)

= 1.21

Now PH +POH = 14

PH = 14 - POH

= 14-1.21

= 12.79

Activity for Students

Example 4:

What is the pH of a solution containing 1.95g pure H_2SO_4, per dm^3 of solution?
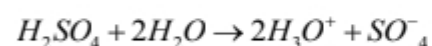
(Ans: pH = 1.4)

Solution:

Mass of H_2SO_4 = 1.95g

Molecular mass of H_2SO_4 = 98g $mole^{-1}$

Number of moles of H_2SO_4 $= \dfrac{1.95}{98} = 0.02$ $mole^{-1}$

The ionization of H_2SO_4 in water is given below

$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO^-_4$

0.02 moles   2 x 0.02 moles

$[H_3O^+]$ is in fact the hydrated proton (H^+)

Therefore $[H^+]$ = 2 x0.02 = 0.04 M

pH = -log (0.04)

= 1.40

Activity for Students

Calculate the fourth parameter when given three of four parameters- molarity of base, volume of base, molality of acid, volume of acid-used in

a titration experiment, assuming a strong acid and strong base reaction. (Analyzing)

Solution:

Titration:

It is defined as a method to find the volume of the standard solution required to react completely with known volume of another solution under analysis".

Procedure:

Acid-base titrations are conducted using burettes and volumetric pipettes

Generally acid solution is placed with the burette

A fixed volume of base is placed into a conical flask along with a few drops of the appropriate acid-base indicator

Acid from the burette is added to the base until the Indicator changes colour

This change of colour indicates the end point of titration

Phenolphthalein as an indicator:

In the neutralization of a strong acid with a strong base, phenolphthalein is used as an indicator. It imparts pink colour to the base solution. At the end point. solution just becomes colourless

The molarity of the acid solution under test is determined with the help of the following equation:

$$M_1V_1 = M_2V_2$$

Where

M_1 = Molarity of the base

V_1 = Volume of the base taken in flask

M_2 = Molarity of the acid

V_2 = Volume of acid used from the burette

Thus by knowing the three parameters, the fourth can be calculated.

Activity for Students

Perform acid-base titrations to calculate molarity and strength of given sample solutions.

Solution:

Take strong acid (HCI) and strong base (NaOH) solutions Molarity of NaOH is known and that of HCI is to be determined. For titration purposes phenolphthalein

is used as an indicator. HCI is taken in the burette while 10 ml of NaOH in the burette. The disappearance of pink colour gives the end point

According to molarity concept

$$M_1V_1 = M_2V_2$$

HCI = NaOH

$$M_1 \times 10 = \frac{1}{10} \times 10 \text{ or } M_1 = \frac{1}{10} = 0.1 \text{ m}$$

Thus molality of the given solution is 0.1m.

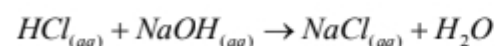Strength dm^3 = molality x molar mass

$$= \frac{1}{10} \times 36.5 = 3.65 g \, dm^{-3}$$

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Activity for Students

In a titration it is found that 25 cm^3 of 0.12M NaOH is neutralized with 30 cm^3 of HCI of unknown concentration. Calculate concentration and strength of HCI solution.

Solution:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O$$

n1=1   n2=2

HCI   NaOH

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

$$\frac{M_1 \times 30}{1} = \frac{0.12 \times 25}{1}$$

$$M_1 = 0.1M$$

Thus Molarity of HCl solution is 0.1M.

Strength of solution = Molarity x Molar mass

Strength of HCl solution = 0.1 x 36.5 = 3.659 dm^3

Q13. What is acid dissociation constant? How it is related to pK, write equation to elaborate.

Ans: Strong and Weak Acids:

i. According to the Bronsted-Lowery definition an acid is a proton donor species. Different acids have a tendency to donate proton but this tendency is different

ii. An acid may donate proton to very high degree, a high degree or to small degree or very small degree. Depending on this ability of donation of proton, an acid is regarded as strong acid or a weak acid.

iii. Strong acids donate proton to a greater degree than the weak acids. The strength of an acid is generally expressed in terms of the acid ionization constant, ka

iv. The extent of ionization and the acid dissociation constant K_a can be used to distinguish between strong and weak acids

Derivation of acid dissociation constant K_a:

Consider the case of ionization of a general acid HX in water. In this aqueous solution the established equilibrium may be represented as follows:

$$HX_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \overline{X_{(aq)}}$$
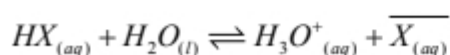
The equilibrium constant K for this ionization process may be written as follows

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$$K = \frac{[H_3O^+][\overline{X}]}{[HX]}$$

or

$$K[H_2O] = \frac{[H_3O^+][\overline{X}]}{[HX]}$$

Since water is a solvent, it is present in excess and therefore its concentration may be regarded as constant. Thus, K (H2O) is another constant and

is designated as K, thus,

$$K[H_2O] = K_a = \frac{[H_3O^+][\overline{X}]}{[HX]}$$

K_a is termed as the acid dissociation constant. It is a measure of the extent to which an acid is ionized or dissociated at the equilibrium state.

"The greater the value of K,, the stronger is the acid".

K_a is temperature dependent:

It must be kept in mind that the acid dissociation constant, K_a, is dependent on temperature. Therefore, the value of K_a should be mentioned along with the temperature at which K, was determined. Dissociation constant, K_a of acetic acid in water at 25°C is 1.8 x 10° The comparison of K, Values of different acids provides a method to compare their strengths.

PK_a:

The value of K, are usually inconvenient numbers, therefore, for convenience these values are converted to pK_a, values. The relationship between K_a, and p K_a, is as follows:

pK_a = -log K_a

Conclusion:

Since pK_a, refers to the negative logarithm of K_a. Thus smaller the value pK_a. stronger shall be the acid because smaller pK_a, value corresponds to a greater

K_a

value. In table 8.2 are listed the ionization constants and pK_a, values of some common acids in water at 25°C.

Table: Ionization constants and pk of Acids

Name of Acid	Formula	K_a	pK_a
Perchloric acid	$HClO_4$	1.0×10^{10}	-10.0
Hydroiodic acid	HI	1.0×10^{10}	-10.0
Hydrobromic acid	HBr	1.0×10^9	-9.7
Hydrochloric acid	HCl	1.0×10^7	-7.0
Sulphuric acid	H_2SO_4	1.0×10^3	-3.0
Hydrofluoric acid	HF	1.0×10^{-4}	+3.1
Formic acid	HCOOH	1.0×10^{-4}	+3.7
Benzoic acid	C_6H_5COOH	1.0×10^{-5}	+4.5
Acetic acid	CH_3COOH	1.0×10^{-5}	+4.7
Phenol	C_6H_5COH	1.0×10^{-10}	+9.3
Water	H_2O	1.0×10^{-15}	+16.0

The K_a and pK_a and given in Table 8.2 show that perchloric acid ($HClO_4$) is the strongest among all the acids given in the table. Also, water is the weakest

acid among all acids listed in it.

Q14. Calculate concentration of H^+ ions of a solution that contain1.0M HF (K_a = 7.2×10^{-4})

Solution:

$$HF_{(aq)} \rightleftharpoons H^+_{(aq)} + F^-_{(aq)}$$
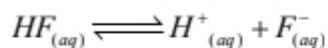
Initial conc. 1.0M

Eq. conc. 1.0 - XXX

(moles dm^3)

$$K_a = \frac{\lfloor H^+ \rfloor \lfloor F^- \rfloor}{[HF]}$$

$$7.2 \times 10^{-4} = \frac{x.x}{1.0 - x}$$

Since x is very small as compared to 1.0, the term in the denominator can be approximated as follows:

1.0-X = 1.0

$$7.2 \times 10^{-4} = \frac{x^2}{1}$$

x= 0.268M

$[H^+]$ = 0.268M

Q15. The pH of a 0.1M solution of an add is 2.85. Calculate the ionization constant K_a of the acid.
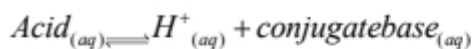
Solution:

Using the pH value, the equilibrium concentration of the acid and the conjugate base can be calculated. These concentrations may then be used to calculate K.

pH= -log $[H^+]$

$2.85 = -\log (H^+)$

Taking antilog "of" both side $[H^+]$ turns out to be 1.4×10^{-3} M.

Now equilibrium is considered:

$$Acid_{(aq)} \rightleftharpoons H^+_{(aq)} + conjugatebase_{(aq)}$$

Before equilibrium 0.100M   0.000   0.000

Change   0.0014M   0.0014M 0.0014M

At equilibrium   0.0986M   0.0014M 0.0014M

$$K_a = \frac{\left[H^+\right]\left[conjugatebase\right]}{\left[acid\right]}$$

$$K_a = \frac{(0.0014)(0.0014)}{0.0986}$$

$= 2.0 \times 10^{-3}$

Thus the ionization constant K is 2.0×10^{-3}

Q16. What is base dissociation constant? How it is related to pk. Write equation to elaborate.

Ans: Strong and Weak Bases:

The strength of a base is the ability to accept a proton form a solvent.

Hydroxides of alkali metals such as sodium hydroxide and potassium hydroxide are strong bases and ionise completely in aqueous solution

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$$KOH_{(aq)} \rightarrow K^+_{(aq)} + OH^-_{(aq)}$$
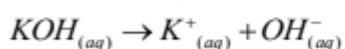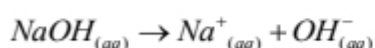
The OH^- ion thus formed is a Bronsted base because it can accept proton H^+

$$OH^- + H^+ \rightarrow H_2O$$

The ability of a base to accept a proton from an acid, usually water, is termed as strength of the base.

The extent of ionization and the base dissociation constant ko is use to

distinguish between strong and weak bases.

Derivation of base dissociation constant K_b:

Consider a base B, an equilibrium reaction with water can be represented by the following equation
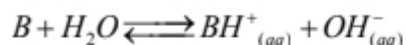
$$B + H_2O \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

Since water is a solvent, it is present in excess and therefore its concentration may be regarded as constant. Thus, K (H_2O) is another constant and is designated as K_b thus.

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

Ky value will be large if degree of ionization of the base B is high i.e. If the base B is strong. The Value of K_b will be small for a weak base B

PK_b:

For convenience, a parameter pK_b has been devised to express K_b value in convenient numbers Thus, OK is defined as the negative logarithm of K_b

pK_b = -log K_b

Table: K_b and PK_b Values of Some Common Bases:

Name of Base	Formula	K_b	pK_b
Diethlyamine	$(C_2H_5)_2 NH$	9.6×10^{-4}	3.02
Ethylamine	$C_2H_5 NH_2$	5.6×10^{-4}	3.25
Methylamine	$CH_3 NH_2$	4.5×10^{-4}	3.34
Ammonia	NH_3	1.7×10^{-5}	4.76
Pyridine	$C_5H_5 N$	5.6×10^{-9}	8.25
Aniline	$C_6H_5 NH_2$	4.3×10^{-10}	9.37

Conclusion:

According to these values' ammonia is a stronger base than pyridine and

aniline but weaker than methylamine and ethylamine. Also, diethyl amine is a strongest base among all those listed in the table

Q17. Prove that $K_a \times K_b = K_w$
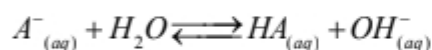
Ans: Relationship of K_a and K_b:

$$K_a \times K_b = K_w$$

This relationship can be proved by considering the ionization of an acid HA and writing equation for its K_a

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$
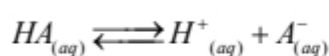
$$K_a = \frac{[H^+][A]}{[HA]}$$

The equilibrium for the conjugate base is

$$A^-_{(aq)} + H_2O \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[H^+][OH^-]}{[A^-]}$$

Multiplying the expression for K, and Ko

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

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

This result leads to an important conclusion that if the value of K, s known K. can be calculated since $K_a \times K_b = K_w$

$$K_a = \frac{K_w}{K_b}$$

$$K_b = \frac{K_w}{K_a}$$

<mark>Conclusion:</mark>

Since Kw is constant at a given temperature, it may be deduced that K, is inversely proportional to K_b.

$$K_a \alpha \frac{1}{K_b}$$

Thus, stronger the acid, weaker is its conjugate base. It can also be said that stronger a base, weaker is its conjugate acid.

Example:

Ammonia is a weaker base (pK_b = + 4.76) than diethylamine (pK_b - 3.02), therefore the conjugate acid of ammonia is stronger acid than the conjugate acid of diethylamine Similarly, the conjugate base of a weak acid, water (PK_b = +6.00) is a stronger base than the conjugate base of stronger acid, hydrochloric acid (pK_b 7.00) Thus hydroxide ion (OH)s a stronger base than the chloride ion (Cl)

Q18. Prove that pK_a + pK_b = 14 at 25°C

Solution: $K_a \times K_b = K_w$

Taking log on both sides

log ($K_a \times K_b$) = log K_w

log K_a + log K_b = log K_w

On changing the signs from plus to minus in the above equation

(-log K_a) + (-log K_b) = (-log K_w)

Note that in terms of PK_a ,& pK_b the equation becomes

PK_a + pK_b - PK_w

As PK_w = 14 at 25°C

$PK_a + PK_b) = 14$ at 25°C

Q19. The pk, of acetic acid at 25°C is +4.76. Calculate the pkb of the conjugate base of acetic acid.

Solution:

$PK_a + PK_b = 14.00$

PK_a of acetic acid is given as + 4.76

$4.76 + pK_b = 14$ or $pK_b = 9.24$

Example 8 (b);

The pK_a of acetic acid at 25°C is + 4.76. Calculate the pK_b of the conjugate base of acetic acid.

Solution:

$PK_a + PK_b = 14.00$

pK_a of acetic acid is given as + 4.76

$4.76 + pK_b = 14$

Solution:

$PK_a + PK_b = 14.00$

pK_a of pyridine = + 8.25

therefore $pK_a + 8.25 = + 14.00$

and pK_a

$=14.00 - 8.25$

$= +5.75$

Therefore the pK_a of the conjugate acid of pyridine turns out to be +5.75 one of the important conclusion of the equation $K_a \times K_b = K_w$ is

Activity for students

What is the percentage ionization of acetic acid in a solution In which 0.1 M of it has been dissolved per dm^3 of the solution
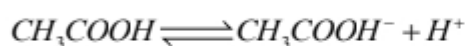
K_a = 1.8 x 10^{-5}

Hint:

Percentage ionization = $\dfrac{concentration\ of\ ionised\ acid}{original\ concentration}$ x100

(Ans: 1.3%)

Solution:

$$CH_3COOH \rightleftharpoons CH_3COOH^- + H^+$$

Initial Conc. 0.1   0   0

(mol/ dm^3)

                          X   X

Equilibrium Conc 0.1-x= 0.1 \since acid is weak:

(mol/ dm^3)

K_a for acetic acid is given by

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]}$$

$K_a = \dfrac{x.x}{0.1} = 1.8 \times 10^{-5}$

$x^2 = 0.1\left(1.8 \times 10^{-5}\right)$

$x^2 = 1.8 \times 10^{-6}$)

Taking square root on both sides

x = 1.3 x 10^{-3} moles

Hence (H^+) = x= 1.3 x 10^{-3} moles

$$\% \text{ Ionization} = \frac{Amount \ of \ acid \ ionized}{Amount \ of \ acid \ initially \ available} \times 100$$

$$\% \text{ ionization} = \frac{1.3 \times 10^{-3}}{0.1} \times 100 = 1.3\%$$

<mark>Activity for Students</mark>

Calculate the [H_3O^+] given the K_a and molar concentration of weak acid.

Solution:

When water is added to a weak acid, It is partially dissociated. Thus an equilibrium is established between the dissociated and un-dissociated molecule,

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

$$K = \frac{\lfloor H_3O^+ \rfloor \lfloor X^- \rfloor}{[HX][H_2O]} \text{ Law of Mass action}$$

The quantities written within brackets indicate activities of reactants and products. As water is always in excess, therefore, its concentration remains almost constant

The above equation is further written as:

$$K[H_2O] = \frac{\lfloor H_3O^+ \rfloor \lfloor X^- \rfloor}{[HX]}$$

$$K_a = \frac{\lfloor H_3O^+ \rfloor \lfloor X^- \rfloor}{[HX]}$$

Where K_a is called dissociation constant of the weak acid.

or $K_a[HX] = \lfloor H_3O^+ \rfloor \lfloor X^- \rfloor$

$$[H_3O^+] = \frac{K_a[HX]}{[X^-]}$$

Thus $[H_3O^+]$ can be calculated if K_a (HX) and (1) are known

<mark>Activity for Students</mark>

Calculate the K, for the system, given the equilibrium concentrations of a weak acid and the $[H_3O^+]$ in the solution.

Solution:

In the equation

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

$$K = \frac{[H_3O^+][X^-]}{[HX][H_2O]}$$

$$K[H_2O] = \frac{[H_3O^+][X^-]}{[HX]}$$

$$K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

where H2O) = K_a

Thus K_a the ionization constant of weak acid can be calculated if $[H_3O^+]$ [X] and (HX) are known $[H_3O^+]$ X and the activities of $[H_3O^+]$ X and HX respectively.

Example 10:

(a) Calculate the pH of an acetic acid-sodium acetate buffer solution

containing 1.0 moles of each component.

(b) What will be the pH of this solution after addition of 0.01 mole of hydrochloric acid gas to 1dm' volume? Assume that the volume of solution remains unchanged on addition hydrochloric acid (ka for acetic acid is 1.8×10^{-5}

(c) The pH of the buffer solutions can be calculated by assuming the equilibrium concentration of both the acid and its conjugate base as starting concentration.
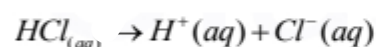
Thus $CH_3COOH = 1.0M$ $CH_3COOH = 1$ OM

For acetic acid dissociation

$$K_a = \frac{[CH_3COOH][H^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} \frac{[1.0][H^+]}{[1.0]}$$

Thus, the pH of buffer solution is 4.745

(d) After HCl addition:

$$HCl_{(aq)} \rightarrow H^+(aq) + Cl^-(aq)$$

0.01 mole 0.01 mole 001 mole

Initially, there were 1.0 mole of CH_3COOH and 1.0 mole of CH_3COOH

present per dm of the solution. After addition of hydrochloric acid 0.01 mole of CH_3COO^- ions are combined with the H^+ ions formed from dissociation of 0.01 mole of added hydrochloric acid. This can be written as.
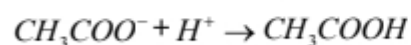
$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

0.01 mole 0.01 mole 0.01 mole

Thus, the numbers of moles of acetic acid and acetate ions, after addition of hydrochloric acid are:

CH_3COOH : (1.0+0.01) mole = 1.01 mole

CH_3COO^- :(1.0-001) mole = 0.99 mole

The equilibrium equation for this new situation can be written

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Or $[H^+] = \frac{[CH_3COOH]}{[CH_3COO^-]}$

$$[H^+] = \frac{1.8x10^{-5}(1.01)}{0.99}$$

$$pH = -\log(2.2 \times 10^{-5}) = 4.736$$

Notice there is a slight change in PH from 4 745 10 4.736, that is only a difference of 0.009. Thus a buffer does a very good job in limiting the change in pH to a very small amount.

Q20. What are buffer solutions? Elaborate with suitable examples. their significance in acid-base reactions. Write three common applications of buffer solutions.

Ans: Definition:

Those solutions which resist the change in their pH when a small amount of an acid or a base is added them are called buffer solutions. They have a specific constant value of pH.

Buffer Capacity:

A buffer solution is that which tends to maintain its pH when small amount of an acid or alkali is added to that. The property of such a solution is called buffer action and the capability to maintain constant pH as buffer capacity

Constitution of buffer:

A buffer solution contains a weak dissociating acid and the salt of that acid with a strong base

$$H_2CO_3 + NaHCO_3$$

e.g. (1) $H_3PO_4 + NaH_2PO_4$

$$CH_3COOH + CH_3COONa$$
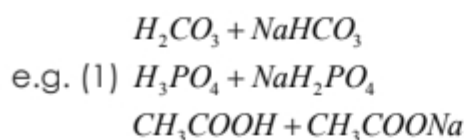
(2) A solution containing a weak base eg, NH_4OH and its salt with a strong acid like NH_4Cl can also act as a buffer.

Equations to explain buffer solution:

Let us take a buffer solution $H_2CO_3 + NaHCO_3$ If HCl is added to it the reaction will be

$$NaHCO_3 + HCl \rightarrow NaCl + H_2CO_3$$
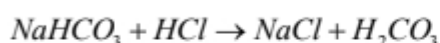
The addition of HCl will result only a little change in the original pH of the butter solution in the same way if NaOH is added to this buffer solution, it reacts with H_2CO_3 as follows:

$$NaOH + H_2CO_3 \rightarrow NaHCO_3 + H_2O$$
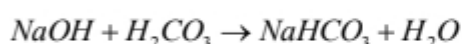
Since $NaHCO_3$ is a much weaker base than NaOH, the resulting rise in pH will be quite small

Composition of a buffer solution:

The composition can be expressed in two ways:

(1) Acidic buffers:

By mixing a weak acid and a salt of it with a strong base. Such solutions give acidic buffers with pH less than 7. e.g. $CH_3COOH + CH_3COONa$

(2) Basic buffers:

By mixing a weak base and a salt of it with a strong acid. Such solutions will give basic buffers with pH more than 7. e.g. $NH_4OH + NH_4Cl$

Buffer Action:

(1) Let us take a buffer solution of CH_3COOH and CH_3COONa Common ion effect helps us to understand how will buffer work. CH_3COOH being a weak electrolyte undergoes very little dissociation. When

CH_3COONa a strong electrolyte is added to CH_3COOH solution, the dissociation of CH_3COOH is suppressed due to common effect of CH_3COO

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

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$
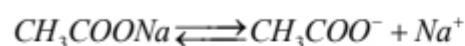
Addition of strong acid:

Suppose we add a few drops of HCl to it is H ions are used up by CH_3COO and the equilibrium is shifted towards left.

Thus the addition of HCl will not change the pH of the buffer solution

(ii) Addition of strong base:

In the same buffer solution, if a strong base is added it is neutralized by the acid.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$H^+ + OH^- \rightarrow H_2O$$
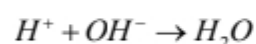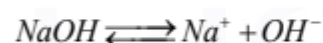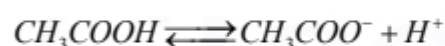
Thus the addition of NaOH will not change value of pH

Applications of buffer solutions:

(i) Buffer solutions play an important role in several industrial processes For example, they are used in the manufacture of photographic materials, leather and dyes

(ii) They are also used in the process of electroplating and analytical procedures.

(iii)The buffer solutions are also used for calibration of pH meters.

(iv) In nature, many biological systems depends upon buffer action to preserve a constant pH e.g. The pk of human blood is maintained between 7.35 to 7.45 The pH of tea's is also maintained at 7.40 whereas the stomach Juices are

known to have pH preserved at 1.65 -1 75. Milk and egg white (protein) show their pH as 6.7 68 and 80-8.1 respectively

(v) Buffers are used to maintain the pH of culture media for the growth of bacteria in bacteriological applications.

Q21. List some important facts about buffer solutions.

Ans: Some important facts about buffer solutions are as follows:

(i) Buffer solution can be prepared by combining, in aqueous solution, a weak acid and its conjugate base or a weak base and its conjugate acid

(ii) A buffer solution resists change in its pH even if a small amount of strong acid or a base is added to it.

(iii) A buffer solution maintains the stability of its pH by shifting their equilibrium to consume added H* ion or to replace H_3O^+ ions which have reacted with the added OH ions.

(iv) An aqueous solution of a strong acid and its conjugate base (as its soluble sat) cannot act as a buffer solution. Since the strong acid is completely ionized already addition of small amount of base (OH ions) will consume the H_3O^+ ions which cannot be replaced and the pH of the solution will change. If a small amount of strong acid is added to this solution, the equilibrium will not shift to the left because the acid already present is a strong acid. Also a solution of strong base and its conjugate acid do not form a buffer solution due to similar reasons.

(v) Some common examples of butters are acetic acid/sodium acetate buffer phosphoric acid/potassium dihydrogen phosphate buffer and formic acid/sodium format buffer.

Q22. What is the pH of buffer if concentration of CH_3COOH is 0.1 M dm^{-3} and CH_3COONa is 1.0 M dm^{-3} P K_a for CH_3COOH is 4.76?

Solution:

Concertation of CH_3COOH = 0.1 M dm^{-3}

Concentration of CH_3COONa = 1,0 M dm^{-3}

The formula to determine pH value is

$$pH = PK_a + \log\text{-}\frac{salt(i.eCH_3COONa)}{acid(i.eCH_3COOH)}$$

$$pH = 4.76 + \log\left(\frac{1.0}{0.1}\right)$$

$$pH = 476 + \log 10 \left(\frac{1.0}{0.1} = \frac{10}{1}\right)$$

$$pH = 4.76 + 100 \ (\log 10 = 1)$$

$$pH = 576$$

==Activity for Students==

Example 12:

Calculate the pH of a buffer solution in which 0.11 Molar CH_3COONa and 0.09

Molar CH_3COOH solutions are present.

K_a **for CH_3COOH is 1.8 x 10-**   **(Ans: 4.83)**

Solution:

K_a of acetic acid = 1.8 x 10-5

pK_a = -log K_a

PK_a = log (1.8 x 10)

PK = 4.745

$[CH_3COOH]$ = 0.09 M

$[CH_3COONa]$ = 0.11 M

$$pH = pK_a + \log \frac{salt(i.eCH_3COONa)}{acid(i.eCH_3COOH)}$$

$$pH = 4\ 745 + \log\left(\frac{0.11}{0.09}\right)$$

pH = 4 745 + 0.087

pH = 4.832

Q23. Briefly describe the concept of salt hydrolysis.

Ans: Salt Hydrolysis (Major Concept):

"The reaction of cations and anions of salts with water is called hydrolysis."

Consider the following observations:

(i) Aqueous solution of NH_4Cl turns blue litmus red

(ii) Aqueous solution of K_2CO_3 turns red litmus blue

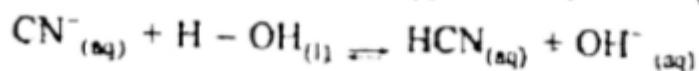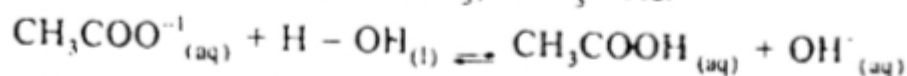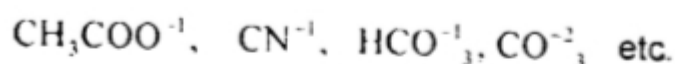**(iii)** Aqueous solution of NaCl has no action on litmus solutions.

Explanation:

These observations can be explained on the base of Bronsted-Lowry acid-e theory. When a salt (MX) is dissolved in water, it splits up into its M and X ions These ions may react with water and give following reactions:
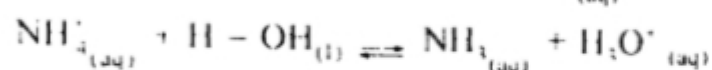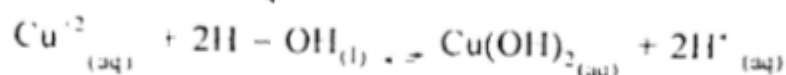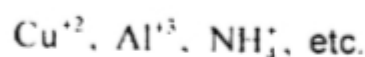
M' + H-OH,.. MOH +H

X + H - OH... HX + OH
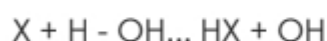
Since H^+ and OH ions are produced in these reactions, the solution of the salt may be acidic or basic. In salts anions are derived from acids and cations from bases. The anions of weak acids are strong conjugate bases. Such anions react with water producing basic solutions

Examples:

$$CH_3COO^{-1}, \quad CN^{-1}, \quad HCO^{-1}_3, CO^{-2}_3 \quad \text{etc.}$$

$$CH_3COO^{-1}_{(aq)} + H-OH_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

$$CN^-_{(aq)} + H-OH_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$

$$CO^{-2}_{3(aq)} + 2H-OH_{(l)} \rightleftharpoons H_2CO_{3(aq)} + 2OH^-_{(aq)}$$
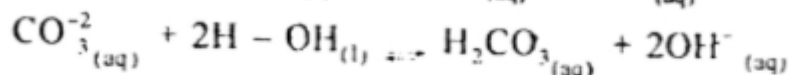
Anions like Cl. NO, SO_4^{-2} are so weak conjugate bases that they do

not react with water. Cations of weak bases are strong conjugate acids Such

cations react with water producing acidic solutions.

Examples:

$$Cu^{+2}, Al^{+3}, NH_4^+, \text{ etc.}$$

$$Cu^{+2}_{(aq)} + 2H-OH_{(l)} \rightleftharpoons Cu(OH)_{2(aq)} + 2H^+_{(aq)}$$

$$NH_4^+{}_{(aq)} + H-OH_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$$

Cations like Na* Ca^{+2} k*, Mg^{+2} etc. are so weak conjugate acids that they

do not react with water.

These reactions, are called hydrolysis reactions.

Types of salts:

There are four types of salts on the basis of their reactivity with water:

1. Salts of strong acids and strong bases do not hydrolyze (pH = 7)

Examples: NaCl, $NaSO_4$, KNO3, etc

2. Salts of weak acids and strong bases hydrolyze producing basis solutions (pH>7).

Examples: CH_3COONa NaCN, Na, etc.

3. Salts of strong acids and weak bases hydrolyze producing acidic solutions (pH <7)

Examples: $CuSO_4$, NH_4Cl, NH_4NO_3 etc.

4. Salts of weak acids and weak bases hydrolyze, but the resulting solution is

either neutral acidic or basic. This depends upon the relative values of K, and

K_b of cations and anions of the salt.

The important aspects of the salt hydrolysis, discussed above, are summarized in Table 8.5
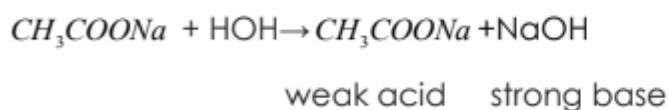
Table 8.5: Summarized discussed as above

| Salt Type		Common Example	Ions which impart Hydrolysis	Solution pH (Nature)
Acid	Base			
Strong	Strong	NaCl, K Br	None	= 7.0 (Neutral)
Strong	Weak	NH_4NO_3, NH_4Cl	Cations	< 7.0 (Acidic)
Weak	Strong	NaCN, K_2CO_3	Anions	> 7.0 (Basic)
Weak	Weak	NH_4CN, NH_4NO_2	Anions & Cations	May be equal, smaller or greater than 7.0

24. Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic.

Ans:

The salts of weak ac.ds and strong bases hydrolyze producing basic solution. Here the value of pH is greater than 7. For examples CH_3COONa , Na,S etc. The equation is

$$CH_3COONa + HOH \rightarrow CH_3COONa + NaOH$$

$$\text{weak acid} \quad \text{strong base}$$

$Na_2S + 2HOH \rightarrow H_2S + 2NaOH$

The salts of strong acids and weak bases hydrolyze producing acidic solution. Here the value of pH is lesser than 7. For example $CuSO_4$, NH_4Cl etc The equation is

$$CuSO_4 - 2HOH \rightarrow Cu(OH)_2 + H_2SO_4$$

weak bases strong acid
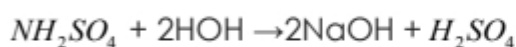
$NH_4Cl + HOH \rightarrow NH_3OH + HCl$
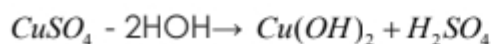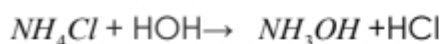
weak bases strong acid

The concept of hydrolysis can be used to explain why the solution of a salt is not necessarily neutral.

The salts of strong acids and strong bases are neutral because the value of

etc.

$NaCl + HOH \rightarrow NaOH + HCl$

strong base strong acid

$NH_2SO_4 + 2HOH \rightarrow 2NaOH + H_2SO_4$

strong base strong acid

However salts of weak acids and strong bases and salts of strong acids and weak bases show acidic or basic behaviour.

Salts of weak acids and weak bases hydrolyses, but the resulting solution is neutral, acidic or basic. This depends upon the relative values of Ka and K_b of cations and anions of the salt

Q25. How hydrolysis is different from hydration?

Ans: Hydrolysis is different from hydration la hydrolysis H-OH bond is broken whereas in hydration water molecule adds up to a substance without bond breakage

<mark>**Activity for Students**</mark>

Calculate concentrations of ions of slightly soluble salts using concept of solubility product.
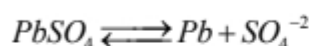
Ans. Solubility Product:

The product of the molar concentration of positive and negative ions in saturated solution in equilibrium with solid salt is called solubility product.

Explanation:

When a sparingly soluble electrolyte is dissolved in water to form a saturated solution an equilibrium is established between the dissociated and un-dissociated

salt eg $PbSO_4$

$$PbSO_4 \rightleftharpoons Pb + SO_4^{-2}$$

$$K_c = \frac{[Pb^{2}] \times [SO_4^{2}]}{[PbSO_4]}$$ Law of mass action

The rate of change of concentration of PbSO4 is so small that it almost remains constant

$$K_c \times [PbSO_4] = [Pb^{+2}] \times [SO_4^{2}] \quad \text{or}$$
$$K_{SP} = [Pb^{+2}] \times [SO_4^{2}] \text{ where } K_c [PbSO_4] = K_{SP}$$

Where Ksp is called as solubility product

The product of the molar concentration of positive and negative ions in saturated solution in equilibrium with solid salt is called solubility product

Q26. Example 13: The solubility of PbF_2 at 25°C is 0.64g dm^{-3} calculate Ksp of PbF_2.

Solution:

Mass of $PbF_2 = 0.649 \, dm^{-3}$

No of moles $PbF_2 = \dfrac{mass of PbF_2}{molar mass of PbF_2}$

$= 26 \times 10$. Mole dm^{-3}

Now from the equation

$$2.6 \times 10^{-1} \, M \, dm \rightleftharpoons 2.6 \times 10^{-3} M + 2 \times 2.6 \times 10^{-3} M$$

$$K_{sp} = [Pb^{-2}] \times [F^{-1}]^2$$
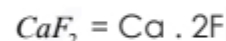
$$= 2.6 x 10^{-3} [2 x 26 x 10^{-3}]^2$$

Activity for Students

The solubility of CaF_2 in H20 at 25°C is found to be 2.05 * 10* Mdm.

What is the value of Ky at this temperature? (Ans: Ksp = 8.405 x 10-2)

Solution:

Solubility of CaF_2 = 2.05 x 10 mole dm^{-3}

According to Balanced chemical eq.

CaF_2 = Ca . 2F

At intial stage 2.05 x 10^{-4}

(mole dm^{-3})

After solubility   0 2.05×10^{-4} $2 \times 2.05 \times 10^{-4}$
(At eq. mol/dm³)

Hence

$$[C_a^{2+}] = 2.05 \times 10^{-4} mole \, dm^3$$
$$[F^-] = 2 \times 2.05 \times 10^{-4} = 4.1 \times 10^{-4} \, mole \, dm^{-3}$$

Therefore

$$KSP = [C_a^{2+}] = F^-]^2$$
$$KSP = [2.05 \times 10^{-4} mole \, dm^{-3}][4.1 \times 10^{-4} mole \, dm^{-3}]^2$$
$$KSP = 3.446 \times 10^{-11} mole^3 \, dm^{-9}$$