Acids and bases

I. Definitions of acids and bases

1. According to Arhenius (1887)

Acid: We call acid any substance capable of releasing H^+ protons .

Notation : An acid is generally noted by **HA**

$$HA \underset{}{\overset{H_2O}{\rightleftarrows}} H^+ + A^-$$

Base: We call base any substance capable of releasing OH^- ions.

Notation : a base is generally noted by **BOH** or **B**

$$BOH \overset{H_2O}{\rightleftarrows} OH^- + B^+$$

Example :

1) CH_3COOH and HCl are acids

$CH_3COOH \overset{H_2O}{\rightleftarrows} H^+ + CH_3COO^-$ (CH3COOH is a weak acid)

$HCl \xrightarrow{H_2O} H^+ + Cl^-$ (HCl is a strong acid)

2) NaOH is a base

$NaOH \xrightarrow{H2O} OH^- + Na^+$ (NaOH is a strong acid)

2. According to Bronsted-Lowerry (1923)

Acid: We call acid any substance capable of releasing H^+ protons .

Base: We call base any substance capable of capturing H^+ protons.

Example :

$CH3COO^-$ is a base

$$CH_3COO^- + H^+ \rightleftarrows CH_3COOH$$

Concept of conjugated acid and base

Let HA be a weak acid

We have:

$$HA \xrightleftharpoons{H_2O} H^+ + A^-$$

HA → Acid ; A^- → conjugate base

To every HA acid corresponds a conjugate base A^-

Example :

The conjugate base of CH3COOH is $CH3COO^-$ and we write:

acid/conjugate base = $CH3COOH/CH3COO^-$

Remark

H^+ cannot exist in the free state , therefore an HA acid can only release an H^+ proton if it is in the presence of a base B which can capture it.

$$HA + B \rightleftharpoons A^- + BH^+$$

HA → Acid1 ; B → base2 ; A^- → conj base1 ; BH^+ → conj acid2

To every pair [acid/ conj base]$_1$ corresponds a pair [acid/base conj]$_2$

Example :

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

CH_3COOH → a1 ; H_2O → b2 ; CH_3COO^- → b1 ; H_3O^+ → a2

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

NH_3 → b1 ; H_2O → a2 ; NH_4^+ → a1 ; OH^- → b2

Concept of ampholyte compound

The H_2O molecule behaved in example 1 as a base and in example 2 as an acid for this reason H_2O is called an ampholyte compound.

Definition of ampholyte compound

Ampholyte is a compound that can behave as acid and as a base.

3. According to Lewis

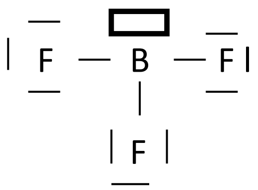
Lewis gave a generalized definition of acid and base, it was extended even to non-hydrogenated compounds.

Acid: We call acid any substance which accepts electronic doublets.

Base: We call base any substance donor of electronic doublets.

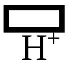
Example :

1) BF3 is an acid

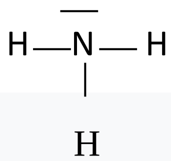


Boron has a vacant cell in which an electronic doublet can be located.

2) H^+ is an acid

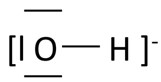


3) NH_3 is a base



Nitrogen has a free doublet

4)The compound ion OH^- is a base



O has 3 free doublets

II. Equilibrium constant:

Let be the equilibrium : $aA + bB \underset{v2}{\overset{v1}{\rightleftarrows}} cC + Dd$

$V_1 = -k_1 [A]^a [B]^b$ (Expression's speed of the direct reaction)

$V_2 = -k2 [C]^c [D]^d$ (Expression's speed of the indirect reaction)

at equilibrium: $V_1 = V_2 \longrightarrow -k_1 [A]^a [B]^b = -K_2 [C]^c [D]^d$

from where : $\frac{k1}{k2} = \frac{[C]^c\ [D]^d}{[A]^a [B]^b}$ = $k_c(T)$ ($k_c(T)$ = equilibrium constant)

Example : The equilibrium constant corresponding to the reaction :

$2NO + Cl_2 \rightleftarrows 2NOCl$ is : $K_c(T) = \frac{[NO\ Cl]2}{[NO]2\ [Cl2]}$

1. Water dissociation equilibrium

Water molecules can act on themselves (self-dissociation of water)

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

And the expression of the equilibrium constant corresponding to this reaction is given by : Kc (T) $= \frac{[H3O+][OH-]}{[H2O]2}$

At T= 25°c Kc(25°)= $3{,}24.10^{-18}$ so the water is very weakly dissociated.

$[H_2O]$ = constant and $[H_2O] = \frac{1000}{18}/1 = 55.5$ mol/l , so we can write :

$[H_3O^+][OH^-] = Kc(T) \, . [H_2O]^2 = 10^{-14} = kw$

(Kw is called the ionic product of water)

2. Acid dissociation equilibrium

Ionic dissociation can be total or partial and depending on the case, the electrolytes (compounds which dissociate in the presence of water) are said to be strong or weak.

Example :

1) HCl in water is a strong electrolyte

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

2) CH3COOH in water is a weak electrolyte

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

a) equilibrium constant of an acid (acidity constant)

Let be HA a weak acid,so:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$Kc\ (T) = \frac{[H3O+]\ [A-]}{[H2O][HA]}$$

Water, in excess, has a concentration which practically does not vary, so $[H_2O]$ is constant.

Therfore $[H_2O].Kc(T)$ = constant = $\frac{[H3O^+]\ [A^-]}{[HA]}$ = ka

ka is called acidity constant, it is characteristic of acid

Example :

Write the expression of the acidity constant of CH_3COOH in water.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Answer : ka = $\frac{[H_3O^+]\ [CH_3COO^-]}{[CH3COOH]}$

b) Ionic dissociation coefficient or degree of ionization (α)

In addition to the equilibrium constant Ka, the dissociation of an acid can be characterized by a coefficient noted α defined as follows:

α = (number of moles dissociated)/(number of initial moles)

if α represents the degree of ionization of an HA acid of concentration C, we can represent the evolution of the dissociation reaction of the acid from t=0 until equilibrium as follows:

	$HA + H_2O$	$\rightleftharpoons$	H_3O^+	$+A^-$
at t=0	C		0	0
at t=eq	C — Cα		Cα	Cα

C: initial number of moles

Cα: number of moles dissociated at equilibrium

C-Cα: number of undissociated moles at equilibrium

$$Ka = \frac{[H3O+]\ [A-]}{[HA]} = \frac{C\alpha.C\alpha}{C-C\alpha} = \frac{C\alpha^2}{1-\alpha}$$

Remarks:

α: ionized fraction

if α = 1 the acid is totally dissociated

if α = 0 the acid is not dissociated

if 0 <α <1 the acid is partially dissociated

c) Oswald's law of dilution

As seen previously : $Ka = \frac{C\alpha^2}{1-\alpha} \longrightarrow ka/c = \alpha^2/1-\alpha$

When C↘ the ratio ka/c↗ so α↗

Dissociation is said to increase with dilution: **Oswald's Dilution Law**

3. Base dissociation equilibrium

Let be B a weak base

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

With the same manner done with the acids, we obtain:

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

Kb is called basicity constant, it characterizes the base

Example:

Write the expression of the constant of basicity of NH_3.

Answer: We have $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

so $Kb = \frac{[NH4^+]\ [OH^-]}{[NH_3]}$

Remarks

1. Ka and Kb depend on the temperature and the nature of the solvent.

2. Ka and Kb are always characteristic constants of acids and bases at a given temperature and with a known solvent.

3. Polyacids and polybases are characterized by the equilibrium constants Ka1, Ka2… of the first and second ...dissociations of the acid and the same for the base Kb1, Kb2…

Example:

Let the diacid H_2CO_3 (weak acid), so we have :

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad Ka_1 = 3.4.10^{-7}$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{-2} \qquad Ka_2 = 5.6.10^{-11}$$

$$H_2CO_3 + 2H_2O \rightleftharpoons 2H_3O^+ + CO_3^{-2} \qquad Ka=?$$

Calculate the equilibrium constant caracterizing of the pair H_2CO_3/ CO_3^{-2}.

Answer:

$$Ka = \frac{[CO_3^{-2}][H3O^+]^2}{[H2CO3]} = \underbrace{\frac{[HCO_3^-][H_3O^+]}{H_2CO_3}}_{Ka1} . \underbrace{\frac{[CO_3^{-2}][H_3O^+]}{[HCO_3^-]}}_{Ka2} = ka_1. Ka_2$$

SO ka = ka1.ka2 = 2.4.10-17

Remark

The constants Ka and Kb characterize the strength of the electrolyte, but on a practical level it is preferable to use more convenient quantities which are denoted pka and pkb such as: **pka = -log ka** and **pkb= - log kb**

4. relationship between ka, kb, pka and pkb

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad Ka= \frac{[H3O^+][A-]}{[HA]}$$

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad Kb= \frac{[H3O^+][A-]}{[HA]}$$

We have: $Ka.Kb = [H3O^+].[OH^-] = kw$

Where b corresponds to the conjugated base of the acid a.

At T= 25°c $\longrightarrow$ $Ka.Kb=Kw= 10^{-14}$ $\longrightarrow$ $- \log (Ka.Kb) = -\log 10^{-14}$

Which corresponds to : pKa + pKb =14

The product ka.kb =constant then ka ↗ ⟶ kb ↘

The conjugate of a strong acid is a weak base and vice versa

III. concept of pH

The concept of pH was introduced with the aim of quantitatively measuring the acidity of a solution.

The pH of a solution is defined as follows: **pH = -log [H3O$^+$]**

In the same way we can define the pOH: **pOH= -log [OH$^-$]**

Remarks :

1. At T= 25°c $[H_3O^+][OH^-] = 10^{-14}$ then $-\log [H_3O^+][OH^-] = 10^{-14}$

So : **pH + pOH=14**

2. The pH of a solution can be measured using the pH meter

3. A neutral medium (pure water) corresponds to:

[H3O+] = [OH-] = 10-7 ⟶ pH =7

An acidic medium corresponds to

[H3O+] > [OH-] ⟶ pH<7

A basic medium corresponds to

[H3O+] < [OH-] ⟶ Ph>7

1.pH of acids and bases

a. pH of a strong acid

$$HA + H_2O \longrightarrow H_3O^+ + A^-$$

At t = 0	Ca	0	0
At t_f	0	Ca	Ca

$$\mathbf{pH = -\log[H_3O^+] = -\log Ca}$$

b. pH of a weak acid

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

We have : $ka = \frac{[H3O^+][A^-]}{[HA]}$ ………. (1)

And : $[H_3O^+] = [A^-]$ ………(2)

$Ca = [HA] + [A^-] \approx [HA]$ ……. (3) because $[A^-] << [HA]$

(2) et (3) reported in (1) gives : $ka = \frac{[H3O^+]^2}{Ca}$

So : $[H_3O^+] = (ka\ .Ca)^{1/2}$

Then : **pH= ½(pKa-logCa)**

c. pH of a strong base

$$BOH \xrightarrow{H_2O} B^+ + OH^-$$

At t = 0	Cb	0	0
At t_f	0	Cb	Cb

We know that : **pOH = -log [OH$^-$] = -log Cb**

At T = 25°c pH+ POH =14 $\longrightarrow$ pH = 14 – POH

So : **pH= 14+Log Cb**

d. pH of a weak base

$$BOH \underset{}{\overset{H_2O}{\rightleftharpoons}} B^+ + OH^-$$

For a weak base POH = $\frac{1}{2}$ (pKb – bg Cb)

And at T = 25°c pH+ pOH = 14 $\longrightarrow$ pH = 14-POH

So : **pH= 14-½(pKb-logCb)**

Note:

as at T= 25°c PKa +PKb =14 PKb =14 –Pka

So : **pH= ½(14+pKa+logCb)**

Note:

The **strengths** of an acid and a base **depend on the concentration** of the medium (Oswald's dilution law) and consequently:

If **$Ka/Ca < 10^{-2}$** the weak acid is diluted to the point where it is not strong and the expression of its pH is that indicated in b.

If **$Ka/Ca > 10^{-2}$** the weak acid is diluted to the point where it is strong and the expression of its pH is that indicated in a.

The same reasoning can be done with the case of bases but this time with the ratio **kb/Cb** compared with **10^{-2}**.

IV.acid-base reaction

1. Salification reaction

The reaction of an acid with a base produces salt and water.

$$HA(acid) + BOH(base) \longrightarrow AB(salt) + H_2O(water)$$

Several cases can be considered, depending on the strength of the acid and the base strength.

a.pH of a salt from strong acid and strong base

$$HA + H_2O \longrightarrow H_3O^+ + A^-$$
$$BOH + H_2O \longrightarrow B^+ + OH^- + H_2O$$
$$HA + BOH \longrightarrow (B^+, A^-) + H_2O$$

The B^+ and A^- ions play no role and therefore the pH of the medium is that of pure water, i.e. pH = 7.

Example:

the pH of a NaCl solution is pH= 7 because the NaCl (salt) comes from the reaction between a strong acid HCl and a strong base NaOH.

b. pH of a salt from a strong acid and a weak base

Example :

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$HCl + NH_3 \rightleftharpoons NH_4^+ + CL^- \text{ (sel = } NH_4Cl)$$

The Cl^- ions play no role (neutral), on the other hand the $NH4^+$ ions react with OH^- coming from the dissociation of H_2O therefore $[OH^-]\searrow$ and the medium is acidic,so the expression of ph is: **pH=1/2 (pka- log CS)**

c. pH of a solution from a weak acid and a strong base

Exemple :

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

$$NaOH + H_2O \longrightarrow Na^+ + OH^- + H_2O$$

$$CH_3COOH + NaOH \rightleftharpoons \underbrace{CH_3COO^- + Na^+}_{\text{salt = } CH_3COONa} + H_2O$$

The Na^+ ions are neutral but $CH3COO^-$ react with $H3O^+$ coming from the dissociation of H_2O therefore $[H3O^+]\searrow$ and the medium is basic, so the expression of ph is: **pH =14 - -$\frac{1}{2}$ (pKb – logCs)**

2. Tompan solution

a. Definition:

Tompan solution is a solution which has the property of maintaining a constant pH .

b. Properties of tompan solutions

A tompan solution is characterized by its pH.

A tompan solution is obtained by mixing a moderately weak acid or base with its conjugate species.

It can be demonstrated that the pH of a tompan solution is given by the expressio: **pH= pka + log ([base])/([acid])**.

To buffer a medium at the desired pH, the volumes or concentrations of acid or base are varied.

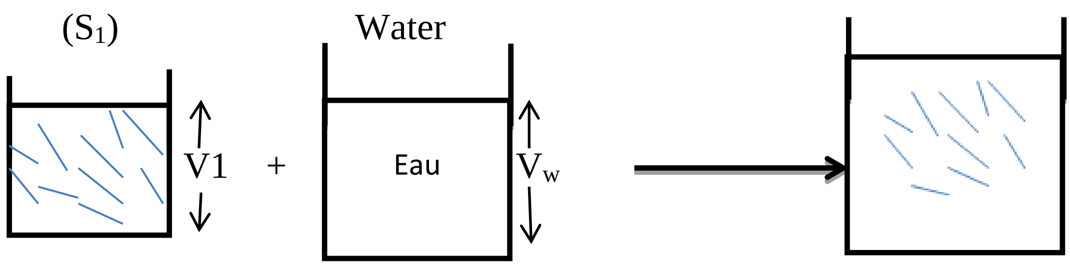
V. dilution and acid-base dosage

1) Dilution

We Consider a solution (S_1) (acid or base) of volume V_1 and concentration C_1.

To dilute (S_1) is to add a volume of water to Calf in order to obtain a solution (S_2) of volume $V_2=V_1+V_w$ and of concentration C_2 such that $C_2<C_1$.

Initial state 1 final state2



(V_1, C_1) ($V_2=V_1+V_w$, C_2)

We have:

quantity of initial solute material = quantity of final solute material

That is to say: n1 = n2 ⟶ $C_1V_1= C_2V_2$ ⟶ $C_1V_1 = C_2(V_1+V_w)$

(which is called dilution law) From where : $\mathbf{Vw = \frac{C_1V_1}{C_2} - V_1}$

Application

Calculate the volume of water necessary to add to a volume V_1 =20ml of a CH_3COOH solution of concentration C_1= 0.5M so that its concentration is 0.25M.

2) the acid-base dosage

The acid-base dosage is the reaction during which an acid reacts with a base to the point where: **number of moles of H^+** = **number of moles of OH^-** in order to determine an unknown concentration of the acid or the base.

At this point:

number of equivalents.g of acid = **number of equivalents.g of base.**

that is to say: **NA.VA = NB.VB**

NA: normality of the acid (eq.g/l)

VA: volume of the acid

NB: normality of the base (eq.g/l)

VB: base volume

Definition of Normality:

It is the number of gram equivalent of solute per liter of solution, it is denoted N and is expressed in gram equivalent per liter (eq.g/l).

Definition of Molarity:

It is the number of moles of solute per liter of solution, it is denoted C or M and is expressed in moles per liter (mole/l).

Relationship between N and C

N= Z.C (Z: acidity or basicity number, N: normality, C: molarity)

Example :

Normal and molar concentrations N and C for the compounds:

HCl, H_2SO_4, H_3PO_4 are linked together by the relationships:

<u>HCl</u> **N=C** ; <u>H_2SO_4</u> **N=2C** ; <u>H_3PO_4</u> **N=3C**