

## Acids, Bases and buffers

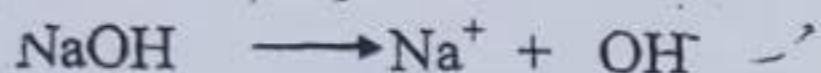
### Acids - base Theories

#### 1- Arrhenius Theory (1884)

Acid is any substance that ionized in water (partially or completely) to give hydrogen ions

Base is any substance that ionized in water to give hydroxyl ions

According to this definition, HCl is an acid NaOH is a base as shown below:



Acid chemically reacts with a base as follow:



#### 2- Brønsted-Lowry Theory (1923)

Acid is any substance that can donate a proton.

Base is any substance that can accept a proton.

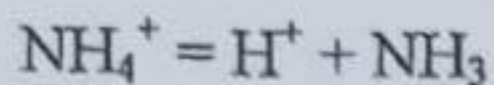
#### 3- Lewis Theory (1923)

Acids is a substance which can accept an electron pair by combining with a second substance with an unshared pair of electrons.

A base is a substance which shares its unshared electron - pair during chemical reaction







$\text{H}_2\text{O}$ : conjugated acid for  $\text{OH}^-$

$\text{NH}_3$ : is conjugated base for ( $\text{NH}_4^+$ )

or  $\text{NH}_4^+$  = is conjugated acid for ( $\text{NH}_3$ ) base



**Acid-Base strength:** When acid or base is dissolved in water it will dissociate or ionize. The degree of ionization depends on the strength of the acid

A strong electrolyte is completely dissociated

A weak electrolyte is partially dissociated

Weak acid has a relatively small dissociation constant ( $K_a$ ) where's strong acid has a large dissociation constant.

The strength of an acid depends on its type and is not related to the concentration.

(e.g.):  $\text{HCl}$  strong acid regardless of whether its concentration.  $1\text{M}$  or  $10^{-4}\text{M}$

Strong base: is a base with relatively large  $K_b$

Weak base: is a base with relatively small  $K_b$

### **Acid bases equilibria in water**

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (ionization content of water)}$$

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

$$[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$$

Conc. of  $[\text{H}^+]$  in a solution is often expressed as the pH of the solution which is the negative of the logarithm of  $[\text{H}^+]$

$$\text{pH} = -\log [\text{H}^+] \quad \text{pOH} = -\log [\text{OH}^-]$$

$$\text{p}K_w = \text{pH} + \text{pOH} = 14$$

**H.W. :** Calculate the pH of  $2 \times 10^{-3}\text{M}$  of hydrochloric acid solution?

In order to determine the pH of weak (partially ionized), strong (completely ionized) acids or bases and salts, different calculations must be followed as shown in the



**1- Strong acid / base**

Since the strong electrolyte is completely dissociated for that the concentration of  $[H^+]/[OH^-]$  is equal of the initial concentration.

Exp: What is the pH of a 0.010 M HCl solution?

Since HCl is a strong acid, the hydronium ion concentration will be equal to the HCl concentration:

$$[H_3O^+] = 0.010 \text{ M}$$

The pH can be found by taking the negative log of the hydronium ion concentration:

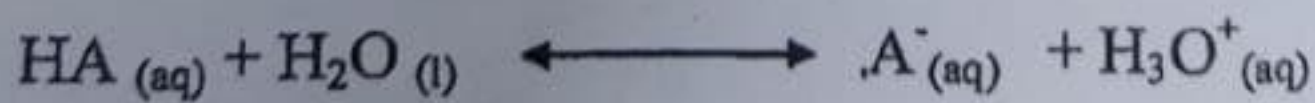
$$\text{pH} = -\log[H_3O^+] = -\log(0.010) = 2.00$$

**2- Weak acid / base**

It's important to realize that a weak acid is not the same thing as a dilute solution of a strong acid. Whereas a strong acid is 100% dissociated in aqueous solution, a weak acid is only partially dissociated. It might therefore happen that the concentration from complete dissociation of a dilute strong acid is the same as that from partial dissociation of a more concentrated weak acid.

Equilibrium exists between the weak acid, water,  $H_3O^+$ , and the anion of the weak acid. The equilibrium lies to the left hand side of the equation, indicating that not much  $H_3O^+$  is being produced. The fact that very little  $H_3O^+$  is being produced is the definition of a weak acid.

The  $K_a$  for a weak acid is small, usually a number less than 1.



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$



Note that water has been omitted from the equilibrium equation because its concentration in dilute solutions is essentially the same as that in pure water and pure liquids are always omitted from equilibrium equations

Exp: The initial concentration of  $\text{HNO}_2$  is 0.45 M,  $K_a = 4.5 \times 10^{-4}$ .

	$\text{HNO}_{2(aq)} + \text{H}_2\text{O}(l) \rightleftharpoons \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)$		
Init	0.45	0	0
Change	-x	+x	+x
Equal.	$0.45 - x$	x	x

$$K_a = \frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]} = \frac{(x)(x)}{0.45 - x} = 4.5 \times 10^{-4}$$

Simplifies to: since  $K_a * 100 \leq C_i$

$$x = [\text{NO}_2^-] = [\text{H}^+] = \sqrt{K_a C_i} = \sqrt{4.5 \times 10^{-4} \times 0.45} = 0.014$$

$$[\text{HNO}_2] = 0.45 - 0.014 = 0.436 \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{0.014} = 7.1 \times 10^{-13}$$

**H.W:** Codeine ( $\text{C}_{18}\text{H}_{21}\text{NO}_3$ ), a drug used in painkillers and cough medicines, is a naturally occurring amine that has  $k_b = 1.6 \times 10^{-6}$ . Calculate the pH and the concentrations of all species present in a 0.0012 M solution of codeine.

### 3- *pH of Salt*

Salts such as NaCl that are derived from a strong base (NaOH) and a strong acid (HCl) yield neutral solutions because neither the cation nor the anion reacts appreciably with water to produce  $\text{OH}^-$  ions. As the conjugate base of a strong acid, has no tendency to make the solution basic by picking up a proton from water. As the cation of a strong base, the hydrated ion has only a negligible tendency to make the solution acidic by transferring a proton to a solvent water molecule.

The following ions do not react appreciably with water to produce either  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions:



- Cations from strong bases: Alkali metal cations of group 1A:  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$   
Alkaline earth cations of group 2A:  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$  except for  $\text{Be}^{+2}$
- Anions from strong monoprotic acids:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_3^-$

Salts that contain only these ions give neutral solutions in pure water ( $\text{pH} = 7$ ).

Salts such as  $\text{NH}_4\text{Cl}$  that are derived from a weak base ( $\text{NH}_3$ ) and a strong acid ( $\text{HCl}$ ) produce acidic solutions. In such a case, the anion is neither an acid nor a base, but the cation is a weak acid



Finally, salt such as  $(\text{NH}_4)_2\text{CO}_3$  in which both the cation and the anion can undergo proton-transfer reactions. Because is a weak acid and is a weak base, the  $\text{pH}$  of an  $(\text{NH}_4)_2\text{CO}_3$  solution depends on the relative acid strength of the cation and base strength of the anion:

We can distinguish three possible cases:

- $k_a > k_b$  If  $k_a$  for the cation is greater than  $k_b$  for the anion, the solution will contain an excess of  $\text{H}_3\text{O}^+$  ions ( $\text{pH} < 7$ ).
- $k_a < k_b$  If  $k_a$  for the cation is less than  $k_b$  for the anion, the solution will contain an excess of  $\text{OH}^-$  ions ( $\text{pH} > 7$ ).
- $k_a = k_b$  If  $k_a$  for the cation and  $k_b$  for the anion are comparable, the solution will contain approximately equal concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions ( $\text{pH} = 7$ ).

- Calculate the  $\text{pH}$  of a 0.10 M solution of  $\text{AlCl}_3$ ;  $k_a$  for  $\text{Al}(\text{H}_2\text{O})_6^{+3}$ , is  $1.4 \times 10^{-5}$ .
- Calculate the  $\text{pH}$  of a 0.10 M solution of  $\text{NaCN}$ ;  $k_a$  for  $\text{HCN}$  is  $4.9 \times 10^{-10}$
- Calculate the  $\text{pH}$  of 0.20 M  $\text{NaNO}_2$ ;  $k_a$  for  $\text{HNO}_2$  is  $4.6 \times 10^{-4}$ .



- Calculate  $k_a$  for the cation and  $k_b$  for the anion in an aqueous  $\text{NH}_4\text{CN}$  solution. Is the solution acidic, basic, or neutral?

#### 4- Solution and indicators for acid/base reaction (titration)

Neutralization titrations depend on a chemical reaction between the analyte and a standard reagent. The point of chemical equivalence is indicated by a chemical indicator or an instrumental method.

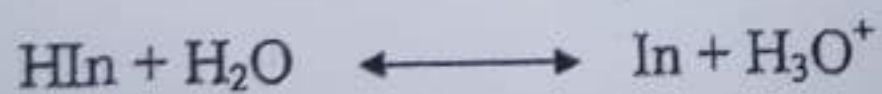
##### - Standard solution

A primary standard is a chemical or reagent which has certain properties such as: 1- High purity (e.g. 99.9% by weight)

- 2- Atmospheric stability
- 3- Absent of hydrate water
- 4- Modest cost
- 5- Reasonable solubility in the titration medium
- 6- Reasonable large molar mass.

##### - Acid/Base Indicators

An acid / base indicator is a weak organic acid or weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HIn}]}{[\text{In}^-]}$$



Water superheated under pressure to 200 °C and 750 atm has  $K_w = 1.5 \times 10^{-11}$

What is  $[H_3O^+]$  and  $[OH^-]$  at 200 °C? Is the water acidic, basic, or neutral?

Water at 500 °C and 250 atm is a supercritical fluid. Under these conditions,  $K_w$  is approximately  $1.7 \times 10^{-19}$ . Estimate  $[H_3O^+]$  and  $[OH^-]$  at 500 °C. Is the water acidic, basic, or neutral?

Calculate the pH to the correct number of significant figures for solutions of Question 1?

Calculate the concentration to the correct number of  $[H_3O^+]$ ,  $[OH^-]$  significant figures for solutions with the following pH values: 4.1, 10.82, 0.00, 14.25, 5.238, -1.0, 9, 14.25, -0.3, 10.75

A solution of NaOH has a pH of 10.50. How many grams of CaO should be dissolved in sufficient water to make 1.00 L of a solution having the same pH?

A solution of KOH has a pH of 10.00. How many grams of SrO should be dissolved in sufficient water to make 2.00 L of a solution having the same pH?

8- Calculate the pH of solutions prepared by:

Dissolving 4.8 g of lithium hydroxide in water to give 250 mL of solution

Dissolving 0.93 g of hydrogen chloride in water to give 0.40 L of solution

Diluting 50.0 mL of 0.10 M HCl to a volume of 1.00 L

(d) Mixing 100.0 mL of HCl and 400.0 mL of  $HClO_4$  (Assume that volumes are additive.)

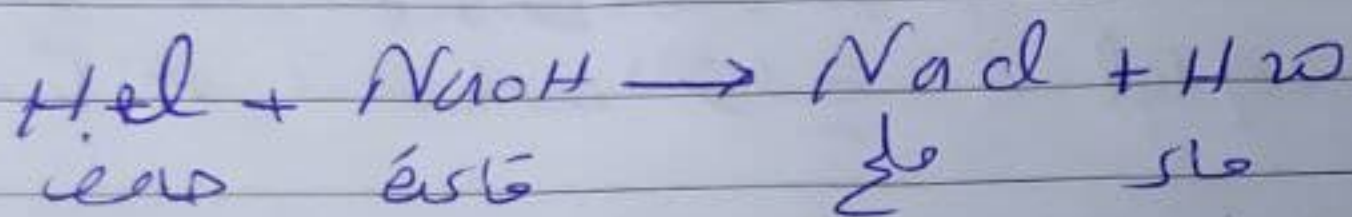
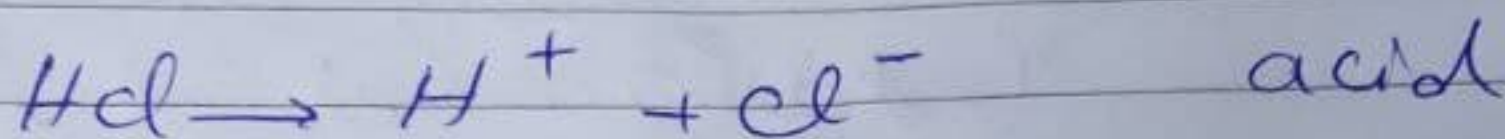
9- Calculate the pH of solutions prepared by:



## Acid-base Theories

1. نظرية أرينيهوس: المادة التي تتأين في الماء لتعطي أيونات تسمى الحمض

المادة التي تتأين في الماء لتعطي أيونات الهيدروكسيل تسمى القاعد



## 2. نظرية بروندستدوري

الحمض: هي المادة التي تمنح بروتون  
 القاعد: هي التي تتقبل البروتون  
 donate Proton      accept Proton

3. قاعد لويس: الحمض: هي المادة التي تتقبل الإلكترونات بأتمها مع مادة ثانية تحتوي على زوج إلكتروني  
 القاعد: هي المادة التي تشارك بزوجها الإلكتروني خلال التفاعل الكيميائي.





## Acid-base strength

عند اذابة حامض اضعف في الماء فانها تتفكك اذتة

درجة التأين لضعف قوة الحامض

\* الا للتروليبي القوي يتفكك طلياً

\* الا للتروليبي اضعف يتفكك جزئياً

\* الحامض الضعيف فقط  $K_a$  لدرجة قليلة - لدرجة الحامض القوي

قيمة ثابت التفكك له عالية

Hel

مما له عن الحامض القوي

\* القاعدية القوية لها  $K_b$  عالية والقاعدية الضعيفة  $K_b$  واطنة

$$K_w = [H^+][OH^-] = 1 \times 10^{-14} \quad (\text{ثابت تفكك الماء})$$

$$[H^+][OH^-] = 1 \times 10^{-14} \Rightarrow [H^+] = [OH^-] = 1 \times 10^{-7}$$

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

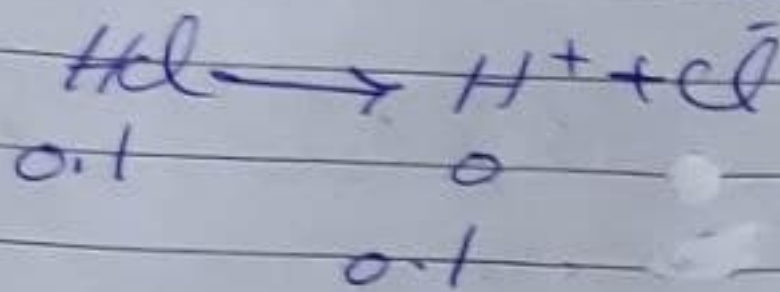
$$pOH = -\log [OH^-]$$

$$pK_w = pH + pOH = 14$$



Strong acid / base

الاحتراب القوي تتفكك كلها اذم تراكيز  $H^+$  ،  $OH^-$  متساوية  
في التراكيز الاحتمالية



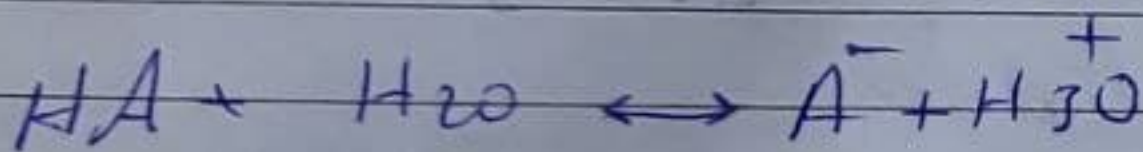
$$pH = -\log [H^+]$$

When  $HCl = 0.1 M \Rightarrow [H^+] = 0.1 M$  also  
لانه يتفكك كلها

$$pH = -\log [H^+] = -\log (0.1) = 2.0$$

Weak acid / base

اما الاحتراب القوي  
فانه يتفكك جزئياً



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

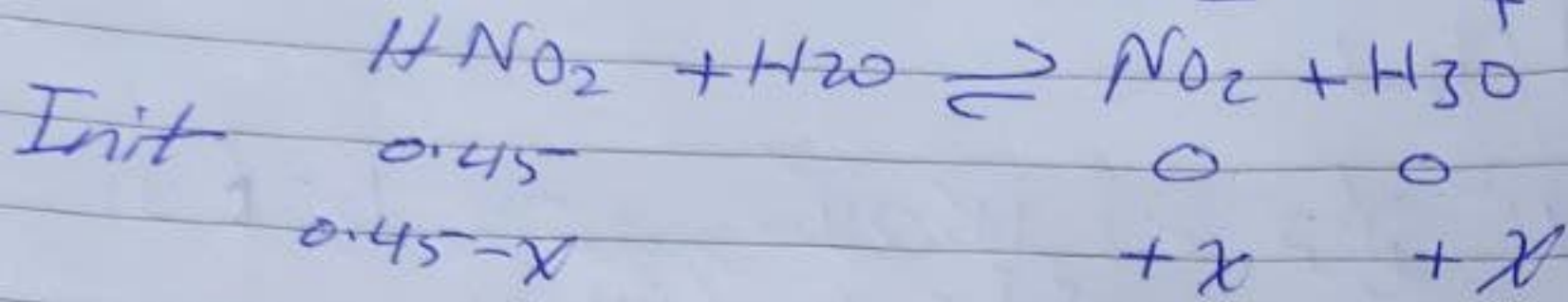
حالة التوازن  
لحامض الضعيف  
والملح

تكون  $K_a$  واهية

وعالية تكون اقل من 1



The Initial conc  $\text{HNO}_2 = 0.45 \text{ M}$  &  $K_a = 4.5 \times 10^{-4}$



$$K_a = \frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]} = \frac{(x)(x)}{0.45 - x} = 4.5 \times 10^{-4}$$

pH of salt

Strong acid  
Weak base

إذا كان الملح مشتق من حامض قوي وقواعد ضعيفة

$$[\text{H}^+] = \sqrt{\frac{[\text{K}_w][\text{Salt}]}{K_b}}$$

يطبق القانون

إذا كان الملح مشتق من حامض ضعيف وقواعد قوية

Strong base and weak acid

$$[\text{H}^+] = \sqrt{\frac{K_w \cdot K_a}{[\text{Salt}]}}$$

يستخدم القانون

Standard Solution

1. نقاوة عالية و مستقرة في الهواء
3. صافي من جزيئات بللار (غير مستقر)
4. تكلفة واهنة
5. سهل الذوبان
6. ويزع عاب

الدلائل Indicators :- هي مواد عضوية (حامضية او قلوية)  
لها ألوان معينة في المحاليل



Q<sub>1</sub> Calculate pH for a 0.5 liter solution containing 3.25 gm of Potassium cyanide (KCN), know that  $K_a(\text{HCN}) = 4.9 \times 10^{-10}$ ,  $MWT(\text{KCN}) = 65 \text{ g/mol}$ .

Sol<sup>n</sup>  $M_{\text{KCN}} = \frac{wt}{MWT} \times \frac{1000}{V(\text{ml})} \Rightarrow \frac{3.25}{65} \times \frac{1000}{500} = 0.1 \text{ M}$

$$[H^+] = \sqrt{\frac{K_w \times K_a}{[\text{Salt}]}} \Rightarrow \sqrt{\frac{10^{-14} \times 4.9 \times 10^{-10}}{0.1}} \Rightarrow [H^+] = 7 \times 10^{-12} \text{ M}$$

$$pH = -\log[H^+] = 11.2$$

Q<sub>2</sub> Calculate  $[OH^-]$  for a 0.5 liter solution containing (5.35) gm of  $\text{NH}_4\text{Cl}$  Ammonium chloride, know that  $K_b(\text{NH}_3) = 2 \times 10^{-5}$ ,  $MWT(\text{NH}_4\text{Cl}) = 53.5 \text{ g/mol}$ .

Sol<sup>n</sup>  $M = \frac{wt}{MWT} \times \frac{1000}{V(\text{ml})} \Rightarrow \frac{5.35}{53.5} \times \frac{1000}{500}$

$M = 0.2$

$$[H^+] = \sqrt{\frac{K_w [\text{Salt}]}{[K_b]}} \Rightarrow \sqrt{\frac{0.2 \times 10^{-14}}{2 \times 10^{-5}}} \Rightarrow [H^+] = \sqrt{10} \text{ M}$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-5}} = 10^{-9} \text{ M}$$



# Examples For - pH -

Ex 12

Calculate number of moles for (salts) required to solve in 100ml of distilled water to prepare a solution with  $pH = [9]$

Know that  $K_a$  for the weak acid is  $= 1 \times 10^{-5}$

Solu  $[H^+] = \sqrt{\frac{K_w \times K_a}{[salt]}}$

$$10^{-9} = \sqrt{\frac{10^{-14} \times 10^{-5}}{[salt]}} = 1 \times 10^{-1} \quad \leftarrow \sqrt[5]{5}$$

$$M = \frac{wt}{Mwt} \times \frac{1000}{V(ml)} \Rightarrow M = \frac{\text{No. of moles}}{V} \times \frac{1000}{V}$$

$$\text{No. of mole} = 1 \times 10^{-2} \quad \leftarrow 10^{-1} = \frac{\text{No. of mole}}{100} \times \frac{1000}{100}$$



Ex 3

calculate PH of a 0.1M solution of NaCN

Know that

$$K_a [\text{HCN}] = 4.9 \times 10^{-10}$$

$$[\text{H}^+] = \sqrt{\frac{K_w * K_a}{[\text{Salt}]}}$$

$$[\text{H}^+] = \sqrt{\frac{1 \times 10^{-14} * 4.9 \times 10^{-10}}{0.1}} \Rightarrow [\text{H}^+] = 7 \times 10^{-12} \text{ M}$$

$$\text{PH} = -\log [\text{H}^+]$$

$$= 11.2 = \text{PH}$$