

MOHAMED KHIDER UNIVERSITY OF BISKRA.

FACULTY OF EXACT SCIENCES AND NATURAL AND LIFE SCIENCES

DEPARTMENT OF BIOLOGY

**Semester2: THERMODYNAMICS AND CHEMISTRY OF
MINERAL SOLUTIONS**

CHAPTER I

Part 1

Level: 1st year LMD

Dr: Ismail DAOUD

Academic year: 2023/2024

1. Chemical equilibrium

1.1. Acid-base equilibrium

We find three definitions: Arrhenius (1887) and Brønsted-Lowry (1923), as well as the model of Lewis (1923). In solution chemistry, the most suitable theory is that of Brønsted-Lowry.

a. Definition of Arrhenius (1887):

An acid: is a chemical substance capable of releasing H^+ ions (protons) in aqueous solution (H_3O^+ : oxonium or hydronium ion).

Example: $HA + H_2O \rightleftharpoons A^- + H_3O^+$ (HCl, CH_3COOH , ...)

A base: is a chemical substance capable of releasing OH^- (hydroxide) ions in aqueous solution

Example: $BOH + H_2O \rightleftharpoons B^+ + OH^-$ (NaOH, KOH, ...)

b. Definition from Bronsted and Lowry (1923):

An acid: is a chemical species capable of releasing one or more H^+ protons; it is a proton donor.

Example: $HA + H_2O \rightleftharpoons A^- + H_3O^+$ (HCl, CH_3COOH , ...)

A base: is a chemical species capable of capturing one or more H^+ protons; it is a proton acceptor.

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

c. Definition from Lewis (1923):

An acid: is a body that accepts a pair of electrons

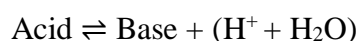
Example: $H_2O + H^+ \rightleftharpoons H_3O^+$ (appearance of a dative bond).

A base: is a body donating a pair of electrons

Example: $NH_3 + H^+ \rightleftharpoons NH_4^+$ (appearance of a dative bond).

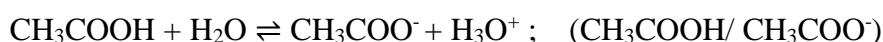
2.2. Monoacid and mono-base:

According to Brønsted, an acid is a species capable of releasing an H^+ proton to give it to another species, and a base is a species capable of capturing a proton coming from another species.



The acid and the base are said: "Conjugates"; they form an acid-base couple noted: Acid/Base).

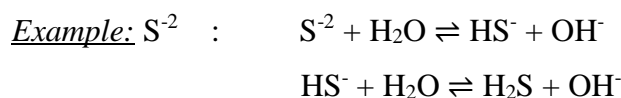
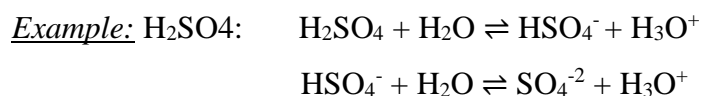
Example:



The acetate ion CH_3COO^- is the conjugate base of acetic acid CH_3COOH .

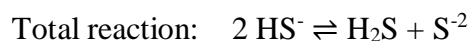
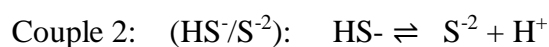
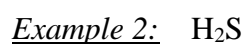
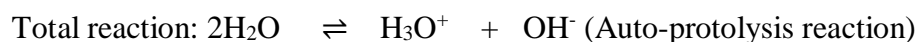
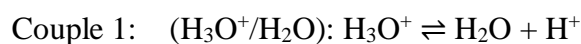
2.3. Poly-acids and Poly-bases:

A polyacid is a species capable of releasing 2 or more protons (H^+) to give them to another species, and a base is a species capable of fixing 2 or more protons (H^+) from another species.



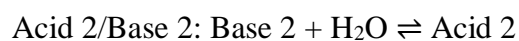
2.4. An ampholytes solution:

An amphoteric (or ampholyte) is a chemical species that can behave either as an acid or as a base. The corresponding solutions are called "Amphoteric).



2.5. Acid-base reaction:

An acid-base reaction is a proton transfer reaction between 2 couples: Acid 1/Base 1 and Acid2/Base2

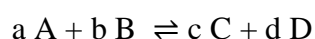


2.5.1. Equilibrium constant: water dissociation, acidity and basicity:

There are four equilibrium constants: K, K_e , K_a , K_b

a. Equilibrium constant of a reaction (K):

The equilibrium constant K of any acid-base reaction is given by the law of mass action:



$$K = \frac{[C]^c * [D]^d}{[A]^a * [B]^b}$$

Or [A], [B], [C] and [D]: are the concentrations of species A, B, C and D at equilibrium.

b. Water dissociation constant (Ke):

The self-protolysis equilibrium of water: $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

$$K = \frac{[\text{H}_3\text{O}^+] \cdot [\text{OH}^-]}{[\text{H}_2\text{O}]} \quad K_e = K \cdot [\text{H}_2\text{O}] = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-]$$

Ke: ionic product of water: $K_e = K \cdot [\text{H}_2\text{O}] = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-]$

Calculate the concentration of water $[\text{H}_2\text{O}]$:

At $t=25\text{ C}^\circ$, $K_e = 10^{-14} \Rightarrow \text{p}K_e = 14$.

We have: $C(\text{H}_2\text{O}) = n(\text{H}_2\text{O})/V(\text{H}_2\text{O})$, and $\rho(\text{H}_2\text{O}) = m(\text{H}_2\text{O})/V(\text{H}_2\text{O}) = 1\text{ g/ml}$ (or: 1 g/cm^3)

We take: $m(\text{H}_2\text{O}) = 1\text{ g} \Rightarrow V(\text{H}_2\text{O}) = 1\text{ ml}$

$n(\text{H}_2\text{O}) = m(\text{H}_2\text{O})/M(\text{H}_2\text{O}) = 1/18 = 0.05555\text{ mol}$ ($M(\text{H}_2\text{O}) = 2(1) + 16 = 18\text{ g/mol}$)

$C(\text{H}_2\text{O}) = 0.0555555/1 \cdot 10^{-3} \Rightarrow C(\text{H}_2\text{O}) = 55.55\text{ mol/l}$.

c. Acidity constant (Ka):

Weak acid: $\text{AH} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$ (Couple: HA/A^-)

The equilibrium constant:

$$K = \frac{[\text{H}_3\text{O}^+] \cdot [\text{A}^-]}{[\text{H}_2\text{O}] \cdot [\text{AH}]}$$

The equilibrium constant of dissociation of the acid called “acidity constant K_a ”:

$$K_a = K \cdot [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+] \cdot [\text{A}^-]}{[\text{AH}]}$$

Knowing that: $\text{p}K_a = -\log K_a$

Noticed:

Increasing acidity: $K_a \nearrow \Rightarrow \text{p}K_a \searrow$

Increasing basicity: $K_a \searrow \Rightarrow \text{p}K_a \nearrow$

d. Basicity constant (Kb):

Weak base: $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$ (Couple: BH^+/B)

The equilibrium constant:

$$K = \frac{[\text{BH}^+] \cdot [\text{OH}^-]}{[\text{H}_2\text{O}] \cdot [\text{B}]}$$

The equilibrium constant of acid dissociation called “acidity constant K_b ”:

$$K_b = K_w \cdot [H_2O] = \frac{[BH^+] \cdot [OH^-]}{[B]}$$

Noticed:

The relationship between K_a and K_b : $K_e = K_a \cdot K_b$

2.5.2. pH (Hydrogen potential):

a. Definition of pH: the acidity of an aqueous solution depends on the concentration of H_3O^+ ions.

$$pH = -\log H_3O^+ \quad (p = -\log ; H = H_3O^+)$$

b. Relationship between pH, pKa and concentrations:

Weak acid: Acid (AH) + $H_2O \rightleftharpoons$ Base (A^-) + H_3O^+ (Couple: HA/ A^-)

$$K_a = \frac{[H_3O^+] \cdot [Base]}{[Acide]} = \frac{[H_3O^+] \cdot [A^-]}{[AH]}$$

$$K_a \cdot [Acide] = [H_3O^+] \cdot [Base] \Rightarrow [H_3O^+] = K_a \cdot [Acid] / [Base]$$

$$-\log[H_3O^+] = -\log (K_a \cdot [Acid] / [Base]); \quad (pH = -\log H_3O^+ ; pK_a = -\log K_a).$$

$$pH = pK_a + \log \frac{[Base]}{[Acide]} \quad \text{Relation d'Henderson}$$

➤ **The pH of the water:**

The water auto-protolysis: $2H_2O \rightleftharpoons H_3O^+ + OH^-$

In pure water the quantities of H_3O^+ and OH^- ions are equal $\Rightarrow [H_3O^+] = [OH^-]$

$$\text{At: } t=25\text{ }^\circ\text{C} \quad K_e = 10^{-14}, [H_3O^+] \cdot [OH^-] = K_e = 10^{-14} \Rightarrow [H_3O^+]^2 = K_e = 10^{-14}$$

$$\Rightarrow [H_3O^+] = \sqrt{K_e} = \sqrt{10^{-14}} = 10^{-7} \Rightarrow -\log[H_3O^+] = -\log 10^{-7}$$

$$pH(H_2O) = 7$$

Noticed:

Neutral solution: $[H_3O^+] = [OH^-] \Rightarrow pH = 7$.

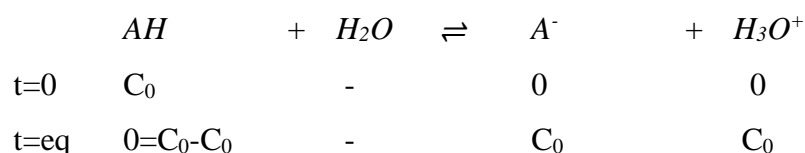
Acid solution: $[H_3O^+] > [OH^-] \Rightarrow pH < 6.5$.

Basic solution: $[H_3O^+] < [OH^-] \Rightarrow pH > 7.5$.

➤ **The pH of a strong monoacid (SA):**

When a Strong Acid (AH) of initial concentration C_0 is dissolved in water, there is total dissociation of the acid:

Couple (HA/ A^-):



In the case of slightly diluted solutions (i.e.: $C_0 > 3 \cdot 10^{-7}$ mol/l), the medium is sufficiently acidic so that $[OH^-]$ resulting from the auto-protolysis of water is negligible compared to $[H_3O^+]$.

This means that: $[H_3O^+] = C_0$; $pH = -\log[H_3O^+] = -\log C_0$.

$\Rightarrow pH = -\log C_0$; ($[H_3O^+] = C_0$).

Validity of the approximation:

For me to be sure and the acid is strong it is necessary that: $[H_3O^+] \geq 10[OH^-]$.

Demonstration:

$$[H_3O^+] \cdot [H_3O^+] \geq 10 [OH^-] \cdot [H_3O^+]$$

$$[H_3O^+]^2 \geq 10 Ke \Rightarrow \text{at } t=25C^\circ, Ke = 10^{-14} \Rightarrow [H_3O^+]^2 \geq 10 \cdot 10^{-14} \Rightarrow [H_3O^+]^2 \geq 10^{-13}$$

$$\Rightarrow [H_3O^+] \geq \sqrt{10^{-13}} = 10^{-6.5} \Rightarrow -\log[H_3O^+] \leq -\log 10^{-6.5} \Rightarrow (\log 10^x = x)$$

$$\Rightarrow pH \leq 6.5$$

Summary:

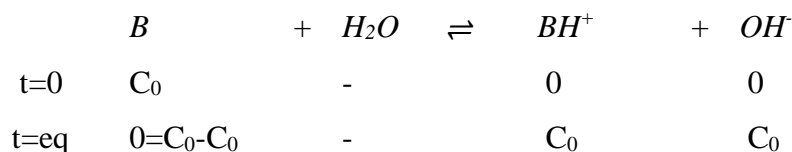
Strong Acid (SA):

pH (SA) = $-\log C_0$ ($[H_3O^+] = C_0$). With **pH ≤ 6.5** (at $t=25C^\circ$)

➤ **The pH of a strong mono-base (SB):**

A Strong base (B) with initial concentration C_0 , We have total protonation of the base:

Couple (BH^+/B):



In the case of slightly diluted solutions (i.e.: $C_0 > 3 \cdot 10^{-7}$ mol/l), the medium is sufficiently basic so that $[H_3O^+]$ resulting from the auto-protolysis of water is negligible compared to $[OH^-]$.

This means that: $[OH^-] = C_0$;

$$[H_3O^+] \cdot [OH^-] = C_0 \cdot [H_3O^+] \Rightarrow Ke = C_0 \cdot [H_3O^+] \Rightarrow [H_3O^+] = Ke / C_0$$

$$-\log[H_3O^+] = -\log(Ke / C_0) \quad (\log A/B = \log A - \log B)$$

$$\Rightarrow pH = -\log Ke + \log C_0, \quad \Rightarrow pH = pKe + \log C_0, \quad [OH^-] = C_0$$

Validity of the approximation:

So that I am sure and the base is strong it is necessary that: $[OH^-] \geq 10 [H_3O^+]$

Demonstration:

$$[OH^-] \cdot [H_3O^+] \geq 10 [H_3O^+] \cdot [H_3O^+]$$

$$K_e \geq 10 [H_3O^+]^2 \Rightarrow \text{at } t=25C^\circ ; K_e = 10^{-14} \Rightarrow 10^{-14} \geq 10 [H_3O^+]^2 \Rightarrow 10^{-15} \geq [H_3O^+]^2$$

$$\Rightarrow \sqrt{10^{-15}} = 10^{-7.5} \geq [H_3O^+] \Rightarrow -\log 10^{-7.5} \leq -\log[H_3O^+] \quad (\log 10^x = x)$$

$$\Rightarrow \text{pH} \geq 7.5$$

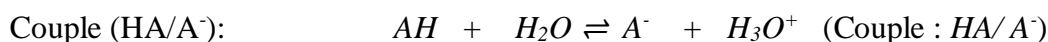
Summary:

Strong Base (SB):

$$\text{pH (SB)} = \text{p}K_e + \log C_0, \quad ([OH^-] = C_0). \quad \text{With} \quad \text{pH} \geq 7.5 \quad (\text{at } t=25C^\circ)$$

➤ **The pH of a weak monoacid (WA):**

When a weak acid (HA) of initial concentration C_0 is dissolved in water, there is a partial dissociation of the acid:



The water auto-protolysis equilibrium: $2H_2O \rightleftharpoons H_3O^+ + OH^-$

Four species are present at equilibrium concentration: $[AH]$, $[A^-]$, $[H_3O^+]$ and $[OH^-]$

We can write four relationships between these four unknowns:

1. Ionic product: $K_e = [H_3O^+] \cdot [OH^-] \dots\dots\dots(1)$

2. Couple acidity constant (HA/A⁻): $K_a = [A^-] \cdot [H_3O^+] / [AH] \dots\dots\dots(2)$

3. Concentration of the constituent elements of the acid-base couple: $C_0 = [AH] + [A^-] \dots\dots\dots(3)$

4. Electro-neutrality of the solution: $[H_3O^+] = [A^-] + [OH^-] \dots\dots\dots(4)$

First approximation:

The medium is acidic: $[H_3O^+] \gg [OH^-]$, i.e. the $[OH^-]$ is negligible compared to $[H_3O^+]$

The relation (4) becomes: $[H_3O^+] = [A^-] \dots\dots\dots(5)$

Second approximation:

The dissociation of the acid is weak, i.e.: the concentration of the conjugated mono-base is negligible compared to that of the acid AH, this means that: $[A^-] \ll [AH]$

The relation (3) becomes: $C_0 = [AH] \dots\dots\dots(6)$

The relation (2) + (5) + (6), we obtain: $K_a = [H_3O^+]^2 / [AH] \Rightarrow [H_3O^+]^2 = K_a \cdot [AH]$

$$\Rightarrow [H_3O^+] = \sqrt{K_a \cdot [AH]} \Rightarrow -\log[H_3O^+] = -\log(K_a \cdot [AH])^{1/2}; \quad (\log A/B = \log A - \log B)$$

$$\Rightarrow \text{pH} = \frac{1}{2} (-\log K_a - \log[AH]) \Rightarrow \text{pH} = \frac{1}{2} (\text{p}K_a - \log[AH]) \Rightarrow \text{pH} = \frac{1}{2} (\text{p}K_a - \log C_0).$$

Validation Domain:

The medium is acidic: $[AH] \geq 10 [A^-]$

Demonstration:

$$[AH] \geq 10 [A^-] \Rightarrow 10^{-1} \geq [A^-]/[AH] \Rightarrow \log 10^{-1} \geq \log [A^-]/[AH] \Rightarrow -1 \geq \log [A^-]/[AH]$$

$$\Rightarrow pK_a - 1 \geq pK_a + \log [A^-]/[AH]$$

According to Henderson relation: $pH = pK_a + \log ([base]/[acid])$

$$\Rightarrow pK_a - 1 \geq pH \quad \Rightarrow \quad pH \leq pK_a - 1.$$

Use of the dissociation coefficient (α_a):

The weak acid approximation relies on the assumption of weak dissociation.

We call: (α_a): dissociation coefficient = Number of moles dissociated from AH/Initial number

of moles of AH, $\alpha_a = x/C_0$

Material equilibrium:

	AH	+	H_2O	\rightleftharpoons	A^-	+	H_3O^+
t=0	C_0		-		0		0
t=eq	$C_0 - X$		-		X		X
$\alpha_a = X/C_0$	$C_0(1 - \alpha_a)$		-		$C_0\alpha_a$		$C_0\alpha_a$

$$K_a = [A^-] \cdot [H_3O^+] / [AH] = C_0\alpha_a \cdot C_0\alpha_a / C_0(1 - \alpha_a) = C_0 \alpha_a^2 / (1 - \alpha_a) \Rightarrow K_a = C_0\alpha_a^2 / (1 - \alpha_a)$$

• If $\alpha_a \leq 0.1$ (the dissociation is weak; less than 10%) \Rightarrow we can neglect the α_a in front of 1:

$$\text{The relationship becomes: } K_a = C_0 \cdot \alpha_a^2 \Rightarrow \alpha_a = \sqrt{(K_a / C_0)} \leq 10^{-1} \Rightarrow K_a / C_0 \leq 10^{-2}.$$

Note:

This is Ostwald's law which indicates that dissociation increases with dilution and a much diluted weak electrolyte behaves like a strong electrolyte. This is why the calculation of the pH of acids and bases is applicable for solutions which are not too diluted.

Summary:

Weak acid (WA):

$$pH (WA) = \frac{1}{2} (pK_a - \log C_0) \quad . \quad (t=25C^\circ)$$

With : 1/ $pH \leq pK_a - 1$; 2/ If $\alpha_a \leq 0.1 \Rightarrow K_a / C_0 \leq 10^{-2}$.

➤ The pH of a weak mono-base (WB):

A weak base (B) with initial concentration C_0 , We have partial protonation of the base:



Four species are present at equilibrium concentration: [B], [BH⁺], [H₃O⁺] and [OH⁻]

We can write four relationships between these four unknowns:

1. Ionic product: $K_e = [H_3O^+] \cdot [OH^-] \dots\dots\dots(1)$
2. Couple basicity constant (BH⁺/B): $K_b = [BH^+] \cdot [OH^-] / [B] \dots\dots\dots(2)$
3. Concentration of the constituent elements of the acid-base couple: $C_0 = [B] + [BH^+] \dots\dots\dots(3)$
4. Electro-neutrality of the solution: $[BH^+] + [H_3O^+] = [OH^-] \dots\dots\dots(4)$

First approximation:

The medium is basic: $[OH^-] \gg [H_3O^+]$, i.e. the $[H_3O^+]$ is negligible compared to $[OH^-]$

The relation (4) becomes: $[BH^+] = [OH^-] \dots\dots(5)$

Second approximation:

The protonation of the base is weak, i.e.: the concentration of the conjugated monoacid is negligible compared to that of base B, this means that: $[BH^+] \ll [B]$.

The relation (3) becomes: $C_0 = [B] \dots\dots\dots(6)$

$K_b = [BH^+] \cdot [OH^-] / [B] \dots\dots(2) \quad (K_a \cdot K_b = K_e ; K_e = [H_3O^+] \cdot [OH^-])$

$\Rightarrow K_e / K_a = [BH^+] K_e / [B] [H_3O^+] \Rightarrow K_e \cdot [B] \cdot [H_3O^+] = K_a \cdot [BH^+] \cdot K_e$

$\Rightarrow K_a = [B] \cdot [H_3O^+] / [BH^+] \dots\dots\dots(7)$

(7) + (5) + (6), we obtained: $K_a = C_0 \cdot [H_3O^+] / [OH^-] \Rightarrow K_a = C_0 \cdot [H_3O^+]^2 / K_e$
 $\Rightarrow [H_3O^+]^2 = (K_a K_e / C_0) \Rightarrow [H_3O^+] = \sqrt{(K_a K_e / C_0)} \Rightarrow -\log[H_3O^+] = -\log(K_e K_a / C_0)^{1/2};$

($\log A/B = \log A - \log B$, $\log A \cdot B = \log A + \log B$)

$\Rightarrow pH = \frac{1}{2} (-\log K_a - \log K_e + \log C_0) \Rightarrow pH = \frac{1}{2} (pK_e + pK_a + \log C_0)$

Validation Domain:

The medium is basic: $[B] \geq 10 [BH^+]$

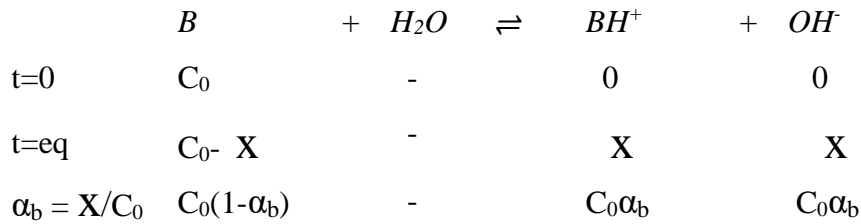
Demonstration:

$[B] \geq 10 [BH^+] \Rightarrow 10^{-1} \geq [BH^+]/[B] \Rightarrow [B]/[BH^+] \geq 10 \Rightarrow \log[B]/[BH^+] \geq \log 10$
 $\Rightarrow pK_a + \log[B]/[BH^+] \geq pK_a + 1$ (Henderson relation: $pH = pK_a + \log ([base]/[acid])$)
 $\Rightarrow pH \geq pK_a + 1.$

Use of the dissociation coefficient (α_b):

The weak basis approximation relies on the assumption of weak protonation
 We call: (α_b): dissociation coefficient = Number of moles dissociated from [B]/ Initial number of moles of [B], $\alpha_b = x/C_0.$

Material equilibrium:



$$K_b = [BH^+] \cdot [OH^-] / [B] \quad (K_a \cdot K_b = K_e ; K_e = [H_3O^+] \cdot [OH^-])$$

$$\Rightarrow K_e/K_a = [BH^+] K_e / [B] [H_3O^+] \Rightarrow K_e \cdot [B] \cdot [H_3O^+] = K_a \cdot [BH^+] \cdot K_e$$

$$\Rightarrow K_a = [B] \cdot [H_3O^+] / [BH^+] \Rightarrow K_a = K_e \cdot [B] / [BH^+] [OH^-] \Rightarrow K_a = K_e C_0(1-\alpha_b) / C_0\alpha_b \cdot C_0\alpha_b$$

$$\Rightarrow K_a = K_e (1-\alpha_b) / C_0\alpha_b^2$$

• If $\alpha_b \leq 0.1$ (the protonation is weak; less than 10%) \Rightarrow we can neglect the α_b in front of 1:

The relationship becomes: $K_a = K_e / C_0\alpha_b^2 \Rightarrow \alpha_b = \sqrt{(K_e / K_a C_0)} \leq 10^{-1} \Rightarrow K_e / K_a C_0 \leq 10^{-2}$.

Summary:

Weak base (WB):

$$pH(WB) = \frac{1}{2} (pK_e + pK_a + \log C_0) \quad . \quad (t=25C^\circ)$$

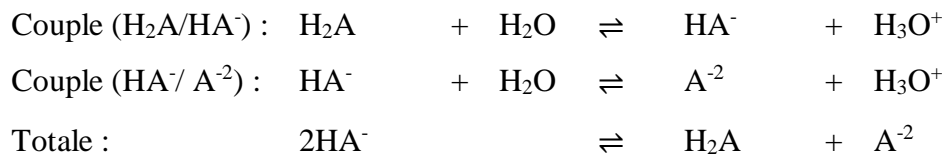
With : **1/** $pH \geq pK_a + 1$; **2/** If $\alpha_b \leq 0.1 \Rightarrow K_e / K_a C_0 \leq 10^{-2}$.

➤ **The pH of an amphoteric solution:**

Consider the solution of a NaHA salt (Example: Na HCO₃) of concentration C.

The total dissociation of salt in water is written as: $NaHA_{(solid)} \rightarrow Na^+ + HA^-$

HA⁻ is an ampholyte since it is the acid pair: HA⁻/A⁻² and the base of H₂A/HA⁻



The balance of this overall reaction indicates that: $[H_2A] = [A^{2-}]$

Ka1: acidity constant: $H_2A/HA^- \Rightarrow Ka_1 = [HA^-] \cdot [H_3O^+] / [H_2A]$

Ka2: acidity constant: $HA^-/A^{2-} \Rightarrow Ka_2 = [A^{2-}] \cdot [H_3O^+] / [HA^-]$

$$Ka_1 \cdot Ka_2 = ([HA^-] \cdot [H_3O^+] / [H_2A]) \cdot ([A^{2-}] \cdot [H_3O^+] / [HA^-]) = [H_3O^+]^2 \cdot ([A^{2-}] / [H_2A])$$

$$[H_2A] = [A^{2-}]$$

$K_{a1} \cdot K_{a2} = [H_3O^+]^2 \Rightarrow pH = \frac{1}{2} (pK_{a1} + pK_{a2})$ (We note that pH is independent of concentration (C)).

Noticed:

An ampholyte is a substance that contains a negative charge and hydrogen (regardless of the number of negative charges or hydrogen atoms).