HINTS & SOLUTIONS WORKBOOK - 2

Ionic Equilibrium

Daily Tutorial Sheet	**Level-0**

Very Short Answer Type (1 Mark)

1. An acid – base pair which differ by a proton (H^+) is known as conjugate acid – base pair.

$HNO_2 \rightleftharpoons NO_2^- + H^+$

Acid Conjugate base

$CN^- + H^+ \rightleftharpoons HCN$

Base Conjugate acid

$HClO_4 \rightleftharpoons ClO_4^- + H^+$

Acid Conjugate base

$F^- + H^+ \rightleftharpoons HF$

Base Conjugate acid

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

Base Conjugate acid

$OH^- \rightleftharpoons O^{2-} + H^+$

Acid Conjugate base

$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$

Base Conjugate acid

$S^2 + H^+ \rightleftharpoons HS^-$

Base Conjugate acid

2. BF_3, H^+ and NH_4^+ act as Lewis acids as they have a vacant orbital and can take up an electron pair.

3. $HF \rightleftharpoons F^- + H^+$; $H_2SO_4 \rightleftharpoons HSO_4^- + H^+$; $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$

F^-, HSO_4^-, CO_3^{2-} = conjugate base

4. $NH_2^- + H^+ \rightleftharpoons NH_3$; $NH_3 + H^+ \rightleftharpoons NH_4^+$; $HCOO^- + H^+ \rightleftharpoons HCOOH$

$NH_3, NH_4^+, HCOOH$ = conjugate acid

5.

Species	**Conjugate acid**	**Conjugate base**
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

6. OH^- and F^- are electron rich species and can donate electron pair. Hence, these act as Lewis base.

$$:\ddot{\underset{\cdot\cdot}{O}}H^- + H^+ \longrightarrow H_2O$$

$$:\ddot{\underset{\cdot\cdot}{F}}^- + BF_3 \longrightarrow BF_4^-$$

H^+ and BCl_3 are electron deficient species and can accept electron pair. Hence, these can act as Lewis acid.

$$H_3N\!: + \overset{+}{H} \longrightarrow NH_4^+$$

$$H_3N\!: + BCl_3 \longrightarrow H_3N \longrightarrow BCl_3$$

Short Answer Type-I (2 Marks)

7. If K_a is the ionization constant of a weak acid (HA) and K_{cb} is the ionization constant of its conjugate base (A^-) then $K_a \cdot K_{cb} = K_w$

$$K_b(F^-) = \frac{1 \times 10^{-14}}{K_a(HF)} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-4}} = 147 \times 10^{-11}$$

$$K_b(HCOO^-) = \frac{1 \times 10^{-14}}{K_a(HCOOH)} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$$

$$K_b(CN^-) = \frac{1 \times 10^{-14}}{K_a(HCN)} = \frac{1 \times 10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$$

8. **(i)** $H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$

$$K_a = \frac{[H_3O^+][HS^-]}{[H_2S]}$$

$$\Rightarrow \quad [H_3O^+] = [HS^-] = \sqrt{K_{a_1} . C} = \sqrt{9.1 \times 10^{-8} \times 0.1} = 9.54 \times 10^{-5}\ M$$

(ii) In the presence of 0.1 M HCl, $[H_3O^+] = 0.1$ M

$$K_{a_1} = \frac{[H_3O^+][HS^-]}{[H_2S]} \quad \Rightarrow \quad 9.1 \times 10^{-8} = \frac{[0.1][HS^-]}{[0.1]} \quad \Rightarrow \quad [HS^-] = 9.1 \times 10^{-8}\,M$$

Hence, concentration of $[HS^-]$ is decreased in the presence of $0.1\,M\,HCl$ due to common-ion effect.

(iii) For second dissociation constant,

$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$ (In absence of HCl)

$$[HS^-] = 9.54 \times 10^{-5} M \quad ; \quad K_{a_2} = \frac{[H_3O^+][S^{2-}]}{[HS^-]}$$

$$[H_3O^+] = [S^{2-}] = \sqrt{K_{a_2} . C} = \sqrt{1.2 \times 10^{-13} \times 9.54 \times 10^{-5}} = 3.38 \times 10^{-9} M$$

(iv) In the presence of 0.1 M HCl,

$$K_{a_2} = \frac{[H_3O^+][S^{2-}]}{[HS^-]} = 1.2 \times 10^{-13} = \frac{[0.1][S^{2-}]}{[9.1 \times 10^{-8}]}$$

$$\Rightarrow \quad \left[S^{2-}\right] = 1.092 \times 10^{-19}\ M$$

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

$$pH = 4.15 = -\log(H^+) \quad \Rightarrow \quad [H^+] = [A^-] = 7.079 \times 10^{-5}\ M$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} = \frac{(7.079 \times 10^{-5})\,(7.079 \times 10^{-5})}{0.01} \simeq 5.0 \times 10^{-7}$$

$$pK_a = -\log K_a = -\log[5.0 \times 10^{-7}] = 7 - 0.699 = 6.301$$

10. $CH_2(Br)\,COOH + H_2O \rightleftharpoons CH_2(Br)\,COO^- + H_3O^+$

	$CH_2(Br)\,COOH$	$CH_2(Br)\,COO^-$	H_3O^+
Initial conc.	C	0	0
Equil. Conc.	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \quad \Rightarrow \quad K_a = C\alpha^2 \qquad [\text{For weak acid } ((1-\alpha) \approx 1]$$

$$K_a = 0.1 \times (0.132)^2 = 0.00174 \approx 1.74 \times 10^{-3}$$

$$pH = -\log\sqrt{K_a C} = -\log\sqrt{1.74 \times 10^{-3} \times 0.1} = 1.88 \qquad [[H^+] = C\alpha = \sqrt{K_a \times C}]$$

11. $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

$$K_b = \frac{[C_6H_5NH_3^+]\,[OH^-]}{[C_6H_5NH_2]} = \frac{[OH^-]^2}{[C_6H_5NH_2]}$$

$$[OH^-] = \sqrt{K_b \cdot C} = \sqrt{4.27 \times 10^{-10} \times 0.001} = 6.534 \times 10^{-7}$$

$$pOH = -\log[6.534 \times 10^{-7}] = 7 + (-0.8152) = 6.18$$

For Base and Conjugate acid pair we have : $pH + pOH = 14$

or $\quad$ pH of conjugate acid $= 14 - 6.18 = 7.82$

12. $pK_a = -\log K_a \quad \Rightarrow \quad K_a = 1.82 \times 10^{-5}$

$$\alpha = \sqrt{K_a / C} \text{ or } \alpha = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} \quad (C = 0.05 \text{ given})$$

$$\alpha = \sqrt{\frac{1.82 \times 10^{-5}}{5.0 \times 10^{-2}}} = \sqrt{0.364 \times 10^{-3}} = \sqrt{3.64 \times 10^{-4}} \quad \Rightarrow \quad \alpha = 1.908 \times 10^{-2}$$

(a) In the presence of $0.01\ M\ H^+$

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

	CH_3COOH	CH_3COO^-	H^+
Initial conc.	$0.05\ M$	0	0
Equili. conc.	$0.05 - C\alpha$	$C\alpha$	$(C\alpha + 0.01)$
	≈ 0.05		≈ 0.01

[CH_3COOH is a weak acid and HCl is a strong acid, so we can assume that $(C\alpha + 0.01) \approx 0.01$]

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} \quad \Rightarrow \quad 1.82 \times 10^{-5} = \frac{C\alpha \times 0.01}{0.05} \quad \Rightarrow \quad \alpha = 1.82 \times 10^{-3}$$

(b) In the presence of 0.1 M HCl: similarly, $K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$$1.82 \times 10^{-5} = \frac{C\alpha \times 0.1}{0.05} \quad \left[[H^+] = (C\alpha + 0.1) \approx 0.1M\right]$$

$$\Rightarrow \quad \alpha = \frac{0.91 \times 10^{-5}}{0.05} = 1.82 \times 10^{-4}$$

Note : In the presence of strong acid, dissociation of week acid i.e., CH_3COOH decreases due to common ion effect. Also observe that we neglect the contribution of common ion from the weak electrolyte in such cases.

Short Answer Type-II (3 Marks)

13. Given, K_b for dimethylamine $= 5.4 \times 10^{-4}$; C for dimethylamine = 0.02 M

$$\alpha = \sqrt{K_b / C} = \sqrt{\frac{5.4 \times 10^{-4}}{0.02}} = 1.64 \times 10^{-1} = 0.164$$

In the presence of 0.1 M NaOH : $(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2\overset{+}{N}H_2 + OH^-$

	$(CH_3)_2NH$	$(CH_3)_2\overset{+}{N}H_2$	OH^-
Initial conc.	0.02M	0	0
Equilibrium conc.	$(0.02 - C\alpha)$ ≈ 0.02	$C\alpha$	$C\alpha + 0.1$ ≈ 0.1

(0.1 M OH^- from 0.1 M NaOH)

$$K_b = \frac{[(CH_3)_2\overset{+}{N}H_2][OH^-]}{[(CH_3)_2NH]} \Rightarrow 5.4 \times 10^{-4} = \frac{C\alpha \times 0.1}{0.02} \Rightarrow \alpha = 0.54\ \%$$

14. $pH = -\log_{10}\left[H^+\right] \Rightarrow [H^+] = 10^{-pH}$

(a) pH of human muscle fluid = 6.83 ⇒ $[H^+] = 1.479 \times 10^{-4}M$

(b) pH of human stomach fluid = 1 ⇒ $[H^+] = 6.31 \times 10^{-2}M$

(c) pH of human blood = 7.38 ⇒ $[H^+] = 4.169 \times 10^{-8}M$

(d) pH of human saliva = 6.4 ⇒ $[H^+] = 3.981 \times 10^{-7}M$

Note : The idea behind this question was to remember the pH of given species (fluids).

15. **(a)** pH of milk = 6.8 ⇒ $[H^+] = 1.585 \times 10^{-7}M$

(b) pH of black coffee = 5.0 ⇒ $[H^+] = 10^{-5}M$

(c) pH of lemon juice = 2.2 ⇒ $[H^+] = 6.310 \times 10^{-3}M$

(d) pH of tomato juice = 4.2 ⇒ $[H^+] = 6.310 \times 10^{-5}M$

(e) pH of egg white = 7.8 ⇒ $[H^+] = 1.585 \times 10^{-8}M$

Note : The idea behind this question was also to remember the pH of given species (Liquids).

16. Solubility of $Sr(OH)_2$ = 19.23 g/L at 298 K.

Solubility in mol/L : $M = \dfrac{19.23}{121.6\ g\ mol^{-1}}$

$$Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^-$$
$$\qquad 0.1581\text{ M} \quad 2 \times 0.1581\text{M}$$

$\Rightarrow \quad [Sr^{2+}] = 0.1581\text{M} \quad$ and $\quad [OH^-] = 0.3163\text{M}$

In an aqueous solution at 25°C :

$$[H^+] \cdot [OH^-] = K_w = 10^{-14} \quad \Rightarrow \quad [H^+] = \frac{10^{-14}}{0.3162} = 3.16 \times 10^{-14}$$

$$\Rightarrow \quad pH = 14.0.4997 = 13.5003 \approx 13.5$$

17. $CH_3CH_2COOH + H_2O \rightleftharpoons CH_3CH_2COO^- + H_3O^+$; $K_a = 1.32 \times 10^{-5}$

$(0.05 - C\alpha) \qquad C\alpha \qquad C\alpha$

From Ostwald's dilution law : $\alpha = \sqrt{K_a / C} = \sqrt{\dfrac{1.32 \times 10^{-5}}{0.05}} \quad \Rightarrow \quad \alpha = 0.016248$

$[H_3O^+] = C\alpha = 0.05 \times 0.016248 = 8.124 \times 10^{-4} \quad \Rightarrow \quad pH \approx 3.09$

When the solution contains 0.01 M HCl : $K_a = \dfrac{[CH_3CH_2COO^-]\,[H_3O^+]}{CH_3CH_2COOH}$

$$1.32 \times 10^{-5} = \frac{C\alpha \times 0.01}{(0.05 - C\alpha)} \simeq \frac{C\alpha \times 0.01}{0.05}$$

$[H_3O^+] = 0.01\text{M}$ from HCl, C = 0.01 M

(In the presence of 0.01 M HCl dissociation of propanoic acid decreases, so degree of ionization is very very less)

Degree of ionization, $\alpha = 1.32 \times 10^{-3}$

18. $HCNO + H_2O \rightleftharpoons H_3O^+ + CNO^-$

pH = 2.34 $\quad \Rightarrow \quad [H^+] = [H_3O^+] = 4.57 \times 10^{-3}$ M

Degree of ionization, $\alpha = \dfrac{4.57 \times 10^{-3}}{0.1} = 4.57 \times 10^{-2}$

Ionization constant, $K_a = \dfrac{[H_3O^+]\,[CNO^-]}{[HCNO]} = \dfrac{4.57 \times 10^{-3} \times 4.57 \times 10^{-3}}{0.1} = 2.089 \times 10^{-4}$

19. Given : $[NaNO_2] = 0.04\text{ M}$; K_a of $HNO_2 = 4.5 \times 10^{-4}$

Note that $NaNO_2$ is a salt of strong base, NaOH and weak acid, HNO_2.

Using standard result for the pH of a solution of salt of Strong base and Weak acid:

$$pH = 7 + \frac{pK_a + \log C}{2}$$

$pK_a = 4 - 0.6532 = 3.3468 \approx 3.35 \quad \Rightarrow \quad pH = 7 + \dfrac{3.35 + \log 0.04}{2} = 7.98$

Degree of hydrolysis, $h = \sqrt{\dfrac{K_w}{K_a C}} = \sqrt{\dfrac{10^{-4}}{4.5 \times 10^{-4} \times 0.04}} \quad \Rightarrow \quad h = 2.36 \times 10^{-5}$

Long Answer Type (5 Marks)

20. The aqueous solution of pyridium hydrochloride is an acidic solution due to hydrolysis. Observe that it is a salt of strong acid, HCl and weak base, Pyridine.

$$C_5H_5N^+HCl^- + H_2O \rightleftharpoons C_6H_5N^+HOH^- + HCl$$

Using standard result of pH :

$$pH = 7 - \frac{pK_b}{2} - \frac{\log C}{2} \quad \Rightarrow \quad 3.44 = 7 - \frac{pK_b}{2} - \frac{\log 0.02}{2}$$

On solving and substituting values, $K_b = 1.5 \times 10^{-9}$

21.

	Salt	Acid	Base	Hydrolysis reaction	Nature of solution
(i)	NaCl	HCl	NaOH	$H_2O \rightleftharpoons H^+ + OH^-$ No hydrolysis	Neutral
(ii)	KBr	HBr	KOH	No hydrolysis	Neutral
(iii)	NaCN	HCN	NaOH	$CN^- + H_2O \rightleftharpoons HCN + OH^-$	Basic
(iv)	NH_4NO_3	HNO_2	NH_4OH	$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$	Acid
(v)	$NaNO_2$	HNO_2	NaOH	$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$	Basic
(vi)	KF	HF	KOH	$F^- + H_2O \rightleftharpoons HF + OH^-$	Basic

22. $CH_2ClCOOH + H_2O \rightleftharpoons CH_2ClCOO^- + H_3O^+$; $K_a = 1.35\ 0^{-3}$

(a) $pK_a = -\log K_a = -\log[1.35 \times 10^{-3}] = 2.87$

By Oswald's dilution law : $[H_3O^+] = \sqrt{K_a .C} = \sqrt{1.35 \times 10^{-3} \times 0.1} = 1.16 \times 10^{-2}$ M

pH acid = $-\log[H_3O^+] = -\log\ (1.16 \times 10^{-2})M = 1.94$

(b) A 0.1 M $CH_2ClCOONa$ aqueous solution (sodium chloro-acetate) is basic due to hydrolysis.

$$CH_2ClCOO^- + H_2O \rightleftharpoons CH_2ClCOOH + OH^-$$

Using standard result for pH of a salt of strong base and weak acid:

$$pH = 7 + \frac{pK_a + \log C}{2} = 7 + \frac{2.87 + \log 0.1}{2} = 7.94$$

23. **(a)** meq of $Ca(OH)_2 = 2 \times 0.2 \times 10 = 4$

meq of $HCl = 1.01 \times 25 = 2.5 \quad \Rightarrow$ Solution is basic.

Excess meq of base = 1.5

$\Rightarrow \quad [OH^-] = \frac{1.5}{35} = 0.043M \quad \Rightarrow \quad pH = 14 + \log[OH^-] = 12.63$

Note : Molarity of OH^- ions = Normality of OH^- ions as n-factor of OH^- ions is 1.

(b) Observe clearly that :

meq of H_2SO_4 = meq of $Ca(OH)_2$

So it is neutral solution as salt is of strong Acid and Strong base. pH = 7

(c) meq of acid = 2 × 0.1 × 10 = 2

meq of base = 1 × 0.1 × 10 = 1 ⇒ Solution is acid.

$[H^+]_{excess} = \frac{1}{20}$ ⇒ $pH = -\log \frac{1}{20} = 1.3$

Note that molority of H^+ ions is some as its normally as n-factor of H^+ ion is 1.

24. Let 's be the solubility of each salt in mol/L.

(a) $Ag_2CrO_4\,(s) \xrightleftharpoons{aq.} 2Ag^+(aq) + CrO_4^{2-}(aq);\ K_{sp} = 1.1 \times 10^{-12}$

2S S

$K_{sp} = [Ag^+]^2 \cdot [CrO_4^{2-}] = [2S]^2 \cdot [S] = 4S^3 \Rightarrow S^3 = \frac{K_{sp}}{4} \Rightarrow S \approx 6.5 \times 10^{-5} M$

$\Rightarrow [CrO_4^{2-}] = S = 6.5 \times 10^{-5}\,M\ \&\ [Ag^+] = 2S = 1.3 \times 10^{-4}\,M$

(b) $BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-};\ K_{sp} = 1.2 \times 10^{-10}$

S S

$K_{sp} = [Ba^{2+}] \cdot [CrO_4^{-2}] = S^2 = 1.2 \times 10^{-10} \Rightarrow S = \sqrt{1.2 \times 10^{-10}} = 1.1 \times 10^{-5} M$

$\Rightarrow [Ba^{2+}] = [CrO_4^{2-}] = 1.1 \times 10^{-5} M$

(c) $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-;\ K_{sp} = 1.0 \times 10^{-38}$

S 3S

$K_{sp} = [Fe^{3+}]\,[OH^-]^3 = s \cdot (3S)^3 = 27S^4 \Rightarrow S^4 = \frac{K_{sp}}{27} \Rightarrow S \approx 1.39 \times 10^{-10}$

$\Rightarrow [Fe^{3+}] = 1.39 \times 10^{-10}\,M\ \&\ [OH^-] = 3S = 3 \times 1.39 \times 10^{-10} = 4.17 \times 10^{-10}\,M$

(d) $PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-;\ K_{sp} = 1.6 \times 10^{-5}$

S 2S

$K_{sp} = [Pb^{2+}]\,[Cl^-]^2 = S \cdot (2S)^2 = 4S^3 \Rightarrow S^3 = \frac{K_{sp}}{4} \Rightarrow S \approx 1.59 \times 10^{-2}\,M$

∴ Solubility of $PbCl_2 = 1.59 \times 10^{-2}$ M

$\Rightarrow [Pb^{2+}] = 1.59 \times 10^{-2} M\ \&\ [Cl^-] = 2 \times 1.59 \times 10^{-2} M = 3.18 \times 10^{-2} M$

(e) $Hg_2I_2 \rightleftharpoons Hg_2^{2+} + 2I^-;\ K_{sp} = 4.5 \times 10^{-29}$

S 2S

$K_{sp} = [Hg_2^{2+}]\,[I^-]^2 = S \cdot (2S)^2 = 4S^3 \Rightarrow S^3 = \frac{K_{sp}}{4} \Rightarrow S = 2.241 \times 10^{-10} M$

Solubility of $Hg_2I_2 = 2.241 \times 10^{-10}$ M

$[Hg_2^{2+}] = 2.241 \times 10^{-10} M\ \&\ [I^-] = 2 \times 2.241 \times 10^{-10}\,M = 4.482 \times 10^{-10}\,M$

25. Let x mol/L and y mol/L be the solubilities of Ag_2CrO_4 and AgBr respectively.

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-};\ K_{sp} = 1.1 \times 10^{-12}$

2x x

$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}] = (2x)^2 \cdot x = 4x^3 \Rightarrow x^3 = \frac{K_{sp}}{4} \Rightarrow x = 6.503 \times 10^{-5} M$

$$AgBr \rightleftharpoons \underset{y}{Ag^+} + \underset{y}{Br^-} \; ; \; K_{sp} = 5.0 \times 10^{-13}$$

$K_{sp} = [Ag^+][Br^-] = y \cdot y = y^2 \qquad \Rightarrow \qquad y = 7.07 \times 10^{-7}$ M

$$\text{The ratio of solubilities} = \frac{x}{y} = \frac{6.5 \times 10^{-5}}{7.07 \times 10^{-7}} \approx 92$$