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

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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: $HA + H_2O \rightleftharpoons A+ + H_2O$ (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: $H_2O + H^+ \rightleftharpoons H_3O^+$ (appearances of a dative bond).

A base: is a body donating a pair of electrons

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

2.2. Monoacid and mono-base:

According to Bronsted, 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.

$$\text{Acid} \rightleftharpoons \text{Base} + (H^+ + H_2O)$$

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

Example:

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$; (CH_3COOH/ CH_3COO^-)

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.

Example: H_2SO4: $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$

$HSO_4^- + H_2O \rightleftharpoons SO_4^{-2} + H_3O^+$

Example: S^{-2} : $S^{-2} + H_2O \rightleftharpoons HS^- + OH^-$

$HS^- + H_2O \rightleftharpoons H_2S + OH^-$

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).

Example 1: H_2O

Couple 1: (H_3O^+/H_2O): $H_3O^+ \rightleftharpoons H_2O + H^+$

Couple 2: (H_2O/OH^-): $H_2O \rightleftharpoons H^+ + OH^-$

Total reaction: $2H_2O \rightleftharpoons H_3O^+ + OH^-$ (Auto-protolysis reaction)

Example 2: H_2S

Couple 1: (H_2S/ HS^-): $H_2S \rightleftharpoons HS^- + H^+$

Couple 2: (HS^-/S^{-2}): $HS- \rightleftharpoons S^{-2} + H^+$

Total reaction: $2 HS^- \rightleftharpoons H_2S + S^{-2}$

2.5. Acid-base reaction:

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

Acid 1/Base 1: Acid 1 $\rightleftharpoons$ Base 1 + H_3O^+

Acid 2/Base 2: Base 2 + $H_2O \rightleftharpoons$ Acid 2

Total reaction: Acid 1 + Base 2 $\rightleftharpoons$ Base 1 + Acid 2

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

There are four equilibrium constants: K, Ke, Ka, Kb

a. *Equilibrium constant of a reaction (K):*

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

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

K= $([C]^c * [D]^d) / ([A]^a * [B]^b)$

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: $2H_2O \rightleftharpoons H_3O^+ + OH^-$

$$K = \frac{[H_3O^+]\ .\ [OH^-]}{[H_2O]} \qquad Ke = K\ .\ [H_2O] = [H_3O^+]\ .\ [OH^-]$$

Ke: ionic product of water: $Ke = K. [H_2O] = [H_3O^+] . [OH^-]$

Calculate the concentration of water $[H_2O]$:

At t=25 C°, $Ke = 10^{-14} \Rightarrow pKe = 14$.

We have: $C(H_2O) = n(H_2O)/V(H_2O)$, and $\rho(H_2O) = m(H_2O)/ V(H_2O) = 1g/ml$ (or: $1\ g/cm^3$)

We take: $m(H_2O) = 1\ g \Rightarrow V(H_2O) = 1\ ml$

$n(H_2O) = m(H_2O)/ M(H_2O) = 1/18 = 0.05555$ mol ($M(H_2O) = 2\ (1) +16 = 18$ g/mol))

$C(H_2O) = 0.0555555/1.10^{-3} \Rightarrow C(H_2O)= 55.55$ mol/l.

c. Acidity constant (Ka):

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

The equilibrium constant:

$$K = \frac{[H_3O^+]\ .\ [A^-]}{[H_2O]\ .\ [AH]}$$

The equilibrium constant of dissociation of the acid called "acidity constant Ka":

$$Ka = K\ .\ [H_2O] = \frac{[H_3O^+]\ .\ [A^-]}{[AH]}$$

Knowing that: pka= - log Ka

Noticed:

Increasing acidity: $Ka \nearrow \Rightarrow pKa \searrow$

Increasing basicity: $Ka \searrow \Rightarrow pKa \nearrow$

d. Basicity constant (Kb):

Weak base: $B + H_2O \rightleftharpoons BH^+ + OH^-$ (Couple: BH^+/B)

The equilibrium constant:

$$K = \frac{[BH^+]\ .\ [OH^-]}{[H_2O]\ .\ [B]}$$

The equilibrium constant of acid dissociation called "acidity constant Kb":

$$Kb = K \ . \ [H_2O] = \frac{[BH^+] \ . \ [OH^-]}{[B]}$$

Noticed:

The relationship between Ka and Kb: Ke = Ka . Kb

2.5.2. pH (Hydrogen potential):

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

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

b. Relationship between pH, pKa and concentrations:

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

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

Ka . [Acide] = $[H_3O^+]$. [Base] ⇒ $[H_3O^+]$ = Ka . [Acid] / [Base]

$-\log[H_3O^+] = -\log$ (Ka . [Acid] / [Base]); ($pH= - \log H_3O^+$; pKa= - log Ka).

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

- **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 ⇒ $[H_3O^+] = [OH^-]$

At: t=25 C° $Ke= 10^{-14}$, $[H_3O^+] . [OH^-] = Ke= 10^{-14} \Rightarrow [H_3O^+]^2 = Ke= 10^{-14}$

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

$$\mathbf{pH(H_2O) = 7}$$

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^-):

	AH	+	H_2O	$\rightleftharpoons$	A^-	+	H_3O^+
t=0	C_0		-		0		0
t=eq	$0=C_0-C_0$		-		C_0		C_0

In the case of slightly diluted solutions (i.e.: $C_0 > 3.10^{-7}$ 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:

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

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

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

$$\Rightarrow \mathbf{pH \leq 6.5}$$

Summary:

Strong Acid (SA):

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

- **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):

	B	+	H_2O	$\rightleftharpoons$	BH^+	+	OH^-
t=0	C_0		-		0		0
t=eq	$0=C_0-C_0$		-		C_0		C_0

In the case of slightly diluted solutions (i.e.: $C_0 > 3.10^{-7}$ 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: $[OH^-] = C_0$;

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

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

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

Validity of the approximation:

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

Demonstration:

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

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

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

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

Summary:

Strong Base (SB):

pH (SB) = pKe + log C_0, ($[OH^-] = C_0$). With **pH $\geq$ 7.5** (at t=25C°)

- **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:

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

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: $Ke = [H_3O^+]. [OH^-]$ ……….(1)

2. Couple acidity constant (HA/A^-): $Ka = [A^-]. [H_3O^+]/ [AH]$ ………(2)

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

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

First approximation:

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

The relation (4) becomes: $[H_3O^+] = [A^-]$ ………(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: $[A^-] << [AH]$

The relation (3) becomes: $C_0 = [AH]$ …….(6)

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

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

$\Rightarrow pH = ½ (-\log Ka - \log[AH]) \Rightarrow pH = ½ (pKa - \log[AH]) \Rightarrow pH = ½ (pKa - \log C_0)$.

Validation Domain:

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

Demonstration:

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

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

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

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

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 equilibruim:

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

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

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

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

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):

$pH\ (WA)= ½\ (pKa - \log C_0)$. (t=25C°)

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

- **The pH of a weak mono-base (WB):**

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

Couple (BH^+/B): $B + H_2O \rightleftharpoons BH^+ + OH^-$

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

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

We can write four relationships between these four unknowns:

1. Ionic product: $Ke = [H_3O^+]. [OH^-]$ ……….(1)

2. Couple basicity constant (BH^+/B): $Kb = [BH^+] . [OH^-] / [B]$ ………(2)

3. Concentration of the constituent elements of the acid-base couple: $C_0= [B] + [BH^+]$…….(3)

4. Electro-neutrality of the solution: $[BH^+] + [H_3O^+] = [OH^-]$ ………..(4)

First approximation:

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

The relation (4) becomes: $[BH^+] = [OH^-]$ …..(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: $[BH^+] << [B]$.

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

$Kb = [BH^+] . [OH^-] / [B]$ ……(2) ($Ka . Kb = Ke$; $Ke = [H_3O^+] . [OH^-]$)

$\Rightarrow Ke/Ka = [BH^+] Ke/ [B] [H_3O^+] \Rightarrow Ke . [B] . [H_3O^+] = Ka . [BH^+] . Ke$

$\Rightarrow Ka = [B] . [H_3O^+] / [BH^+]$ ……..(7)

(7) + (5) + (6), we obtained: $Ka = C_0. [H_3O^+] / [OH^-] \Rightarrow Ka = C_0. [H_3O^+]^2 / Ke$

$\Rightarrow [H_3O^+]^2 = (Ka\ Ke /C_0) \Rightarrow [H_3O^+] = \sqrt{}(Ka\ Ke /C_0) \Rightarrow -\log[H_3O^+] = -\log(Ke\ Ka /C_0)^{1/2}$;

(log A/B= log A – log B, log A.B= log A+log B)

$\Rightarrow pH= ½ (-\log Ka - \log Ka + \log C_0) \Rightarrow pH= ½ (pKe + pKa + \log C_0)$

Validation Domain:

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

Demonstration:

$[B] \geq 10 [BH^+] \Rightarrow 10^{-1} \geq [BH^+]/[B] \Rightarrow [B]/[BH^+] \geq 10 \Rightarrow \log[B]/[BH^+] \geq \log 10$

$\Rightarrow pKa + \log[B]/[BH^+] \geq pKa + 1$ (Henderson relation: $pH = pKa + \log ([base]/[acid])$

$\Rightarrow pH \geq pKa + 1$.

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 equilibruim:

	B	$+ \; H_2O$	$\rightleftharpoons$	BH^+	$+ \; OH^-$
t=0	C_0	-		0	0
t=eq	C_0- X	-		X	X
$\alpha_b = X/C_0$	$C_0(1-\alpha_b)$	-		$C_0\alpha_b$	$C_0\alpha_b$

$Kb = [BH^+] \,.\, [OH^-] / [B]$ $\quad$ ($Ka \,.\, Kb = Ke$; $Ke = [H_3O^+] \,.\, [OH^-]$)

$\Rightarrow Ke/Ka = [BH^+]\, Ke / [B]\,[H_3O^+] \quad \Rightarrow Ke \,.\, [B] \,.\, [H_3O^+] = Ka \,.\, [BH^+] \,.\, Ke$

$\Rightarrow Ka = [B] \,.\, [H_3O^+]/[BH^+] \Rightarrow Ka = Ke \,.\, [B]/[BH^+]\,[OH^-] \Rightarrow Ka = Ke\, C_0(1-\alpha_b)/C_0\alpha_b \,.C_0\, \alpha_b$

$\Rightarrow Ka = Ke\,(1-\alpha_b) / C_0\, \alpha_b^2$

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

The relationship becomes: $Ka = Ke/C_0\alpha_b{}^2 \Rightarrow \alpha_b = \sqrt{}\,(Ke/ KaC_0) \leq 10^{-1} \Rightarrow Ke/KaC_0 \leq 10^{-2}$.

Summary:

Weak base (WB):

$pH(WB) = ½\,(pKe + pKa + \log C_0)$. (t=25C°)

With : **1/** $pH \geq pKa + 1$; **2/** If $\alpha_b \leq 0.1 \Rightarrow Ke/KaC_0 \leq 10^{-2}$.

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

Consider the solution of a NaHA salt (Example: Na HCO_3) 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 H_2A/HA^-

Couple (H_2A/HA^-) :	H_2A	$+ \; H_2O$	$\rightleftharpoons$	HA^-	$+ \; H_3O^+$
Couple (HA^-/ A^{-2}) :	HA^-	$+ \; H_2O$	$\rightleftharpoons$	A^{-2}	$+ \; H_3O^+$
Totale :	$2HA^-$		$\rightleftharpoons$	H_2A	$+ \; A^{-2}$

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

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

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

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

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

$Ka_1 . Ka_2 = [H_3O^+]^2 \Rightarrow pH = \frac{1}{2} (pKa1 + pKa2)$ (We note that pH is independent of concentration (C)).

<u>Noticed:</u>

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