1. Details of Module and its structure

Module Detail			
Subject Name	Chemistry		
Course Name	Chemistry 01 (Class XI, Semester 01)		
Module Name/Title	Equilibrium: Part 4		
Module Id	kech_10704		
Pre-requisites	Degree of ionization, weak acids and bases, K_a , K_b and K_w .		
Objectives	 After going through the contents of this module the learner will be able to: Derive an expression for ionization constant of a weak acid Workout an expression for dissociation constant of a weak base Derive a relation between K_a and K_b Appreciate the series of ionization constants of a polybasic acid and a polyacidic base Deduce the factors that affect the acidic strength Explain the dependence of degree of ionization on concentration of the electrolyte and that of the common ion. 		
Keywords	Ionization constant, K _a and K _b , polybasic acid, polyacidic base, acid strength, common ion effect.		

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1. Introduction

In Module 3, you learnt how to classify acids and bases as weak or strong in terms of their ionization constants and describe pH scale for representing hydrogen ion concentration; in this module you will derive expressions for their ionization constants. This task will not be difficult for you at all as you have also learnt about the ionization of water and its dual role as acid and base. Ionization constant for a weak acid or a base may be found in the same manner.

2. Ionization Constants of Weak Acids

Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by:

$HX(aq) + H_2 O(l)$	\rightarrow	$H_3 O^+(aq) + X^-$				
(aq)						
Initial concentration ((M)					
С	0	0				
Let α be the extent of	ionization					
Change (M)						
		+cα				
-cα	+cα					
Equilibrium concentration (M)						
		сα				
с-са	сα					

Here, c = initial concentration of the undissociated acid, HX at time, t = 0, $\alpha =$ extent up to which HX is ionized into ions. Using these notations, we can derive the equilibrium constant for the above discussed acid-dissociation equilibrium:

 $K_a = c^2 \alpha^2 / c(1-\alpha) = c \alpha^2 / 1-\alpha$

K_a is called the **dissociation or ionization constant** of acid HX. It can be represented alternatively in terms of molar concentration as follows:

K_a= [H⁺][X⁻] / [HX] (1)
 At a given temperature T, K_a is a measure of the strength of the acid HX i.e., larger the value of K_a, the stronger is the acid. K_a is a dimensionless quantity with the understanding that the standard state concentration of all species is 1M.

The values of the ionization constants of some selected weak acids are given in Table 1.

Acid	Ionization Constant,		
		K	K _a
		3.	
Hydrofluoric Acid Nitrous Acid	(HF)	5 4.	× 10 ⁻⁴
(HNO ₂)		5	× 10 ⁻⁴
		1.	
Formic Acid (HCC	OH)	8 1.	× 10 ⁻⁴
Niacin (C ₅ H ₄ NCOC	DH)	5	× 10 ⁻⁵
Acetic Acid (CH ₃ C	OOH)	1.7	/4 × 10 ^{−5}
Benzoic Acid	(C ₆ H ₅	6.	
COOH) Hypochlorous	Acid	5 3.	× 10 ⁻⁵
(HCIO)		0 4.	× 10 ⁻⁸
Hydrocyanic Acid Phenol (C ₆ H ₅	(HCN)	9 1.	× 10 ⁻¹⁰
OH)		3	$\times 10^{-10}$

Table 1 The Ionization Constants of Some Selected Weak Acids (at 298K)

The pH scale for the hydrogen ion concentration has been so useful that besides pK_w , it has been extended to other species and quantities. Thus, we have:

$$pK_a = -\log(K_a) \tag{2}$$

Knowing the ionization constant, K_a of an acid and its initial concentration, c, it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution.

A general step-wise approach can be adopted to evaluate the pH of the weak electrolyte as follows:

Step 1. The species present before dissociation are identified as Brönsted-Lowry acids / bases.

Step 2. Balanced equations for all possible reactions i.e., with a species acting both as acid as well as base are written.

Step 3. The reaction with the higher K_a is identified as the primary reaction whilst the other is a subsidiary reaction.

Step 4. Enlist in a tabular form the following values for each of the species in the primary reaction

(a) Initial concentration, c.

(b) Change in concentration on proceeding to equilibrium in terms of α , degree of ionization.

(c) Equilibrium concentration.

Step 5. Substitute equilibrium concentrations into equilibrium constant equation for principal reaction and solve for α.

Step 6. Calculate the concentration of species in principal reaction.

Step 7. Calculate $pH = -\log[H_3O^+]$

The above mentioned methodology has been elucidated in the following examples.

Problem 1

The ionization constant of HF is 3.2×10^{-4} . Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H₃O⁺, F⁻ and HF) in the solution and its pH.

Solution

The following proton transfer reactions are possible:

1) $HF + H_2O \rightleftharpoons H_3O^+ + F^ K_a = 3.2 \times 10^{-4}$ 2) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

 $K_w = 1.0 \times 10^{-14}$

As $K_a >> K_w$, [1] is the principal reaction.

$HF + H_2O$	=	$H_3 O^+$	+ F-
Initial			
concentration (M)			
0.02		0	0
Change (M)			
-0.02α	+0.02	2α	+0.02α
Equilibrium			
concentration (M)			
0.02 - 0.02			
α		0.02 α	0.02α

Substituting equilibrium concentrations in the equilibrium reaction for principal reaction gives:

$$K_a = (0.02\alpha)^2 / (0.02 - 0.02\alpha) = 0.02 \alpha^2 / (1 - \alpha) = 3.2 \times 10^{-4}$$

We obtain the following quadratic equation:

 $\alpha^{2} + 1.6 \times 10^{-2} \alpha - 1.6 \times 10^{-2} = 0$

The quadratic equation in α can be solved and the two values of the roots are:

 $\alpha~=+~0.12~and-0.12$

The negative root is not acceptable and hence,

 $\alpha = 0.12$

This means that the degree of ionization, $\alpha = 0.12$, then equilibrium concentrations of other species viz., HF, F⁻ and H₃O⁺ are given by:

 $[H_3O^+] = [F^-] = c\alpha = 0.02 \times 0.12 = 2.4 \times 10^{-3} M$

 $[HF] = c(1 - \alpha) = 0.02 (1 - 0.12) = 17.6 \times 10^{-3} M$

 $pH = -\log[H^+] = -\log(2.4 \times 10^{-3}) = 2.62$

Problem 2

The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species H^+ , A^- and HA at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid.

Solution:

 $pH = -\log [H^+]$

Therefore, $[H^+] = 10^{-pH} = 10^{-4.50} = 3.16 \times 10^{-5}$

 $[H^+] = [A^-] = 3.16 \times 10^{-5}$

Thus, $K_a = [H^+][A^-] / [HA]$

$$\begin{split} [HA]_{eqlbm} &= 0.1 - (3.16 \times 10^{-5}) ~\approx 0.1 \\ K_a &= (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8} \end{split}$$

 $pK_a = -\log(10^{-8}) = 8$

Alternatively, "Percent dissociation" is another useful method for measure of strength of a weak acid and is given as:

Percent dissociation

 $= [HA] dissociated / [HA] initial \times 100\%$ (3)

Problem 3

Calculate the pH of 0.08M solution of hypochlorous acid, HOCl. The ionization constant of the acid is

 2.5×10^{-5} . Determine the percent dissociation of HOCl.

Solution

$$HOCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$$

Initi	al co	oncent	ration (N	(N				
0.08				C)	0		
Chang	ge	to	rea	ach	e	equili	briun	n
conce	ntra	tion(N	1)					
- x				-	+ x		$+_{X}$	
Equil	ibriu	ım con	centrati	on (M))			
0.08	- X					x	Х	
	=	{[H	30 ⁺][C	2l0-]	/			
Ka	[HC) []}						

$$= x^{2} / (0.08 - x)$$

As x << 0.08, therefore $0.08-x~~\approx~~0.08$

$$x^2 / 0.08 = 2.5 \times 10^{-5}$$

$$x^2 = 2.0 \times 10^{-6}$$
, thus, $x = 1.41 \times 10^{-3}$

$$[H^+] = 1.41 \times 10^{-3} M.$$

Therefore, Percent dissociation

= {[HOCI]dissociated / [HOCI]undissociated }* 100

$$= 1.41 \times 10^{-3} / 0.08 = 1.76 \%.$$

$$pH = -log(1.41 \times 10^{-3}) = 2.85$$

3. Ionization of Weak Bases

The ionization of base MOH can be represented by equation:

$$MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$$

In a weak base there is partial ionization of MOH into M^+ and OH^- , the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called **base ionization constant** and is represented by K_b . It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

K _b = $[M^+][OH^-] / [MOH]$ (4)

Alternatively, if c = initial concentration of base and $\alpha =$ degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

 $K_b = (c\alpha)^2 / c (1-\alpha) = c\alpha^2 / (1-\alpha)$

The values of the ionization constants of some selected weak bases, K_b are given in Table 1.

Constant of some Weak Bases at 298 K

Base	K _b
Dimethylamine, (CH	H_3)5.4 × 10 ⁻⁴
2NH	
Triethylamine, (C ₂ H ₅) ₃ N	6.45×10^{-5}
Ammonia, NH_3 or N_3	$H_4 1.77 \times 10^{-5}$
ОН	
Quinine, (A pla	1.10×10^{-6}

product)	
Pyridine, C₅ H₅N	1.77×10^{-9}
Aniline, C ₆ H ₅ NH	$4.27 imes 10^{-10}$
Urea, CO (NH ₂) ₂	$1.3 imes 10^{-14}$

Many organic compounds like amines are weak bases. Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by another group. For example, methylamine, codeine, quinine and nicotine all behave as very weak bases due to their very small K_b . Ammonia produces OH^- in aqueous solution:

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

The pH scale for the hydrogen ion concentration has been extended to get:

p $K b = -\log(K)$ (5)

Problem 4

The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

Solution

 $NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$. From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of hydroxyl ions. Thus we have:

 $[H^+]$ = antilog (–pH)

= antilog (-9.7) = 1.67×10^{-10}

 $[OH^{-}] = K_w / [H^{+}] = 1 \times 10^{-14} / 1.67 \times 10^{-10} = 5.98 \times 10^{-5}$

The concentration of the corresponding hydrazinium ion is also the same as that of hydroxyl ion. The concentration of both these ions is very small so the concentration of the undissociated base can be taken equal to 0.004M.

Thus,

 $K_b = [NH_2NH_3^+][OH^-] / [NH_2NH_2]$

$$= (5.98 \times 10^{-5})^2 / 0.004 = 8.96 \times 10^{-7}$$

 $pK_b = -logK_b = -log(8.96 \times 10^{-7}) = 6.04.$

Problem 5

Calculate the pH of solution formed on mixing 0.2M NH_4Cl and 0.1M NH_3 . The pK_b of ammonia solution is 4.75.

Solution

 $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

The ionization constant of NH₃,

 K_b = antilog ($-pK_b$) i.e.

$$K = 10^{-4.75} = 1.77 \times 10^{-5} M$$
b

NH

 $_{3}$ + H₂O = NH₄ + OH⁻

Initial concentration (M)

 $_{0.10}$ 0.20 0

Change to reach

equilibrium (M)

 $_{-x}$ +x +x +x

At equilibrium (M)

 $_{0.10-x}$ 0.20 + x x

K = [NH⁺][OH⁻] / [NH]

b 4 3

= (0.20 + x)(x) / (0.1 - x) = 1.77 \times 10^{-5}

As K_b is small, we can neglect x in

comparison to 0.1M and 0.2M. Thus,

[OH⁻] = x = 0.88 × 10^{-5}

Therefore, [H⁺] = 1.12 × 10^{-9}

pH = $_{10}$ [H⁺] = 8.95.

4. Relation between K_a and K_b

As seen earlier in this module, K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if

one is known, the other can be deduced. Considering the example of NH₄⁺ and NH₃ we see,

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$
$$K_a = [H_3O^+][NH_3] / [NH_4^+] = 5.6 \times 10^{-10}$$
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

 $K_{b} = [NH_{4}^{+}][OH^{-}] / NH_{3} = 1.8 \times 10^{-5}$ Net: 2 H₂O(l) \rightleftharpoons H₃O⁺(aq) + OH⁻(aq) $K_{w} = [H_{3}O^{+}][OH^{-}] = 1.0 \times 10^{-14} M$

where K_a represents the strength of NH_4^+ as an acid and K_b represents the strength of NH_3 as a base.

It can be seen from the net reaction that the equilibrium constant is equal to the product of equilibrium constants K_a and K_b for the reactions added. Thus,

 $= \{ [H_3O^+][NH_3] / K_a \times K_b [NH^+4] \} \times \{ [NH^+4] [OH^-] / [NH_3] \}$ $= [H_3O^+][OH^-] = K_w$

 $= (5.6 \times 10^{-10}) \times (1.8 \times 10^{-5}) = 1.0 \times 10^{-14} M$

This can be extended to make a generalisation. The equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions:

 $K_{\text{NET}} = K_1 \times K_2 \times \dots$ (6) Similarly, in case of a conjugate acid-base pair,

$$K_a \times K_b = K_w \tag{7}$$

Knowing one, the other can be obtained. It should be noted that a strong acid will have a weak conjugate base and vice-versa.

=

It may be noted that if we take negative logarithm of both sides of the equation, then pK values of the conjugate acid and base are related to each other by the equation:

 $pK_a + pK_b = pK_w = 14$ (at 298K)

Problem 6

Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 2. Also, calculate the ionic constant of the conjugate acid of ammonia.

Solution

The ionization of NH₃ in water is represented by equation:

 $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

We use equation (4) to calculate hydroxyl ion concentration,

$$[OH^{-}] = c \alpha = 0.05 \alpha$$

$$K_b = 0.05 \alpha^2 / (1 - \alpha)$$

The value of α is small, therefore the quadratic equation can be simplified by neglecting α in comparison to 1 in the denominator on right hand side of the equation.

Thus,

$$K_b = c \alpha^2$$
 or $\alpha = \sqrt{(1.77 \times 10^{-5} / 0.05)}$

= 0.018.

 $[OH^{-}] = c \alpha = 0.05 \times 0.018 = 9.4 \times 10^{-4} M.$

$$[H^+] = K_w / [OH^-] = 10^{-14} / (9.4 \times 10^{-4}) = 1.06 \times 10^{-11}$$

 $pH = -log(1.06 \times 10^{-11}) = 10.97.$

Now, using the relation for conjugate acid-base pair,

 $K_a \times K_b = K_w$

and using the value of K_b of NH_3 from Table 2, we can determine the ionization constant of conjugate acid NH_4^+ .

 $K_a = K_w \ / \ K_b = 10^{-14} \ / \ 1.77 \ \times \ 10^{-5} \ = 5.64 \ \times \ 10^{-10}$

5. Di- and Polybasic Acids and Di- and Polyacidic Bases

Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids.

The ionization reactions for example for a *dibasic acid* H₂X are represented by the equations:

 $H_2X(aq) \rightleftharpoons H^+(aq) + HX^-(aq)$

 $HX^{-}(aq) \rightleftharpoons H^{+}(aq) + X^{2-}(aq)$

And the corresponding equilibrium constants are given below:

 $K_{a1} = \{ [H^+][HX^-] \} / [H_2X] \text{ and}$ $K_{a2} = \{ [H^+][X^{2-}] \} / [HX^-]$

Here, \mathbf{K}_{a1} and \mathbf{K}_{a2} are called the first and second ionization constants respectively of the acid H_2 X. Similarly, for tribasic acids like H_3PO_4 we have three ionization constants. The values of the ionization constants for some common polyprotic acids are given in Table 3.

Table 3 The Ionization Constants of Some Common Polyprotic Acids (298K)

Acid	K _{a1}	K _{a2}	K _a 3
Oxalic Acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic Acid	$7.4 imes 10^{-4}$	$1.6 imes 10^{-12}$	
Sulphurous Acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric Acid	Very large	$1.2 imes 10^{-2}$	
Carbonic Acid	4.3×10^{-7}	5.6×10^{-11}	
Citric Acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

It can be seen that higher order ionization constants $\tilde{1} \mathbf{K}_{a2}$, \mathbf{K}_{a3} $\tilde{1}$ are smaller than the lower order ionization constant (\mathbf{K}_{a1}) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. This can be seen in the case of removing a proton from the uncharged H₂CO₃ as compared from a negatively charged HCO₃⁻. Similarly, it is more difficult to remove a proton from a doubly charged HPO₄²⁻ anion as compared to H₂PO₄⁻.

Polyprotic acid solutions contain a mixture of acids like H_2A and HA^- in case of a

diprotic acid. H_2A being a strong acid, the primary reaction involves the dissociation of H_2A , and H_3O^+ in the solution comes mainly from the first dissociation step.

6. Factors Affecting Acid Strength

Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid depends on the **strength** and **polarity** of the H-A bond.

In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity.

But it should be noted that while comparing elements in the same *group* of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. For example,

Size increases

HF << HCl << HBr << HI

Acid strength increases

Simlarly, H₂S is stronger acid than H₂O.

But, when we discuss elements in the same *row* of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example,

Electronegativity of A increases

 $CH_4 < NH_3 < H_2O < HF$

Acid strength increases

7. Common Ion Effect in the Ionization of Acids and Bases

Consider an example of acetic acid dissociation equilibrium represented as:

 $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$ or $HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$

 $K_a = [H^+][Ac^-] / [HAc]$

Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions, $[H^+]$. Also, if H^+ ions are added from an external source then the equilibrium moves in the direction of undissociated acetic acid i.e., in a direction of reducing the concentration of hydrogen ions, $[H^+]$. This phenomenon is an example of **common ion effect**. It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. Thus, we can say that common ion effect is a phenomenon based on the Le Chatelier's principle discussed in module 2 In order to evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M

acetic acid solution, we shall consider the acetic acid dissociation equilibrium once again,

 $HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$

Initial concentration (M)

0.05 0 0.05

Let x be the extent of ionization of acetic acid.

Change in concentration (M)

-x +x +x

Equilibrium concentration (M)

0.05-x x 0.05+x

Therefore,

 $K_a = [H^+][Ac^-]/[H Ac] = \{(0.05+x)(x)\}/(0.05-x) \text{ As } K_a \text{ is small for a very weak acid, } x << 0.05.$ Hence, $(0.05 + x) \approx (0.05 - x) \approx 0.05$

Thus,

 $1.8 \times 10^{-5} = (x) (0.05 + x) / (0.05 - x)$

 $= x(0.05) / (0.05) = x = [H^+] = 1.8 \times 10^{-5} M \text{ pH} = -\log(1.8 \times 10^{-5}) = 4.74$

9. Summary

The expressions for ionization (equilibrium) constants of weak acids (K_a) and weak bases (K_b) are developed using Arrhenius definition.

The equilibrium constant for acid ionization is called **acid ionization constant** and is represented by K_a . It can be expressed in terms of concentration in molarity of various species in equilibrium by $K_a = [H^+][X^-] / [HX]$ the equation:

Dissociation or Ionization constant K_a of an acid is : $K_a = c^2 \alpha^2 / c(1-\alpha) = c \alpha^2 / 1-\alpha$.

At a given temperature T, K_a is a measure of the strength of the acid HX i.e., larger the value of K_a , the stronger is the acid. K_a is a dimensionless quantity with the understanding

that the standard state concentration of all species is 1M.

The equilibrium constant for base ionization is called **base ionization constant** and is represented by $K_b = [M^+][OH^-] / [MOH]$ K_b . It can be expressed in terms of in molarity of various species in equilibrium by the equation:

If c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

$$K_b = (c\alpha)^2 / c (1-\alpha) = c\alpha^2 / (1-\alpha)$$

Percent dissociation is measure of strength of a weak acid or a base. Which may be given for a weak acid as-

The degree of ionization and its dependence on concentration and common ion are discussed.

 $pK_a = -\log[K_a]$; $pK_b = -\log[K_b]$; and $pK_w = -\log[K_w]$

The ionization of water has been considered and we note that the equation: $pH + pOH = pK_w$ is always satisfied.

The role of common ion on dissociation of a weak electrolyte has been discussed. The common ion effect is the suppression of the degree of dissociation of a weak electrolyte by addition of a salt containing a common ion. If the concentration of any one of the ions of a weak electrolyte is increased, then, according to Le Chatelier's principle, some of the ions in excess should be removed from solution, by combining with the oppositely charged ions; i.e. reverse reaction is favoured.