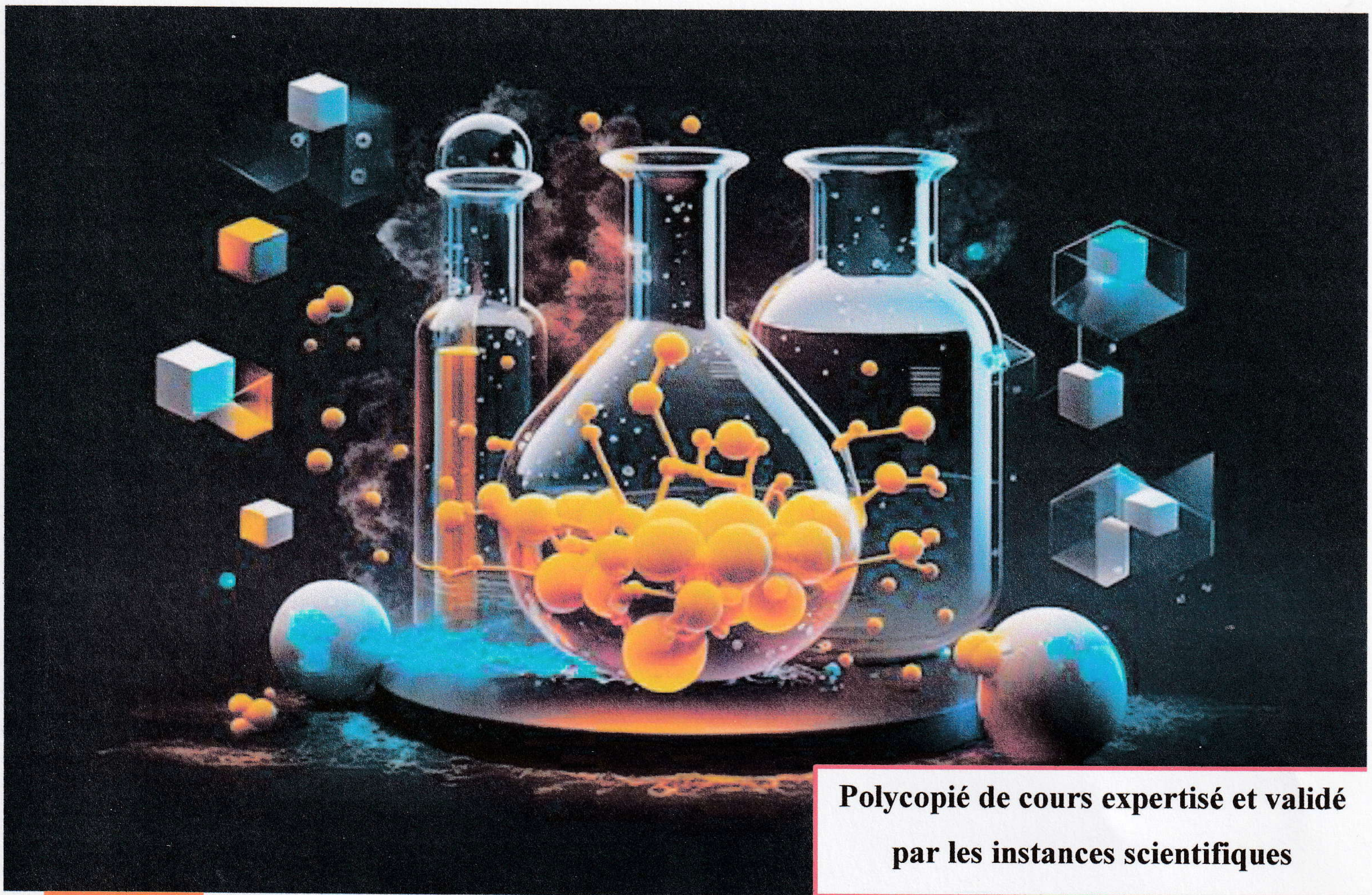

Polycopié de cours expertisé et validé par les instances scientifiques

ANALYTICAL CHEMISTRY

Course and exercises

Second year undergraduate chemistry

المجلس العلمي

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Foreword

This manuscript presents a course in analytical chemistry, illustrated by solved exercises. It is aimed in particular at second year undergraduate students of fundamental chemistry who wish to broaden their knowledge of analytical chemistry. It would also be useful for analytical and mineral teachers and researchers in fundamental sciences.

The course is devoted to the basic concepts of analytical chemistry and is divided into six chapters, each of which contains a series of classical exercises involving reflection and others involving simple calculations based on bibliographical data.

This analytical chemistry course manuscript provides a comprehensive and easily understandable presentation of all the key concepts. It has been specifically designed to align with the new Licence-Master-Doctorate (LMD) degree programme. It covers a wide range of topics, including the fundamental principles of solution chemistry. It delves into important areas such as expressing the concentration of a solution, theories related to acids, bases, and salts, ionisation, pH, solubility product, hydrolysis, complexometry, oxidation-reduction, and precipitation. These concepts are particularly crucial for students pursuing Master's and Doctoral degrees, as well as those engaged in scientific research.

We hope that this manuscript will provide students with a more concise teaching than standard textbooks, and that they will get the most out of the course and the exercises available to them.

Mrs Lynda MITICHE-KLALECHE

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Chapter 1 Fundamental Concepts

1.1. What is a mixture ?

A mixture arises from the combination of two or more distinct substances within a single container. The components do not necessarily blend in fixed proportions to constitute a mixture. Examples include blends of salt and sugar, combinations of sand and water, and amalgams of oil and vinegar. Mixtures generally fall into two main categories: heterogeneous mixtures and homogeneous mixtures.

1.1.1. Heterogeneous mixture

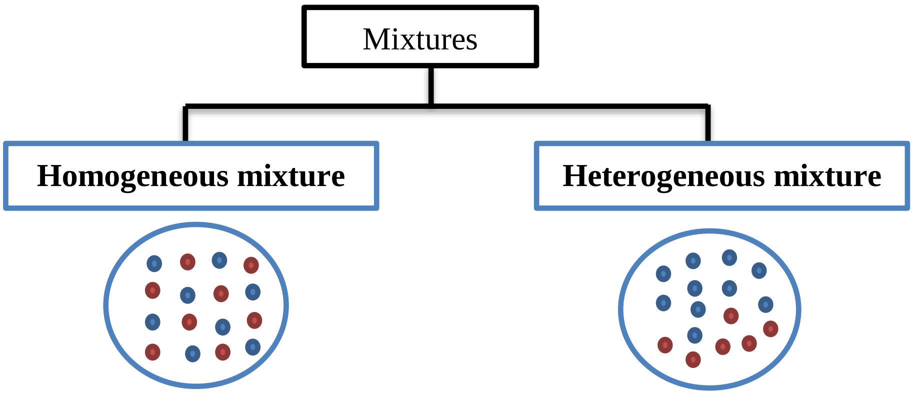
A mixture is classified as heterogeneous when two or more of its components remain discernible to the naked eye even after thorough agitation. Such mixtures are characterized by their non-uniform composition, comprising multiple phases. Examples of heterogeneous mixtures include:

- two liquids like water and oil or water and petroleum.
- a liquid and a solid like water and sand or water and flour.
- a liquid and a gas, as in a lemonade exposed to open air.

1.1.2. Homogeneous mixture

A homogeneous mixture is the opposite of a heterogeneous mixture: it is a mixture where the different components cannot be distinguished by the naked eye after agitation. It consists of a single phase.

- ➢ Water can form homogeneous mixtures with other liquids, like alcohol or ink.



1.2. Definition of a solution

The dissolution of a chemical species in a large volume of liquid results in a mixture known as a solution.

Solution = solute + solvent

A solution is a mixture of two or more components. The major component is called the solvent, while the minor component is called the solute.

- The solute can be solid, liquid, or gaseous, but it is always present in small quantities compared to the solvent.
- A solution can contain either molecules, ions, or both.
- The solvent is a liquid; if the solvent is water, it has referred to as an aqueous solution.

1.3. Solutions concentrations

The concentration of a solution refers to the amount of solute dissolved in a specified amount of solvent.

- A concentrated solution contains a large proportion of solute.
- A diluted solution contains a small amount of solute.

There are several ways to express the concentration of solutions, the most important of which are:

1.3.1. Molar Concentration or Molarity (M)

The molarity (M) or molar concentration of a solution is used to represent the amount of moles of the solute per litre of the solution

$$\boxed{\mathbf{M} = \frac{\mathbf{n}}{\mathbf{V}}}$$

M: molar concentration (mol/l)

n: amount of substance (moles)

V: volume of the solution (litres)

Example 1:

A 2 Litres of a solution is composed of 0.5 g KCl dissolved in water. Find its molarity. M_{KCl} = 74.5 mol/L.

Answer: $n = \frac{m}{M} = \frac{0.5}{74.5} = 0.0067\ mol\ KCl$

Molarity is: $\text{M} = \frac{moles\ of\ the\ solute}{litres\ of\ the\ solution} = \frac{0.0067}{2} = 0.0335$ M.

Example 2:

What is the molarity of a solution containing 150 g of NaCl in 3 litres of the solution? $M_{(NaCl)}$ = 58.5 g/mol.

Answer: $\text{M} = \frac{\text{Mass}}{\text{molar mass x volume}} = 0.85\ \text{M}$

$$\text{M} = \frac{150}{58.5 \text{ x } 3} = 0.85\ \text{M}$$

1.3.2. Mass Concentration (T)

The mass concentration of a solution is the mass of the solute contained in one litre of that solution. It is denoted by T and expressed in g/L.

$$\boxed{\mathbf{T} = \frac{\mathbf{m}}{\mathbf{V}}}$$

m: mass of the solute (g)

V: volume of the solution (L)

There exists a relationship between the mass concentration T and the molarity M:

$$\boxed{\mathbf{M} = \frac{\mathbf{T}}{\mathbf{Molar\ mass}}}$$

1.3.3. Mole fraction (x)

The mole fraction, denoted by x, is the number of moles of specific component in solution divided by the total number of moles in the given solution.

Mole fraction is unitless and dimensionless expression.

$$\boxed{x_i = \frac{ni\ (mol)}{\sum_i ni(mol)}}$$

If we have a solution composed of two compounds A and B

$$x_A = \frac{moles\ of\ A}{moles\ of\ A + moles\ of\ B}$$

$$x_B = \frac{moles\ of\ B}{moles\ of\ A + moles\ of\ B}$$

$$x_A + x_B = 1$$

Also, keep in mind that the sum of each of the solution's substances mole fractions equals 1.

Example:

Calculate the molar fractions in a solution consisting of 26 g of NaCl in 150 g of water. $M_{(NaCl)} = 58.5$ g/mol.

$$x_{NaCl} = \frac{nNaCl}{nNaCl + nH2O}$$

$$n_{NaCl} = \frac{\text{M NaCl}}{molar\ mass\ of\ NaCl} = \frac{26}{58.5} = 0.44\ moles$$

$$x_{NaCl} = \frac{nNaCl}{nNaCl + n\ H2O} = \frac{\frac{26}{58.5}}{\frac{26}{58.5} + \frac{150}{18}} = \frac{0.44}{0.44 + 8.33} = 0.05$$

$$x_{H2O} = 1 - 0.05 = 0.95$$

1.3.4. Mass Fraction(w_i)

Let m_i be the mass of a constituent i of the solution. The mass fraction *wi* of this constituent is expressed as the ratio of its mass to the total mass m of the solution:

$$\boxed{w_i = \frac{masse\ i\ (g)}{solution\ mass(g)} = \frac{mi}{\sum_i mi}}$$

Where $\sum_i wi = 1$

m_i and m are expressed in the same unit of mass. w_i is dimensionless.

In practice, the mass percentage is commonly used: P (%) = $wi \times 100$.

Example:

A concentrated commercial solution of hydrochloric acid at 78% contains 78 g of HCl in 100 g of solution, which means 78 g of HCl for 28 g of water.

1.3.5. Percentage Concentration (%)

a) Weight percent (wt-wt)

It is the number of grams of the solute per 100 g of the solution.

$$\boxed{\text{Weight percent (wt-wt)} = \frac{\text{wt.of solute}}{\text{wt.of solution}} \times 100}$$

Example:

HCl at 98%: This means that 100g of solution contains 98 g of HCl.

b) Volume percent (V/V)

It is the volume of the solute contained in 100 mL of solution.

$$\boxed{\text{Volume percent (V/V)} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100}$$

Example:

Alcohol at 10 %: We have 10 mL of alcohol per 100 mL of the solution.

1.3.6. Molal Concentration or Molality (m)

Molal concentration or molality is the number of moles of the solute contained in one kilogram (1000g) of the solvent. It is expressed as mol/Kg_{solv}.

$$\boxed{\mathbf{m} = \frac{\textbf{\textit{number of moles of solute}}}{\textbf{number of Kg of solvent}}}$$

Molality is the preferred unit for certain types of calculations, although it is used less in laboratory work.

Note:

In the case of sufficiently diluted aqueous solutions, molarity and molality are numerically equal (M = m). Indeed, under these conditions, the mass of one litre of solution is practically equal to the mass of one litre of water (1kg).

1.3.7. Equivalent concentration or Normality (N)

Equivalent concentration is defined by the number of gram-equivalents contained in one litre of solution. It is expressed in Eq /L.

The gram-equivalent of a compound is the quantity of a substance that, in a chemical reaction, involves one gram-equivalent of an electron (redox reaction) or one gram-equivalent of a proton (acid-base reaction).

$$\boxed{\textbf{\textit{Normality}} = \frac{n_e}{V}}$$

Where:

n_e: number of gram-equivalents

V: volume (L)

There exists a relationship between normality and molarity:

Z = the number of equivalents

For some chemicals, when Z = 1**,** N and M are the same.

$$\boxed{\textbf{\textit{Normality}} = \mathbf{Z} \times \mathbf{M}}$$

Example:

Calculate the normality of a solution containing 7 g of H_2SO_4 in 3 litres of the solution. $M_{(H2SO4)} = 98$ g/mol.

$$\text{Number of gram-equivalents} = \frac{98}{2} = 49g$$

$$N = \frac{\frac{7}{49}}{3} = 0.047\ N$$

It is important to note that the gram-equivalent is a concept applied to acid-base and redox reactions.

- **In the case of acids:** Z corresponds to the number of H^+

Example:

HCl (Z = 1); H_2SO_4 (Z = 2) ; H_3PO_4 (Z = 3)

HCl Z = 1 → E (HCl) = 36.5/1 = 36.5 g
H_2SO_4 Z = 2 → E (H_2SO_4) = 98 / 2 = 49 g
H_3PO_4 Z = 3 → E (H_3PO_4) = 98 / 3 = 32.66 g

- **With a base:** Z corresponds to the number of OH^-

Example:

NaOH (Z=1); Ca $(OH)_2$ (Z = 2)

NaOH Z = 1 → E (NaOH) = 40 g

$Mg(OH)_2$ Z = 2 → E ($Mg(OH)_2$ = 58.3/2 = 29.15 g

- **With a redox reaction:** Z corresponds to the number of electrons involved. Z is the number of electrons donated or accepted.

Example:

$KMnO_4 = K^+ + MnO_4^-$

$$\mathbf{MnO_4^- + 5e^- + 8\,H^+ \rightleftarrows Mn^{2+} + 4\,H_2O}$$

For MnO_4^- : Z = 5 → E ($KMnO_4$) = 158/5 = 31.6 g

1.3.8. Relative density (Specific gravity)

The relative density (R.D) of a substance is the ratio of the mass of a certain volume of that substance to the mass of the same volume of water.

R.D is dimensionless.

Relative density = $\rho_{solution}/\ \rho_{water}$

$\rho_{water} = 1\ g/cm^3$

The density of a substance corresponds to the ratio of its mass (m) to its volume (V). It is denoted by ρ and can be calculated using the following relation: m/V.
ρ is expressed in g/cm^3.

1 Litre of solution weighs m = (1000 x R.D) (g)

Example:

We have a solution of sulfuric acid with 96% of purity and a relative density of 1.83 (M_{H2SO4} = 98 g/mole). What are the volumes of water and acid to mix if we want to get 1Litre of the H_2SO_4 at 1.79 mol/L?

For the first example, with sulfuric acid:
Given that 1 litre of H_2SO_4 weighs 1830 g, the initial molarity of H_2SO_4 for 100 % of purity would be:
C = n/V = (1830/98)/1 = 18.67 mol/L
Considering the 96% of purity, the concentration becomes:
C =17.63 mol/L= 35.86 N
Since H_2SO_4 is a diacid, a solution containing 1 mole per litre releases 2 moles of H_3O^+ ions per litre. Therefore, to achieve a concentration of C/10 = 1.79 mol/L, we need to take 100 mL of H_2SO_4 and 900 mL of water.

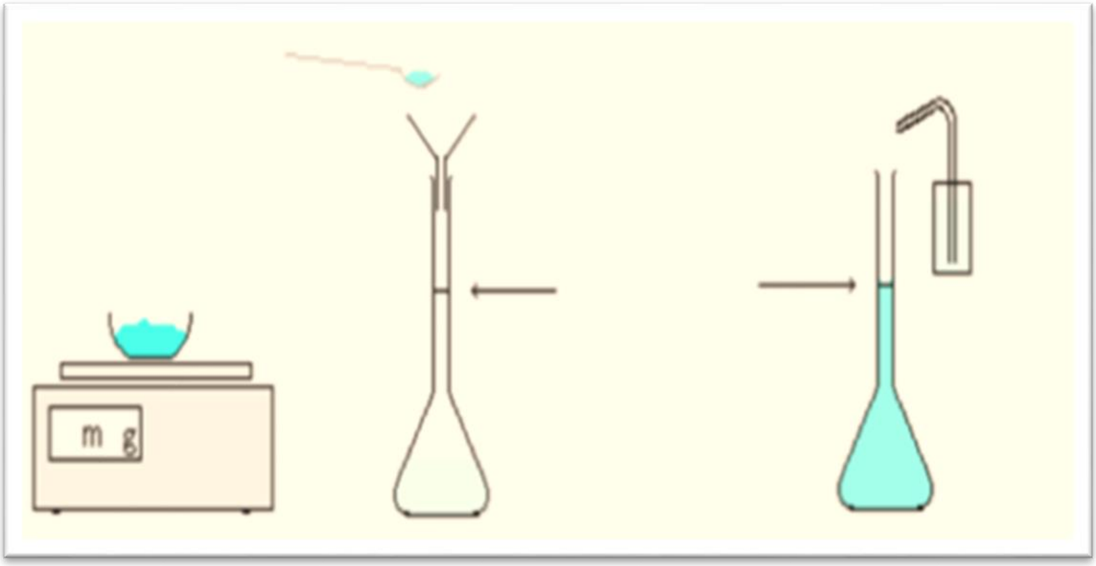
1.4. Preparation of Solutions

Solutions can be prepared using different methods depending on the nature of the solute (solid or liquid).

1.4.1. Dissolution Method

First, calculate the mass of the salt and the volume of water required. Weigh this quantity on a balance, and then quantitatively transfer the salt into a volumetric flask. Next, add distilled water to fill the flask halfway. To dissolve the salt in the water, shake the contents of the flask. Then, add water until it reaches the mark on the flask. To obtain a solution prepared by weighing, the substance must possess certain characteristics:

- be of defined chemical composition: NaCl, $CuSO_4$…
- be chemically pure.
- be stable in the solid or dissolved state.



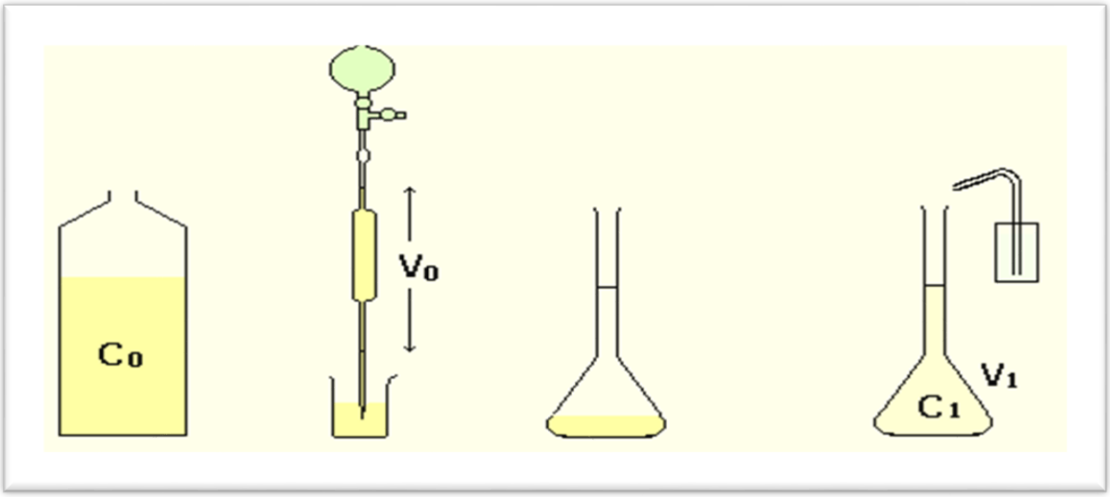
1.4.2. Dilution Method

Diluting a solution involves increasing the volume of the solvent in the solution without changing the amount of the solute. The solution to be diluted is called the stock solution. Its volume is denoted by V_0, and its concentration is denoted by C_0. The solution obtained from the stock solution is called dilute solution. Its volume is denoted by V_1, and its concentration is denoted by C_1.

Since the amount of solute remains constant, we can write

$$n = C_0 \times V_0 = C_1 \times V_1$$

This relation allows us to easily obtain a daughter solution of the desired concentration.



Example:

Preparation of a dilute solution of desired concentration:

We have a stock solution of hydrochloric acid with a concentration of 1.0 mol/L. We want to obtain a dilute solution with a volume of 100 mL and a concentration of 0.10 mol/L.

First, we calculate the volume of the stock solution to be taken: According to the dilution law: $C_0 \times V_0 = C_1 \times V_1$ we find $V_0 = 10$ mL.

- We extract this volume of stock solution using a volumetric or graduated pipette of 10 mL.
- We transfer this volume into a volumetric flask with a capacity of 100 mL.
- We fill the volumetric flask with distilled water up to the mark.

1.4.3. Using a commercial solution

Preparation of 100 mL of a 1N solution of HCl (R.D = 1.2 and 38%)

$HCl \longrightarrow H^+ + Cl^-$ **Normality = Molarity**

1000 mL ⟶ 36.46 g

100 mL ⟶ m **m = 3.646 g**

3.646 g of solution HCl ⟶ 38 g
100 g HCl ⟶ m

$$m = \frac{100 \text{ x } 3.646}{38} = 9.59 \text{ g}$$

Whereas HCl is a liquid, its volume can be measured as the mass m = 9.11g

$$d = \frac{\rho_{solution}}{\rho_{water}} = \rho_{solution} = \frac{m}{V} \Rightarrow V = \frac{m}{\rho_{solution}}$$

$$V = \frac{9.59}{1.2} = 8.0 \text{ mL}$$

1.5. Exercises

Exercise 1:

1. Calculate the molarity of a phosphoric acid (H_3PO_4) solution that contains 6 moles of solute in 3000 cm^3 of solution.

2. Calculate the quantity of sodium sulfate (Na_2SO_4) needed to obtain 250 mL of a sodium sulfate solution with a molarity of 0.5 M.

3. Calculate the volume of a 6 M aqueous solution of sulfuric acid (H_2SO_4) that needs to be taken to obtain 500 mL of a 0.3 M aqueous solution of sulfuric acid.

4. Calculate the weight percent of Na_2SO_4 solution which prepared by dissolving 32 g in 150 g of solution.

Molar mass (M) (g/mol): H (1); O (16); Na (23); S (32)

Answer:

1. The molarity is the molar concentration (mol/L): the amount of substance (mol)/ volume of solution (L).

C = 6 / 3 = 2 mol/L.

2. Amount of the substance Na_2SO_4 : n = 0.5 x 0.25 = 0.125 mol.

Molar mass of Na_2SO_4: M = 2 x 23+32+4 x 16 = 142 g/mol.

Mass of Na_2SO_4 : m = n M = 0.125 x 142 = 17.8 g.

3. The final solution contains 0.5 x 0.3 = 0.15 mol of sulfuric acid.

So, it is necessary to take V= 0.15/6 = 0.025 L = 25 mL of 6 M sulfuric acid solution.

4. The Weight percent = (32 x 100)/150 = 21.3 %.

Exercise 2:

1. Calculate the molarity of a calcium hydroxide ($Ca(OH)_2$) solution with a mass percentage of 24% and a density equal to d = 1.155.

2. Calculate the normality of a phosphoric acid solution that contains:

   a) 98 g of solute per 500 mL of solution

   b) 0.2 gram-equivalents of solute per 50 mL of solution

M (g/mol): Ca (40); O (16); P (31)

Answer:

1. One litre of the solution has a mass of 1.155 kg = 1155 g.

This solution contains 1155 x 0.24 = 277.2 g of calcium hydroxide.

Molar mass of Ca $(OH)_2$: M = 40+2 x (1+16) = 74 g/mol

Quantity of substance of solute: m(g) / molar mass (g/mol) = 277.2/74 = 3.74 mol in 1L.

2. The normality N of an acidic solution is the number of moles of $H^+_{(aq)}$ ions that can be liberated per litre of this solution.

Phosphoric acid (H_3PO_4) is a triacid: normality = 3 times the molarity.

The molar mass of phosphoric acid: M = 98 g/mol.

a) Quantity of substance in 0.5 L of solution: 98/98=1 mol, which means 2 mole in 1 L. Molarity = 2 mol/L; Normality = 3 ×2 = 6 N.

b) The gram-equivalent corresponds to normality. 0.2 gram-equivalent in 0.05 L,

So: 0.2/0.05 = 4 N

Exercise 3:

We have a solution of acetic acid with a density of 1.14 and a purity of 99.8%. What volume does 100 g of this acid occupy? What is its molarity?

$M_{(CH3COOH)}$ = 60 g/mol.

Answer:

1 litre of CH_3COOH with 99.8 % purity weighs 1.14 x 0.998 = 1138 g

So, 100 g of this acid occupies a volume V equal to V = 100 / 1138 = 8.79 x 10^{-2} L. Calculation of the molarity of the acid:

C = (1140/60) x 0.998 = 18.96 mol/L

Exercise 4:

We have a solution at 1.75 mol/L. What volume of this solution and what volume of water should be mixed to get :

a) 0.5 L of a 0.75 mol/L solution
b) 0.75 L of a 0.5 mol/L solution
c) 1 L of a 0.375 mol/L solution

Answer:

During the dilution, the number of moles of H_3O^+ ions is preserved.

$$\mathbf{C_{initial}\,V_{initial} = C_{final}\,V_{final}}$$

$n_{final} = C_{final}\,V_{final} = 0.375$ moles

We therefore deduce Vi

1.75 Vi = 0.375 hence Vi = 0.214 L

The volume of water to be added is therefore in each case equal to:

a) $V_{water} = V_f - V_i$
$= 0.5 - 0.214 = 0.286$ L

b) $V_{water} = V_f - V_i$
$= 0.75 - 0.214 = 0.536$ L

c) $V_{water} = V_f - V_i$
$= 1- 0.214= 0.786$ L

Exercise 5:

The density of an aqueous solution of sulfuric acid contained in a car battery is 1.25, and this solution contains 33.3 % H_2SO_4 by weight.

a) What is the weight of one litre of the solution?
b) What weight of H_2SO_4 is there in one litre of the solution?

c) What is the molarity of the solution?

d) What is the weight of H_2SO_4 per kilogram of water?

e) What is the normality of the solution?

M $_{(H2SO4)}$ = 98 g/mole

Answer:

$$\text{R.D} = \frac{\rho_{\text{acid}}}{\rho_{\text{water}}} = 1.25$$

$$\rho_{\text{acid}} = 1.25 \ g/cm^3$$

$$\rho_{water=1g/cm^3}$$

a) The weight of 1 litre of the solution is:

1000 cm^3 of the acid solution weighs 1250 g.

b) The mass of the acid contained in 1000 cm^3 of the solution is:

$$m = \frac{1250 \text{ g x } 33.3}{100} = 416.25 \text{ g}$$

c) The molarity of the solution:

$$\text{molarity} = \frac{m}{M} = \frac{416.25}{98} = 4.25 \text{ M}$$

d) 33,3 g of acid is contained in 100 g of water.

For 1000 g of water, we have: 33.3 x 10 = 333 g of acid.

e) Normality = number of grams equivalent of the solute contained in 1 litre of the solution.

1 gram equivalent of sulfuric acid weighs 49 g.

$$\text{Number of grams equivalent of acid} = \frac{416{,}25 \text{ g}}{49g} = 8.50 \text{ g eq.}$$

The normality of the solution is 8.50 N.

Exercise 6:

The titrant solution of hydrochloric acid used has a concentration of C = 0.10 mol/L. This solution is prepared using a stock solution (mother solution) of hydrochloric acid with a mass percentage equal to 30 % and a density of d = 1.15.

1. Calculate the molar concentration C of the stock solution.
2. What volume *V* of the commercial solution should be used to prepare 200 mL of this titrant solution? M (g/mol): H (1); Cl (35.5), T = 298 K.

Answer:

1. Density of a liquid = mass of a volume V of the liquid/mass of the same volume of water for 1 L of stock solution, its mass is 1.150 g;

In this solution, the mass of HCl is 30 % × 1.150 g = 345 g.

Now, $M_{HCl} = 1 + 35.5 = 36.5$ *g/*mol.

In 1 L of the stock solution, we thus have 345 / 36.5 = 9.45 moles of HCl,

hence, C = 9.45 mol/L.

2. the stock solution	the dilute solution
$C = 9.45$ mol/L	$C' = 0.10$ mol /L
$V = ?$	$V' = 0.200$ L
$n_{HCl} = C \times V$	$n_{HCl} = C' \times V'$

We have $n_{HCl} = C \times V = C' \times V'$

therefore $V = C' \times V' / C = 2.1$ mL.

Exercise 7:

A concentrated solution of nitric acid (HNO_3) with a density of 1.4536 contains 78 % by weight of nitric acid.

a) What is the mass of the acid contained in one litre of the solution?

b) What is the volume of this concentrated solution containing one mole of acid?

$M_{(HNO3)} = 63$ g/mol

Answer :

a) One litre of the nitric acid solution weighs 1453.6 g.

The mass of the acid in one litre of solution is $m = \frac{1453.6 \text{ x } 78}{100} = 1133.8\ g$

b) Number of moles of acid in one litre of solution: $\frac{m}{M} = \frac{1133.8}{63} = 18$ moles

18 moles of acid are contained in 1000 cm^3 of concentrated solution,

and 1 mole of acid is contained in a volume: $v = \frac{1000}{18} = 55.52$ mL.

Exercise 8:

What is the procedure of preparation of 100 mL of 0.5M NaOH ? ($M_{(NaOH)}$ = 40 g/mol)

Answer:

Molar mass of NaOH = 40 g/mol

The solubility of NaOH in water at 25 °C is 1000 g/L or 1 g/mL.

1. First, we have to calculate the amount of NaOH required for the preparation of the solution.
2. To do that, we calculate the number of moles in 100 mL of 0.5 M NaOH solution

0.1 L x 0.5 M = 0.05 mol.

3. Next, by definition, moles of solute = (mass of solute/molar mass of solute).
4. Therefore, mass of NaOH required for the preparation of solution

= 0.05 x 40 = 2 g

5. Dissolve it in the beaker with 100 mL of distilled water.
6. Top up the flask carefully to the mark with more distilled water.
7. Stopper the flask and mix well.

This is your 100 mL of 0.5 M NaOH solution.

Chapter 2

Equilibrium in solution

2.1. Notion of chemical equilibrium

Reversible reactions are in a state of equilibrium when the direct and reverse reactions occur at the same rate. An equilibrium is characterized by its equilibrium constant K_c^t.

$$\alpha\, \mathbf{A} + \beta\, \mathbf{B} \rightleftharpoons \gamma\, \mathbf{C} + \delta\, \mathbf{D}$$

$$K^t_C = \frac{[C]^\gamma \times [D]^\delta}{[A]^\alpha [B]^\beta}$$

If the concentration of one of the constituents *increases*, the system evolves in the direction of its *disappearance*.

Conversely, if the concentration of one of the constituents *decreases*, the system evolves in the direction of its *formation*.

In other words, a reaction is said to be reversible when, as the reagents combine to give the products, they react with each other to give the reagents. This reversibility is represented by a double arrow:

Example :

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\,HI_{(g)}$$

→ : direct reaction

← : back reaction

Chemical equilibrium is the situation that is reached when, in a chemical reaction, the concentrations of reagents and products arrive at a constant value that does not change over time.

Thus, for reactions that involve, for example, a solution (or a gas) and a solid, the solid phase can be considered as a reservoir of material with respect to the solution (or the gas) where the reaction (s) take place. The concentration in the homogeneous phase of the solid substance is constant and does not intervene in the expression of K_c^t.

Example :

$$CaCO_{3\ solid} \rightleftharpoons CaO_{\ solid} + CO_{2\ gaz} \qquad K_c^t = [CO_2]$$

Another constant K_p^t is thus defined for the equilibria in the gas phase, which connects the partial pressures of the constituents of the equilibrium.

$$\alpha\ \mathbf{A}_{\ gaz} + \beta\ \mathbf{B}_{\ gaz} \rightleftharpoons \gamma\ \mathbf{C}_{\ gaz} + \delta\ \mathbf{D}_{\ gaz}$$

$$K^t_p = \frac{P_C^{\ \gamma} \times P_D^{\ \delta}}{P_A^{\ \alpha} P_B^{\ \beta}}$$

2.2. Homogeneous equilibrium. Heterogeneous equilibrium

All the substances in equilibrium form a medium with a homogeneous or heterogeneous appearance.

Depending on the case, there are two types of equilibrium:

2.2.1. Homogeneous equilibrium

The substances are all in the gaseous state, or all in the fully miscible liquid state, or in the dissolved state in the same solvent.

Examples :

Gazeux : $2\ SO_{2(gaz)} + O_{2\ (gaz)} \rightleftharpoons 2\ SO_{3(gaz)}$

Liquide: $CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5\ (aq)} + H_2O_{(aq)}$

2.2.2. Heterogeneous equilibrium

The medium consists of gases and solids, or solids and liquids, or immiscible liquids..

Examples :

$CaO_{(solid)} + CO_{2(gaz)} \rightleftharpoons CaCO_{3(solid)}$

$H_2O_{(ice)} \rightleftharpoons H_2O_{(liquide)}$

Changes in physical state or structure are heterogeneous equilibria.

2.3. Equilibrium constant

2.3.1. Mass action law or Guldberg and Waage law

Consider the reaction:

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

- When chemical equilibrium is reached: $\mathbf{\Delta r\ G_{(T)} = 0}$ (**Δr G** is the Gibbs free energy)
- Equilibrium is defined by a thermodynamic quantity called ***equilibrium constant K*** given by the ***law of mass action***:

Equilibrium constant at the temperature T

$$\boxed{K_{(T)} = \frac{a^{c}_{eq\,(C)}\ a^{d}_{eq\,(D)}}{a^{a}_{eq\,(A)}\ a^{b}_{eq\,(B)}}}$$

A pure solid : $a_{(X)} = 1$

A pure liquid : $a_{(X)} = 1$

- K depends only on temperature

- K is without units

$a_{eq(X)}$: activity of constituent (x) at quilibrium

(concentrations and pressures) at equilibrium

$$\boxed{\begin{array}{ll} \text{Solution :} & a_{(x)} = \frac{C_i}{C^\circ} \\ \text{Gaz parfait :} & a_{(x)} = \frac{P_i}{P^\circ} \end{array}}$$

C_i : Concentration
C° : Reference concentration = 1 mol/L
P° : Reference pressure = 1 bar.

K is also related to the standard reaction enthalpy $\mathbf{\Delta r\ G^\circ_{(T)}}$ by the relationship:

$$\boxed{\boldsymbol{\Delta_r G^\circ_{(T)} = -\,RT\ Ln\ K}}$$

The current interest of the Guldberg-Waage law is to lead to the expression of equilibrium constants.

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

$$K_C = \frac{[C]^c \text{ x } [D]^d}{[A]^a [B]^b}$$

If K_c is large, the equilibrium promotes product formation (sense →)
Similarly, a small value of K_c, the reverse reaction is favored (sense ←) and the reagents are

Note:

In an equilibrium constant, concentrations are in mol/L and pressures are in atm.

2.3.2. Variation of the equilibrium concentration with T: Van't Hoff equation

The equilibrium constants K (K_c or K_p) vary with temperature.

$\Delta_r G° = \Delta_r H° - T \Delta_r S° = - RT \operatorname{Ln} K$

$\Delta_r G° / RT = \Delta_r H° / RT - T \Delta_r S°/RT = - RT \operatorname{Ln} K / RT$

It is assumed that at temperature T, $\Delta_r H°$ and $\Delta rS°$ are constant. Meaning:

$$\frac{d}{dT}(Ln\ K) = \frac{\Delta_r H^{\circ}}{RT^2}$$

Van’t Hoff's Law

$$\boxed{d(Ln\ K) = \frac{\Delta_r H^{\circ}}{RT^2}\ d\ T}$$

By integration we can determine $K_{(T2)}$ and its relationship with $K_{(T1)}$

$$\int_{K_{T1}}^{K_{T2}} d(Ln\,K) = \frac{\Delta_r H^\circ}{R} \int_{T1}^{T2} \frac{dT}{T^2}$$

$$Ln\,K_{(T2)} - Ln\,K_{(T1)} = Ln\,\frac{K_{(T2)}}{K_{(T1)}} = -\,\frac{\Delta_r\,H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\boxed{K_{(T2)} = K_{(T1)}.\ exp\,\left(-\frac{\Delta_r\,H^\circ}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Two cases: $\Delta_r H^\circ > 0$: K increases with temperature;

$\Delta_r H^\circ < 0$: K decreases with temperature.

2.4. Displacement and equilibrium factors

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

$\Delta_r G^\circ_{(T)}$ = - RT Ln K

$$LnK = -\frac{\Delta_r G^\circ_{(T)}}{RT}$$

If the value of one of the terms $\frac{\Delta_r G^\circ_{(T)}}{RT}$ or K (K_p or K_c) varies, equality is no longer respected, the system is no longer in equilibrium. It therefore evolves to reach a new balance.

The transition from a state of equilibrium to a new state of equilibrium under the influence of a disturbance external to the system is called ***“equilibrium shift”***.

We act on the quantities on which depend ΔG:

- Temperature T
- Total pressure P
- Concentration or partial pressures

These quantities are called ***equilibrium factors.***

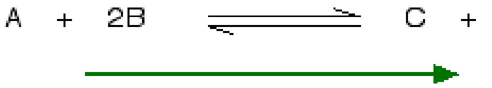
2.5. Displacement of chemical equilibrium

2.5.1. Law of moderation or LE CHATELIER'S principle

When a system at equilibrium is subjected to a disturbance, it moves in the direction that tends to oppose this disturbance to return to its state of equilibrium.

Example:

According to Le Châtelier, the position of equilibrium will move in such a way as to counteract the change. In this case, the equilibrium position will move so that the concentration of A decreases again by reacting it with B to form more C and D. The equilibrium moves to the right (indicated by the green arrow below).



$$A + 2B \rightleftharpoons C + D$$

The position of equilibrium moves to the right if you increase the concentration of A.

In the opposite case in which the concentration of A is decreased, according to Le Châtelier, the position of equilibrium will move so that the concentration of A increases again. More C and D will react to replace the A that has been removed. The position of equilibrium moves to the left.

2.5.2. Influence of the temperature

If, at constant total pressure P_{tot}:

- the temperature T of the system at equilibrium is decreased, then it evolves in the direction of the exothermic reaction (heat release).
- the temperature T of the system at equilibrium is increased, then it evolves in the direction of the endothermic reaction (heat absorption).

The modification of T has no effect on an athermal reaction: $\Delta rH_0 \approx 0$.

Note:

When the temperature increases, the equilibrium moves in the endothermic direction, i.e. in the direction where $\Delta_r H$ is positive.

- $\Delta_r H < 0$ the reaction is exothermic, the equilibrium releases heat by moving from left to right:

- The temperature is increased: $T_2 > T_1$: $T_1 - T_2 < 0$ hence, $\Delta_r G > 0$

by increasing the temperature of an exothermic reaction the reaction regresses,

- The temperature is decreased:, $T_2 < T_1$: $T_1 - T_2 > 0$ hence, $\Delta_r G < 0$

by decreasing the temperature of an exothermic reaction, the reaction progresses.

- $\Delta_r H > 0$, the reaction is endothermic the equilibrium absorbs heat by moving from left to right:

- The temperature is increased:, $T_2 > T_1$: $T_1 - T_2 < 0$, hence, $\Delta_r G < 0$ by increasing the temperature of an endothermic reaction, the reaction progresses,
- We decrease the temperature: $T_2 < T_1$: $T_1 - T_2 > 0$, hence , $\Delta_r G > 0$ by decreasing the temperature of an endothermic reaction, the reaction regresses.

To summarize

A temperature increase at constant pressure shifts the equilibrium in the direction that opposes this increase, the endothermic direction.	**Conversely, a decrease in temperature at constant pressure shifts the equilibrium in the direction that opposes this decrease, the exothermic direction.**

2.5.3. Influence of the pressure

In the case of a system comprising a gas phase, if, at constant temperature *T*:

- The pressure P_{tot} of the system at equilibrium is increased, then it evolves in the direction that decreases the number of moles of gas (Le Chatelier's Law).
- The pressure P_{tot} of the system at equilibrium is decreased, then it evolves in the direction that increases the number of moles of gas.

Note:

When the pressure increases, the system moves in the direction that lowers it, therefore in the direction that decreases the number of moles of gas.

2.5.4. Introduction of a constituent

- Inert constituent, i.e. a constituent that is not involved in the reaction, solid or liquid: no displacement of the equilibrium if T remains constant.
- Inert gas component:
  - no displacement of the equilibrium if T and V remain constant.
  - shift of the equilibrium in the direction that increases the number of moles of gas if T and P remain constant.
- Solid or liquid constituent of the reaction: no shift of the equilibrium if T and V remain constant.
- Gaseous constituent of the reaction: displacement or not, if T and P remain constant, depending on the case.

Note:
The system evolves in the direction that consumes the added reactant.

2.6. Exercises :

Exercise 1:

Let the equilibrium in the gas phase be:

$$N_2O_4 \rightleftharpoons 2\ NO_2$$

At 25°C the constant K_c of this equilibrium is 172.

At this temperature, 2 moles of N_2O_4 and 5 moles of NO_2 are introduced into a 10 litres reactor. Calculate at equilibrium the number of moles of each species.

Answer:

	N_2O_4	$\rightleftharpoons$	**$2\ NO_2$**
Initial mols	2		5
mols at equilibrium	2 - x		5 + 2 x
Concentrations at equilibrium	(2 - x) / 10		(5 + 2 x) / 10

At equilibrium $$K_C = \frac{[NO_2]^2}{[N_2O_4]}$$

$$172 = \frac{(\frac{5+2x}{10})^2}{(\frac{(2-x)}{10}} \Longrightarrow x = 1.95$$

At equilibrium there are :

the number of moles of **NO_2 is (5+2x) = 8.9 mol**

and the number of moles of **N_2O_4. is (2-x) = 0.05 mol**

Exercise 2:

The synthesis of ammonia gas is carried out, industrially, according to the chemical equilibrium of equation:

$$N_{2(g)} + 3H_{2(g)} = 2\ NH_{3(g)}$$

1. Knowing that this reaction is exothermic in nature, at equilibrium temperature, what is the effect of a temperature change on this equilibrium ?
2. What is the effect of a pressure change on this equilibrium (at constant temperature)? justify.
3. What is the effect of an addition of gaseous dinitrogen N_2 on the equilibrium, at constant temperature and volume?

Answer:

1. A decrease in temperature shifts the equilibrium in the direction of the exothermic reaction (NH_3 synthesis).

2. An increase in P_{tot} causes an evolution of the system in the direction of a decrease in the number of moles of gas (law of moderation), that is to say, for the reaction studied, in the direction of formation of NH_3.

3. At constant T and V, the introduction of gaseous dinitrogen: the system then evolves spontaneously in the forward direction, therefore in the direction that consumes N_2.

Exercise 3:

At temperature 817°C, the K_p of the reaction between pure CO_2 and an excess of carbon is equal to 10.

$$CO_{2(gaz)} + C_{(solid)} \rightleftharpoons 2\ CO_{(gaz)}$$

1. Write the equation of K_p in the homogeneous phase.

2. Calculate the partial pressures of CO_2 and CO at equilibrium, knowing that at 817°C the total pressure in the reactor is 4 atm.

3. The reactor volume was 5 litres. Determine the number of moles of CO and CO_2 at equilibrium.

Answer:

$K_p = (P_{CO})^2 / P_{CO2} = 10$

with $P_{CO} + P_{CO2} = 4$

$(P_{CO})^2 + 10.P_{CO} - 40 = 0$

$$\mathbf{P_{CO} = 3.06\ atm} \quad \text{and} \quad \mathbf{P_{CO2} = 0.94\ atm}$$

Let's apply the ideal gas relationship to the gas mixture:

$$P_T.V = N_T.R.T$$

$$4.5 = N_T\ .0{,}082.(273 + 817)$$

So $\mathbf{N_T = 0.224\ mole.}$

There is proportionality between number of moles and pressure:

$$N_{CO}/\ 3.06 = N_{CO2}/\ 0.94 = 0.224\ /\ 4.$$

we find $\mathbf{N_{CO} = 0.171\ mol}$ and $\mathbf{N_{CO2} = 0.053\ mol.}$

Exercise 4:

How the equilibrium volves:

$$CH_4 \rightleftharpoons C + 2\,H_2 \qquad \Delta H > 0$$

1. If we raise the temperature
2. If we raise the pressure
3. If constant volume methane is added
4. If we add carbon
5. If an inert gas is added at a constant volume
6. If an inert gas is added at constant pressure.

Answer:

1. Move to the right
2. Move to the left
3. Move to the right
4. No change: carbon is the only constituent of the solid phase, its concentration is 1 whatever its mass
5. No evolution
6. Move to the right.

Chapter 3 Oxidation-Reduction Reactions

3.1. Oxidation, reduction, redox couples, oxidation-reduction reactions

An oxidation-reduction reaction is a type of chemical reaction that involves a transfer of electrons between two species. A redox reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron.

For example, when zinc metal is dissolved in an aqueous hydrochloric acid, the zinc is oxidized from Zn^0 to Zn^{2+}, and the acid hydrogen is reduced from H^+ to $H_{2(g)}$.

$$\mathbf{Zn_{(s)} + 2\,HCl \rightarrow Zn^{2+} + H_{2\,(g)} + 2\,Cl^-}$$

3.1.1. Oxidation, reduction

- **Oxidation**

Oxidation is a chemical transformation in which electrons are lost by an atom, molecule, or ion.

Oxidation half-reaction: $\mathbf{Red \rightleftharpoons Ox + n\,e^-}$

Example:

$\mathbf{Cu \rightleftharpoons Cu^{2+} + 2e^-}$ the Cu atom is oxidized to Cu^{2+} ion

- **Reduction**

Reduction is a chemical transformation in which electrons are gained by an atom, molecule, or ion.

Reduction half-reaction: $\mathbf{Ox + ne^- \rightleftharpoons Red}$

Example: $\mathbf{I_2 + 2\,e^- \rightleftharpoons 2\,I^-}$ molecular iodine is reduced to ion I^-

A reduction corresponds to a gain of electrons, while an oxidation corresponds to a loss of electrons.

Oxidation and reduction always occur simultaneously because the total number of electrons must be kept.

Example:

In the reaction of elemental calcium and oxygen to produce calcium oxide:

$$\mathbf{Ca_{(s)} + \tfrac{1}{2} O_{2\,(g)} \rightarrow CaO_{(s)}}$$

Oxygen gains two electrons and calcium loses two electrons. Although the two events occur simultaneously, they may be written as two separate half-reactions:

Reduction half-reaction: $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$

Oxidation half-reaction: $Ca \rightarrow Ca^{2+} + 2e^-$

3.1.2. Reducer, oxidizer

- **Reducer (reducing agent)** (noted red): it is a chemical species capable of yielding one or more electrons.
- **Oxidizer (oxidizing agent)** (noted Ox): it is a chemical species capable of capturing one or more electrons.

3.1.3. Redox couple

A redox couple (Ox/Red) is such that it is possible to change from the oxidized form (Ox) to the reduced form (Red) by transfer of n electrons.

$$\mathbf{Ox + n\,e^- \rightleftharpoons Red}$$

An oxidizing-reducing couple is noted as an **Ox / Red couple**.

Oxidized species ***Ox*** of a couple undergoes reduction, while a reduced species ***Red*** undergoes oxidation.

Examples:

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ the copper ion undergoes a reduction

$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ solid copper undergoes oxidation

$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2\,(g)}$ the couple H^+/H_2

Oxidizer **Reducer**

$Cl_{2\,(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$ the Cl_2/Cl^- couple

$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$ the Al^{3+}/Al couple

This writing reflects the possibility of switching from *Ox* to *Red* and vice versa by electron transfer. This writing is formal since electrons do not exist in the free state in aqueous solution.

The oxidant and the reducing agent thus connected are said to be conjugate: they form a redox couple, denoted *Ox*/*Red*.

3.1.4. Oxidation-reduction (redox) reaction

An oxidation-reduction or redox reaction is a reaction in which the electrons are exchanged between two redox couples Ox_1/Red_1 and Ox_2/Red_2.

The total number of electrons lost by oxidation must be equal to the number of electrons gained by reduction.

Either the two pairs Ox_1/Red_1 and Ox_2/Red_2 such as:

$$\mathbf{Ox_1 + n_1\,e^- \rightleftharpoons Red_1} \qquad (\times\, n_2)$$

$$\mathbf{Red_2 \rightleftharpoons Ox_2 + n_2\,e^-} \qquad (\times\, n_1)$$

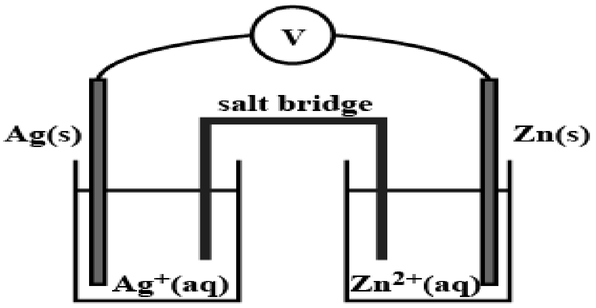
The redox reaction equation is written by combining the electronic half equations, but in such a way that the transferred electrons do not appear in the balance.

$$\mathbf{n_2\,Ox_1 + n_1\,Red_2 \rightleftharpoons n_1\,Ox_2 + n_2\,Red_1}$$

Example 1:

The galvanic cell in which the given reaction takes place is depicted as:

$Zn_{(s)}|Zn^{2+}_{(aq)}||Ag^{+}_{(aq)}|Ag_{(s)}$



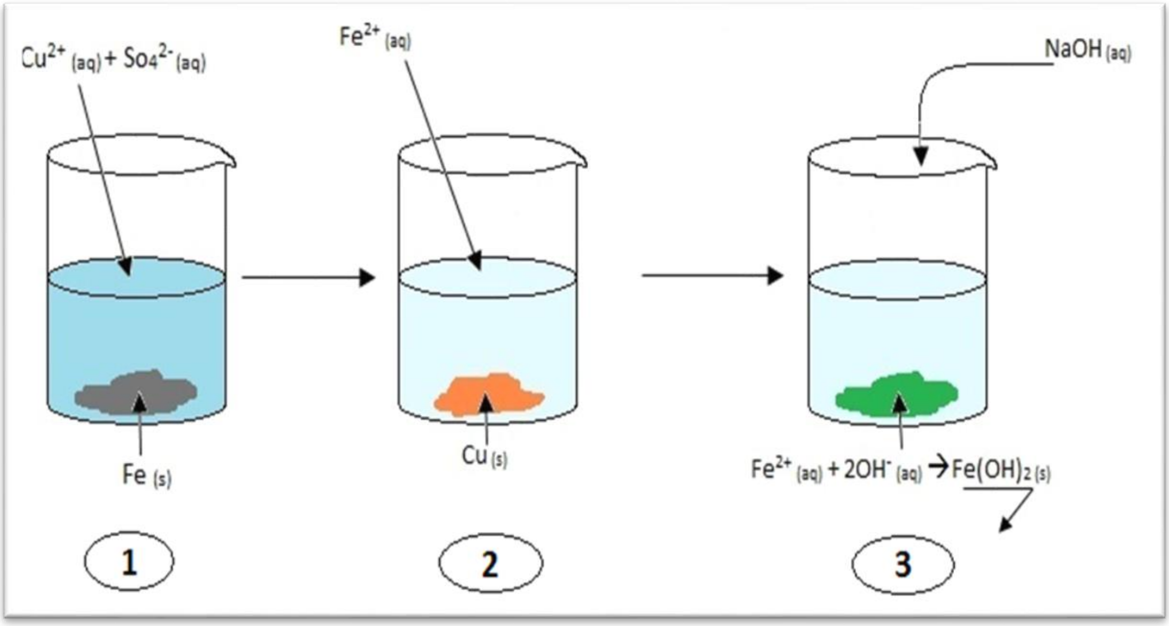
Oxidation at anode: $Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2\,e^-$

Reduction at cathode: $2\,Ag^{+}_{(aq)} + 2\,e^- \rightleftharpoons 2\,Ag_{(s)}$

The overall reaction is: $\mathbf{Zn + 2\,Ag^+ \rightleftharpoons Zn^{2+} + 2\,Ag}$

Example 2:

Oxidation of iron straw in copper (II) sulfate solution. Diagram of the oxidation-reduction reaction (Diagram: Samuel Renaud)



Step 1: The grey iron straw is introduced into a blue solution of copper (II) sulfate ($CuSO_4$) (presence of Cu^{2+} ions).

Step 2: The initially blue aqueous solution has become discolored, indicating that the Cu^{2+} ions have been consumed. In addition, the iron straw is completely covered with a red-brown precipitate after several days characteristic of a Cu deposit.

The Cu^{2+} ions were converted to Cu^0.

Step 3: Soda (NaOH) is added to the discolored aqueous solution. A green precipitate is then formed characteristic of a deposit of iron hydroxide ($Fe(OH)_{2\,(s)}$). This makes it possible to highlight the presence of Fe^{2+} ions in the discolored solution.

Iron(II) has been converted to Fe^{2+} ions.

On balance, the equation for this oxidation-reduction reaction can be written:

$$\boxed{Fe_{(s)} + Cu^{2+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Cu_{(s)}}$$

3.2. Oxidation numbers

3.2.1 Definition

The oxidation number (denoted n.o.) makes it possible to determine the oxidation state of an element, whether this element is alone or engaged in a molecular or ionic structure. Its value is either negative, zero, or positive and is expressed in Roman numerals.

3.2.2. Rules for assigning oxidation numbers

- **The oxidation number of any free element always remains zero**

The oxidation number of the elements or simple bodies is equal to 0.

Example: For simple bodies Cl_2, O_2, N_2, Na, H_2 and Cl_2 n.o. = 0

For Cu metal, n.o.(Cu) = 0;

- **The oxidation number in the case of a monatomic ion is always equal to the value of the charge of the ion.**

- **The oxidation number of group 1A and 2A in periodic table (group1 and group2) elements are +I and +II respectively :**

Example: For Al^{3+} ion, n.o.(Al) = + III Na^{+} ion, n.o.(Na) = + I

Cl^{-} ion, n.o.(Cl^{-}) = -I; O^{2-} ion, n.o.(O) = - II .

- **To determine the oxidation number of an element in a building, it is necessary to:**

  - Establish Lewis' representation of this edifice;
  - Assign the binding doublet(s) to the most electronegative atom;
  - Take stock of expenses.

- The algebraic sum of the n.o. of the atoms of a molecule is zero (in general for hydrogen is n.o. (H) = + I and for oxygen it is - II.

For the molecule HBr, n.o. (H) + n.o. (Br) = 0 therefore n.o. (Br) = -I

- The oxidation number of oxygen in compounds is equal to (-II).

- The most common exception is in peroxides (H_2O_2 for example), when the n.o. (O) = - I and in F_2O the n.o. (O) = +II.

- In compounds, the oxidation number of hydrogen in is almost always +I. The most common exception occurs when hydrogen combines with metals [LiH; NaH; ....], in this case the n.o of hydrogen is typically –I.

- For an electrically neutral compound, the sum of the positive and negative oxidation number of all elements in the compound equals zero.

- For a complex ion, the sum of the positive and negative oxidation numbers of all elements in the ion equals the charge on the ion.

- Chloride has not changed its oxidation state. It is a spectator ion in this reaction.

Example:

For $Cr_2O_7^{2-}$

Let x be the degree of oxidation of Cr

The n.o. of oxygen = - II and the charge of the complex is equal to - 2

$2x + 7(-2) = -2$ so $x = +VI$

For CO_2: n.o.(C) + 2 n.o.(O) = 0 with n.o.(O) = -II, therefore n.o.(C) = +IV.

For NO_3^-, n.o (N) + 3 n.o (O) = -I, with n.o.(O) = -II, therefore n.o (N) = + V

3.2.3. Redox reactions and oxidation numbers

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that always occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases.

$$\underset{\textbf{n.o. = + II}}{Cu^{2+}} + 2e^- \rightarrow \underset{\textbf{n.o. = 0}}{Cu}$$

The n.o. goes from (+II) to 0 (decreases)

a) Definition

- An oxidizer is a chemical entity whose n.o. may decrease.
- A reducer is an entity whose n.o. may increase.
- Oxidation corresponds to an increase in n.o.
- A reduction corresponds to a decrease in n.o.

Note :

If the oxidation number is constant Δno = 0, the envisaged reaction is not an oxidation-reduction reaction.

When an element is oxidized, its oxidation number increases; it decreases when the element is reduced.

This property can be used to detect if a species has undergone oxidation or reduction.

b) Identifying oxidized and reduced elements

$$\mathbf{Zn_{(s)} + 2\,H^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2\,(g)}}$$

n.o. = 0 n.o. = +I n.o. = +II n.o. = 0

The oxidation state of H^{+} changes from (+I) to 0, and the oxidation state of Zn changes from 0 to (+II). Hence, **Zn is oxidized and acts as the reducing agent**.

The oxidation state of H^{+} changes from (+I) to 0, and the oxidation state of Zn changes from 0 to (+II). Hence, **H^{+} ion is reduced and acts as the oxidizing agent**.

c) Dismutation reaction

It is a chemical reaction in which an element acts as an oxidant and a reductant.

Example:

Chlorine disproportionation

We have two redox couples:

$$\mathbf{Cl_2 + 2\,OH^{-} \rightleftharpoons ClO^{-} + Cl^{-} + H_2O}$$

n.o. = 0 n.o. = +I n.o. = -I

- Cl_2/Cl^{-}: chlorine acts as an oxidant.
- ClO^{-}/Cl_2: chlorine acts as a reducing agent.

Therefore, chlorine plays the role of a redox ampholyte.

d) Water redox couples

Water has acid-base properties and redox properties: It has two redox couples:

- **H^+/H_2 in acidic medium or H_2O/H_2 in basic medium**

$2\ H^+ + 2e^- \rightleftharpoons H_2$ in acid medium

$2\ H_2O + 2e^- \rightleftharpoons H_2 + 2\ OH^-$ in basic medium

- **O_2/H_2O in acidic medium or O_2/OH^- in basic medium**

$O_2 + 4\ H^+ + 4e^- \rightleftharpoons 2\ H_2O$ in acidic medium

$O_2 + 2\ H_2O + 4e^- \rightleftharpoons 4\ OH^-$ in basic medium

3.3. Equilibration of an oxidation-reduction reaction

3.3.1. Balancing a redox reaction using the half-reactions

Step 1: Write the half equations associated with each couple in the direction they unfold.

How to balance half-reactions?

We balance the chemical elements other than O and H. (Cl, I, Mn...).

The element O is balanced: if necessary, H_2O is added.

We balance the element H: if necessary, we add H^+.

Then the charges are balanced by adding electrons on the oxidizer side.

Step 2: The half-reactions are optionally multiplied so that the number of electrons exchanged is the same in each half-reaction. (Electrons should not appear in the balanced reaction).

Step 3: Sum of the two half-reactions. The species that are found on the products and reagents side are optionally simplified.

The reaction can now be checked to make sure that it is balanced.

Example 1:

Couple $S_4O_6^{2-}/S_2O_3^{2-}$

To find the four sulfur atoms, we must double the species $S_2O_3^{2-}$

hence: $S_4O_6^{2-} \rightleftharpoons 2\ S_2O_3^{2-}$

We have two electrons on the left side and four on the right side, so we must add two electrons: **$S_4O_6^{2-} + 2\ e^- \rightleftharpoons 2\ S_2O_3^{2-}$** ***The reaction is balanced***

Example 2:

Couple MnO_4^-/Mn^{2+}

When the oxidizer contains oxygen atoms and the reducer no longer contains oxygen atoms, it is usually sufficient to add water molecules.

$MnO_4^- \rightleftharpoons Mn^{2+}$ Mn atoms are balanced

$MnO_4^- \rightleftharpoons Mn^{2+} + 4\ H_2O$

4 molecules of water are added to balance the oxygen number

$MnO_4^- + 8\ H^+ \rightleftharpoons Mn^{2+} + 4\ H_2O$

8 H^+ protons corresponding to the 4 water molecules are added.

5 electrons are added for electroneutrality.

$MnO_4^- + 8\ H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$ ***The reaction is balanced***

Example 3:

Either the Fe^{3+}/ Fe^{2+} and MnO_4^-/ Mn^{2+} couples in an acid medium

***Step 1*: Each half reaction should be multiplied by the number of electrons in the other half equation. Oxidizer of couple 1 will react with reducer of couple 2.

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (x 5) Oxidation half - reaction

$MnO_4^- + 5e^- \rightarrow Mn^{2+}$ Reduction half - reaction

$5Fe^{2+} + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+}$

Step 2: Balance O and H^+ with H_2O

$$5\,Fe^{2+} + MnO_4^- \rightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$$

Step 3: Balancing loads with H^+

$$5\,Fe^{2+} + MnO_4^- + 8\,H^+ \rightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$$

Final equation

The charges are already balanced: no electrons should appear in the final equation

$$\boxed{5\,Fe^{2+} + MnO_4^- + 8\,H^+ \rightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O}$$

Example 4:

The same Fe^{3+}/Fe^{2+} and MnO_4^-/Mn^{2+} couples are considered in basic medium

In the above, the balance reactions were balanced using H^+ ions. This is the method to be used when the reaction takes place in an acidic medium.

When it takes place in a basic medium, it is necessary to balance this time with OH^- hydroxide ions instead of H^+ ions.

To do this, the easiest way is to start by equilibrating in an acidic medium, then switch to a basic medium thanks to the fact that: $H^+ + OH^- \rightleftharpoons H_2O$.

Example 5:

We take the balanced equation of the previous example in an acid medium, and we go to a basic medium:

$$5\,Fe^{2+} + MnO_4^- + 8\,H^+ \rightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$$

$$5\,Fe^{2+} + MnO_4^- + 8\,H^+ + 8\,OH^- \rightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O + 8\,OH^-$$

$$5\,Fe^{2+} + MnO_4^- + 8\,H_2O \rightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O + 8\,OH^-$$

$$5\,Fe^{2+} + MnO_4^- + 4\,H_2O \rightarrow 5\,Fe^{3+} + Mn^{2+} + 8\,OH^-$$

3.3.2. Balancing redox reactions using oxidation numbers

Consider the Cu^{2+}/Cu couple: the oxidizer has the oxidation number (+II) while the reducer has the oxidation number 0.

The n.o. is lower in the Red species than in the Ox species.

During reduction: $Cu^{2+} + 2e^- \rightarrow Cu$ copper n.o. decreases

During oxidation: $Cu \rightarrow Cu^{2+} + 2e^-$ copper n.o. increases

During a reduction, the n.o. of an element decreases, during an oxidation it increases.

Step 1: Write the equation $Ox_1 + Red_2 \rightarrow Red_1 + Ox_2$.

Step 2: For each pair, identify the element whose oxidation number varies. Adjust the stoichiometric numbers so that this element is balanced.

Step 3: For each pair, determine the variation of the n.o. of this element. This corresponds to n (number of exchanged electrons)

Step 4: Adjust the stoichiometric numbers so that the value of n is the same for each pair.

Step 5: Balance oxygen atoms and charges using H_2O and H^+.

Step 6**:** In reactions occurring in an acid medium, it is necessary to involve as many H^+ ions in the reagents as necessary to achieve equilibrium of charges. The presence of n H^+ ions in the reagents requires the appearance of n/2 molecules of water (H_2O) in the products.

Step 7**:** In a basic medium, it is necessary to involve as many OH^- ions in the reagents as is necessary to achieve equilibrium of charges. The presence of n OH^- ions in the reagents requires the appearance of n/2 molecules of water (H_2O) in the products.

Step 8**:** In an aqueous medium with the appearance of an acidic medium or a basic medium, it is necessary to involve in the products as many H^+ or OH^- ions as necessary. The presence of n OH^- or n H^+ ions in the products requires the intervention of n/2 molecules of water (H_2O) in the reagents.

Example 1:

Action of dilute nitric acid (HNO_3) on copper

Oxidation: $\mathbf{Cu \rightarrow Cu^{2+} + 2\,e^-}$ x 3 the n.o. goes from 0 to +II

n.o. = 0 n.o. = + II

Reduction: $\mathbf{NO_3^- + 3\,e^- + 4\,H^+ \rightarrow NO + 2\,H_2O}$ x 2

n.o.(N) = + V n.o.(N) = +II

Δ n.o. = - III

$$\boxed{\mathbf{3\,Cu + 2\,NO_3^- + 8\,H^+ \rightarrow 3\,Cu^{2+} + 2\,NO + 4\,H_2O}}$$

Example 2:

Balance the following equation: $a\,HCl + b\,O_2 \longrightarrow c\,Cl_2 + d\,H_2O$.

n.o.(H) = +I and n.o.(Cl) = -I in HCl molecule

n.o.(O) = 0 in the O_2 molecule

n.o.(Cl) = 0 in the Cl_2 molecule

n.o.(H) = +I and n.o.(O) = - II in the H_2O molecule

During the reaction:

n .o.(H) does not vary Δn.o. (H) = 0

n.o. (Cl) increases from -I to 0: Δn.o.(Cl) = 0 - (-1) = 1

n.o. (O) decreases from 0 to -II: Δn.o.(O) = -2 - 0 = -2

The total charge transferred by the Cl atoms and that captured by the O atoms must compensate each other (conservation of charges during the reaction).

$$\Delta n.o.\ (O) + \Delta n.o.\ (Cl) = -2 + 2 \times 1 = 0.$$

So one molecule of O_2 is compensated by four molecules of HCl (a = 4 b).

All that remains is to balance the products in such a way as to preserve all the elements.

$$\boxed{\mathbf{4\,HCl + O_2 \longrightarrow 2\,Cl_2 + 2\,H_2O}}$$

3.4. Exercises

Exercise 1:

Determine the oxidation number of the underlined atoms in the following compounds: $Na\underline{Cl}$, $\underline{K}H$, $\underline{H}_2O$, $\underline{N}O_2$, $\underline{Cu}O$, $K\underline{Mn}O_4$, $H_3\underline{P}O_4$, $H_2\underline{O_2}$, $H\underline{Cr}O_3$, $\underline{Cr_2}O_3$.

Answer:

$Na\underline{Cl}$: n.o (Na) = + I, **n.o (Cl) = -I**

$\underline{K}H$: n.o (H) = - I, **n.o (K) = +I**

$\underline{H}_2O$: n.o (O) = - II, **n.o (H) = +I**

$\underline{N}O_2$: n.o(O) = - II or x the n.o of N then: x - 4 = 0 ⇒x = 4, **n.o(N) = + IV**

$\underline{Cu}O$: n.o (O) = - II, x the n.o of Cu then: x - 2 = 0 ⇒x = 2, **n.o (Cu) = +II**

$K\underline{Mn}O_4$: the sum of the n.o = +1 +x + 4(-2) = 0, **n.o.(Mn) = +VII**

$H_3\underline{P}O_4$: the sum of the n.o = +3 +x + 4(-2) = 0, **n.o (P) = +V**

$H_2\underline{O_2}$: the sum of the n.o = +2 +2x = 0, **n.o (O) = -I**

$H\underline{Cr}O_3$: the sum of the n.o = 1+x-6 = 0, **n.o (Cr) = +V**

$\underline{Cr_2}O_3$: the sum of the n.o = 2x-6 = 0, **n.o (Cr) = +III**

Exercise 2:

Balance the following redox reactions by writing in each case the two redox half reactions.

$Cr(OH)_3 + ClO^- \longrightarrow CrO_4^{2-} + Cl^-$ (in basic medium)

$MnO_4^- + SO_3^{2-} \longrightarrow Mn^{2+} + SO_4^{2-}$ (in acidic medium)

$IO_3^- + Cr(OH)_3 \longrightarrow CrO_4^{2-} + I^-$ (in basic medium)

$Cr + NO_3^- \longrightarrow Cr^{3+} + NO$ (in acidic medium)

$KMnO_4 + K_2SO_3 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + H_2O$ (in acidic medium)

Answer:

Balance the redox reactions

$Cr(OH)_3 + ClO^- \longrightarrow CrO_4^{2-} + Cl^-$ (in basic medium)

Oxidation: $(Cr(OH)_3 + 5\,OH^- \longrightarrow CrO_4^{2-} + 4\,H_2O + 3e^-) \times 2$

Reduction: $(ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2\,OH^-) \times 3$

$2\,Cr(OH)_3 + 3\,ClO^- + 4\,OH^- \longrightarrow 2\,CrO_4^{2-} + 3Cl^- + 5\,H_2O$

$MnO_4^- + SO_3^{2-} \longrightarrow Mn^{2+} + SO_4^{2-}$ (in acidic medium)

Reduction: $(MnO_4^- + 8\,H^+ + 5e^- \longrightarrow Mn^{2+} + 4\,H_2O)$ x 2

Oxidation: $(SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2\,H^+ + 2e^-)$ x 5

$2\,MnO_4^- + 5SO_3^{2-} + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,SO_4^{2-} + 3\,H_2O$

$IO_3^- + Cr(OH)_3 \longrightarrow CrO_4^{2-} + I^-$ (in basic medium)

Reduction: $IO_3^- + 6\,e^- + 3\,H_2O \longrightarrow I^- + 6\,OH^-$

Oxidation: $(Cr(OH)_3 + 5\,OH^- \longrightarrow CrO_4^{2-} + 3\,e^- + 4\,H_2O\,)$ x 2

$IO_3^- + 2\,Cr(OH)_3 + 4\,OH^- \longrightarrow I^- + 2\,CrO_4^{2-} + 5\,H_2O$

$Cr + NO_3^- \longrightarrow Cr^{3+} + NO$ (in acidic medium)

Reduction: $NO_3^- + 3e^- + 4\,H^+ \longrightarrow NO + 2H_2O$

Oxidation: $Cr\,(s) \longrightarrow Cr^{3+} + 3e^-$

$Cr\,(s) + NO_3^- + 4\,H^+ \longrightarrow Cr^{3+} + NO + 2H_2O$

$KMnO_4 + K_2SO_3 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + H_2O$ (in acidic medium)

Reduction: ($MnO_4^- + 8H^+$ + 5 é $\longrightarrow Mn^{2+} + 4\,H_2O$) x 2

Oxidation: ($SO_3^{2-} + H_20 \longrightarrow SO_4^{2-} + 2\,H^+$ + 2 é) x 5

$2\,KMnO_4^- + 3\,H_2SO_4 + 5\,K_2SO_3 \longrightarrow 2MnSO_4 + 6\,K_2SO_4 + 3\,H_2O$

Exercise 3:

Determine the oxidation number of the underlined atoms in the following compounds:

$\underline{Cu}Cl_2$, $\underline{O}_2$, $\underline{P}O_4^{3-}$, $\underline{Cr}_2O_3$, $\underline{Ag}^+$, $\underline{Mn}O_4^-$, $\underline{Na}$, $\underline{S}O_4^{2-}$, $[\underline{Fe}(CN)_6]^{3-}$

Answer :

a) **The oxidation number in the following compounds:**

$\underline{Cu}Cl_2$: n.o. (Cu) = + IV

$\underline{O}_2$: n.o.(O) = 0

$\underline{Cr}_2O_3$: n.o.(Cr) = + III

$\underline{Mn}O_4^-$: n.o.(Mn) = + VII

$\underline{Ag}^+$: n.o.(Ag) = + I

$\underline{Na}$: n.o.(Na) = 0

$\underline{S}O_4^{2-}$: n.o.(S) = + VI

$[\underline{Fe}(CN)_6]^{3-}$: n.o.(Fe) = + III

$\underline{P}O_4^{3-}$: n.o.(P) = + V

Exercise 4:

Balance the following redox reactions by writing in each case the two redox half reactions and indicate the acid-base couple.

$I^- + C_2O_7^{2-} \longrightarrow Cr^{3+} + I_2$ (in acidic medium)

$NO_2^- + Al \longrightarrow NH_3 + AlO_2^-$ (in basic medium)

$Cr_2O_7^{2-} + C_2H_6O \longrightarrow Cr^{3+} + C_2H_4O_2$ (in acidic medium)

Answer:

$I^- + Cr_2O_7^{2-} \longrightarrow Cr^{3+} + I_2$ (in acidic medium)

Reduction: $Cr_2O_7^{2-} + 14\,H^+ + 6e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$

Oxidation: $(2\,I^- \longrightarrow I_2 + 2e^-)$ x 3

$6\,I^- + Cr_2O_7^{2-} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$

NO_3^{-} + Al $\longrightarrow$ NH_3 + AlO_2^{-} (in basic medium)

Reduction: $(NO_3^{-} + 6\,H_2O + 8e^{-} \longrightarrow NH_3 + 9\,OH^{-})$ x 3

Oxidation: $(Al + 4\,OH^{-} \longrightarrow AlO_2^{-} + 2\,H_2O + 3e^{-})$ x 8

$$\boxed{3\,NO_3^{-} + 8\,Al + 5\,OH^{-} + 2\,H_2O \longrightarrow 3\,NH_3 + 8\,AlO_2^{-}}$$

$Cr_2O_7^{2-}$ + C_2H_6O $\longrightarrow$ Cr^{3+} + $C_2H_4O_2$ (in acidic medium)

Reduction: $(Cr_2O_7^{2-} + 14\,H^{+} + 6e^{-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O)$ x 2

Oxidation: $(C_2H_6O + H_2O \longrightarrow C_2H_4O_2 + 4\,H^{+} + 4e^{-})$ x 3

$$\boxed{2\,Cr_2O_7^{2-} + 3\,C_2H_6O + 16\,H^{+} \longrightarrow 4\,Cr^{3+} + 3\,C_2H_4O_2 + 11\,H_2O}$$

Exercise 5:

Balance the following redox reactions by writing in each case the two redox half reactions.

1. $MnO_4^{-} + SO_4^{2-} \longrightarrow Mn^{2+} + S_2O_8^{2-}$ (in acidic medium)
2. $CrI_3 + Cl_2 \longrightarrow CrO_4^{2-} + IO_4^{-} + Cl^{-}$ (in basic medium)
3. $MnO_4^{-}{}_{(aq)} + Fe^{2+} \longrightarrow Mn^{2+}{}_{(aq)} + Fe^{3+}$ (in acidic medium)

Answer:

Balance the redox reactions

$$MnO_4^- + SO_4^{2-} \longrightarrow Mn^{2+} + S_2O_8^{2-}$$ **(in acidic medium)**

The two redox couples Ox$_1$/Red$_1$ and Ox$_2$/Red$_2$ are:

MnO_4^-/Mn^{2+} and $S_2O_8^{2-}/SO_4^{2-}$

Reduction: $(MnO_4^- + 8\,H^+ + 5e^- \longrightarrow Mn^{2+} + 4\,H_2O) \times 2$

Oxidation: $(2\,SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-) \times 5$

$$\boxed{2\,MnO_4^- + 10\,SO_4^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,S_2O_8^{2-} + 8\,H_2O}$$

$$CrI_3 + Cl_2 \longrightarrow CrO_4^{2-} + IO_4^- + Cl^-$$ **(in basic medium)**

The two redox couples Ox$_1$/Red$_1$ and Ox$_2$/Red$_2$ are:

Cl_2/Cl^- and CrO_4^{2-}/Cr^{3+}

Reduction: $(Cl_2 + 2e^- \longrightarrow 2\,Cl^-) \times 27$

Oxidation: $(CrI_3 + 32\,OH^- \longrightarrow CrO_4^{2-} + 3\,IO_4^- + 16\,H_2O + 27e^-) \times 2$

$$\boxed{2\,CrI_3 + 27\,Cl_2 + 64\,OH^- \longrightarrow 2CrO_4^{2-} + 6\,IO_4^- + 54Cl^- + 32\,H_2O}$$

$$MnO_4^-\,(aq) + Fe^{2+} \longrightarrow Mn^{2+}\,(aq) + Fe^{3+}$$ **(in acidic medium)**

The two redox couples Ox$_1$/Red$_1$ and Ox$_2$/Red$_2$ are:

MnO_4^-/Mn^{2+} and Fe^{3+}/Fe^{2+}

Reduction: $MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$

Oxidation: $(Fe^{2+} \longrightarrow Fe^{3+} + 1e^-) \times 5$

$$\boxed{MnO_4^- + 8\,H^+ + 5\,Fe^{2+} \longrightarrow Mn^{2+} + 4\,H_2O + 5Fe^{3+}}$$

Chapter 4

Ionic Solutions

Acids and Bases

4.1. Generalities

There are three primary theories that definite the chemistry of acids and bases: Arrhenius theory (1887), Lewis theory (1923) and Brönsted-Lowry theory (1923).

4.1.1. Arrhenius theory

- **An acid** according to Arrhenius is a hydrogen-containing compound which, in aqueous solution, releases one or more protons (H^+) or (H_3O^+).

$$HCl \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

$$H_2SO_4 \xrightarrow{H_2O} 2\,H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

$$H_3PO_4 \xrightarrow{H_2O} 3\,H^+_{(aq)} + PO_4^{3-}{}_{(aq)}$$

- **A base** is a hydroxide compound which releases OH^- ions on dissociation in water.

$$NaOH \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

$$Ca(OH)_2 \xrightarrow{H_2O} Ca^{2+}_{(aq)} + 2\,OH^-_{(aq)}$$

Arrhenius' definition of acids and bases has two key limitations: first, because acids and bases were defined in terms of ions obtained from water, the Arrhenius definition applied only to molecules in aqueous solution. Second, and more important, the Arrhenius definition predicted that only materials that dissolve in water to give H^+ and OH^- ions can have the properties of acids and bases. But there are many examples where this is not true, such as NH_3. We need to go beyond Arrhenius to understand some acids and bases. In 1923, the Brønsted-Lowry theory is thus proposed.

4.1.2. Lewis theory

Lewis proposed a theory of acids and bases based on electron exchanges. He put forward a new theory that substances that do not contain hydrogen can also be classified as acids or bases.

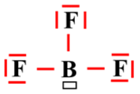
- **An acid** according to Lewis is a substance capable of accepting one or more electronic doublets. Acids must have empty molecular orbitals where electrons can be lodged.

Example:

Ag^+, Fe^{2+}, Al^{3+} cations and molecules whose central atom has not completed the byte (BF_3, $AlCl_3$)

H^+ $1s^0$ □ OA empty, so H^+ is an acid according to Lewis.

BF_3

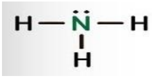


B has 1 empty OA

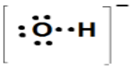
- **A base** is a substance capable of giving one or more electron doublets.

Example:

OH^-, Cl^-, S^{2-} anions and molecules with free electron doublets (NH_3, OH^-)



N has 1 free doublet



O has 3 free doublets

The bases must have unshared electron doublets that can be yielded to form a dative covalent bond. The formation of this bond is then called neutralization.

4.1.3. Brønsted-Lowry theory

Among the different theories of acids and bases, the theory proposed by Johannes Brønsted and Thomas Lowry in 1923 is still the most widely used today.

4.1.3.1. Definition of an acid

An acid is a chemical species, ion or molecule, capable of releasing (yielding) a proton (H^+). Acids are described as proton donors.

An acid $HA \rightleftharpoons A^- + H^+$

Examples:

HCl, H_2SO_4, HSO_4^-, H_3O^+, HNO_3, CH_3COOH and H_2O are acids in the sense that they can yield a proton.

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

$$HCl \rightarrow H^+ + Cl^-$$

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

$$HSO_4 \rightleftharpoons H^+ + SO_4^{2-}$$

4.1.3.2. Definition of a base

A base is a chemical species, ion or molecule, capable of accepting (fixing) a proton (H^+). Bases are also called proton acceptors.

A base $B + H^+ \rightleftharpoons BH^+$

Examples:

$CHCOO^-$, NH_3, CO_3^{2-} and H_2O are bases because they can capture a proton.

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

It should be noted that compounds such as KOH, NaOH, ... in water dissociate giving OH^- ions which are bases since they can fix a proton:

$$\mathbf{OH^- + H^+ \rightleftharpoons H_2O}$$

All of the two species associated in the same equilibrium constitute an acid/base pair. The acid and the base of the same couple are said to be ***conjugate***.

$$\mathbf{Acid \rightleftharpoons Base + H^+}$$

4.2. Conjugated Acid-base couples

$$\text{acid + base} \rightleftharpoons \text{Conjugate Base + Conjugate Acid}$$

The conjugate base of an acid is referred to as the molecule that remains after releasing a proton. The conjugate acid of a base is the molecule that attached the proton (the proton attached to this base molecule).

Example 1:

$$HCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons HCOO^-_{(aq)} + H_3O^+_{(aq)}$$

acid **base** **Conjugate base** **Conjugate acid**

The acid-base couple is written: Acid/its conjugate base

Example 2:

$HCOOH/ HCOO^-$, NH_4^+/NH_3, H_2SO_4/HSO_4^-

Let us take the following example:

$$HA \rightleftharpoons A^- + H^+ \qquad (1)$$

$$B + H^+ \rightleftharpoons BH^+ \qquad (2)$$

In the reaction (1), the direct direction HA is an acid. If we consider the reverse opposite direction, A^- fixes a proton it is the conjugate base of HA

In reaction (2), the direct direction B is a base. If we consider the reverse opposite direction, BH^+ is the conjugate acid of B. We consider the acid/base couples HA/ A^- and BH^+/B.

In any acid-base reaction, two conjugated acid-base couples are involved.

Example 3:

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ the two couples are: NH_4^+/ NH_3 and H_2O / OH^-

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ the two couples are: CH_3COOH/CH_3COO^- and H_3O^+/H_2O

4.3. Acid-base reactions

In aqueous solution, H^+ protons do not exist in the free state. Their release by an acid can therefore only take place in the presence of a base capable of capturing it.

An acid-base reaction in water always involves the HA acid of one couple and the B base of another couple. It can therefore be interpreted as the sum of two acid-base half reactions:

$$\left.\begin{array}{l} HA \rightleftharpoons A^- + H^+ \\ B + H^+ \rightleftharpoons BH^+ \end{array}\right\} \qquad HA + B \rightleftharpoons A^- + BH^+$$

$$\left.\begin{array}{l} HCl \rightarrow H^+ + Cl^- \\ NH_3 + H^+ \rightleftharpoons NH_4^+ \end{array}\right\} \qquad HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

4.4. Ampholytic or amphoteric compounds

Some species may behave both as acids and as bases depending on the nature of the partner with whom it reacts. Species with this character are said to be amphoteric, such as HCO_3^-, H_2O, HS^-, etc.

Example:

Water acts like an acid in the presence of a base and acts like a base in the presence of an acid.

- **water behaves like an acid**

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

The two couples involved are: H_2O / OH^- and BH^+/ B.

- **water behaves like a base**

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

Two couples involved are: H_3O^+/H_2O and HA/A^- .

The HS^- ion behaves like an acid and like a base.

Couple (1): H_2S/HS^- HS^- is a base

$$\underset{\textbf{Base 1}}{HS^-} + \underset{\textbf{Acid 2}}{H_3O^+} \rightleftharpoons \underset{\textbf{Acid 1}}{H_2S} + \underset{\textbf{Base 2}}{H_2O}$$

Couple (2): HS^-/S^{2-} HS^- is an acid

$$\underset{\textbf{Acid 1}}{HS^-} + \underset{\textbf{Base 2}}{H_2O} \rightleftharpoons \underset{\textbf{Acid 2}}{H_3O^+} + \underset{\textbf{Base 1}}{S^{2-}}$$

Note:

Polyacids are also amphoteric substances.

4.5. Solution properties

A solution is a homogeneous mixture. There are two types of electrolytes

4.5.1. Strong electrolytes

These are compounds that completely dissociate in the solvent: the reaction is total. They are strong acids and bases. The acidity and basicity constants are high.

***Example*:** HCl, $HClO_4$, $NaOH$, HNO_3.

	HCl	$+$	H_2O	$\longrightarrow$	Cl^-	$+$	H_3O^+
$t=0$	C_a		Excess		0		0
$t=t_{final}$	0				C_a		C_a

At the end of the reaction, we have only H_3O^+ and $Cl^−$ but no HCl.

4.5.2. Low electrolytes

These are compounds that partially ionized in the solvent: the reaction is partial. These are weak acids and bases. The acidity and basicity constants are low. The dissociation equilibrium is clearly in favour of the opposite reaction.

Example: CH_3COOH, NH_3, C_2H_5COOH

	CH_3COOH	$+$	H_2O	$\rightleftharpoons$	CH_3COO^-	$+$	H_3O^+
$t = 0$	C_a		Excess		0		0
$t = t_{final}$	$C_a - x$				x		x

At the end of the reaction, the solution contains H_3O^+, $CH_3COO^−$ ions and CH_3COOH molecules which are not dissociated.

If an acid is very strong, it easily releases a proton. Its conjugate base will then be very weak. In an acid-base pair, if the acid is strong, the base is weak and vice versa.

4.6. Study of equilibrium in solution

4.6.1. Ionic product of water (Autoprotolysis constant)

Pure water contains H_3O^+ ions and OH^- ions formed by the reaction, called autoprotolysis of water, of equation:

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + H_3O^+_{(aq)}$$

$$K_{eq} = \frac{[\quad][\quad]}{[\quad][\quad]} \quad OH_2O \quad H_3O$$

$$K_{eq} = \frac{[OH^-]\ [H_3O^+]}{[H_2O]\ [H_2O]}$$

We have: $[H_2O]_{t=0} = \frac{1000}{18} = 55.5\ M \approx [H_2O]_{eq}$

It can be considered that water is very weakly dissociated

$$[H_3O^+]\ [HO^-] = \underbrace{K_{eq}\ [H_2O]^2}_{K_w = 10^{-14}}$$

$$\boxed{K_w = [H_3O^+][OH^-] = 10^{-14} \quad \text{at} \quad 25°C}$$

Note: *K_w takes the name of ionic product of water; it depends on the temperature according to Van't Hoff's law:*

$$\frac{d}{dT}(Ln\ K_W) = \frac{\Delta_r H^\circ}{RT^2}$$

The electrical neutrality of pure water implies that $[H_3O^+] = [OH^-]$

At 25°C pH = 7 *$[H_3O^+] = [HO^-] = 10^{-7}$ mol/L*

The quantity pK_w is associated with the ionic product K_w by the formula: $pK_W = -\log K_w$

4.6.2. Acidity constant of an acid-base couple

The acidity constant is a numerical measure of the strength of the acid, i.e. its reactivity with the molecules of the solvent. An acid is all the stronger when its acidity constant is high.

Consider an HA acid. The dissociation equilibrium is written:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)}$$

The concentration equilibrium constant is:

$$Kc = \frac{[A^-] \text{ x}[H_3O^+]}{[\text{HA}] \text{ x}[H_2O]}$$

The acidity constant is written: $K_a = \text{K}_C \text{ x } [H_2O] = \frac{[A^-] \text{ x}[H_3O^+]}{[\text{HA}]}$

$$\boxed{\mathbf{K}_{\boldsymbol{a}} = \frac{[\boldsymbol{A}^-] \ [\boldsymbol{H_3O}^+]}{[\mathbf{HA}]}}$$

K_a called acidity constant (also known as an acid dissociation constant, or acid-ionization constant) characterizes the dissociation of acid HA in a solution.

Example:

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$\boldsymbol{K_a} = \frac{[\text{CH}_3\text{COO}^-] \text{ x}[\boldsymbol{H_3O}^+]}{[\text{CH}_3\text{COOH}]}$$

4.6.3. Basicity constant of an acid-base couple

The strength of a base can be measured by its basicity constant K_b. A base is said to be strong in a given solvent, if the corresponding acid-base reaction is total, it is said to be weak otherwise.

Let's also consider a base B in water

The ionization reaction is written:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant is written: $K_C = \frac{[\text{BH}^+] \text{ x } [\text{OH}^-]}{[B] \text{ x } [H_2O]}$

$$\Rightarrow K_b = \text{K}_C \text{ x } [H_2O] = \frac{[\text{BH}^+] \text{ x } [\text{OH}^-]}{[B]}$$

The solution being very dilute (water in very large excess),

$$[H_2O] \;=\; 55.5 \text{ M}$$

So: $K_b = K_C \times 55.5$

K_b like K_C only depend on the temperature

$$\boxed{\mathbf{K}_b = \frac{[OH^-]\;[BH^+]}{[\mathrm{B}]}}$$

***Example**:*

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

The basicity constant is written: $K_b = \dfrac{[NH_4^+] \times [OH^-]}{[NH_3]}$

The strength of an acid or base is measured by the tendency to yield or fix a proton. The higher the acidity constant of an acid, the more it is dissociated. Similarly for a base, the greater its basicity constant, the greater its strength.

4.6.4. Relationship between K_a and K_b

For a couple (HA/A^-)

$$\text{Acid} + H_2O \rightleftharpoons \text{base} + H_3O^+ \qquad K_a = \frac{[\text{base}] \times [H_3O^+]}{[\text{acid}]}$$

The conjugate base A^- of HA acid can react with water according to the reaction:

$$\text{Base} + H_2O \rightleftharpoons \text{acid} + OH^- \qquad K_b = \frac{[\text{acid}] \times [OH^-]}{[\text{base}]}$$

Since there is a relationship between $[H_3O^+]$ and $[OH^-]$ ($K_w = [H_3O^+] \times [OH^-]$),

$$K_b = \frac{[\text{acid}] \times [OH^-]}{[\text{base}]} = \frac{[acid]}{[base]} X \frac{K_w}{[H_3O^+]}$$

$$\frac{K_w}{K_b} = \frac{[\text{base}] \times [H_3O^+]}{[\text{acid}]} = K_a$$

$$\boxed{\mathbf{K_a \times K_b = [H_3O^+][OH^-] = K_w = 10^{-14}} \quad \text{at } 25°\text{C}}$$

Thus if we know either Ka for an acid or Kb for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid base pair.

We can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$\mathbf{pK_a = -\log_{10} K_a,} \qquad \mathbf{pK_b = -\log_{10} K_b}$$

The stronger the acid, the higher the K_a value and the lower the pKa value.

The same is true for K_b.

$$K_a \times K_b = K_w \quad \Rightarrow \; -\log_{10} K_a - \log_{10} K_b = -\log_{10} K_w$$

$$\boxed{\mathbf{pK_a + pK_b = pK_w = 14}} \qquad \text{At } 25\ °C$$

Note:

The smaller values of pKa, the stronger the acid of a couple and the weaker the conjugate base

The higher values of the pKa, the stronger the base of a couple and the weaker the conjugate acid

The pKa of the two acid-base couple of water (H_3O^+/H_2O) and (H_2O/HO^-) can be defined.

- **The first couple corresponds to the equilibrium:**

Acid-base couple (H_3O^+/H_2O): $H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$

$$Ka = \frac{[H_3O^+]}{[H_3O^+]} = 1 \longrightarrow \mathbf{pKa = 0}$$

- **The second acid-base couple corresponds to the equilibrium:**

Acid-base couple (H_2O/HO^-): $H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$

$$Ka = [HO^-] \times [H_3O^+] = 10^{-14} \longrightarrow \mathbf{pKa = 14}$$

Since H_3O^+ is the strongest acid in water, and OH^- is the strongest base, both pairs of water limit the pKa scale, for acid-base couple in water, except strong acids and strong bases.

$$\mathbf{0 \leq pKa \leq 14 \qquad At\ 25\ °C}$$

4.7. Leveling effect

The dissociation reaction of a strong acid is complete; that is, this acid no longer exists in the solution; it has been completely replaced by an equal amount of H_3O^+. Therefore, acids stronger than H_3O^+ cannot be differentiated in water.

It is said that there is a "Leveling" of their forces to that of H_3O^+. The H_3O^+ ion is the strongest acid that can exist in water.

The dissociation reaction of a strong acid is total; that is, this acid no longer exists in the solution; it has been totally replaced by an equal amount in moles of H_3O^+.

Therefore, acids stronger than H_3O^+ cannot be differentiated in water. It is said that there is a "Leveling" of their forces to that of H_3O^+. The hydronium ion H_3O^+ is the strongest acid that can exist in water.

Similarly, the hydroxide ion OH^- is the strongest base that can exist in water. If there are stronger bases, their strengths will be levelled at the level of that of OH^-.

In order to be able to classify strong acids, it is necessary to use a less basic solvent than water, i.e. a solvent where these acids are partially dissociated. Similarly, to be able to classify strong bases, a less acidic solvent than water must be used.

Example:

$$\underset{A_1}{HCl} + \underset{B_2}{CH_3COOH} \rightleftharpoons \underset{A_2}{CH_3COOH_2^+} + \underset{B_2}{Cl^-}$$

The solvent is acetic acid.

Each solvent has an acidity scale. The acidity scale regarding water is the most used because aqueous solutions are the most widespread.

In a solvent comprising liquid NH_3, the acids are levelled at NH_4^+ and the bases are levelled at NH_2^-.

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

The reference couples are: NH_4^+/ NH_3 and NH_3/ NH_2^-

NH_3 (liquid) being more basic than water, in this solvent the HCl and CH_3COOH acids will have the same strength.

In the acidity scale regarding water, the reference couples are H_3O^+/H_2O and H_2O/OH^-.

4.8. Relationship between pKa and acid strength

Stronger acids (pKa < 0), do not differentiate in water. Similarly, bases stronger than OH^- (pKa > 14) do not differentiate in water.

For weak acids and bases, $0 < pKa < 14$. To classify them, we use a scale of pKa.

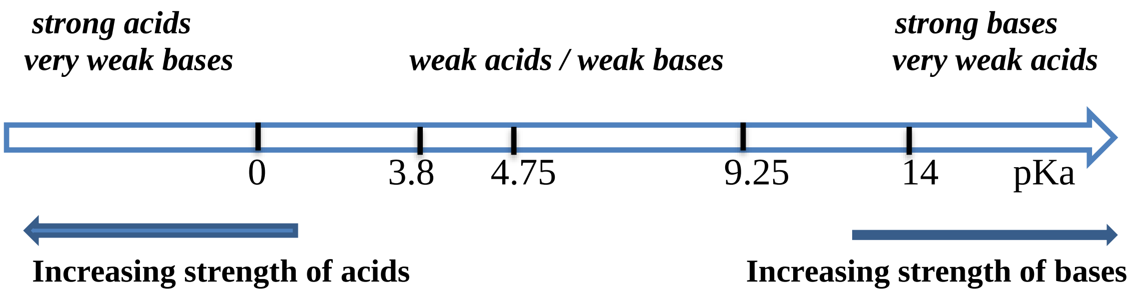
The value of Ka (therefore pKa) characterizes the ability of the acid and its conjugate base to react with water: Therefore, we can classify the acid-base couples using the diagram below.

Scales have been established for several solvents. Water is the most used. In this scale, the (H_3O^+/H_2O) and (H_2O/OH^-) couples were taken as reference.

Example:

pKa ($HCOOH/HCOO^-$) = 3.8 pKa (CH_3COOH/CH_3COO^-) = 4.75

pKa (NH_4^+/NH_3) = 9.25



Strong acids refer to acids that are almost completely ionized in aqueous solution(pKa< 0),

Medium acids are those with a pKa between 0 and 4 ($0 \leq pKa \leq 4$),

Medium weak acids have a pKa between 4 and 7 ($4 \leq pKa \leq 7$),

Weak acids have a pKa greater than 7 (pKa > 7).

The larger the acidity constant K_a of a couple HA/A^-, the smaller the pKa and the more the acid is dissociated in water.

4.9.Relationship between pH and pKa of couple (predominance diagram)

The pH of a solution containing a weak acid HA and its conjugate base A^- is related to the pKa of the HA/A^- pair by the relationship:

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

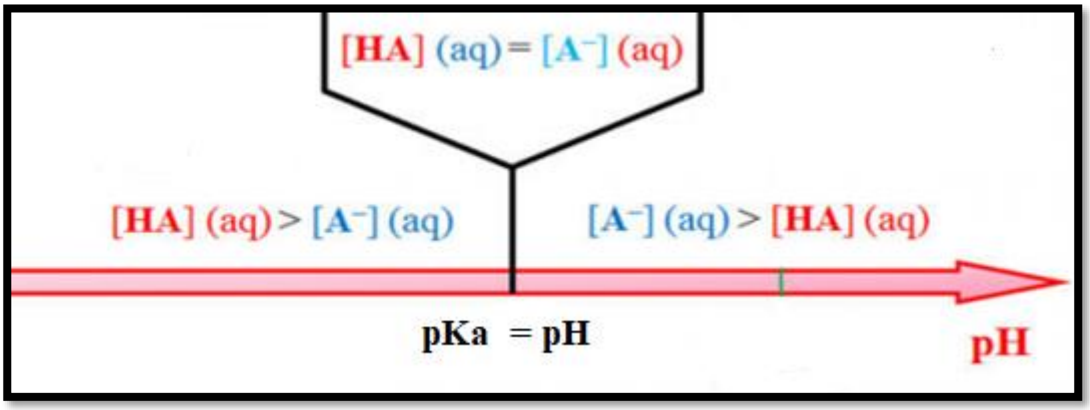
$pK_a = -\log K_a$, $pH = -\log [H_3O^+]$

This relationship derives from the definition of the acidity constant K_a and the properties of log :

$$\boxed{pH = pKa + \log \frac{[A^-]}{[HA]}}$$

- if **[A⁻] = [AH],** the logarithm becomes zero, and therefore pH = pKa: acidic and basic species have the same concentration in solution.
- if **[A⁻] < [AH],** the logarithm is a negative number, more HA means more acid, and thus a lower pH. therefore pH < pKa: the acid species predominates.
- if **[A⁻] > [AH]**, the solution goes more basic because the logarithm now is greater than zero, therefore pH > pKa: the basic species predominates.

This can be summarized in a predominance diagram:



4.10. Displacement of acid-base balances

We can use the relative strengths of acids and bases to predict the direction of an acid-base reaction by following a single rule: an acid-base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\textbf{Stronger acid + Stronger base} \rightleftharpoons \textbf{Weaker acid + Weaker base}$$

Consider the balance:

$$HA + H_2O \overset{1}{\underset{2}{\rightleftharpoons}} H_3O^+ + A^-$$

HA is a strong acid. The dissociation equilibrium will be moved in direction 1

Since HA acid is strongly dissociated, its conjugate base is a weak base.

Example:

Hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

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

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$CH_3COOH + H_2O \overset{1}{\underset{2}{\rightleftharpoons}} CH_3COO^- + H_3O^+$$

Since the ionization constant Ka of H_3O^+ is stronger than that of CH_3COOH, the acid CH_3COOH is weaker than the acid H_3O^+ and the base CH_3COO^- is stronger than H_2O.

Note:

The acid-base equilibrium moves in the direction of weaker acid and weaker base formation (direction 2).

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

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

Example:

The addition of a common ion to the equilibrium causes a retreat of ionization.

$$\mathbf{HA + H_2O \underset{2}{\overset{1}{\rightleftharpoons}} H_3O^+ + A^-}$$

The addition of H_3O^+ ions or A^- ions to the solution in equilibrium causes the reaction to move in direction 2 (LE CHATELIER's law).

4.11. Degree of dissociation α

An electrolyte is a chemical compound which, in the molten or dissolved state, can undergo electrolysis, that is, which decomposes by the passage of an electric current. The decomposition of a molecule into two or more pieces can be done in two ways.

- **Ionization**: If the products obtained are ions.

Example:

$$\mathbf{NaCl \rightleftharpoons Na^+ + Cl^-}$$

- **Dissociation**: If the products obtained are neutral.

Example:

$$\mathbf{2\ NH_3 \rightleftharpoons N_2 + 3\ H_2}$$

Such reactions often result in equilibrium; dissociation or ionization are rarely complete. The noted ionization (or dissociation) degree gives α us a measure of the displacement of this equilibrium. It represents the number of moles of ionized acid or base.

It is defined as follows:

$$\boxed{\alpha = \frac{\textit{amount of substance of the reactant dissociated}}{\textit{amount of substance of the reactant present initially}}}$$

The degree of ionization is between 0 and 1.

α = 0: means that there is no ionization,
α = 1: means that the ionization is complete (strong electrolytes),
0 ≤ α ≤ 1: means ionization is partial (weak electrolytes).

The dissociation of a weak acid HA can therefore be written:

	HA	+	**H_2O**	$\rightleftharpoons$	**A^-**	+	**H_3O^+**
$t_{initial}$	C_0		0				
After dissociation	$C_0 - \alpha C_0$				αC_0		αC_0

$$\alpha = \frac{[A^-]}{C_0} = \frac{[H_3O^+]}{C_0}$$

$$K_a = \frac{[A^-]\ [H_3O^+]}{[HA]} = \frac{\alpha^2 C_0}{(1-\alpha)}$$

Within the framework of the approximations valid for weak acids slightly dissociated at the usual concentrations, we can write

$$\alpha << 1 \quad \text{and} \quad Ka = C_0\,\alpha^2$$

These relationships express Ostwald's dilution law; they are not valid for strong electrolytes. They show that for a given weak acid (or weak base), if the initial concentration decreases, the more it will tend to dissociate (increase in the ionization coefficientα), since Ka is a constant quantity at a given temperature.

This means that the percentage of ionized acid (or base) increases as the initial acid concentration decreases.

4.12. Exercises

Exercise 1:

Which of the following species are acid-base pairs? In these couples, what is the acid and what is the base?

H_2S, OH^-, H_2O, CH_3^-, AlH_3, NH_3, CH_4, O^{2-}, AlH_4^-, NH_2^-, NaH, H_3O^+, NH_4^+, Na^+, Cl^-, NaOH, HS^-, HBr, S^{2-}, CH_3^+, CH_4

Answer:

If the acid is electrically neutral, the conjugate base is an anion.

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

Example 1: $HCOOH \rightleftharpoons HCOO^- + H^+$

The acid can be a cation, the conjugate base is then a neutral molecule.

Example 2: $CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+$

The acid is an anion; the base is then an anion carrying a greater charge (in absolute value).

Example 3 :

$$HS^- \rightleftharpoons S^{2-} + H^+$$

The acid-base pairs are:

NH_4^+/ NH_3	NH_3/NH_2^-
CH_4/CH_3^-	H_3O^+/H_2O
H_2S/HS^-	HS^-/ S^{2-}
H_2O /OH^-	OH^-/O^{2-}

The species AlH_3, AlH_4^-, NaH and Na^+ as well as CH_3^+ and CH_4 are not acid-base pairs because the transition from one to the other involves an H^- hydride ion and not an H^+ proton.

Exercise 2:

1. Find the conjugate bases of the following acids:

H_3O^+, $HClO_4$, HNO_3, HNO_2, HCOOH, C_6H_5COOH

2. Find the conjugate acids of the following bases:

OH^-, Cl^-, HS^-, NH_3, C_5H_5N

3. Do the following species constitute acid-base pairs?

$NaHCO_3$/ HCO_3^-, LiH / Li^+, CH_3NH_2/ $CH_3NH_3^+$, SH^-/ S^{2-} , NH_3/ N_2H_4 , HNO_3/NO_3^-

Answer:

1. Conjugated bases are of the following acids are:

H_3O^+ / H_2O

$HClO_4$ / ClO_4^-

HNO_3 / NO_3^-

HNO_2 / NO_2^-

HCOOH / $HCOO^-$

C_6H_5COOH / $C_6H_5COO^-$

2. Conjugated acids of the following bases are:

H_2O / OH^-

HCl / Cl^-

$C_5H_6N^+$ / C_5H_5N

H_2S / HS^-

NH_4^+ / NH_3

4. The acid/base pairs are:

$CH_3NH_3^+$ / CH_3NH_2 ; SH^-/S^{2-} and HNO_3/NO_3^-

Exercise 3:

1. Indicate the equations of the reactions of the acids below with the H_2O base:

a) HI b) CH_3COOH c) HF d) HNO_2

2. Indicate the equations of the reactions of the bases below with H_2O acid:

a) HSO_4^- b) PH_2^- c) Cl^- d) CH_3NH_2 e) H^-

Answer:

1. The reactions of the acids with the H_2O base are:

a) $HI + H_2O \rightleftharpoons H_3O^+ + I^-$

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

c) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

d) $HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$

3. The reactions of the bases with H_2O acid are:

a) $HSO_4^- + H_2O \rightleftharpoons OH^- + H_2SO_4$

b) $PH_2^- + H_2O \rightleftharpoons OH^- + PH_3$

c) $F^- + H_2O \rightleftharpoons OH^- + HF$

d) $CH_3NH_2 + H_2O \rightleftharpoons OH^- + CH_3NH_3^+$

e) $H^- + H_2O \rightleftharpoons OH^- + H_2$

Exercise 4:

Predict whether the equilibrium for each reaction lies to the left or the right as written.

1. $NH_4^+{}_{(aq)} + PO_4^{3-}{}_{(aq)} \rightleftharpoons NH_{3(aq)} + HPO_4^{2-}{}_{(aq)}$
2. $C_2H_5COOH_{(aq)} + CN^-{}_{(aq)} \rightleftharpoons C_2H_5COO^-{}_{(aq)} + HCN_{(aq)}$

Answer:

- Identify the conjugate acid-base pairs in each reaction.
- Determine which the stronger acid is and base.
- Equilibrium always favors the formation of the weaker acid-base pair.

1. The conjugate acid-base pairs are NH_4^+ / NH_3 and HPO_4^{2-} / PO_4^{3-}.

NH_4^+ is a stronger acid (pKa = 9.25) than HPO_4^{-2} (pKa = 12.32),

and PO_4^{-3} is a stronger base (pK_b=1.68) than NH_3 (pK_b = 4.75).

The equilibrium will therefore lie to the right, favoring the formation of the weaker acid-base pair:

$$\underset{\text{Stronger acid}}{NH_4^+{}_{(aq)}} + \underset{\text{Stronger base}}{PO_4^{3-}{}_{(aq)}} \longrightarrow \underset{\text{Weaker base}}{NH_{3(aq)}} + \underset{\text{Weaker acid}}{HPO_4^{2-}{}_{(aq)}}$$

2. The conjugate acid-base pairs are C_2H_5COOH / $C_2H_5COO^-$ and HCN/CN^-

HCN is a weak acid (pKa = 9.3) and CN^- is a moderately weak base (pK_b = 4.7). Propionic acid (C_2H_5COOH is not listed in Table, however. In a situation like this, the best approach is to look for a similar compound whose acid-base properties are listed.

For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($-CH_2CH_3$ versus $-CH_3$-CH_3), so we might expect the two compounds to have similar acid-base properties. In particular, we would expect the pKa of propionic acid to be similar in magnitude to the pKa of acetic acid. (In fact, the pKa of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.)

Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid-base pair:

$$\mathbf{C_2H_5COOH_{(aq)} + CN^-_{(aq)} \rightleftharpoons C_2H_5COO^-_{(aq)} + HCN_{(aq)}}$$

Stronger acid Stronger base Weaker base Weaker acid

Chapter 5

pH of aqueous solutions

5.1 . Definition

In various industries and medical practices, the ability to assess the acidity of solutions is crucial. This assessment is typically based on the molar concentration of H_3O^+ ions.

For this purpose, a mathematical operator was introduced, corresponding to p = -log (decimal logarithm) of the H_3O^+ ion concentration (pH = H^+ ion potential), explained by the relationship:

$$\boxed{\mathbf{pH = -\log_{10} [H_3O^+]}}$$

The H_3O^+ ion concentration is expressed in $mol.L^{-1}$.

It can also be written: $[H_3O^+] = 10^{-\,pH}$

By analogy with pH, we can define p OH:

$$\boxed{\mathbf{p\,OH = -\log_{10} [OH^-]}}$$

The smaller the pH, the more acidic the solution.

The smaller the p OH, the more basic the solution.

The higher the concentration of H_3O^+ ions, the lower the pH of the solution and vice versa.

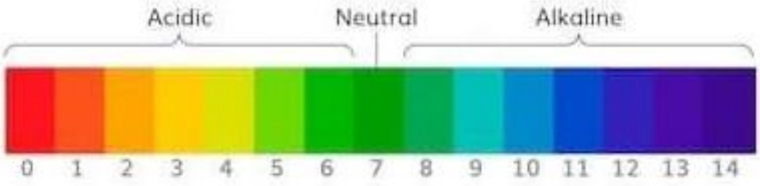
The higher the pH of a solution, the more basic it becomes

5.2. pH scale in water

In pure water, at 25°C, $[H_3O^+] = [OH^-] = 10^{-7}\ mol.l^{-1}$ $\Rightarrow$ **$pH = -\log 10^{-7} = 7$**

In an acid solution, $[H_3O^+] > [OH^-] \Leftrightarrow [H_3O^+] > 10^{-7}\ mol.l^{-1}$ $\Rightarrow$ **$pH < 7$**

In a basic solution, $[H_3O^+] < [OH^-] \Leftrightarrow [H_3O^+] < 10^{-7}\ mol.l^{-1}$ $\Rightarrow$ **$pH > 7$**



Examples:

Acid	**Neutral**	**Basic**
Gastric juices (pH ~2)	Pure water (pH = 7 to 25 ^{0}C)	Soap (pH ~8)
Vinegar (pH ~4)	Blood (pH ~7.4)	Bleach(11.5 <pH<12.5)
Lemon juice (pH ~2)		

Similarly, from the autoprotolysis constant of water, it is possible to write:

$$K_w = [H_3O^+] \times [OH^-] \Leftrightarrow -\log K_w = (-\log [H_3O^+]) + (-\log [OH^-])$$

$$\boxed{pH + pOH = 14}$$

The pH of a solution is usually measured either by a pH meter, which is a battery where the electromotive force measured is related to the concentration of H_3O^+ ions, or using colored indicators or pH paper that give a quick, economical, but inaccurate indication of the acidity of a solution.

Example:

a) Calculate the pH of a 4 x10^{-4} M NaOH solution

Sodium hydroxide is a strong base: it is completely dissociated in solution.

$$NaOH \rightarrow Na^+ + OH^-$$

$[OH^-] = 4 \times 10^{-4}$M

pOH = - log (4 ×10^{-4}) = 3.39

pH = 14 - pOH = 14 - 3.39 = 10.61.

b) 200 mL of a solution containing 0.01 moles of HCl is prepared. Calculate its pH.

$[HCl] = [H_3O^+] = n / V = 0.01/0.2 = 0.05$ M

$pH = -\log [H^+] = -\log 0.05 = 1.30$.

5.3. Determination of the pH of solutions

For the calculation of the pH of acidic or basic solutions, it is important to lay down several equations and make approximations. These equations have special names. These are:

- ***The law of mass action***, corresponding to the expression of the equilibrium constant: K
- ***Ionic product of water*** • or autoprotolysis of water: K_w
- ***Electro-neutrality:*** in this equation, we write that the sum of the concentrations of the positively charged species is equal to the sum of the concentrations of the negatively charged species.
- ***The conservation of mass (mass balance)***: in this equation, it is written that the initial concentration of a compound is equal to the sum of the concentrations of this compound and its conjugate, formed during the reaction considered.

5.3.1. pH of acids solutions

- **Dissociation of acid in water (law of mass action)**

Let C_a be the initial concentration of an HA acid:

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

The species present in the solution are HA, A^-, H_2O, OH^- and H_3O^+

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

The acidity constant

- **Partial water dissociation equilibrium**

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

$K_w = [OH^-]\ [H_3O^+] = 10^{-14}$

- The electroneutrality equation, applied to the solution:

$$[H_3O^+] = [OH^-] + [A^-]$$

- Conservation of the mass:

$$C_a = [A^-] + [AH]$$

To calculate the pH of the solution, many approximations are made, leading to simplifications that must be justified according to the case studied.

1st approximation: The [OH$^-$ ions] produced by the dissociation of water can be neglected in front of those coming from the dissociation of acid.

2nd approximation: The acid is little dissociated to be able to neglect [A$^-$] in front of [HA].

Sample

Weak acid: $[H_3O^+] = [A^-] + [OH^-]$

Weak base: $[BH^+] + [H_3O^+] = [OH^-]$

Make valid approximations in a not too diluted medium ($C > 10^{-6}$ N)

- In an acidic medium not too diluted: $[OH^-] << [H_3O^+]$
- In basic medium not too diluted: $[H_3O^+] << [OH^-]$
- For weak electrolytes, not too dilute ($\alpha \leq 10^{-3}$) the concentration of ions in solution is negligible compared to that of non-ionized species.

The conservation of mass equation becomes: $C_a = [AH]$ $([A^-] <<< [AH])$.

5.3.1.1. Calculation of pH: Strong acid

Strong acids (HNO_3, $HClO_4$, HBr, HCl, HI) have a pKa of less than 0 and react so totally (quantitatively) with water to give H_3O^+.

- **Consider a strong acid solution that is not too dilute ($C_a > 10^{-6}$ N)**

Let C_a be the initial concentration of a strong acid HA:

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

As a result, the concentration of H_3O^+ ions from the dissociation of water can be neglected compared to that from the dissociation of acid.

Similarly, the concentration of OH^- ions from water is neglected compared to that of the conjugate base.

Electrical neutrality: $[H_3O^+] = [A^-]$

Mass balance: $C_a = [AH] + [A^-] = [A^-]$

The acid is fully dissociated: [A-] >>> [AH] so $[H_3O^+] = C_a$

Hence

$$\boxed{\mathbf{pH = -\log C_a}}$$

Example: Calculate the pH of the following solution: 0.01 M hydrochloric acid (HCl) (pKa = -3.7).

Answer :

HCl is a dissociated strong acid so

$$pH = -\log C_a = -\log 0.01 = 2$$

➢ Consider a highly dilute strong acid solution ($C_a < 10^{-6}$ N)

In the case of a very dilute strong acid solution, the concentration of OH^- ions is no longer negligible compared to that of H_3O^+ ions.

Ionic product of water: $K_w = [OH^-][H_3O^+] = 10^{-14}$ (1)

Mass balance: $C_a = [A^-]$ ([AH] = 0, totally dissociated acid) (2)

Electrical neutrality: $[A^-] + [OH^-] = [H_3O^+]$ (3)

These three equations must be combined to determine the H_3O^+ ion concentration.

From (1) $\longrightarrow$ $[OH^-] = \frac{K_e}{[H_3O^+]}$ (4)

From (2) and (3) $\longrightarrow$ $[H_3O^+] = C_a + [OH^-]$ (5)

by replacing (4) in (5), we obtain

$$[H_3O^+] = \frac{C_a + \sqrt{{C_a}^2 + 4K_e}}{2}$$

$$\boxed{\mathbf{pH = \log_{10} 2 - \log}\ (C_a + \sqrt{{C_a}^2 + 4K_w})}$$

5.3.1.2. Calculation of pH: Weak acid and little dissociated

In a solution of a weak acid HA (**$[A^-] << [HA]$**)

- Two equilibria coexist:

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

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

- The species present are HA, A^-, H_3O^+, OH^-, and H_2O

- There are relationships between their concentrations:

* mass action law: $Ka = [A^-][H_3O^+]/[HA]$ and $K_w = [H_3O^+][OH^-]$

* Electrical neutrality: $[H_3O^+] = [A^-] + [OH^-]$

* Conservation of mass: $C_a = [HA] + [A^-]$

If the weak acid is little dissociated ($[A^-] << [HA]$ 2nd approximation) the relationship of the conservation of matter becomes $C_a = [HA]_0$ and as $[H_3O^+] = [A^-]$ (1st approximation), the acidity constant gives:

$$K_a = [H_3O^+]^2 / C_a,$$

we deduce $[H_3O^+] = \sqrt{K_a C_a}$

$$\boxed{\mathbf{pH = \frac{1}{2}(pKa - \log C_a)}}$$

Example:

Calculate the pH of the following solution: 0.15 M formic acid (HCOOH) (pKa = 3.8).

Answer :

HCOOH is a weak acid so:

$$pH = \frac{1}{2}(pKa - \log C_a) = \frac{1}{2} pKa - \frac{1}{2}\log 0.15 = 1.9 + 0.41 = 2.3$$

5.3.1.3. Calculation of pH: a mixture of two acids

a) A mixture of two strong acids, HA_1 and HA_2

In an aqueous solution, the strong acids are completely dissociated:

$$HA_1 + H_2O \longrightarrow A_1^- + H_3O^+$$

$$HA_2 + H_2O \longrightarrow A_2^- + H_3O^+$$

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

Either a mixture of two acids, HA_1 of concentration C_1 and HA_2 of concentration C_2.

$$[H_3O^+] = [A_1^-] + [A_2^-] + [OH^-]$$

1st approximation $[OH^-] << [H_3O^+]$ => $[H_3O^+] = C_1 + C_2$

$$\boxed{pH = - \log (C_1 + C_2)}$$

Note:

If $C_1 >> C_2$ ==> $pH = - \log C_1$

$C_2 >> C_1$ ==> $pH = - \log C_2$

b) A mixture of strong acid HA_1 and weak acid HA_2

$$HA_1 + H_2O \longrightarrow A_1^- + H_3O^+$$

$$HA_2 + H_2O \rightleftharpoons A_2^- + H_3O^+$$

The presence of H_3O^+ ions from the total dissociation of the strong acid downgrades the dissociation balance of the weak acid, making the amount of H_3O^+ from the weak acid ($HA_2 >> A_2^-$) even more negligible.

The pH of the mixture is then imposed by the strong acid hence: $[H_3O^+] = C_1$

$$\boxed{pH = - \log C_1}$$

c) A mixture of two weak acids, HA_1 and HA_2

$$HA_1 + H_2O \rightleftharpoons A_1^- + H_3O^+$$

$$HA_2 + H_2O \rightleftharpoons A_2^- + H_3O^+$$

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

$C_1 = [HA_1] + [A_1^-]$ $C_2 = [HA_2] + [A_2^-]$

$[H_3O^+] = [A_1^-] + [A_2^-] + [OH^-]$

$$K_{a1} = \frac{[A_1^-] x [H_3O^+]}{[HA_1]} \qquad K_{a2} = \frac{[A_2^-] x [H_3O^+]}{[HA_2]}$$

Approximations:

$[OH^-] <<< [H_3O^+]$ $[HA_1] \approx C_1$ and $[HA_2] \approx C_2$

$[A_1^-] = Ka_1\, C_1/ [H_3O^+]$ $[A_2^-] = Ka_2\, C_2/ [H_3O^+]$

$[H_3O^+]^2 = Ka_1C_1 + Ka_2C_2$

$$\boxed{\mathbf{pH = - \tfrac{1}{2} \log (Ka_1C_1 + Ka_2C_2)}}$$

Note:

If $Ka_1 >> Ka_2$ ***and*** $C_1 \approx C_2 \approx C$ $pH = \frac{1}{2}\, pKa_1 - \frac{1}{2} \log C$

$Ka_1 \approx Ka_2$ ***and*** $C_1 >> C_2$ $pH = \frac{1}{2}\, pKa - \frac{1}{2} \log C_1$

Example:

Calculate the pH of the solutions obtained by mixing equal volumes of the following 0.2 M solutions: $CH_3COOH + HCOOH$; $HCl + HClO_4$.
($HClO_4$: pKa = - 9.9; HCl: pKa= - 3.7; HCOOH: pKa = 3.8; CH_3COOH; pKa = 4.75)

Answer:

After mixing, the concentration of each of the compounds is equal to 0.1 M.

- **The mixture (HCOOH + CH_3COOH)**: these two acids are weak

$[H_3O^+]^2 = Ka_1C_1 + Ka_2C_2$

$[H_3O^+] = \sqrt{Ka_1C_1 + Ka_2C_2} = 10^{-2.37}$ M   pH = 2.4

- **The mixture (HCl+ $HClO_4$)**: these two strong acids (pKa < 0) are dissociated in water. The pH of the solution is calculated using the following formula.

pH = - log ($C_1 + C_2$) = - log (0.1 + 0.1) = - log 0.2 = 0.7.

5.3.2. Calculation of pH: Strong base

Strong bases have a pKa greater than 14 (NaOH, KOH) and therefore react almost totally with water to give OH^-.

Let C_b be the initial concentration of a strong base:

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

Total dissociation: $[BH^+] >> [B]$

The expression of the conservation of matter becomes $C_b= [BH^+]$

The electrical neutrality relationship $[BH^+] = [OH^-]$ (1st approximation).

Ultimately $[OH^-]= C_b$ and pOH = **-** log C_b

As pH + pOH = 14

$$\boxed{\mathbf{pH = 14 + \log C_b}}$$

Example:

Calculate the pH of the following solution: sodium hydroxide (NaOH) at 0.05M (pKa > 14).

Answer:

NaOH is a strong base so,

$$pH = 14 + \log C_b = 14 + \log 0.05 = 14-1.3 = 12.7$$

5.3.2.1. Calculation of pH: Weak base and little dissociated ($[BH^+] << [B]$)

Two balances coexist:

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

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

The species present are B, BH^+, OH^-, H_3O^{+}, and H_2O.

There are between their concentrations the relationships:

- mass action law: $Kb = [BH^+]\,[OH^-] / [B]$

  and $K_w = [H_3O^+] \times [OH^-]$

- Electrical neutrality of the solution: $[H_3O^+] + [BH^+] = [OH^-]$

- Balance mass: $C_b = [BH^+] + [B]$

If the reaction of base B in water is exceptionally low ($[BH^+] << [B]$ 2nd approximation)

$C_b = [B]$ and as $[OH^-] = [BH^+]$ (1st approximation),

The basicity constant gives:

$$K_b = [OH^-]^2 / C_b$$

hence $[OH^-] = (K_b \cdot C_b)$ ½

Thus $pOH = ½\,(pK_b - \log C_b)$.

Hence the relationship

$$\boxed{pH = 7 + ½\, pK_a + ½ \log C_b}$$

Example:

Calculate the pH of the following solution: 0.2 M ammonia (NH_3) ($pK_a > 9.25$).

Answer:

NH_3 is a weak base so

$$pH = 7 + ½\, pK_a + ½ \log C_b = 7 + 4.625 - 0.35 = 11.275$$

5.3.2.2. Calculation of pH: Mixture of two bases

The reasoning for calculating the pH of base mixtures will be identical to that adopted in the case of acid mixtures:

a) A mixture of two strong bases B_1 and B_2

$$B_1 + H_2O \longrightarrow B_1H^+ + OH^-$$
$$B_2 + H_2O \longrightarrow B_2H^+ + OH^-$$

Either a mixture of two bases B_1 of concentration C_1 and B_2 of concentration C_2.

The approximation

$$[H_3O^+] << [OH^-]$$

$$\Rightarrow \quad [OH^-] = C_1 + C_2$$

The equation is established by replacing pH with pOH

$\Rightarrow pH + pOH = pK_w = 14$

$pOH = - \log (C_1 + C_2)$

$$\mathbf{pH = 14 + \log (C_1 + C_2)}$$

Note:

If $C_1 >> C_2 \implies pH = 14 + \log C_1$

$C_2 >> C_1 \implies pH = 14 + \log C_2$

b) A mixture of strong base B_1 and weak base B_2

$$B_1 + H_2O \longrightarrow B_1H^+ + OH^-$$
$$B_2 + H_2O \rightleftharpoons B_2H^+ + OH^-$$

The presence of OH^- ions from the total dissociation of the sturdy base B_1 downgrades the dissociation equilibrium of the weak base, making the amount of OH^- from the weak base B_2 even more negligible.

The pH of the mixture is then imposed by the strong base hence: $[OH^-] = C_1$

$$\boxed{\mathbf{pH = 14 + \log C_1}}$$

c) A mixture of two weak bases, B_1 and B_2

$$B_1 + H_2O \rightleftharpoons B_1H^+ + OH^-$$

$$B_2 + H_2O \rightleftharpoons B_2H^+ + OH^-$$

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

The equations are established by replacing pH with pOH and Ka with K_b

$pH + pOH = pK_w = 14$

$pKa + pK_b = 14$

$pOH = -\tfrac{1}{2}\log(K_{b1}C_1 + K_{b2}C_2)$

$$\boxed{\mathbf{pH = 14 + \tfrac{1}{2}\log(K_{b1}C_1 + K_{b2}C_2)}}$$

Note:

If $K_{b1} \gg K_{b2}$ *and* $C_1 \approx C_2 \approx C$ $\quad pH = 7 + \tfrac{1}{2}pK_{a1} + \tfrac{1}{2}\log C$

$K_{b1} \approx K_{b2}$ *and* $C_1 \gg C_2$ $\quad pH = 7 + \tfrac{1}{2}pK_a + \tfrac{1}{2}\log C_1$

Example:

Calculate the pH of the solutions obtained by mixing equal volumes of the following 0.2 M solutions: NH_3 and KOH; NaOH and KOH.

NH_3 : (pKa = 9.25); KOH: (pKa > 14); NaOH: (pKa > 14).

Answer:

After mixing, the concentration of each of the compounds is equal to 0.1 M.

- **NaOH + KOH**: these two strong bases are dissociated in water. The pH of the solution is calculated using the following formula.

$$pH = 14 + \log (C_{NaOH} + C_{KOH})$$
$$= 14 + \log (0.1+0.1) = 14 + \log 0.2$$
$$pH = 13.3$$

- **NH_3 + KOH**: NH_3 is a weak base and KOH is a strong base. The pH of the solution is calculated using the following formula.

$$pH = 14 + \log C_{KOH}$$
$$= 14 + \log 0.1$$
$$pH = 13$$

5.3.3. Ionization of polyprotic acids

Acids with more than one acidic hydrogen ionize in steps.

An ionization-constant expression may be written for each step.

The dissociation equilibria of H_2A are written :

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+ \qquad K_{a_1} = \frac{[HA^-] \text{x} [H_3O^+]}{[H_2A]}$$

$$HA^- \rightleftharpoons A^{2-} + H_3O^+ \qquad K_{a_2} = \frac{[A^{2-}] \text{x} [H_3O^+]}{[HA^-]}$$

The methods used for calculating the pH of solutions contaning various combinations of the species H_2A, HA^- , and A^{2-} from the ionization constants are summarized as follows :

a) A solution containing H_2A, or $H_2A + HA^-$

If $K_{a1} << K_{a2}$, the second ionisation will have very little effect and can be ignored. The pH of thesolution is calculated from the K_{a1} expression.

b) A solution containing HA^-

Here both ionizations affect the composition of the solution and must be considered. In the second ionization, $[H^+]$ is not equal to $[A^{2-}]$ because some H^+ combines with HA^- to form H_2A. Therefore,

$$[A^{2-}] = [H^+] + [A_2H]$$

$$K_{a2} = \frac{\left[A^{2-}\right] x \left[H_3O^+\right]}{\left[HA^-\right]} \qquad \left[A^{2-}\right] = \frac{K_{a2}\ x \left[HA^-\right]}{\left[H_3O^+\right]}$$

Equating the right sides of these two equations,

$$[H_3O^+] + [A_2H] \quad = \frac{K_{a2}\ x \left[HA^-\right]}{\left[H_3O^+\right]}$$

We can replace $[A_2H]$ with a quantity obtained from the K_{a1} expression:

$$\left[H^+\right]^2 = \frac{K_{a1}\ K_{a2}\ x \left[HA^-\right]}{\left[HA^-\right] + K_{a1}}$$

At usual concentrations, $[HA^-]$ will generally be much larger than K_{a1}.

$$\left[H^+\right]^2 = \frac{K_{a1}\ K_{a2}\ x \left[HA^-\right]}{\left[HA^-\right]} = K_{a1}K_{a2}$$

$$\mathbf{[H_3O^+]} \quad = \quad \sqrt{K_{a1}\ K_{a2}}$$

$$\boxed{\mathbf{pH} = \frac{pK_{a1}+pK_{a2}}{2}}$$

c) A solution containing HA^- + A^{2-}

If K_{a1} is 100 times or more greater than K_{a2} ($K_{a1} << K_{a2}$), there will very little H_2A in the solution at equilibrium, and the first ionization-constant didn't need to be used. The pH is very easily by using the K_{a2} expression.

Example:

Calculate the pH of a 0.15 M solution of malonic acid $CH_2(COOH)_2$. The ionization constant for malonic acid are $K_{a1} = 1.4 \times 10^{-3}$ and $K_{a2} = 2.2 \times 10^{-6}$.

Answer:

K_{a1} is enough larger than K_{a2} that the second ionization can be safely ignored and the pH calculated only from the K_{a1} expression.

Note that K_{a1} is large enough that the equilibrium concentration of malonic acid(H_2A) must be taken as 0.15- $[H^+]$.

$$K_{a_1} = \frac{[HA^-] \text{x} [H_3O^+]}{[H_2A]}$$

$$K_{a_1} = \frac{[H_3O^+]^2}{0.15 - [H^+]}$$

$$[H_3O^+] = 1.38 \text{ x } 10^{-2} \longrightarrow \quad pH = 1.86$$

5.4. Neutralization reaction

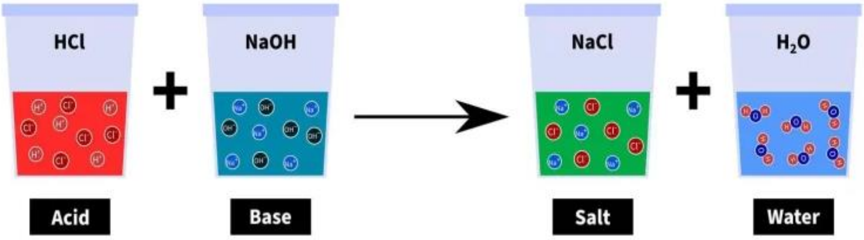
The action of an acid on a (hydroxylated) base is a neutralization that leads to the formation of a salt in water.

$$\textbf{Acid + Base} \longrightarrow \textbf{Salt + Water}$$

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow NaCl + H_2O$$

$$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COONa + H_2O$$

Neutralization is used to change the pH of a medium



5.5. Salt hydrolysis

AB salt is the product of the reaction between an HA acid and a BOH base.

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

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

Salt Water

- Action of water on A^-: $A^- + H_2O \rightleftharpoons HA + OH^-$

  The hydrolysis constant: $K_h = \frac{[HA] \text{ x } [OH^-]}{[A^-]} = K_b$

- Action of water on BH^+: $BH^+ + H_2O \rightleftharpoons B + H_3O^+$

$$\boxed{K_h = \frac{[B] \text{ x } [H_3O^+]}{[BH^+]} = K_a}$$

Note:

Hydrolysis of salts results in a change in pH. When we introduce a salt into a solvent (water), we have:

- Destruction of the crystalline network

- Reaction between these ions and the solvent: hydrolysis

Since the AB salt is an ionic compound, in aqueous solution, it is completely dissociated into A^- and B^+ ions.

Example:

$$NH_4Cl + H_2O \longrightarrow NH_4^+ + Cl^-$$

To determine the pH of a salt, it must be broken down into ions. When the dissociation is done, look at which category these ions fall into (strong acid, weak, bases..). This classification will make it possible to see on which element the acidity and therefore the pH depends.

The pH always depends on the "strongest" substance.

The parameters that can influence hydrolysis are the concentration and strength of the electrolyte.

a) According to Oswald's dilution law, dissociation is even more important when the solution is diluted. The lower the concentration of the solution, the more it is hydrolyzed.

b) Influence of the strength of the acid or base: a salt is all the more hydrolyzed as the acid HA (or base B) is weaker.

5.5.1. Strong acid and strong base salt

Either the KCl salt, in aqueous solution, the salt is dissociated into K^+ and Cl^- ions.

$$KCl \xrightarrow{H_2O} K^+_{(aq)} + Cl^-_{(aq)}$$

$[K^+]$ and $[Cl^-]$ do not influence the medium. They are inert (spectator ions). pH is determined by water. However, the pH of water is 7.

5.5.2. Strong acid and weak base salt

Example:

$$NH_4Cl + H_2O \longrightarrow NH_4^+ + Cl^-$$

Cl^-: is a neutral base

NH_4^+: conjugate acid of weak base NH_3

$$\begin{array}{lccccc} & NH_4^+ & + & H_2O \longrightarrow & NH_3 & + H_3O^+ \\ t=0 & C & & & 0 & 0 \\ t\ eq & C(1-\alpha) & & & C\alpha & C\alpha \end{array}$$

$$K_a = \frac{[NH_3] x [H_3O^+]}{[NH_4^+]} = \frac{[H_3O^+]^2}{Cs}$$

$$\boxed{\mathbf{pH = ½ \, (pK_a - \log C_s)}}$$

5.5.3. Weak acid and strong base salt

Example:

Weak acid: acetic acid (CH_3COOH)

Strong base: sodium hydroxide (NaOH)

Salt: Sodium acetate (CH_3COONa)

$$CH_3COONa + H_2O \longrightarrow CH_3COO^- + Na^+ \quad \text{(ionization)}$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \quad \text{(hydrolysis)}$$

$$K_b = \frac{[CH_3COOH] \times [OH^-]}{[CH_3COO^-]}$$ where $[CH_3COO^-]_{eq} = [OH^-]_{eq}$

$CH_3COO^- = CH_3COONa = Cs$ $$K_b = \frac{[OH^-]^2}{Cs}$$

$$\boxed{\mathbf{pH = 7 + \tfrac{1}{2}\, pK_a + \tfrac{1}{2} \log C_s}}$$

5.5.4. Weak acid and weak base salt

Example: Weak acid: CH_3COOH

Weak base: NH_3

Salt: Sodium acetate (CH_3COONH_4)

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$CH_3COONH_4 + H_2O \longrightarrow CH_3COO^- + NH_4^+ \text{ (ionization)}$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \text{ (hydrolysis)}$$

$$NH_4^+ + CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + NH_3$$

$$K_b = \frac{[CH_3COOH] \times [OH^-]}{[CH_3COO^-]}$$

$$K_a = \frac{[NH_3] \times [H_3O^+]}{[NH_4^+]}$$

$[CH_3COO^-]_{eq} = [NH_4^+]$

$[CH_3COOH] = [NH_3]$

$$\frac{K_a}{K_b} = \frac{[H_3O^+]}{[OH^-]} \quad ==> \quad \frac{K_a}{K_b} = \frac{[H_3O^+]^2}{Ke}$$

$$\boxed{\mathbf{pH = 7 + \tfrac{1}{2}\, pK_a - \tfrac{1}{2} \log pK_b}}$$

The pH of a weak acid and a weak base does not depend on the concentration.

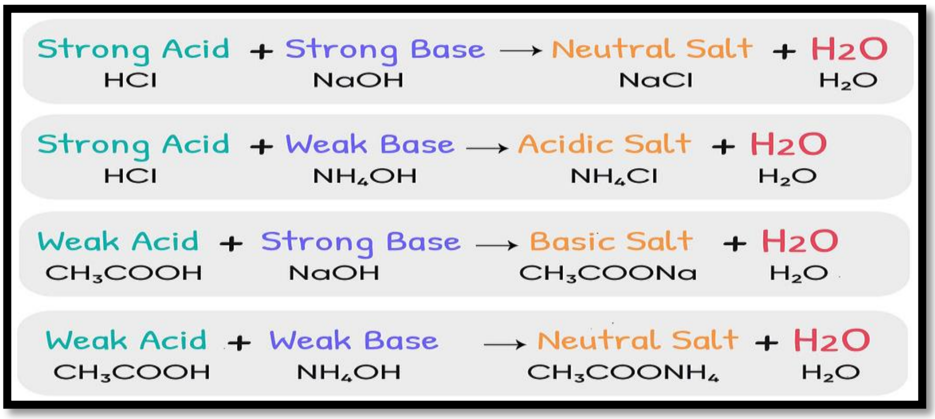
The easiest method to remember which cations/anions relate to acidic /basic salts is:

- a salt is always the product of an acid-base neutralization reaction;
- you must first derive the parent acid and parent base of the salt in order to use this chart;
- the cation of the salt is always from the base of the neutralization reaction, and the anion of the salt is always from the acid of the neutralization reaction;
- Then, determine whether the parent acid and parent base are strong or weak.

Example:

In an aqueous solution, NH_4Cl dissociates to form NH_4^+ and Cl^-. These ions are derived from the parent weak base (NH_3) and parent strong acid (HCl), respectively. Based on the above chart, the neutralization reaction between a weak base and strong acid yields an acidic salt.

Exemples:



Strong Acid + Strong Base ⟶ Neutral Salt + H_2O
HCl NaOH NaCl H_2O

Strong Acid + Weak Base ⟶ Acidic Salt + H_2O
HCl NH_4OH NH_4Cl H_2O

Weak Acid + Strong Base ⟶ Basic Salt + H_2O
CH_3COOH NaOH CH_3COONa H_2O

Weak Acid + Weak Base ⟶ Neutral Salt + H_2O
CH_3COOH NH_4OH CH_3COONH_4 H_2O

5.6. Buffer solution

5.6.1. Definition

A Buffer is a compound or mixture that, when added to a solution, helps maintain a specific pH.

A buffer solution is made by mixing appropriate amounts of a weak acid and its salt of strong base or a mixing of a weak base and its salt of strong acid.

Example:

CH_3COOH and $CH_3COO^-Na^+$ is acidic buffer because it is a mixture of weak acid (CH_3COOH) and its salt ($CH_3COO^-Na^+$) with strong base (NaOH).

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

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \text{ (hydrolysis)}$$

The CH_3COOH is a weak acid, CH_3COO^- in solution reverses its ionization. Similarly, CH_3COOH reduces the hydrolysis of CH_3COO^-.

- An acidic buffer solution (3-7) is composed of a weak acid and a strong base salt of that acid.
- A basic buffer solution (7-11) is composed of a weak base and a strong acid salt of this base.

5.6.2. pH of a buffer solution

The pH of a buffer solution is determined by the pKa of the acid present and the ratio of the concentrations of the acid and its conjugate base.

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

t_0	C_a	C_{salt}	
t_{eq}	$C_a\,(1-\alpha)$	$C_{salt} + C_a\alpha$	$C_a\alpha$

$[CH_3COO^-] = C_b$

$[CH_3COOH] = C_a$

The acidity constant of acetic acid

$$K_a = \frac{[CH_3COO^-] x [H_3O^+]}{[CH_3COOH]}$$

$$[H_3O^+] = \frac{[CH_3COOH] x K_a}{[CH_3COO^-]} \quad ==> \quad [H_3O^+] = \frac{Ca \text{ x } Ka}{Cb}$$

$$pH = -\log [H_3O^+] \quad ==> \quad pH = -\log K_a + \log \frac{Cb}{Ca}$$

$$\boxed{pH = pK_a + \log \frac{[\text{conjuguate base}]}{[\text{acid}]}}$$

5.6.3. Ownership of a buffer solution

- A buffered solution resists large changes in pH that otherwide would occur if the solution were diluted or if either a strong acid or a strong base were added to the solution.
- pH = pKa, maximum buffering capacity corresponds to an equimolar mixture of the weak acid and its conjugate base.
- Buffers are very important in many chemical and biochemical systems

Example 1:

A solution containing 0.4 M of formic acid HCOOH and 0.1 M of its conjugate base HCOONa with pKa = 3.8.

This buffer solution has a $pH = pKa + \log \frac{[HCOO^-]}{[HCOOH]}$

$$pH = 3.8 + \log \frac{0,1}{0,4} = 3.19$$

5.7. pH Indicators

pH indicators are substances that are added to the acid-base solutions to be assayed to visually identify the equivalent volume during an assay.

A colored indicator is a weak organic acid or base whose undissociated molecules have a distinct color from their ions.

These colored indicators are substances that are often of overly complex formula but can be schematized by the formula HIn, namely the formula of a weak acid.

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-.$$

For the formula indicator HIn, we will have the existence of an acidity constant Ka:

$$\boxed{K_a = \frac{[H_3O^+].[In^-]}{[HIn]}}$$

We will then have a pKa for the colored indicator.

A colored indicator is chosen when its conjugate base In- is of an assorted color from the acid form HIn.

With bromothymol blue, the HIn form is yellow and the In- form is blue.

In the case of phenolphthalein, the HIn form is colorless and the In- form is pink.

For pH values of a solution < pKa indicator -1, the HIn form is the majority.

For pH values > pKa indicator +1, the In- form is the majority.

The pH zone, pK a indicator – 1< pH < and pK a indicator + 1, in which no color dominates, is called the turning zone.

❖ Main colored indicators

Table 5.1: Indicators and their colours in acid and alkaline solution.

Indicator Name	**pKa**	**pH transition range**	**"Color change".**
Methyl orange	3.4	$3.1 < pH < 4.4$	Red to yellow
Methyl red	5.2	$4.2 < pH < 6.2$	Red to yellow
Bromothymol blue (BTB)	7.3	$6.0 < pH < 7.6$	Yellow to blue
Phenolphthalein	8.7	$8.0 < pH < 10.0$	Colorless to pink

Note:

To choose the right color indicator, during an acid-base assay, the pH at equivalence should ideally be equal to the pK_a ***of the color indicator.***

- ***If a weak base (***NH_3***) is assayed with a strong acid (NaOH), in this case, the equivalent point for*** $C=10^{-2}$ ***mol/L is located at*** $pH = ½ (pKa-\log_{10} C) = 5.6$***. Thus, methyl red is the most suitable.***
- ***If a strong acid (HCl) is assayed by a strong base (NaOH), the equivalent point is pH= 7, among the three indicators mentioned in the table, the choice will preferably be on the BTB.***

5.8. Neutralisation of an acid by a base

When an acid and a base are mixed, the H_3O^+ ions of the acid react with the OH^- ions of the base. Neutralization is complete if the ion concentrations are equivalent.

Table 5.2: pH Levels at the Equivalence Point.

Strength of Acid and Base	**pH Level**
Strong Acid-Strong Base	7
Strong Acid-Weak Base	< 7
Weak Acid-Strong Base	> 7
Weak Acid-Weak Base	pH < 7 if Ka > Kb pH =7 if Ka = Kb pH >7 if Ka < Kb

5.8.1. Neutralization of a strong acid by a strong base

Consider the titration of a strong HCl acid by a strong NaOH base.

$$\begin{array}{llll} & HCl + & NaOH \longrightarrow & Na^+ Cl^- + H_3O^+ + OH^- \\ t_0 & n_a & n_b & 0 \\ & C_a V_a & C_b V_b & \end{array}$$

$n_b = C_b V_b$ moles of OH^- are added to $n_a = C_a V_a$ moles of H_3O^+.

- **Before neutralization**:

$C_a V_a > C_b V_b$ H_3O^+ in excess: strong acid medium: pH= -log $[H_3O^+]$ = -log Ca

$$\boxed{pH = -\log \frac{C_aV_a - C_bV_b}{V_a + V_b}}$$

- **Half-neutralization**: strong acid

$$\boxed{\frac{C_aV_a}{2} = C_bV_b}$$

- **Medium: pH = -log [H_3O^+]**

$$\boxed{pH = -\log \frac{C_aV_a}{2}}$$

- **At neutralization: point of equivalence:**

$C_a V_a = C_b V_b$ (number of moles of acid = number of moles of base).

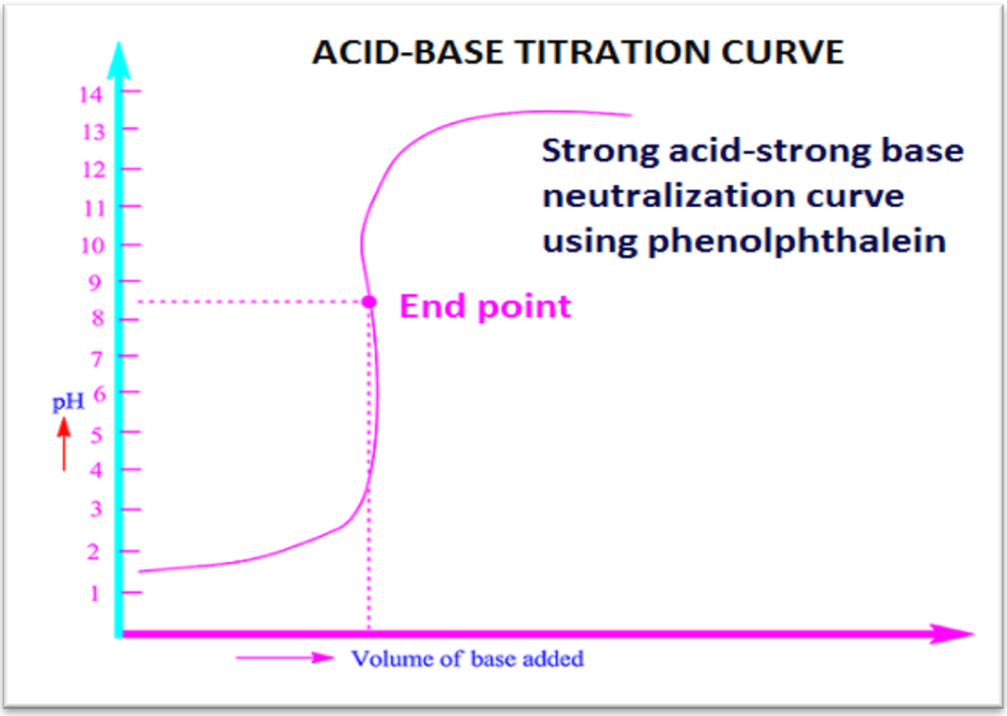
The medium is neutral: **$pH = pH_{salt} = pH_{water} = 7$**

- **After neutralization:**

$C_a V_a < C_b V_b$. strong base medium:

$$\boxed{pH = pK_w + \log \left[\frac{C_bV_b - C_aV_a}{V_a + V_b}\right]}$$

Figure 5.1: Neutralisation of a strong acid by a strong base.



5.8.2. Neutralisation of a weak acid by a strong base

Consider dosing a CH_3COOH weak acid with a strong NaOH base.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

The pH of the starting weak acid medium is calculated by the relationship:

$$pH = 1/2\ (pK_a - \log C_a)$$

- **Before neutralization**:

$C_a V_a > C_b V_b$ H_3O^+ in excess: weak acid medium:

$$\boxed{\mathbf{pH = pK_a + \log\ [\ C_aV_a - \frac{C_bV_b}{V_a + V_b}]}}$$

- **Half-neutralization:**

equimolar $\frac{C_aV_a}{2} = C_bV_b$ mixture of weak acid + its conjugate base = buffer solution:

$$\boxed{\mathbf{pH = pK_a + \log\ [\frac{C_bV_b}{C_aV_a}] = pK_a}}$$

- **At neutralisation: point of equivalence:**

$C_a V_a = C_b V_b$ mixture is weak base $C_{salt} = \frac{C_aV_a}{V_a + V_b}$

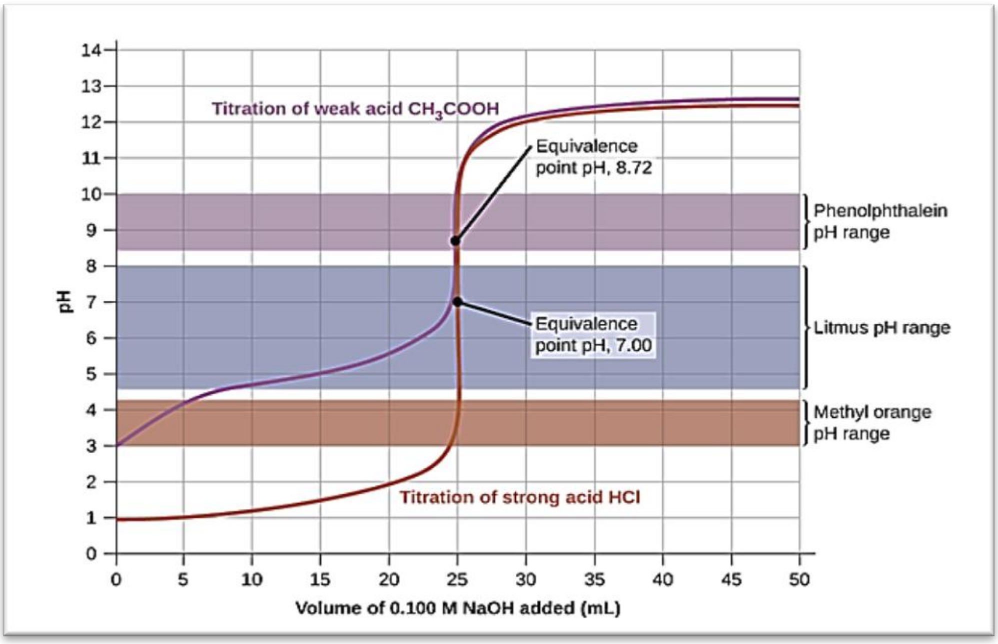
$$\boxed{\mathbf{pH = ½\ (14 + pK_a + \log C_{salt})}}$$

- **After neutralization:**

$C_a V_a < C_b V_b$. strong base medium:

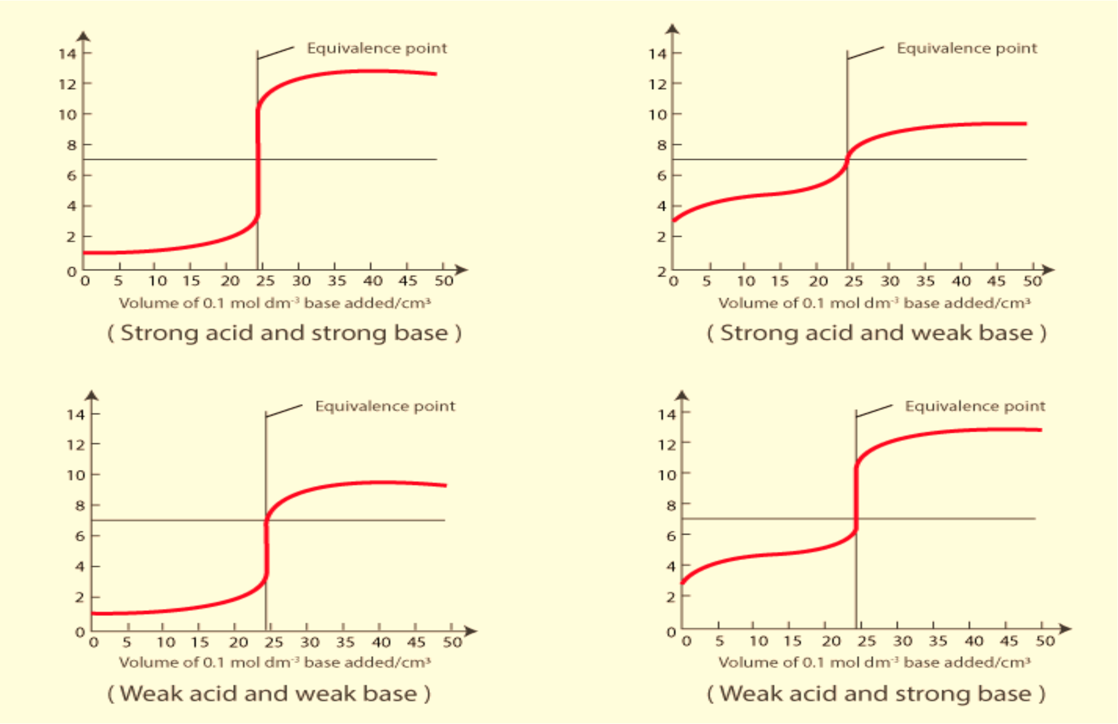
$$\boxed{\mathbf{pH = pK_w + \log\ [\frac{C_bV_b - C_aV_a}{V_a + V_b}]}}$$

Figure 5.2: Neutralisation of a weak acid by a strong base.



The titration curves below show how the pH changes with added volumes of a base to an acid, for strong and weak acid-base reactions.

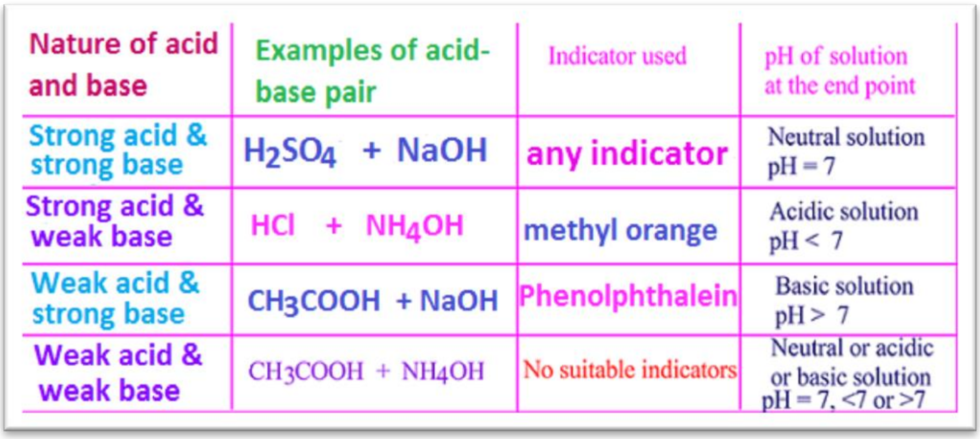
Figure 5.3 : Titration curve-equivalence point.



(Strong acid and strong base) (Strong acid and weak base)

(Weak acid and weak base) (Weak acid and strong base)

Table 5.3: A list of indicators those used for different types of acid-base neutralization reactions.



Nature of acid and base	Examples of acid-base pair	Indicator used	pH of solution at the end point
Strong acid & strong base	H_2SO_4 + NaOH	any indicator	Neutral solution pH = 7
Strong acid & weak base	HCl + NH_4OH	methyl orange	Acidic solution pH < 7
Weak acid & strong base	CH_3COOH + NaOH	Phenolphthalein	Basic solution pH > 7
Weak acid & weak base	CH_3COOH + NH_4OH	No suitable indicators	Neutral or acidic or basic solution pH = 7, <7 or >7

5.9. Exercise

Exercise 1:

A solution A of nitric acid HNO_3 with a concentration of 18M is available.

1. What volume of this solution should be used to prepare 500 mL of a 5 M HNO_3 (solution B).
2. We have now a 0.02 M of HNO_3 solution C with a volume of 4 litres.

In what proportion should solutions B and C be mixed to obtain 4 litres of HNO_3 0.5 M (solution D) ?

Answer:

1. $M_1V_1 = M_2V_2$

V_1 = volume of solution A V_2 = volume of solution B

M_1 = molarity of the solution A M_2 = molarity of the solution B

$$V_1 = \frac{M_2 \text{ x } V_2}{M_1} = \frac{5 \text{ x } 500}{18} = 139 \text{ml}$$

2. $V_B + B_C = V_D$ $B_C = V_D - V_B$

$$V_B \text{ x } C_B + V_C \text{ x } C_C = V_D x C_D$$

$$V_B \text{ x } C_B + (V_D - V_B) \text{ x } C_C = V_D \text{ x } C_D$$

$$V_B \text{ x } C_B + V_D \text{ x } C_C - V_B \text{ x } C_C = V_D \text{ x } C_D$$

$$V_B (C_B - C_C) = V_D (C_D - C_C)$$

$$V_B = \frac{V_D (C_D - C_C)}{C_B - C_C} \qquad V_B = \frac{4000(0{,}5 - 0{,}02)}{5 - 0{,}02}$$

$V_B = 387.9$ mL $\quad V_C = 3612.1$ mL

Exercise 2 :

A commercial solution of hydrochloric acid with a density d = 1.19 and containing 37% by mass of HCl acid is considered. Molar mass of HCl = 36.5 g/mol.

1. Calculate the molar concentration of this commercial hydrochloric acid solution
2. What volume should be taken from this commercial solution to prepare 1 litre of a dilute hydrochloric acid solution with a concentration of 0.1 mol/L.
3. Calculate the pH of the dilute HCl solution.

Answer:

1. The density of the solution is d = 1.19

$\rho = 1190$ g/dm^3, so: 1 litre of a solution weighs 1190 g.

The mass m of HCl contained in 1 litre of solution is: $\boldsymbol{m = \frac{1190 \text{ x } 36.5}{100}}$

m = 434.35 g HCl.

The number of moles n of HCl contained in 1 litre of a solution is $\boldsymbol{n = \frac{434.35}{36.5}}$

n = 11.9 moles, therefore: the concentration of this solution is 11.9 M.

2. $C_i \, V_i = C_f . V_f$

C_i = concentration of the stock solution = 11.9 M

V_i = volume of the stock solution = ?

C_f = concentration of the diluted solution = 0.1 M

V_f = volume of the diluted solution = 1000 mL

$$\boldsymbol{V_i = \frac{Cf . Vf}{Ci} = \frac{0.1 . 1000}{11.9}} \quad \text{hence : } V_i = 8.4 \text{ mL}$$

3. HCl is a strong acid in the medium not too diluted.

$$\text{pH} = -\log [H_3O^+] = -\log 0.1, \text{ hence: pH} = 1.$$

Exercise 3:

1. Nitric acid HNO_3 is a strong acid. We will take T = 298 K

a. Write the equation of its reaction with water.

b. Dissolve 2.0×10^{-4} moles of nitric acid in 100 cm^3 of pure water; what is the pH of the solution obtained?

2. Perchloric acid $HClO_4$ is a strong acid.

0.12×10^{-4} moles of perchloric acid are dissolved in 100 L of pure water; what is the *p*H of the solution obtained?

Answer:

$$\mathbf{HNO_3 + H_2O \rightarrow NO_3^- + H_3O^+}$$

the reaction of HNO_3 with water is total.

b. $C = 2.0 \times 10^{-4}/100 \times 10^{-3} = 2{,}0 \times 10^{-3}$ mol.L^{-1} $> 10^{-6{,}5}$.

We use the relationship: pH = - log C therefore pH = 2.7.

2. $C = n/V = 0.12 \times 10^{-4}/100$

$= 1.2 \times 10^{-7}$ mol.L^{-1} $< 10^{-6{,}5}$

we cannot use the relation $pH = -\log C$.

For perchlorate ions: $[ClO_4^-] = C = 1.2 \times 10^{-7}$ mol/L

Electro-neutrality: $[H_3O^+] = [ClO_4^-] + [OH^-]$

Or $[H_3O^+] \times [OH^-] = 10^{-14}$.

We deduce:

$$[H_3O^+]^2 - 1.2 \times 10^{-7} [H_3O^+] - 10^{-14} = 0$$

The only positive solution gives:

$$[H_3O^+] \approx 1.8 \times 10^{-7} \text{ mol/L}$$

hence pH = 6.8

Exercise 4:

Calculate the pH variation in the following two cases:

a) 0.1 mole of HCl is added to one litreof water,

b) 0.1 mole of HCl is added to one litreof a solution containing a mixture 1M of acetic acid (CH_3COOH) and 1M of sodium acetate (CH_3COONa).

Answer

a) The initial pH of pure water equal to 7, after addition of HCl, the solution contains 0.1 mole of H_3O^+ its pH equal to (– log C).

$$pH = - \log C = - \log 0.1 = 1$$

The pH therefore varied by 6 units.

b) Mixture of 1M acetic acid (CH_3COOH) and 1M sodium acetate (CH_3COONa).

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = 4.75 + \log 1 = 4.75$$

$pH = 4.75 + \log \frac{1,1}{0,9} = 4.66$ The pH therefore varied by 0.09 unit, which is negligible.

Exercise 5:

One litre of 0.02 M sodium hydroxide (NaOH) solution is available.

1. Calculate its pH.

2. Add 2.14 g of NH_4Cl to 1 litre of the solution A. Calculate the pH of this new solution.

$pK_{a\ (NH4+/\ NH3)} = 9.25$; $M_{\ NH4Cl} = 53.5$ g/mol

Answer

1. Since NaOH is a strong base, its pH is given by the relationship: $pH = 14 + \log C_0$

$pH = 14 + \log 0.02 = 12.3$

2. NaOH reacts quantitatively with NH_4^+ according to the reaction:

The initial mole number of NH_4Cl is m/ M = 2.14/53.5 = 0.04 moles

$$\begin{array}{ccccc} NaOH & + NH_4^+ & \rightleftharpoons & NH_3 & + H_2O + Na^+ \\ 0.02\ mol & 0.04\ mol & & & \end{array}$$

After the reaction, we will have 0.04 - 0.02 = 0.02 mole of NH_4^+ and 0.02 mole of NH_3.

A mixture of a weak NH_3 base with its conjugate NH_4^+ base constitutes a buffer solution.

Its pH is given by the following relationship:

$$pH = pKa + \log \frac{[NH_3]}{[NH_4^+]} \qquad pH = pKa = 9.25$$

Exercise 6:

1. A solution contain 6.1 g/L of benzoic acid C_6H_5COOH, the Ka for benzoic acid is $10^{-4.2}$.
   Calculate the pH. $M_{(C6H5COOH)} = 122$ g/L
2. A solution contain 0.2 M of pyridine, the $K_b = 1.5 \times 10^{-9}$. Calculate the pH.

Answer:

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

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

The concentration of free benzoic acid HA must be expressed as molarity. To do this, divide the number of grams per litreby the formula weight :

$$[AH] = \frac{6.1}{122} = 0.05 \text{ M}$$

Because $[A^-] = [H^+]$, the numerator of Ka expression is $[H_3O^+]^2$

$$K_a = \frac{[H_3O^+]^2}{[HA]}$$

$$[H_3O^+] = \sqrt{Ka\, x [HA]}$$

$$= \sqrt{10^{-4.2}\, x\, 0.05} = 2.24\ 10^{-3.1} \text{ M}$$

$pH = - \log [H_3O^+] = 2.75$

2. $$K_b = \frac{[OH^-]^2}{C}$$

$[OH^-] = \sqrt{Kb\ x\ C} = \sqrt{0.2\ x\ 1.5\ 10^{-9}} = 1.7 \text{ x } 10^{-5}$

pOH = 4.76

pH + pOH = 14

pH = 14 - 4.76 = 9.24.

Exercise 7:

Consider a commercial solution of sulphuric acid H_2SO_4 with a specific gravity of 1.84 and a mass percentage of 95%. (Molar mass of H_2SO_4 = 98 g/mol).

1. Calculate the mass concentration, molarity and normality of the commercial solution.
2. What volume must be taken from the commercial solution to prepare 10 litres of a dilute 0.05N sulphuric acid solution?
3. Calculate the pH of the dilute solution thus prepared.
4. Mix 500 mL of a 0.025 mol/L sulphuric acid solution with 200 mL of a 0.45 mol/L sulphuric acid solution. What is the pH of the solution obtained ?

Answer:

d = 1,84 ⇒ mass of one litre of commercial solution = 1000 * 1,84 = 1840 g/L

% H_2SO_4= 95 ⇒ quantity of H_2SO_4 in one litre of commercial solution.

- the mass concentration = 1840*0,95 = 1840 g/L

- the molar concentration C ou M = 1748 /98 = 17,83 mol/L.

- Normality N = 17,83 * 2 = 35,66 eq /L.

2- Diluted Solution : Vi * 17,83 = 10 * 0,025 ⇒ Vi = 14 mL.

3- H_2SO_4 is a strong diacid ⇒ pH = - log (2*0,025) = 1,3

4- Vf = 500 + 350 = 850 mL

$n_t = M_1V_1 + M_2V_2$ = 0,5*0,025+ 0,2*0,45 = 0,1025 mol

$\Rightarrow M_f = nt / V_f = .01025/0,850 = 0,12$ M

Exercise 8:

Consider an ammonia solution containing 1.7g of NH_3 per litre. The basicity constant of NH_3 is given by K_b, its molar concentration is given by C and α its degree of dissociation.

1. Write down the dissolution reaction of NH_3 in water.
2. Establish the relationship between C, Kb et α .
3. Knowing that the acidity constant of the couple NH_4^+/NH_3 is $5\ 10^{-10}$, determine the value of α for this solution (use the necessary approximations).
4. Calculate the pH of this solution.
5. A volume 20 mL of the ammonia solution is neutralised with a 0.2 N HCl solution..
   - a- Write down the overall neutralisation reaction.
   - b- What volume of HCl solution must be added to reach equivalence ?
   - c- Calculate the pH value of the mixture at equivalence.

Answer:

1. The dissolution reaction NH_3 in water :

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

2. The relationship between the dissociation coefficient α and the concentration C and the basicity constant K_b : $\alpha = NH_4^+] /C = [OH^-] / C$

$$K_b = [NH_4^+][OH^-] / [NH_3] = C\alpha^2 / 1-\alpha$$

3. In the case of a weak base with little dissociation: $(\alpha << 1) \Rightarrow K_b = C\alpha^2$

$$\Rightarrow \alpha = \sqrt{Kb/C}$$

$K_b = K_w/K_a = 10^{-14}/10^{-9,2} = 10^{-4,8}$ and C= 0,1M $\Rightarrow \alpha = 0,013$ or 1,3%

4. pH = 7 + ½ pKa+ ½ logC =7 + 9,2 / 2 + ½ log (0,1) =11,1

5. $NH_3 + HCl \rightarrow NH_4Cl + H_2O$

$C_{HCl}\, V_{HCl} = C_{NH3}\, V_{NH3} \Rightarrow V_{HCl} = 0,1*20/0,2 = 10$ mL

Species present in solution at the equivalent point : NH_4^+, Cl^-

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \Rightarrow \text{weak acid}$$

$\Rightarrow pH = ½\ pKa - ½\ [NH_4^+]$ $[NH_4^+] = 0,1*20/30 = 0,067M$

$pH = ½ \times 9,2 - ½ \log(0,067) = 5,2$

Chapter 6 Salts in Solution

6.1. Concept of solubility-saturation

The maximum amount of a substance that can be dissolved in a given volume of solvent is called solubility. A solution that has not reached its maximum solubility is called an unsaturated solution. This means that more solute could still be added to the solvent and dissolving would still occur. Once this limit is reached, the substance cannot dissolve further, marking the maximum solubility.

A solution that has reached the maximum solubility is called a saturated solution. If more solute is added at this point, it will not dissolve into the solution. Instead it will remain precipitated as a solid at the bottom of the solution.

Within the realm of water-soluble substances encountered in daily life, two common examples are sugar and table salt. Chemically, these substances dissolve in water through distinct processes.

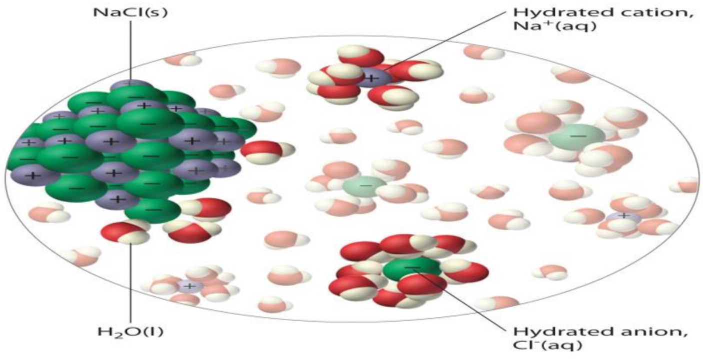
a) Ionic solutions

In the case of an ionic solution, the dissolution of the solute by the solvent leads to the formation of ions dispersed in this latter.

Example: Dissolution of sodium chloride (salt) in water

A grain of cooking salt (NaCl) is a small crystal consisting of Na^+ and Cl^- ions, linked by ionic bonds. When this grain of salt is dissolved in water, the ionic bonds are broken and the ions will be free in the solution, each being surrounded by water molecules, the ion is said to be *hydrated*.

$$NaCl_{(S)} \xrightarrow{water} Na^+_{(aq)} + Cl^-_{(aq)}$$



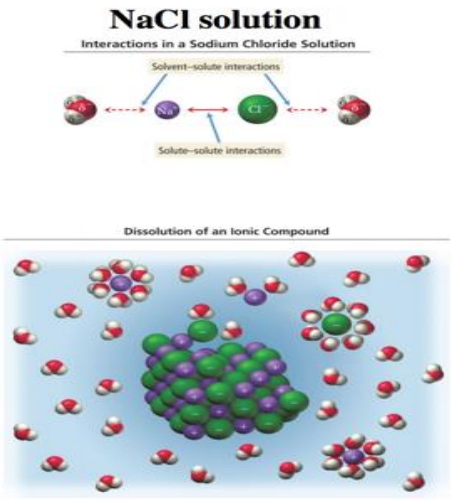
b) Molecular solutions

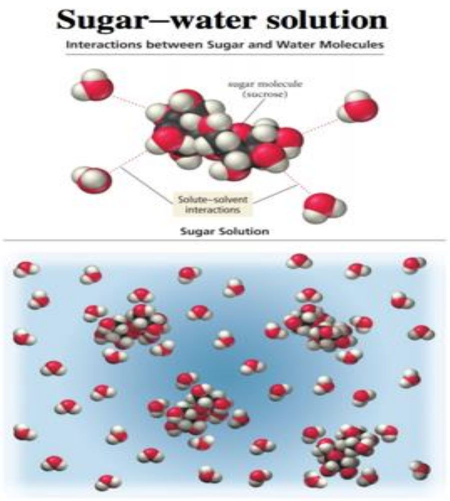
In the case of a molecular solution, the solute comprises molecules that disperse within the solvent without undergoing any modification.

***Example**:* Dissolution of glucose (sugar) in water

A sugar grain (*glucose*) is a small crystal consisting of molecules (of formula $C_6H_{12}O_6$) all of whose internal bonds are covalent. When this sugar grain is dissolved in water, each molecule is surrounded by water molecules and isolated from the other sugar molecules. The covalent bonds are not broken; each molecule remains whole.

$$C_6H_{12}O_{6\,(S)} \xrightarrow{\text{water}} C_6H_{12}O_{6\,(aq)}$$





6.2. Definition of solubility

The solubility S of a substance (a poorly soluble salt) is the maximum amount that can be dissolved in a given volume of solvent. This solubility can be expressed in:

- Gram of solute per litre of solution (g/L),
- Number of moles of solute dissolved in one litre of solution (mol/L).

A salt is considered poorly soluble if the maximum amount that can be dissolved is less than 10^{-2} mol/L.

Examples:

AgCl: S ≈ 10^{-5} mol/L, AgCl is said to be a very poorly soluble compound.
NaCl: S ≈ 6 mol/L, NaCl is said to be a very soluble compound.

- In a litre of pure water, you can dissolve:
  - 24 moles of solid $AgClO_4$
  - 0.00023 moles of solid AgCl

  $AgClO_4$ is said to be more soluble than AgCl

- Examples of the water solubility threshold of different chemical species, at a temperature of 20°C.

Novel compounds	**Copper sulphate**	**Calcium carbonate**	**Sodium chloride**
Solubility (g/l)	220	0153	360

Note:

Solubility concerns a solid in a liquid, but also a gas in a liquid (carbonated water for example) or a liquid in another liquid.

6.3. Solubility rules

The solubility rules make it possible to predict whether a compound is soluble or sparingly soluble.

1) Sodium, potassium, and ammonium salts are soluble (NaCl, KCl, NH_4OH).
2) The salts of nitrates, chlorates, and acetates are soluble (KNO_3, $NaClO_3$, and CH_3COONa).
3) Carbonates, chromates, and phosphates are insoluble, except for their salts with ammonium cations and alkali metal cations ($CaCO_3$, $PbCrO_4$, and Ag_3PO_4 are all insoluble while compounds like Na_3PO_4 and $(NH_4)_2CO_3$ are soluble).

4) Chloride, bromide, and iodide compounds are soluble, except for those of silver, lead, and mercury (I).

5) Most hydroxylated compounds are insoluble. The hydroxide salts formed with the elements of group 1 are an exception because these elements are still soluble ($Fe(OH)_3$, $Co(OH)_2$, and $Al(OH)_3$ are insoluble, but NaOH and LiOH are soluble.

6) Sulfate salts are soluble except their salts containing silver, lead, mercury (I), barium, strontium, and calcium ($CaSO_4$, $BaSO_4$….) are insoluble.

6.4. Solubility product K_{sp}

A solution in which maximum solubility is reached is said to be a: saturated solution. The system is then composed of two phases in equilibrium:

- a solid phase (undissolved solute)
- a liquid phase containing dissolved solute

Therefore, the study of precipitation dissolution equilibria is a direct application of the general laws of equilibria. The equilibrium constant in this case is called solubility product K_{sp}.

For a body of formula AnBm, following what we have seen for the equilibrium constants:

$$A_nB_{m\,(solid)} \rightleftharpoons n\,A^{m+}{}_{(aq)} + m\,B^{n-}{}_{(aq)}$$

By applying the mass action law to the ionization of A_nB_m, one can write the following formula:

$$\boxed{K_c = \frac{[A^{m+}]^n\,[B^{n-}]^m}{[A_nB_m]} = \frac{[A^{m+}]^n\,[B^{n-}]^m}{S}}$$

$K_{sp} = K_c \times S = [A^{m+}]^n \times [B^{n-}]^m = \text{constant}$

K_{sp} is called the solubility product constant.

$[A^{m+}]$ and $[B^{n-}]$ represent the ion concentrations at equilibrium (mol/L).

n and m correspond to the coefficients of each of the ions.

Note:

- The solubility product is dimensionless

- The solubility products have low values, often expressed as 10^{-x}, which justifies the frequent use of pK_{sp}.

$$pK_{sp} = -\log K_{sp} \quad \text{so} \quad K_{sp} = 10^{-pK_{sp}}$$

When K_{sp} is small (pK_{sp} is high), the salt is less soluble.

6.5. Relationship between solubility (S) and solubility product (K_{sp})

General case: the cation and the anion do not have the same valence A_nB_m.

Either the following balance:

	A_nB_m (solid)	$\rightleftharpoons$	$n\,A^{m+}$(aq)	$+\ m\,B^{n-}$ (aq)
t=0	x mol		0	0
$t_{equilibrium}$	(C-S) mol		n S mol	m Smol

$$K_{sp} = [A^{m+}]^n \times [B^{n-}]^m$$
$$= (nS)^n \times (mS)^m$$
$$= n^n\, m^m\, S^{n+m}$$

$$\boxed{S = \sqrt[n+m]{\frac{Ks}{n^n\ m^m}}}$$

Note:

A compound is characterized by its solubility product (K_{sp}) and not by its solubility (S).

Two special cases are most often encountered:

- ***The cation and the anion have the same valence,***
- ***One ion is monovalent and the other divalent.***

Example:

Calculate the solubility of silver chloride AgCl in water in moles per litre. The solubility product at 20 °C is 10^{-10}.

Answer : $AgCl\ (S) \rightleftharpoons Ag^+ + Cl^-$

$$K_{sp} = [Ag^+] \times [Cl^-]$$

Each mole of dissolved AgCl gives 1 moles of Ag^+ and 1 mole of Cl^-.

$$[Ag^+] = [Cl^-]$$

$$K_{sp} = [Ag^+]^2$$

$$[Ag^+] = \sqrt{K_{sp}} = 1.0 \times 10^{-5}\ M.$$

a) Salt type AB

Example 1:

- **Dissolution of AgI**

The solubility of silver iodide AgI is 1.2×10^{-8} mol/L at a certain temperature. Calculate its solubility in g/L and its solubility product.

$$AgI \rightleftharpoons Ag^+ + I^-$$

To calculate the solubility in g/L, we need the molar mass of AgI:

$$M = 107.9 + 126.9 = 234.8\ g/mol$$

We can therefore find the solubility in g/L:

$$S = C_{AgI} = 234.8 \cdot 1.2 \cdot 10^{-8} = 2.82 \cdot 10^{-6}\ g/L$$

The solubility product is:

$$K_{sp} = [Ag^+] = [I^-] = S^2$$

$$K_{sp} = S^2 = (1.2 \cdot 10^{-8})^2 = 1.44 \cdot 10^{-16}.$$

Example 2:

- **Dissolution of $CaSO_4$**

$$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$$

Solubility: $S = [Ca^{2+}] = [SO_4^{2-}]$

$K_{sp} = [Ca^{2+}] \times [SO_4^{2-}] = S^2$

$$\boxed{S = \sqrt{K_{sp}}}$$

b) Salt type A_2B or AB_2

Examples 1:

- **Dissolution of CaF_2**

$$CaF_2 \rightleftharpoons Ca^{2+} + 2\,F^-$$

$S = [Ca^{2+}] = ½\,[F^-]$

$K_{sp} = [Ca^{2+}] \times [F^-]^2 = 4S^3$

$$\boxed{S = \sqrt[3]{\frac{K_{sp}}{4}}}$$

Examples 2:

- **Dissolution of PbI_2**

$$PbI_2 \rightleftharpoons Pb^{2+} + 2\,I^-$$

Solubility: $S = [Pb^{2+}] = ½\,[I^-]$

Such that at equilibrium: $K_{sp} = [Pb^{2+}] \times [I^-]^2 = 4S^3$

$$\boxed{S = \sqrt[3]{\frac{K_{sp}}{4}}}$$

Examples 3:

- **Dissolution of Ag_2CrO_4**

$$Ag_2CrO_4 \rightleftharpoons 2\,Ag^+ + CrO_4^{2-}$$

$S = ½\,[Ag^+] = [CrO_4^{2-}]$

$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}] = 4S^3$

hence:

$$\boxed{S = \sqrt[3]{\frac{K_{sp}}{4}}}$$

6.6. Precipitation conditions

Consider the following equilibrium:

$$M_xX_y \rightleftharpoons x\,M^{y+}_{(aq)} + y\,X^{x-}_{(aq)}$$

In a solution with a concentration C of metal ions M^{y+}, the anion X^{x-} is gradually added to this solution.

The ionic product (P_i) is the product of the molar concentrations of the ions in the solution of a poorly soluble compound, affected by their exponent. Thus, as and when t increases, the program gets complicated for increasingly rare cases.

-When:

$$\boxed{P_i = [M^{y+}]^x\,[X^{x-}]^y < K_{sp}}$$

No precipitate; the solution is therefore not saturated

- When:

$$\boxed{P_i = [M^{y+}]^x\,[X^{x-}]^y = K_{sp}}$$

Precipitation limit, the solution obtained is a saturated solution and its concentration represents the solubility of the salt (S).

So the precipitation condition is:

$$\boxed{P_i = [M^{y+}]^x\,[X^{x-}]^y > K_{sp}}$$

6.7. Factors influencing solubility

6.7.1. External factors

Several factors influence solubility:

a) **Structure**: is what determines the polarity of the molecules of the substance.
b) **Pressure**: it greatly influencing the solubility of gases in liquids, but it has no influence on the solubility of solids; its increase increases the solubility of gases.
c) **Temperature**: since most dissolution processes are endothermic, an increase in temperature increases the solubility of solids but decreases the solubility of gases.

6.7.2. Internal factors

a) **Relative ion volume**: Salts with ions of neighbouring radius are poorly soluble.
b) **The nature of the solvent**: In most cases, polar solute will dissolve in a polar solvent while a nonpolar solute will dissolve a nonpolar solvent. The reason fat does not dissolve in water is because fats are nonpolar and water is polar.

6.8. Effect of common ion

A salt becomes less soluble when it is dissolved in a solution that contains one of its ions. So far, we have considered a single electrolyte dissolved in water.
Consider, for example, the solubility of a very sparingly soluble salt such as $BaSO_4$.

$$BaSO_4 \downarrow \underset{2}{\overset{1}{\rightleftharpoons}} Ba^{2+} + SO_4^{2-}$$

If sulphuric acid (H_2SO_4) is added to the heterogeneous mixture in equilibrium (solid + aqueous phase), the system reacts to absorb this excess of SO_4^{2-} ions added, the equilibrium moves in direction 2 (precipitation) according to the principle of Le Chatelier. The solubility of $BaSO_4$ therefore decreased by adding a common ion (here SO_4^{2-}).

Note:

The introduction of a solution of a common ion leads to a decrease in the solubility of the ionic compound.

6.9. Effect of the pH of the solution

For example, in the equilibrium:

$$CaCO_{3\,(S)} \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

If an acid (H^+) is added, the carbonate ion reacts:

$$CO_3^{2-} + 2\,H^+ \rightleftharpoons H_2CO_3 \longrightarrow CO_{2(g)} + H_2O$$

As the carbonate ion is consumed, the equilibrium shifts to the right and the $CaCO_3$ precipitate dissolves.

Note:

Acidification of the medium leads to redissolution of the precipitate.

6.10. Effect of complexation

For example, in the equilibrium: $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

If ammonia is added, the Ag^+ ion reacts to form a complex:

$$Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+ \text{ soluble}$$

As the Ag^+ ion is consumed, the equilibrium shifts to the right and the AgCl precipitate dissolves.

Note:

The formation of the complex enhances the dissolution of a salt.

6.11. Exercises

Exercise 1:

Calculate the concentration of silver ion in the aqueous solution in equilibrium with a precipitate of silver chromate, when the solution contain sodium chromate so that $[CrO_4^{2}]$ = 10^{-2} M. K_{sp} $(Ag_2CrO_4) = 1.1 \times 10^{-12}$

Answer: $Ag_2CrO_4 \rightleftharpoons 2\ Ag^+ + CrO_4^{2-}$

$K_{sp} = [Ag^+]^2\ [CrO_4^{2-}]$

The silver-ion concentration is unknown and is to be calculated; the chromate ion concentration is 10^{-2}M. Substituting into the solubility product expression,

$[Ag^+]^2\ [CrO_4^{2-}] = 1.1 \times 10^{-12}$

$[Ag^+]^2 = 1.1 \times 10^{-12} / [CrO_4^{2-}]$

$= 1.1 \times 10^{-10}$

$[Ag^+] = 1.05 \times 10^{-5}$ M

Exercise 2:

1. A solution of $Pb(NO_3)_2$ at 0.01 mol/L is mixed in equal volumes with a 0.1 mol/L solution of KCl. Will there be a precipitate of $PbCl_2$?

   K_{sp} $(PbCl_2) = 1.5.10^{-5}$

2. A 10^{-4} mol/L solution of NaCl is mixed in equal volumes with a 10^{-4} mol/L solution of $AgNO_3$. Will there be an AgCl precipitate?

   K_{sp} $(AgCl) = 1.6.10^{-10}$

Answer:

$PbCl_2 \rightleftharpoons Pb^{2+} + 2\ Cl^-$

$K_{sp} = [Pb^{2+}] \times [Cl^-]^2 = 1.5.10^{-5}$

In the mixture $[Pb^{2+}] = 0.01 \times V/ V+ V = 0.005$ mol/L

Idem for Cl^- ions: $[Cl^-] = 0.1 \times V /V + V = 0.05$ mol

$Pi = [Pb^{2+}] \times [Cl^-]^2 = 0.005 \times (0.05)^2 = 1.25.10^{-5}$ $P_i < K_{sp}$

A value lower than Ks is obtained, so there will be no precipitation of $PbCl_2$

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$K_s = [Ag^+][Cl^-] = 1.6.10^{-10}$

In the mixture $[Ag^+] = 10^{-4}$ x V/ V+ V = 5.10^{-5} mol/L

Idem for Cl^- ions: $[Cl^-] = 10^{-4}$x V / V+ V = 5.10^{-5} mol/L

$Pi = [Ag^+][Cl^-] = 5.10^{-5} x\ 5.10^{-5} = 2.5 \times 10^{-9}$

$$P_i > K_{sp}$$

We obtain a value greater than K_{sp}, so there will be no precipitation of AgCl.

Exercise 2:

One solution contains Fe^{2+} ions and Cu^{2+} ions and hydrogen sulfide H_2S. The concentrations are all equal to 0.1 mol/L. The solution is buffered to pH = 5. We then have $[S^{2-}] = 10^{-20}$ mol/L. What is the sulfide that precipitates?

K_{sp} (CuS) = 10^{-35} and K_{sp} (FeS) = $6.3\ 10^{-18}$.

Answer:

Precipitation equations: $CuS \rightleftharpoons Cu^{2+} + S^{2-}$

$$FeS \rightleftharpoons Fe^{2+} + S^{2-}$$

We have:

$K_{sp1} = [Cu^{2+}]\ [S^{2-}] = 10^{-35}$ for CuS

$K_{sp2} = [Fe^{2+}][S^{2-}] = 6.3\ 10^{-18}$ for FeS

CuS : $Pi_1 = [Cu^{2+}][S^{2-}]$

FeS: $Pi_2 = [Fe^{2+}]\ [S^{2-}]$

It is noted that $Pi_1 = [Cu^{2+}][S^{2-}] = 0.1\ x10^{-20} = 10^{-21} > 10^{-35}$

$P_i > K_{sp}$ ⟶ **CuS precipitation**

$Pi_2 = [Fe^{2+}]\ [S^{2-}] = 0.1x10^{-20} = 10^{-21} < 6.3\ 10^{-18}$

$P_i < K_{sp}$ ⟶ **no precipitation of FeS.**

Exercise 3:

For silver chloride, the solubility product K_{sp} is 1.6 10^{-10} at 25 °C.

a) Calculate the solubility of AgCl in pure water.
b) Calculate the solubility of AgCl in 0.1M NaCl solution.

Molar mass of AgCl = 143.5 g /mol

Answer

a) Solubility of silver chloride in pure water

Let x be the amount (mol) of AgCl that is introduced into one litre of pure water. The solubility S of silver chloride is the maximum amount of this solid that passes into solution.

	$AgCl$	$\rightleftharpoons$	Ag^+	+	Cl^-
Initially	x mol		0		0
After dissolution	(x-S) mol		S mol		S mol

a) In pure water $[Ag^+] = [Cl^-] = S$ mol/l

$$K_{sp} = [Ag^+].\,[Cl^-] = S^2$$

We get $$S = \sqrt{K_{sp}}$$

S = $\sqrt{1,6\ x\ 10^{-10}}$ = 1.26 x 10^{-5} mol/L

Or 1.26 x 10^{-5} x 143.5 = 1.8 10^{-3} g/L (M (AgCl) = 143.5 g/mol).

b) Solubility in NaCl solution (presence of common ion Cl^-)

We have: $[Cl^-]_{total} = [Cl^-]_{NaCl} + [Cl^-]_{AgCl}$

Let S ′ be the solubility of AgCl in the 0.1 M NaCl solution, the expression of K_s becomes:

$$K_{sp} = [Ag^+]\,[Cl^-] = S' \text{ x } (S' + 0.1) = 1.6 \text{ x } 10^{-10}$$

We arrive at a second-order equation that is easy to solve.

However, AgCl is very poorly soluble in water and $[Cl^-]_{AgCl}$ can be neglected in front of $[Cl^-]_{NaCl}$ so:

$$K_{sp} = S' \times 0.1 = 1.6 \times 10^{-10}$$

hence $S' = 1.6 \times 10^{-9}$ mol/L

or $S' = 1.6 \times 10^{-9} \times 143.5 = 2.29 \times 10^{-7}$ g/L

$S' < S$ The solubility of silver chloride in sodium chloride solution is less than its solubility in pure water.

Verification of the calculation hypothesis:

$1.6\ 10^{-9}$ mol/L << 0.1 mol /L (justified approximation)

It was therefore possible to make the approximation.

Exercise 3:

An aqueous solution contains a mixture of calcium Ca^{2+} ion, magnesium Mg^{2+} ion and chloride Cl^- ion such that :

$[Ca^{2+}] = 0.10$ mol/L and $[Mg^{2+}] = 0.30$ mol/L.

A sodium hydroxide solution (NaOH) of molar concentration C = 0.010 mol/L is slowly added to one litre of this solution with stirring. It is considered that this addition does not significantly modify the volume.

1. Determine, with justification, the precipitate that forms first.
2. Determine the hydroxide ion concentration $[OH^-]$ when observing this first precipitate
3. Calculate the volume of the NaOH solution poured from which the formation of this precipitate is observed.

K_{sp2} $Mg(OH)_2 = 1.3\ 10^{-11}$

Solubility $S_2 = 1.48\ 10^{-4}$ mol/L.

Answer :

1.

$$Ca^{2+}_{aq} + 2\ OH^-_{aq} \rightleftharpoons Ca(OH)_{2\ solid}$$

The constant of this reaction is $K_1 = 1/\ (\ [Ca^{2+}_{aq}][\ OH^-_{aq}]^2)$

$$= 1/K_{sp1} = 1\ /\ 8.0\ 10^{-6} = 1.3\ 10^5$$

$$Mg^{2+}_{aq} + 2\ OH^-_{aq} \rightleftharpoons Mg(OH)_{2\ solid}$$

The constant of this reaction is $K_2 = 1/ ([Mg^{2+}_{aq}][OH^-_{aq}]^2)$

$$= 1/K_{sp2} = 1/1.3 \times 10^{-11} = 7.7 \times 10^{10}.$$

$K_2 >> K_1$ So **$Mg(OH)_{2solid}$ precipitates first**.

2. $Ca(OH)_2$ precipitates as soon as the solubility product $K_{sp1} =[Ca^{2+}_{aq}][OH^-_{aq}]^2$ is reached:

$[OH^-_{aq}]^2 = K_{sp1} / [Ca^{2+}_{aq}]$

$$[OH^-_{aq}] = \sqrt{\frac{K_{sp1}}{[Ca^{\,2+}_{\,aq}]}}$$

with $[Ca^{2+}_{aq}]_{\text{ initial}} = 0.10$ mol/L

$[OH^-_{aq}] = (8.0\ 10^{-6}/ 0.10)^{½}$

$= 8.9 \times 10^{-3}$ mol/L.

$Mg(OH)_2$ precipitates as soon as the solubility product $K_{sp2} = [Mg^{2+}_{aq}]\ [HO^-_{aq}]^2$ is reached:

$[OH^-_{aq}]^2 = K_{sp2} / [Mg^{2+}_{aq}]$;

$$[OH^-_{aq}] = \sqrt{\frac{K_{sp2}}{[Mg^{\,2+}_{\,aq}]}}$$

with $[Mg^{2+}_{aq}]_{\text{ initial}} = 0.30$ mol/L

$[OH^-_{aq}] = (1.3\ 10^{-11}/ 0.30) = 6.6\ 10^{-6}$ mol/L.

$Mg(OH)_2$ therefore precipitates first, as soon as the OH^- ion concentration reaches $6.6\ 10^{-6}$ mol/L.

3. Volume V_{NaOH} of sodium hydroxide solution poured:

$V_{NaOH} = 6.6\ 10^{-6}/ 0.010 = 6.6\ 10^{-4}$ L (0.66 mL).

Exercise 4:

The solubility product of silver nitrite $AgNO_2$, at 25°C, is $K_{sp} = 7.23.10^{-4}$.

1. Calculate the solubility in pure water, expressed in mol/L and g/L, of this salt at this temperature.

2. What is the new solubility of silver nitrite in a 0.118 mol/l solution of silver nitrate $AgNO_3$, fully soluble salt? Compare these two results. What does that tell us?

M ($AgNO_2$) = 154 $g.mol^{-1}$

Answer :

1) Calculation of the solubility of $AgNO_2$:

Either the following heterogeneous equilibrium:

$$AgNO_2 \rightleftharpoons \underset{S}{Ag^+} + \underset{S}{NO_2^-}$$

Dissociation of an $AgNO_2$ entity releases 1 ion of Ag^+ and 1 ion of NO_2^-

$[Ag^+]$ = [Cl-] = S

$K_{sp} = [Ag^+][NO_2^-] = S \times S$

Hence $S = \sqrt{K_{sp}}$

$K_{sp} = 7.23 \times 10^{-4}$

$S = 2.69.10^{-2}$ mol/L = $2.69.10^{-2} \times 154$ = 4.14 g/L

2) Calculation of the new solubility S' in a silver nitrate solution $AgNO_3$ with C = 0.118mol/L.

Regression equations are as follows:

$$AgNO_3 \longrightarrow Ag^+ + NO_3^- \qquad \text{fully soluble salt}$$

$$AgNO_2 \rightleftharpoons Ag^+ + NO_2^- \qquad K_{sp} = [Ag^+][NO_2^-]$$

$[Ag^+] = S' + C$

and $[NO_2^-] = S'$ with C = 0.118

$K_{sp} = (S' + C) S'$

or $S' <<< C$

hence $K_{sp} = S' C$ $\qquad S' = \frac{K_S}{C}$

$K_{sp} = 7.23.10^{-4}$

$S' = 6.10^{-3}$ mol/L (low value before 0.118, the hypothesis is verified)

Conclusion:

The solubility of a poorly soluble salt decreases considerably when a soluble salt with a common ion is added to the solution.

Exercise 5:

We have a neutral solution A of cadmium ions at 10^{-3} M. Sodium hydroxide is added to 500 cm^3 of solution A until the cadmium hydroxide begins to precipitate (solution B). At this point the pH is 8.5.

1. Calculate the solubility product of cadmium hydroxide.
2. Sodium hydroxide is added to solution B (without changing the volume) so as to precipitate 90% of the cadmium originally present (solution C). Calculate the pH of solution C.
3. Calculate the quantity of sodium hydroxide to be added to solution B to obtain solution C.

Answer :

1.

$$Cd^{2+} + 2\,OH^- \rightleftharpoons Cd(OH)_2$$

$K_{sp} = [Cd^{2+}][OH^-]^2$

pH + pOH = pKe

pOH = (pKe – pH) = - log [OH⁻]

$[OH^-] = 10^{(pH - pKe)} = 10^{(8,5-14)} = 10^{-5,5}$

$K_{sp} = [10^{-3}][10^{-5,5}]^2$ **$K_{sp} = 10^{-14}$**

2. We have 90 % of $Cd(OH)_2$ précipites . 10 % Will remain: $10^{-3} \times 0,1 = 10^{-4}$ M.

$$Ks = [Cd^{2+}][OH^-]^2$$

$$\Rightarrow [OH^-]^2 = \frac{K_s}{[Ca^{2+}]}$$

$$\Rightarrow [OH^-] = \sqrt{\frac{K_s}{[Ca^{2+}]}} = \sqrt{\frac{10^{-14}}{10^{-4}}}$$

$$[OH^-] = 10^{-5}\ M$$

pOH = - log [OH⁻] = 5

pH = pKe – pOH = 14 – 5 = 9 pH = 9

3. The volume of the solution has not changed and is now 0.5 litres.

The number of moles of OH^- ions present in solution C of pH = 9 is determined.

$n = [OH^-] \times 0{,}5 = 10^{-5} . 0{,}5 = 5 \times 10^{-6}$ mole

2 moles of OH^- ions are needed to precipitate 1 mole of Cd^{2+} ions, the number of moles of OH^- ions needed to precipitate 90% of the cadmium in solution B will be :

$n = 2 \times 0{,}9 \times 10^{-3} \times 0{,}5 = 9 \times 10^{-4}$ mole

Exercise 6:

The solubility product of silver chloride AgCl is 1.6×10^{-10} at 25°C.

1. Calculate the solubility in g/l of this salt in pure water at this temperature.

2. Take 950 mL of a saturated aqueous solution of silver chloride and add 50 mL of a normal solution of hydrochloric acid HCl. State the nature of the reaction and calculate :

   a) The pH of the solution

   b) The solubility of the silver chloride in the medium.

   c) The mass of precipitate.

M (g/mol) : Ag (108) , Cl (35,5).

Answer:

$$AgCl\,(s) \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

$$K_{sp} = [Ag^+]\,[Cl^-] = S \times S = S^2$$

$$S = \sqrt{K_{sp}} = \sqrt{1.6x\ 10^{-10}} = 1.26 \times 10^{-5}\ M$$

$$S = 1.26 \times 10^{-5}\ M$$

$$S = 1{,}26 \times 10^{-5} \times 143{,}5 = 1.8 \times 10^{-3}\ g/L$$

2. Adding a volume of 50 mL of HCl solution to the AgCl solution amounts to adding Cl^- ions.

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

According to LE CHATELIER's law, the addition of common ions shifts the solubility equilibrium in the direction of AgCl precipitation.

a) 1 eq.g. of HCl $\longrightarrow$ 1000 mL

x eq.g. of HCl $\longrightarrow$ 50 mL => X = 0.05 Eq. g

[HCl] = 0.05 N = 0.05 M

HCl is a strong acid pH = -log C

$$pH = -\log(0.05) = 1.3$$

b) $$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

S' (S' + C)

Avec S' << C

$$K_{sp} = [Ag^+][Cl^-] = S' \times C \Rightarrow S' = \frac{K_{sp}}{C} = \frac{1{,}6 \times 10^{-10}}{0{,}05}$$

$$= 3.2 \times 10^{-9}\ M$$

c) Masse of Ag^+ before adding HCl : m_1

$m_1 = S \times V \times M_{Agcl} = m_1 = 1{,}26 \times 10^{-5} \times 0{,}950 \times 143{,}5 = 1.7 \times 10^{-3}$ g

Masse of Ag^+ after adding HCl : m_2

$m_2 = S' \times V \times M_{AgCl} = 3{,}2 \times 10^{-9} \times 0{,}950 \times 143{,}5 = 4.36 \times 10^{-7}$ g

Masse de AgCl précipité : m_3

$$m_3 = m_1 - m_2 = 1{,}70 \times 10^{-3} - 4.36 \times 10^{-7}.$$

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Appendixes

Appendix 1

Table 1 : Acidity constants and pKa of some acid-base couples in aqueous solution at 25°C.

Name	Acid formula	Base formula	pK_a à 25°C
Sulfuric acid	H_2SO_4	HSO_4^-	-4,0
Hydrochloric acid	HCl	Cl^-	-3,7
Nitric acid	HNO_3	NO_3^-	-1,4
Hydronium	H_3O^+	H_2O	0,0
Oxalic acid	$H_2C_2O_4$	$HC_2O_4^-$	1,2
Hydrogen oxalate	$HC_2O_4^-$	$C_2O_4^{2-}$	4,3
Sulfurous acid	H_2SO_3	HSO_3^-	1,8
Hydrogen sulfite	HSO_3^-	SO_3^{2-}	7,2
Hydrogen sulfate	HSO_4^-	SO_4^{2-}	2,0
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	2,1
Dihydrogen phosphate	$H_2PO_4^-$	HPO_4^{2-}	7,2
Hydrogen phosphate	HPO_4^{2-}	PO_4^{3-}	12,4
Nitrous acid	HNO_2	NO_2^-	3,3
Formic acid	$HCOOH$	$HCOO^-$	3,8
Acetic acid	CH_3CO_2H	$CH_3CO_2^-$	4,75
Carbonic acid	H_2CO_3	HCO_3^-	6,4
Hydrogen carbonate	HCO_3^-	CO_3^{2-}	10,3
Hydrogen sulfide	H_2S	HS^-	7,0
Hydrosulfide	HS^-	S^{2-}	12,9
Hypochlorous acid	$HClO$	ClO^-	7,3
ammonium	NH_4^+	NH_3	9,25
Hydrogen cyanide	HCN	CN^-	9,3
Ethanol	C_2H_5OH	$C_2H_5O^-$	15,9

Appendix 2

Table 2 : Constants Solubility Product of metal hydroxides.

$M(OH)_n \rightleftharpoons M^{n+} + n\,OH^- \qquad K_{sp} = [M^{n+}][OH^-]^n$

Ions	pK_{sp}
Al^{3+}	32,5
Ag^+	7,6-7,7
Ba^{2+}	2,3
Bi^{3+}	30,4
Cd^{2+}	13,5-14,2
Ca^{2+}	5,3
Cr^{2+}	17
Cr^{3+}	30
Cu^{2+}	19.7
Sn^{2+}	26,2
Sn^{4+}	56
Fe^{2+}	15,1-15,32
Fe^{3+}	37,2-38,2
Mn^{2+}	10,92-11
Hg^{2+}	23-24
Hg_2^{2+}	25,5-25,85
Ni^{2+}	14,7-17,2
Pb^{2+}	14,5-15,6
Sr^{2+}	3,5
Zn^{2+}	16,1-16,9

Table 3 : Constants of Solubility Product of metal Sulfides (MS).

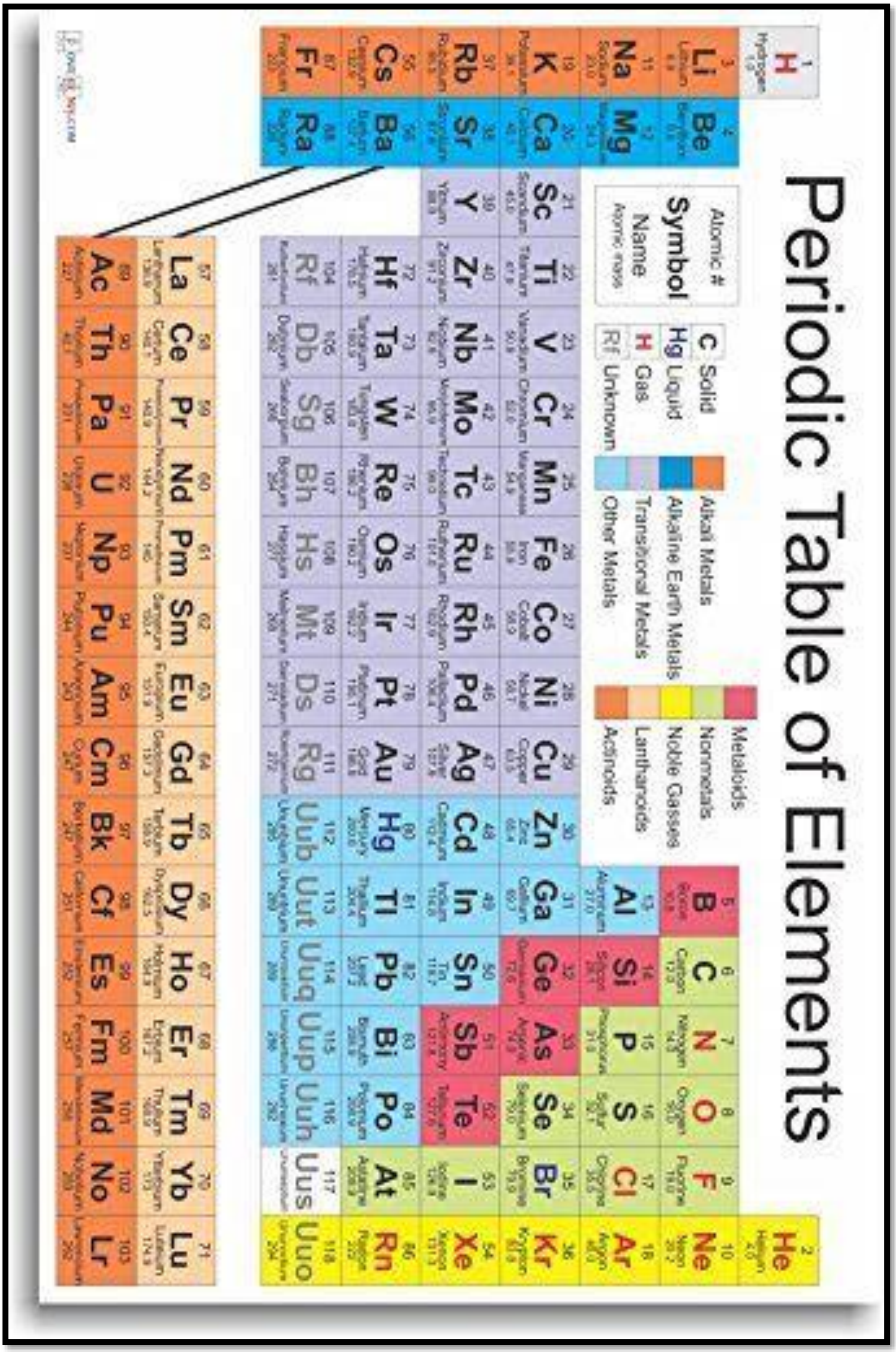
Ions	pK_{sp}
Ag^+	49,80
Cd^{2+}	27,85
Cu^+	47,6
Cu^{2+}	35,2
Co^{2+}	20,4-24,7
Sn^{2+}	25
Fe^{2+}	17,2
Mn^{2+}	9,6
Hg^{2+}	51,8
Ni^{2+}	18,5-25,7
Pb^{2+}	27,9
Zn^{2+}	21,6-23,8

Table 4 : Constants Solubility Product of other salts.

This is the equilibrium constant for the process of dissolution. Consider the generic salt

$$M_xA_{y(s)} \rightleftharpoons x\,M^{m+}_{(aq)} + y\,A^{n-}_{(aq)}$$

Métal	Ions	pK_{sp}
Ag	AgBr	12,48
	Ag_2CO_3	11,96
	AgI	16
	AgCl	9,77
Ba	$BaCO_3$	8,31
	$BaCrO_4$	9,7
	$Ba(C_2O_4)$	6,77
	$BaSO_4$	10
Ca	$CaCO_3$	8,32
	$CaSO_4$	4,22
	$Ca(C_2O_4)$	8,64
Cu	CuCl	6,74
	CuSCN	13,5
	CuBr	8,28
Mg	$MgCO_3$	5
	$MgNH_4PO_4$	12,6
	$Mg(C_2O_4)$	4,07
Hg	Hg_2Cl_2	17,96
	$Hg_2(C_2O_4)$	13
	Hg_2I_2	28,35
Pb	$PbCO_3$	12,82
	$PbCrO_4$	13,74
	$PbSO_4$	7,65
	PbI_2	8,06
	$Pb(C_2O_4)$	10,46
K	$KClO_4$	1,97
Sr	$SrCO_3$	8,8
	$SrSO_4$	6,55
	$Sr(C_2O_4)$	7,3


Periodic Table of Elements
Atomic #
Symbol
Name
Atomic mass
C Solid
Hg Liquid
H Gas
Rf Unknown
Alkali Metals
Alkaline Earth Metals
Transitional Metals
Other Metals
Metalloids
Nonmetals
Noble Gasses
Lanthanoids
Actinoids