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 2

Level: 1st year LMD

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3. The pH of saline solutions:

We call salt any neutral species which, in solution. They are always trained in neutralization by reaction between acid and base.

Acid : (na, Ca, Va) + base : (nb, Cb, Vb) $\rightarrow$ Salt + H_2O

Examples: NaCl, NH_4NO_3.

3.1. The pH of a solution of strong acid and strong base:

Consider the following neutralization reaction:

HCl + NaOH $\rightarrow$ $NaCl_{(s)}$ + H_2O
(S.A) (S.B) Salt

In aqueous solution, there is total dissolution of the salt: NaCl(s) (Sodium chloride)

$NaCl_{(s)} + H_2O \rightarrow Na^+ + Cl^-$

Cl^-: Conjugate base (very weak) of a strong acid (HCl), Cl^-: does not modify the pH of the solution: Cl^-: is inactive (indifferent or spectator ion), it does not participate in any acid-equilibrium basic.

Na^+: Conjugated acid (very weak) of a strong base (NaOH), Na^+: does not modify the pH of the solution: Na^+: is inactive (indifferent or spectator ion), it does not participate in any acid-base equilibrium.

$$pH(NaCl)= pH(H_2O)= ½ pke =7 \qquad \text{at } t=25\ C°$$

Conclusion: Salts of strong acids and strong bases dissociate in water without changing the pH, the solution remains neutral.

3.2. The pH of a solution of strong acid and weak base:

Consider the following neutralization reaction:

HCl + NH_3 $\rightarrow$ $NH_4Cl_{(s)}$ + H_2O
(S.A) (W.B) Salt

In aqueous solution, there is total dissolution of the salt: NH_4Cl(s) (Ammonium chloride)

$NH_4Cl_{(s)} + H_2O \rightarrow NH_4^+ + Cl^-$

Cl^-: Conjugate base (very weak) of a strong acid (HCl), Cl^-: does not modify the pH of the solution: Cl^-: is inactive (indifferent or spectator ion), it does not participate in any acid-equilibrium basic.

NH_4^+: Conjugated acid (very weak) of a weak base (NH_3), it participates in acid-base equilibrium.

If : $[H_3O^+] >> [OH^-]$ and $[NH_4^+] >> [NH_3]$ $\Rightarrow$ the acid is weakly dissociated.

$pH(NH_4Cl) = pH(NH_4^+) = pH(\text{Conjugate w. acid}) = ½ (pka - \log[NH_4^+])$ at t=25 C°

3.3. The pH of a solution of weak acid and strong base:

Consider the following neutralization reaction:

CH_3COOH + $NaOH$ → $CH_3COONa_{(s)}$ + H_2O
(W.A) (S.B) Salt

In aqueous solution, there is total dissolution of the salt: $CH_3COONa(s)$ (Sodium acetate)

$CH_3COONa_{(s)}$ + H_2O → CH_3COO^- + Na^+

CH_3COO^-: Conjugate base (very weak) of a weak acid (CH_3COOH), it participates in acid-base equilibrium.

Na^+: Conjugated acid (very weak) of a strong base ($NaOH$), Na^+: does not modify the pH of the solution: Na^+: is inactive (indifferent or spectator ion), it does not participate in any acid-base equilibrium.

If : $[OH^-] >> [H_3O^+]$ and $[CH_3COO^-] >> [CH_3COOH]$ ⇒ the base is weakly protonated.

$pH(CH_3COONa) = pH(CH_3COO^-) = pH(\text{Conjugate w. base}) = \frac{1}{2}(pke + pka + \log[CH_3COO^-])$

at t=25 C°

3.4. The pH of a weak acid and weak base solution:

Consider the following neutralization reaction:

CH_3COOH + NH_3 → $CH_3COONH_{4(s)}$ + H_2O
(W.A) (W.B) Salt

In aqueous solution, there is total dissolution of the salt: $CH_3COONH_{4(s)}$ (Ammonium acetate) of concentration = C

$CH_3COONH_{4(s)}$ + H_2O → CH_3COO^- + NH_4^+

CH_3COO^-: Conjugate base (very weak) of a weak acid (CH_3COOH), it participates in acid-base equilibrium.

CH_3COOH + H_2O → CH_3COO^- + H_3O^+ ………… Ka1

NH_4^+: Conjugated acid (very weak) of a weak base (NH_3), it participates in acid-base equilibrium.

NH_4^+ + H_2O → NH_3 + H_3O^+ …………Ka2

However, the mixture between a w. A and a w. B gives a weakly acidic or weakly basic solution ⇒ pH is close to 7.

If : $C >> [H_3O^+]$ and $C >> [OH^-]$ ⇒ by making the product Ka1. Ka2

$pH(CH_3COONH_4) = \frac{1}{2}(pka1 + pka2)$, the pH is independent of the initial concentration C.

3.5. The pH of a buffer solution:

A buffer solution is defined as a mixture of a weak acid AH and their conjugates base A^- in equal or similar proportions.

The expression for the acidity constant Ka of the HA/A^- couple is:

$$K_a = \frac{[A^-].[H_3O^+]}{[AH]} \Rightarrow [H_3O^+] = \frac{K_a.[AH]}{[A^-]}$$

$$pH = pk_a - log\frac{[AH]}{[A^-]} \Leftrightarrow pH = pk_a - log\frac{[Acid]}{[Base]}$$

Noticed:

A buffer solution can be obtained from:

- Weak acid AH + a weak base A.
- Weak acid HA + strong base.
- Weak base A^- (NaA salt) + strong acid.

Buffer solutions have the property of minimizing pH variations caused by:

- An addition of acid or base.
- An addition of solvent (dilution).