

3. Ionic Equilibrium.

* Equilibrium.

- The equilibrium between ions and unionized molecules in solution is called ionic equilibria.

* Degree of Dissociation.

$$\alpha = \frac{\text{no. of moles dissociated}}{\text{total no. of mass}}$$

$$\text{Percent dissociation} = \alpha \times 100$$

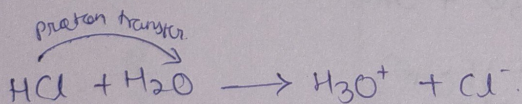
* Arrhenius Theory

- An acid is any substance that releases hydrogen (H^+) ions in water. eg. HCl.

- An base is any substance that releases OH^- ions in water. eg. NaOH.

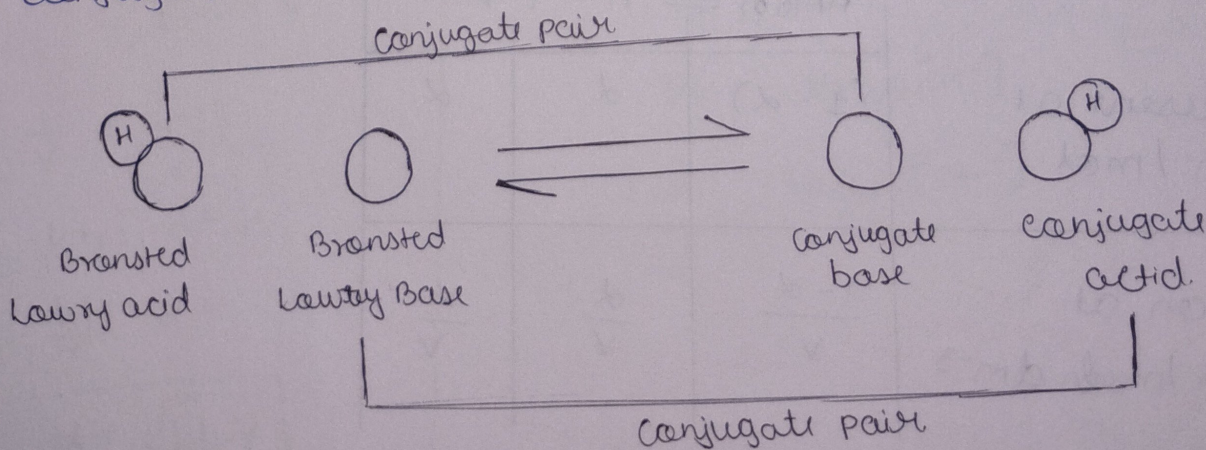
* Acc. to Bronsted-Lowry Theory:

- An acid is any species that donates a proton (H^+) to another species.



↑
Bronsted-Lowry
theory

* Conjugate acid base pair.



* Lewis acid

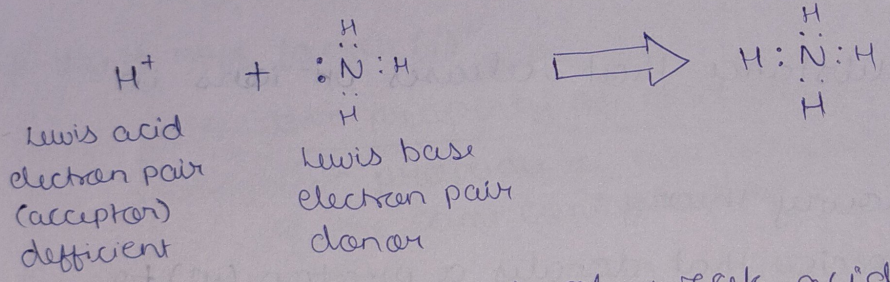
- Electron pairs acceptor
- Electron loving (Electrophile)
- All the positively charged species and molecules with central atoms which needs one or more lone pair of electrons to complete their valence shells.

and

Lewis Base.

- Electron pairs donor
- Nucleus loving (Nucleophile)
- All the negatively charged species and neutral species bearing one or more lone pair of electrons.

Weak acid
 $K_A \rightleftharpoons H^+$
 $K_A = \frac{[H^+][A^-]}{[HA]}$



* Dissociation constant of weak acids and weak bases

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

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

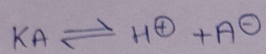
$$BOH \rightleftharpoons B^+ + OH^-$$

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

* Ostwald's dilution law

	$HA(aq) \rightleftharpoons H^+ + A^-$		
Amount present at equilibrium / mol.	$(1 - \alpha)$	α	α
Concentration at equilibrium / mol dm ⁻³	$\frac{1 - \alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

a) weak acids



$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

$$K_a = \frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{V}\right)}{\left(\frac{1-\alpha}{V}\right)}$$

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

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

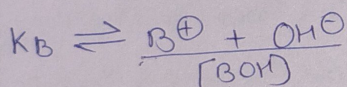
$$\frac{1}{V} = C$$

$$K_a = \alpha^2 \cdot C$$

$$\frac{K_a}{C} = \alpha^2$$

$$\boxed{\sqrt{K_a \cdot V} = \alpha}$$

b) weak bases:



$$K_b = \frac{(\alpha/V)(\alpha/V)}{\left(\frac{1-\alpha}{V}\right)}$$

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

$$K_b = \frac{\alpha^2}{(1-\alpha) \cdot V}$$

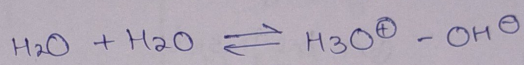
$$\frac{1}{V} = C$$

$$K_b = \alpha^2 \cdot C$$

$$\frac{K_b}{C} = \alpha^2$$

$$\boxed{\therefore \alpha = \sqrt{K_b \cdot V}}$$

* Autoionization of water:



$$K = \frac{[H_3O^{\oplus}][OH^{\ominus}]}{[H_2O]^2}$$

$$K = \frac{[H_3O^{\oplus}][OH^{\ominus}]}{K'} \dots \left([H_2O]^2 = K'\right)$$

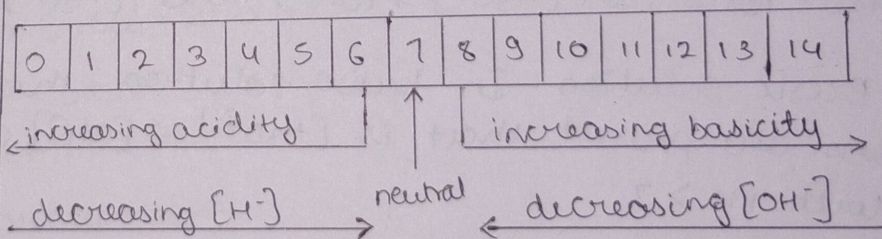
$$K \cdot K' = [H_3O^{\oplus}][OH^{\ominus}]$$

$$\boxed{K_w = [H_3O^{\oplus}][OH^{\ominus}]}$$

$$K_w = 1 \times 10^{-7} \times 1 \times 10^{-7}$$

$$\boxed{K_w = 1 \times 10^{-14}}$$

* pH and pOH scale



$$pH = -\log_{10}[H^{\oplus}]$$

$$pOH = -\log_{10}[OH^{\ominus}]$$

* Relationship between P_H and P_{OH} .
[Feb 24, March 22, Sep 21]

$$K_w = [H_3O^+][OH^-]$$

$$K_w = 1 \times 10^{-14}$$

$$1 \times 10^{-14} = [H_3O^+][OH^-]$$

Taking log on both sides

$$\log_{10}(1 \times 10^{-14}) = \log_{10}[H_3O^+] + \log_{10}[OH^-]$$

$$-14 = \log_{10}[H_3O^+] + \log_{10}[OH^-]$$

Multiplying by "-" on both side

$$14 = -\log_{10}[H_3O^+] + -\log_{10}[OH^-]$$

$$\boxed{14 = P_H + P_{OH}}$$

* Acidity, basicity and neutrality of aqueous solution.

1) Neutral solution: For pure water or any aqueous neutral solution at 298 K

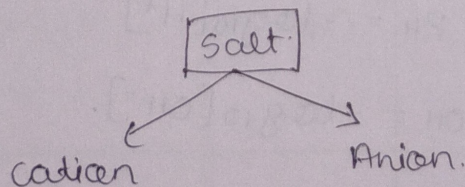
$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} M.$$

$$\text{Hence, } P_H = -\log_{10}[H^+] = -\log_{10}[1 \times 10^{-7}] = 7.$$

2) Acidic solution: In acidic solution, there is excess of H_3O^+ ions, or $[H_3O^+] > [OH^-]$ hence, $[H_3O^+] > 1 \times 10^{-7}$ and $P_H < 7$

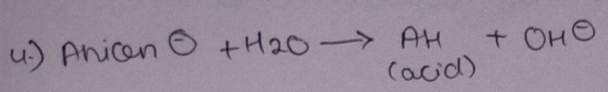
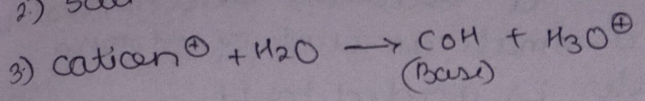
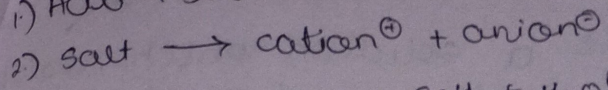
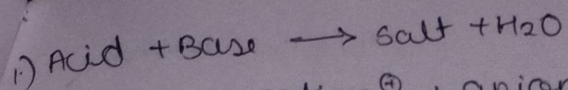
3) Basic solution: In basic solution, the excess of OH^- ions are present that is $[H_3O^+] < [OH^-]$ or $[H_3O^+] < 1 \times 10^{-7}$ with $P_H > 7$

ASC no. 1 Trick!!



Acid: H^+ $\frac{d}{dt} \frac{1}{\epsilon}$

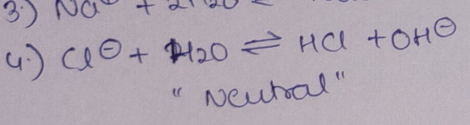
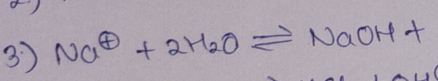
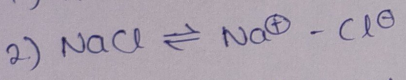
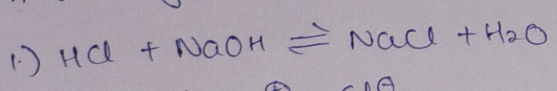
Base: OH^- $\frac{d}{dt} \frac{1}{\epsilon}$



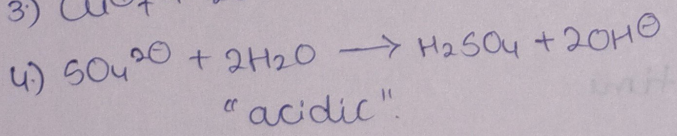
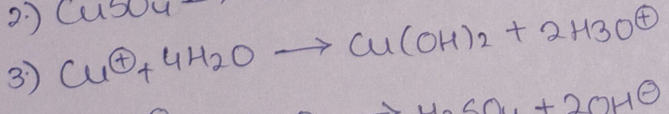
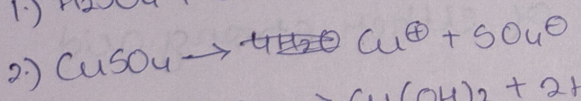
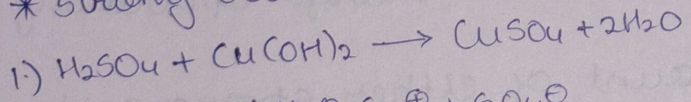
* Hydrolysis of salts:

Acid		Base	
Strong	Weak	Strong	Weak
1) HCl	1) CH ₃ COOH	1) KOH	1) Cu(OH) ₂
2) H ₂ SO ₄		2) NaOH	2) NH ₄ OH
3) HNO ₃			

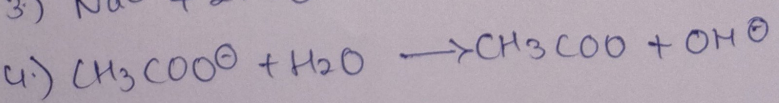
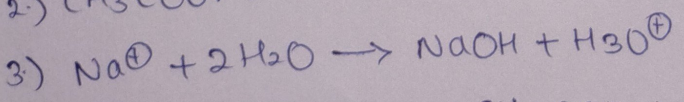
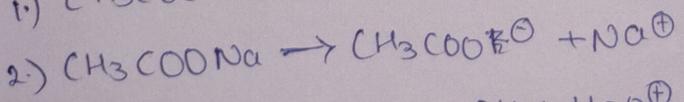
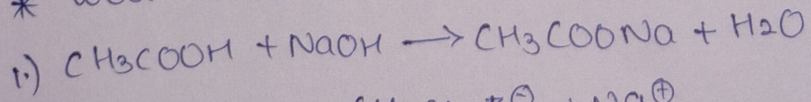
* Strong acid and strong base.



* Strong acid and weak base



* weak acid and strong base.



* Buffer solutions: [July 23, 24]

- Buffer solution is defined as a solution which has drastic changes in pH when a small amount of strong acid or strong base or water is added to it.

i) acidic buffer solution:

- A solution containing a weak acid and its salt with strong base is called an acidic buffer solution.

weak acid . salt . strong base
weak base . salt . strong acid.

$$pH = pK_a + \log_{10} \frac{\text{salt}}{\text{acid}}$$

$$pK_a = -\log_{10} [K_a]$$

$$pOH = pK_b + \log_{10} \frac{\text{salt}}{\text{base}}$$

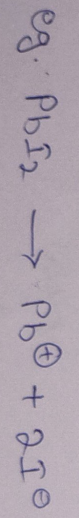
$$pK_b = -\log_{10} [K_b]$$

* Properties of buffer solution.

- The pH of a buffer solution does not change appreciably
- i) by addition of small amount of either strong acid or strong base.
- ii) on dilution.
- iii) or when it is kept for long time.

* Solubility product

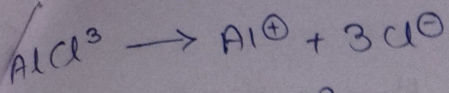
$$K_{sp} = x^x \cdot y^y \cdot S^{x+y}$$



$$K_{sp} = (1)^1 (2)^2 \cdot S^{1+2}$$

$$K_{sp} = 4S^3$$

resists



$$x=1, y=3$$

$$K_{sp} = (1)^1 (3)^3 \cdot S^{1+3}$$

$$K_{sp} = 27 S^4$$

Q. Define solubility product.

⇒ In the saturated solutions of sparingly soluble salt, the product of equilibrium concentrations of the constituent ions raised to the power equal to their respective coefficients in the balanced equilibrium expression at a given temperature is called the solubility product.

