SEM-III (PHYSICAL CHEMISTRY)

1. Chemical Energetics 2. Chemical Equilibrium

3. Ionic Equilibrium

IONIC EQUILIBRIUM 8L

Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ... application of solubility product

[* Ionization Constant and ionic product of water, Ionization of wk acids and bases, pH scale, Common ion effect; Salt hydrolysis - Calculation of hydrolysis constant, degree of hydrolysis and pH for different salts; Buffer solutions; Solubility and solubility product of sparingly soluble salts - applications of solubility product principles]

Principles.

Electrolytes.

Electrolytes
- NaCl, KCl, CaCl$_2$, NaOH → Strong (ionophore) : (True electrolyte)
- CH_3COOH, ... → Weak (Ionizers) : (Potential ")
- H_3BO_3 ... → Intermediate ...

Strong electrolytes: practically present wholly as ions, law of mass action will result no fruitful out come.

Weak electrolytes are only partially dissociated to ions and so, law of mass action is valid. -

Arrhenius idea (revolutionary at that time) (1887) → extensive reversible dissociation of molecules of electrolytes — e.g. $NaCl \rightleftharpoons Na^+ + Cl^-$ (molecule)

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$

and so on.

He even proposed methods for determination of d
of dissociation (α).

Today we know that though his basic idea o
existence of ions in solution is correct, h
further development of idea, as far as Sti
electrolyte is concerned was completely erro
the latter being practically completely ionized
all dilutions.

Strong electrolyte : (a) $NaCl(s) \rightleftharpoons Na^+ + Cl^-$

(b) $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

Weak electrolyte : (c) $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + C$

(d) $HgCl_2 \rightleftharpoons HgCl^+ + Cl^-$

HCl and CH_3COOH being covalent compound
suffer a proton partition reaction (protol
with water to form ions, the former react
completely while the latter (a weak elect
only partially.

NaCl on the other hand being an electro
compound which is present wholly as Na^+
ions in the solid state just falls apart (no d
ociation is necessary); hydration of the ions
such cases probably also take place but is no
an essential part of the ionization proce

Dissociation of weak acids and bases

Following Brönsted theory of acids and bases it is simpler to view dissociation of weak acids and bases as proton partition reaction with the solvent (water).

e.g.;

2/9/2022

(i) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

(ii) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

@ In water the free H^+ (proton) has practically no existence and it exists wholly in the hydrated form H_3O^+ (H^+, H_2O) called oxonium or hydronium ion. However, we use H^+ for H_3O^+ for the sake of simplicity.

(Brönsted theory)

(Proton donor acceptor)

Conjugate acid base pairs

(b) Note that we need not bother with the intermediate formation of NH_4OH ($NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$). because the concentration of NH_4OH has been found to be negligible.

29/8/2022 — Class-I
5 students

Ostwald's Dilution Law:

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

Say one mole of a binary electrolyte is dissolved in 'v' litre of water. (V litre/soln contains one mole → 1 litre contains 1/V mole, $c = \frac{1}{V}$.) At equilibrium a fraction 'α' of it dissociated into ions.

Since concentration = no of moles/volume (1/v), we have,

$[CH_3COOH] = (1-\alpha)/V$

$[H^+] = [CH_3COO^-] = \alpha/V$

Dilution law: $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{\alpha/v \cdot \alpha/v}{(1-\alpha)/v}$

$\frac{\alpha^2 \cdot v}{(1-\alpha)v^2} = \frac{\alpha^2}{(1-\alpha)v} = \frac{\alpha^2 c}{(1-\alpha)}$ --- (1)

K_a: Ionization constant or the Dissociation constant of the acid.

K_a: like any other equilibrium constant, is constant at const. temp. Its value changes with Temp and ionic strength (μ)

$\mu = \frac{1}{2}\sum c_i z_i^2$

z_i: valency of ion; c_i: conc. of ith ion.

This equation relates the variation of the degree of dissociation with dilution is known as 'Ostwald's Dilution Law'.

'α' is generally determined by conductivity measurements, the above formula can be put in a different form, — as $\alpha = \Lambda/\Lambda_0$ ↕ $\alpha = \frac{\Lambda}{\Lambda_0}$

(Λ = equivalent conductivity; Λ_0 → 100% dissociation)

$\Lambda = \frac{1000\,k}{c}$; $\Lambda = kV$

k: sp. conductance

c: Conc^n gm eqvt/litre

$\Lambda = kV$

V: volume of the soln (cc) containing one gm eqvt. of electrolyte

Unit: $k = ohm^{-1}cm^{-1}$

c = in gm eqvt/L

c: gm eqvt/litre

c: gm eqvt/1000 cc.

1 cc → $\frac{c}{1000}$

c gm eqvt → 1000 cc

1 gm eq → $\frac{1000}{c}$ cc. = V (1)

or, $K_a = \frac{(\Lambda/\Lambda_0)^2 c}{(1-\Lambda/\Lambda_0)} = \frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)}$

Ostwald's dilution Law holds good fairly well for weak acids and bases.

The following table shows some data:

c (moles/litre)	α (%)	$K_a \times 10^5$
1·006	0·40	1·62
0·501	1·614	1·88
0·0629	1·66	1·76
0·000134	30·1	1·72

K_a for acetic acid remains fairly constant over a wide range of concentration.

For bases dissociation const is represented by K_b

Approximate Form of Ostwald's dilution Law

If the degree of dissociation is very small, as is the case of weak electrolytes at ordinary concentration, then

$(1-\alpha) \approx 1$

$K_a = \frac{(\alpha/v)(\alpha/v)}{(1-\alpha)/v} \approx \frac{\alpha^2}{v^2}\frac{v}{(1-\alpha)} \approx \frac{\alpha^2}{(1-\alpha)v} \approx \frac{\alpha^2}{v}$

$K_a = \frac{c\alpha \cdot c\alpha}{(1-\alpha)c} = \frac{\alpha^2 c}{(1-\alpha)}$

$K_a = \alpha^2 c = \frac{\alpha^2}{v}$

$\alpha = \sqrt{K_a \cdot v} = \sqrt{\frac{K_a}{c}}$

$\alpha \to$ very small $\therefore \alpha \ll 1$

For weak electrolyte

$[H^+] = \alpha c = \sqrt{\frac{K_a}{c}}\, c = \sqrt{K_a \cdot c} = (K_a c)^{\frac{1}{2}}$

$-\log[H^+] = -\frac{1}{2}\log K_a - \frac{1}{2}\log c$

$pH = \frac{1}{2} pK_a - \frac{1}{2}\log c$: Proof

Degree of dissociation (ionization) (α)

The fraction of the total number of molecules present as ions is known as the degree of dissociation (α) of the electrolyte.

'α' of course depends on dilution and as a general rule, 'the more dilute the solution the greater is the degree of dissociation'.

P-321:

$CH_3COOH \longrightarrow CH_3COO^- + H^+$: Forward reaction is a unimolecular process and dissociation is proportional to $[CH_3COOH]$. On the other hand the recombination. $CH_3COO^- + H^+ \longrightarrow CH_3COOH$ is a bimolecular process and so is proportional to the square of 'α'

∴

So, on diluting to say, double volume, the speed of the direct reaction falls to only half but that of the reverse reaction reaction falls to one fourth, and so, the reaction goes towards the forward direction and the equilibrium gets displaced to the right. * to make ionic

$r_f \propto [CH_3COOH]$ ✓ : Unimolecular, $a \to |a|^1$. $C \to C$

$r_f \to \frac{1}{2} r_f$: $\frac{1}{2^1}$

but $r_b \propto [CH_3COO^-][H^+]$: Bimolecular

$a \to 2a$

$r_b \to \left(\frac{1}{2}\right)^2 r_b$.

(Eqlm. is displaced to the right on dilution.)

Ionization (Auto-protolysis) of Water:

: Ionic product of water :

Even the purest water is not an absolute non-conductor but conducts current very feebly suffering electrolysis. So, water is a weak electrolyte, due to the presence of very small quantities of hydrogen $[H^+]$ and hydroxyl $[OH^-]$ ions, which are in equilibrium with undissociated water molecules according to the equation,

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

or more correctly, $2H_2O \rightleftharpoons H_3O^+ + OH^-$

[One molecule of water donates a proton (acting as an acid) to another molecule of water which accepts the same i.e. acts as a base. So the same kind of molecule is acting as a proton-donar (i.e. an acid) and a proton acceptor (i.e. a base) at the same time and so this is auto protolysis of water]

Applying the law of mass-action:

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

$$K = \frac{[H^+][OH^-]}{[H_2O]} \quad \text{or,} \quad [H^+][OH^-] = K \times [H_2O] \quad \cdots (1)$$

Since in water the active mass of H_2O is constant, we have

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

where K_w is called the **Ionic Product** for water.

In pure water $[H^+] = [OH^-] = \sim 10^{-7}$ gmion per litre at 25°C. the value of $K_w \sim 10^{-14}$ at mean R.T i.e. 25°C and independent of whether the solution is acidic or alkaline.

K_w has got this value in all aq. solns at 25°C. Pure water contains very few H^+ and OH^- ions; at 25°C 1 gm ion H^+ in 10 million litre of H_2O.

Suppression of dissociation by Common Ion:

Later detailed discussion

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

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

or, $[H^+][CH_3COO^-] = K_a[CH_3COOH]$

If to a solution of acetic acid some sodium acetate is added, the equilibrium will change. Acetic acid ionizes giving H^+ and CH_3COO^- ions and there is established the equilibrium.

Here, $CH_3COONa \longrightarrow CH_3COO^- + Na^+$

$[CH_3COO^-]$ increases, since the concentration of un-ionised acetic acid can not increase very much, as the dissociation is usually small, $[H^+]$ will thus be proportionately decrease to maintain the same value of the equilibrium const. The introduction of a salt with a common ion decreases the degree of dissociation of a weak electrolyte. (Salting out)

Thus, the degree of dissociation is approximately inversely proportional to the concentration of the added substance.

Common ion effect

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

Le Chatelier's principle

$\therefore \alpha = \sqrt{K v} = \sqrt{\frac{K}{c}}$ ——— (1)

For weak electrolyte, the degree of dissociation is inversely proportional to the square root of concentration, and directly proportional to the square root of dissociation const.

On the other hand, if α is not negligible in comparison with unity, the equation is a quadratic equation w.r.t α and on solving gives

$$\alpha = -\frac{Kv}{2} + \sqrt{Kv + \frac{K^2 v^2}{4}} \quad \text{——— (11).}$$

Eqn (1) valid only under the approximation of $\alpha \to 0$, i.e., α is negligible in comparison to 1.

P-32

1. A decinormal solution of acetic acid is ionised to the extent of 1.3%, find the ionization const (K_a) of acetic acid.

decinormal : (0.1N)

Here, $\alpha = 1.3\%$.

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

$$= \frac{(1.3 \times 10^{-3})^2}{0.987 \times 0.1} = \frac{(1.3)^2 \times 10^{-6}}{0.987 \times 10^{-1}}$$

$$= 1.71 \times 10^{-5}$$

$[H^+] = \alpha C$

$= 0.1N \times 1.3\%$

$= 0.1N \times 0.013$

$= 1.3 \times 10^{-3} N$

$[CH_3COO^-] = [H^+] = 1.3 \times 10^{-3} N$

$[CH_3COOH] = (1-\alpha)C$

$= (1 - 0.013) \times 0.1$

$= 0.987 \times 0.1$

(i) K_{a} = NH_4^+ : acid
NH_3 : base

Here:

$K_a \times K_b = \frac{[NH_3][H^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_3]}$

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

Proof of $K_a \times K_b = K_w$

$\log K_w = \log K_a + \log K_b$

$-\log K_w = -\log K_a - \log K_b$.

$pK_w = pK_a + pK_b$.

$pK_a = pK_w - pK_b$

$pK_b = pK_w - pK_a$.

(i) $NH_4^+ \rightleftharpoons NH_3 + H^+$.

$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$

(ii) $NH_3 + OH_2 \rightleftharpoons NH_4^+ + OH^-$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$.

(g/g) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]}$.

$pK_w = pK_a + pK_b$.

$K_w = K_a \times K_b$.

Ex: at 25°C, for NH_3, $K_b = 10^{-5}$

pK_b is 5

$pK_a = 9$; (14 - 5)

(*) $pK_a \uparrow$ $K_a \downarrow$ acidity ↓
$pK_b \downarrow$ $K_b \uparrow$ basicity ↑

Few Data:

	pKa
CH_3COOH :	4.74
$ClCH_2COOH$:	2.81
$Cl_2CHCOOH$:	1.28
Cl_3CCOOH :	−0.92 (as strong as HNO_3)

Which one is stronger

Less pKa, more K_a, strong acid

Inorganic acids: $HClO_4 > HI > HBr > HNO_3 > HCl > H_2SO_4 > H_3PO_4$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$; K_a ↑ $[H^+]$ ↑ Speed is high.

Strength of Acids and Bases:

* K_a is a measure of acid strength. K_b is a measure of base strength.

K_a or K_b: Value is very low (~ 10^{-5} etc.), so popular method of expression is $-\log K_a$ or $-\log K_b$. i.e. pK_a or pK_b

Similarly $[H^+]$ Conc^n ... $pH = -\log[H^+]$

K_a ↑ pK_a ↓ Acidity ↑

Examples:

$pK_a \simeq 1-2$: $Cl_2CHCOOH$, $(COOH)_2$ ...

$pK_a \simeq 4-5$: C_6H_5COOH, CH_3COOH (4.74) ...

Less strong acid.

K_b ↑ pK_b ↓ basicity ↑

$pK_b \simeq$ (2-3) (pKa) (11-12) : $(C_2H_5)_2NH$ (11.09), K_b 1.2×10^{-3}

pK_b ↓ K_b ↑ Basicity ↑.

pK_b ↓ K_b ↑ Basicity ↑

$K_a + K_b = 14$ ∴ K_b ↑ base strength ↑

For bases: The strength of a base is expressed as the pKa of the conjugate acid of the base.

Conjugate base acid (stable)

e.g. NH_3 is a base. ⇒ Conjugate acid, $NH_3 + H^+ \rightleftharpoons NH_4^+$

NH_4^+: Conjugate acid of the base NH_3.

pK_a ↑ K_a ↓ $NH_4^+ \rightleftharpoons NH_3 + H^+$

NH_4^+ — $NH_3 + H^+$.

basicity ↑

pK_b ↓ basicity ↑.

pK_a: of the NH_4^+ ion: K_a ↓ $NH_4^+ \rightleftharpoons H^+ + NH_3$

pK_a: of the $C_6H_5NH_3^+$ (anilinium ion)

(stable) pK_a ↑ pK_b ↓ K_b ↑ Basicity ↑

Basicity ↑ K_b ↑ pK_b ↓.

$NH_4^+ \rightleftharpoons NH_3 + H^+$

K_a ↑ Acidity ↑ pK_a ↓ pK_b ↑ strong base ↑ pK_a ↑.

Acid (Base) ↓ strength ↓ pK_a ↑ pK_b ↑

Temp (°C)	0°C	10°C	25°C	40°C	50°C	100°C
pH	7.47	7.27	7.00	6.76	6.63	6.12
$K_w \times 10^{14}$	0.1139	0.2920	1.008	2.919	5.494	58

$K_w = K[H_2O]$ or. $K = K_w/[H_2O]$

1 litre of H_2O = 1000 gm

$= \frac{1000}{18}$ moles

$= 55.5$ moles

$[H_2O] = 55.5$ (moles/Litre).

$= \frac{K_w}{55.5}$ i.e $\frac{1}{55.5}$ times that of K_w.

Unit of Conductance / Specific Conductance, equivalent Conductance, molar Conductance

Prob. Sp. conductivity of pure water at 25°C is 0.58×10^{-7} ohm^{-1} cm^{-1}. Calculate K_w.

[$\lambda^0_{H^+} = 350$ unit, $\lambda^0_{OH^-} = 198$ unit]

Q. How to measure K_w?

by Conductivity measurements

$\Lambda = \frac{1000\,K}{C}$ [$C = \frac{1000}{18} = 55.58$ moles/L] $\alpha = \Lambda/\Lambda_0$

$= \frac{1000 \times 0.58 \times 10^{-7}}{55.58} \simeq \frac{10^3 \times 58.0 \times 10^{-2} \times 10^{-7}}{55.58}$

$= 1.045 \times 10^{-6}$ $= 1.045 \times 10^{-6}$

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

$= \alpha C \alpha C$

$= \alpha^2 C^2$

$K[H_2O] = [H^+][OH^-]$

$\Lambda_0 = \lambda^0_{H^+} + \lambda^0_{OH^-} = 350 + 198$

$= 548$

$\alpha = \Lambda/\Lambda_0 = \frac{1.045 \times 10^{-6}}{548} = 1.9 \times 10^{-9}$

$\frac{1.045 \times 10^{-6}}{0.548 \times 10^{3}} = 1.9 \times 10^{-9}$

$K_w = \alpha^2 C^2 = (1.9 \times 10^{-9} \times 55.58)^2$

$K_w = [H^+][OH^-] = 1.10 \times 10^{-14}$.

Polybasic acid: (H_3PO_4)

(i) $H_3PO_4 \overset{K_1}{\rightleftharpoons} H^+ + H_2PO_4^-$; $K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 1.1 \times 10^{-2}$;

(ii) $H_2PO_4^- \overset{K_2}{\rightleftharpoons} H^+ + HPO_4^{2-}$; $K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 7.5 \times 10^{-8}$

(iii) $HPO_4^{2-} \overset{K_3}{\rightleftharpoons} H^+ + PO_4^{3-}$; $K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13}$

$K_1 > K_2 > K_3$ as successive steps in ionization become increasingly more difficult because of the increasing -ve charge of the acid residue. This makes $K_1 > K_2 > K_3$ for H_3PO_4.

Why $K_3 < K_2 < K_1$: Chance of recombination is high for K_3 than K_2 than K_1.

H_2CO_3. $K_1 = 4.31 \times 10^{-7}$; $K_2 = 5.6 \times 10^{-11}$; $K_1 > K_2$

$H_3\ddot{N}$, $CH_3\ddot{N}H_2$, $\frac{CH_3}{CH_3}>NH$, $(CH_3)_3N$

Stability

The strength ↑ upto 2° amine, but drops to 3° amine as crowding ↑.

Stability $(CH_3)_3\overset{+}{N}H$ less than $(CH_3)_2\overset{+}{N}H_2$

3° amine → Conjugate base is not very stable

Conjugate ~~acid~~ base more stable → acid strong.

Conjugate acid more stable → base strong.

$CH_3COOH \rightleftharpoons CH_3COO^-$ Conjugate base. (I)

$ClCH_2COOH \rightleftharpoons ClCH_2COO^-$ Conjugate base (II)

(II) is more stable than (I).

Brönsted - Lowry Theory of acids and bases:

Acids: H^+ donor
Bases: OH^- donor
} both in aqueous sol^n.

But, for the non aq. solution, difficulty arises for non-aqueous solutions. Even OH^- ions can not have any universal significance in respect of basic properties. —

$NaNH_2$: (base) in liq. ammonia.

Amines in acetic acid or ketone in benzene and so on.

Brönsted – Lowry (1923) proposed acid-base behaviour in all solvents.

Acid: i) molecular species having tendency to lose a proton.

ii) The extent of ionization of an acid in a given solvent will depend on the capacity of the solvent for acceptance of the proton.

Base: Base is a molecular species having a tendency to combine with a proton.

Base is proton acceptor
or
An acid is a proton donor
Base is a proton acceptor

We got the following imp points

i) Absoluteness of the Acid-Base Concept.

ii) Existence of Conjugate acid base pair

iii) All reactions involving an Acid and/or Base conform to the following general eqn.

The basic eqn of Brönsted theory:

$$(Acid)_1 + (Base)_2 \rightleftharpoons (Base)_1 + (Acid)_2$$

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

CH_3COOH: Acid 1, Base 1

CH_3COO^-: Conjugate to the acid CH_3COOH.

Conjugate acid base pair:

$HCN - CN^-$

$NH_4^+ - NH_3$

$HSO_4^- - SO_4^{2-}$

The basic Brönsted Equation:

The general equation (Brönsted eqn):

$$(Acid)_1 + (Base)_2 \rightleftharpoons (Base)_1 + (Acid)_2$$

It is a common prototype of all reactions of acids and bases, this is discussed below for four types of reactions:

(i) dissociation of acids and bases
(ii) Acid base neutralization (iii) Hydrolysis
(iv) Buffer action

Example: i) N/1000 HCl sol^{n}

$$pH = -\log[H^+]$$
$$= -\log\left[\frac{1}{1000}\right]$$
$$= -\log 10^{-3}$$
$$= 3.$$

ii) N/500 HCl sol^{n}

$$pH = -\log\left[\frac{1}{500}\right]$$
$$= -\log[2\times10^{-3}]$$
$$= -\log 2 + 3$$
$$= 3 - \log 2$$
$$= 3 - 0.30 = 2.70$$

So dubling the $[H^+]$ will decrease the pH by only 0.30 units

Usual pH Value:

$pH = 3 \approx \frac{N}{1000}$ HCl sol^{n}

$pH = 11 \approx \frac{N}{1000}$ NaOH sol^{n}

$[pH + pOH = 14]$

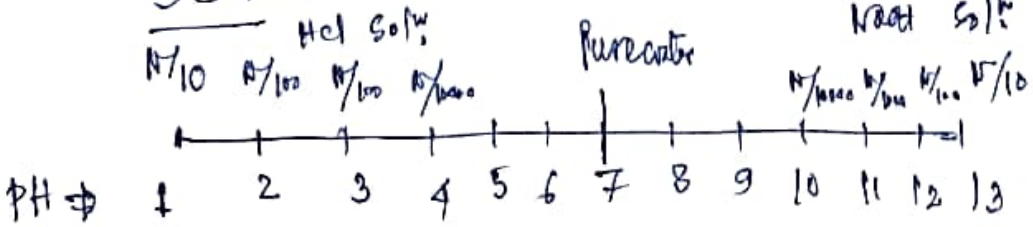
$pH = 11$

$pOH = 3$

$[OH^-] = 10^{-3}$

$pH = 2.3$ means an acid strength somewhere b/w Centinormal and a thousandth normal HCl sol^{n}.

Scale:



Through the usual range of pH is considered to extend from pH = 0 (i.e. an 'N' acid sol^{n}) to pH = 14 (an 'N' alkali sol^{n}), it is conceivable that under stranger conditions of acidity the pH may fall and also fall below zero. Similarly a strongly alkaline

(i) It is arithmetically simpler and covers a wide range

(ii) The percentage error in pH is the same as the experimental percentage error in EMF determination. This is however not so for the calculated a_{H^+} or $[H^+]$.

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* $pH = -\log a_{H^+}$.

as no method exists for determination of a_{H^+} for that matter any single ion activity. The nearest that can be done in a theoretical sound way is the determination of mean ionic activity in say a HCl soln.

$(f_\pm^2 = f_+ . f_-)$

Simpler definition of H-ion Exponent or pH -

Since we have agreed to equate concentration with activity, pH is defined as 'negative exponent (power) of its hydrogen ion concentration

$pH = -\log[H^+]$ (approx. definition)

space of activity coefficient. 16-16.

~~$\log f_\pm = -A$~~

If 'a ten fold decrease/increase of H+ ion concentration corresponds to a one unit of pH increase or decrease of pH.)

pH scale, common ion effect, Buffer solutions Solubility and solubility product of Sparingly soluble Salts – applications of Solubility product principle.

P-220 (Palit)

Introduction: (i) H^+ does not have any free existence, it remains as hydronium or oxonium ion, H_3O^+, but for the simplicity it is used as H^+.

(a) On discussing ionic equilibrium, activity of ions (i.e. a_{H^+}) is the quantity that directly matters. Here however for simplicity's sake we shall continue to use concentrations, such as $[H^+]$, $[OH^-]$ etc. which should really be activity terms.

$$[a = f.c]$$

The difference is by no means negligible but this can not be helped in studies at the elementary level.

Background of pH:

The hydrogen ion activity of any solution can be measured conventionally by using the hydrogen electrode – (P-412). Sørensen expressed this hydrogen ion activity in pH unit (pH is Potenz of H; potenz means power in German), defining pH as follows:

Definition of pH: $pH = -\log a_{H^+}$: where a_{H^+} : activity of hydrogen ion.

Two advantages in this notation.

Reverse.

ii) Calculate of $[H^+]$ from pH:

$[H^+] = A \times 10^{-z}$.

z = whole no. next to pH and A = Antilog

Say: If pH = 10·2, $z = 11$

A = Antilog (11 - 10·2)

= Antilog 0·8 = 6·31

$\therefore [H^+] = 6·31 \times 10^{-11}$

H.T. Calculate the $[H^+]$ of the following Solution.

(i) pH = 3·4 : 0·000398 (N)

(ii) pH = 2·1 : $7·94 \times 10^{-3}$ (N)

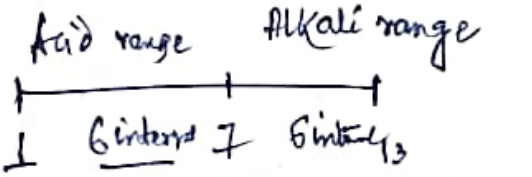
(iii) pH = 10·0 : 10^{-10} (N)

pH :

$pH = -\log a_{H^+}$

$\approx -\log [H^+]$

Scale:



i) pH of acid solution :

Say 10^{-2} N HCl : pH = 2

ii) pH of alkaline solution : 10^{-2} N (NaOH)

$pH = p.pOH$

$= 14 - 2 = 12$

$pOH = 2$

$pH = 14 - 2 = 12$

Conversion of $[H^+]$ into pH and vice versa

(i) Calculation of pH from $[H^+]$:

N/100 = 10^{-3} (N) : $pH = -\log\{10^{-3}\}$

$= 3 - \log 10 = 3.$

$\frac{N}{200} = 0.5 \times 10^{-3}$ (N).

$= 5.0 \times 10^{-4}$ (N) : $pH = -\log [H^+]$

$= -\log [5 \times 10^{-4}]$

$= -\log 5 + 4$

$= 4 - \log 5$

$= 4 - 0.699$

$= 3.31$

H.T.

pH : N/40 HCl solution pH = 1.6

N/200 HCl " pH = 2.3

N/100 NaOH " pH = 11

N/50 NaOH : pH = 12.3

10^{-8} (N) HCl : pH = ?

solution may have a pH above pH = 14. However since pH has merely an operational (~~practical~~) definition and no sound theoretical basis, the interpretation of such extreme values is none too clear.

pH of pure water.

$[H^+] = 10^{-7}$ at 25°C.

$pH = -\log_{10}(10^{-7})$

$= 7.$

pH < 7 Acidic

pH > 7 Alkaline

pH = 7 Neutral

pH of acidic Soln.

$[H^+] = 0.01$ N.

pH = 2

$[H^+] = 10^{-6}$ N.

pH = 6

$[H^+] = 10^{-3}$ N

pH = 3

$(N/5000)$ HCl Soln

pH = 3.7. Calculate ?

$N/5000 = \frac{2}{10000}(N)$

$= 2 \times 10^{-4}$

$pH = 4 - \log 2$

$= 4 - 0.3$

$= 3.7$

pH of alkaline Soln

$N/1000$ (NaOH) $\Rightarrow$ pH = 7.

$[OH] = 10^{-3}$ (N)

pOH = 3.

pH + pOH = 14.

pH = 14 - 3

= 11 at 25°C

iii) Calculate of PH at different Degree of Neutralisation.

The pH of a weak acid can be Calculated with a fair degree of accuracy over a considerable range of neutralization (roughly for 10% to 90% neutralization) with the help of following equation, Called Henderson's Equation, which is easily obtained from O stand d'lw law:

$$HA \rightleftharpoons H^+ + A^-$$

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

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

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

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

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

$$pH = pK + \log \frac{[salt]}{[acid]} \quad \text{--- (1)}$$

Equation (1) is a very important eqn and the pH value of buffer solutions are easily Calculated with the help of this eqn

At neutralization point the solution is merely that of the neutral salt formed, hence the $[H^+]$ and so pH at neutralization point can be easily Calculated with the help of hydrolysis eqn.

Say Acetic acid:

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

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

$$pH = pK + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

Example: Calculate pH of (i) a 10 cc acetic acid Solution (0·1N) to which has been added 3 cc of decinormal caustic soda and (ii) a N/100 ammonia Solution after 60 percent neutralisation.

Given: $pK_a = 4.75$, pK_b (NH₄OH) = 4.74

10 cc 3
CH_3COOH + NaOH
(1) CH_3COONa +
(3)

(i) $pH = pK_a$ (acetic acid) + $\log \frac{\text{salt}}{\text{acid}}$

$= 4.75 + \log 3/7 = 4.37$

(ii) $pH = pK_a$ (ammonium ion) + $\log (40/60)$

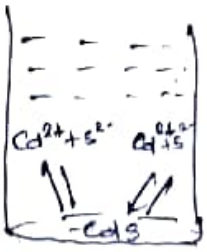
$= -\log K_w$ (water) + $\log K_b$ (ammonia) + $\log 2/3$

$= 14 - 4.75 + (0.30 - 0.48)$

$= 9.08$

It is noted that calculated pH is independent of dilution which is experimentally not quite true and shows the approximate nature of Henderson's equation.

Solubility Product:



⇐ Equilibrium between Ion and Precipitate.

Principle: Although the law of mass action can not be profitably applied to the process of electrolytic dissociation except in the case of weak electrolyte, it can be usefully applied with considerable accuracy to saturated solutions of sparingly soluble salts because it is a case of heterogeneous equilibrium, as illustrated below for a saturated solution of silver chloride —

$$AgCl\ (solid) \rightleftharpoons Ag^+ + Cl^-\ (in\ solution)$$

$$AgCl\ (solid) \rightleftharpoons AgCl\ (soln.) \longrightarrow Ag^+ + Cl^-\ (solution)$$

→ Applying the laws of mass action, we get [Heterogeneous equ.]

$$\frac{[Ag^+][Cl^-]}{[AgCl]_{(solid)}} = K$$

or, $$[Ag^+][Cl^-] = K\,[AgCl]_{(s)}$$

The Concentration of 'Solid silver chloride' is indeed Constant, and by Convention is put equal to unity

Nevertheless, the eq^{n} $[Ag^+][Cl^-] = K_{sp} = s^2$ will still hold good.

If the new solubility of AgCl be s', we should have, since the salts are completely dissociated, s' and $(s'+c)$ as the final Conc^{n} of Ag^+ and Cl^- ions respectively in the saturated solution.

So we have:

Effect of Common ion: $(s') \times (s'+c) = K_{s.p} = s^2$

Where the Concentrations are expressed in gm moles/L or gram ions/L. Similar eq^{n}s for more complicated cases of unsymmetrical types of salts can be usually deduced.

KHTa : KCl

$K_{sp} = [K^+]_s [HTa^-]_s = s^2$

$K_{sp} = [K^+][HTa^-]$

$(s+c)(s')$

$s' < s$

Example:

Solubility of lead sulphate in water is 1.03×10^{-4}. Calculate the solubility in Centinormal sol^{n} of sulphuric acid.

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

$K_{sp} = [Pb^{2+}][SO_4^{2-}] = s^2$

$K_{sp} = s^2 = (1.03 \times 10^{-4})^2 = 1.06 \times 10^{-8}$

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

Now $c = 0.01\ N\ H_2SO_4 = 0.005\ (M)$,

Now, $K_{sp} = s'(s' + 0.005) = 1.06 \times 10^{-8}$

$s'^2 + 0.005\, s' = 1.06 \times 10^{-8}$

$s' = 2.1 \times 10^{-6}$

s' = less

s'^2 = much less, neglected

i.e. $s' < s$.