Analytical chemistry

By

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University of Salahaddin
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Course Book
Analytical chemistry
Second year chemistry
Academic year 2022-2023 one semester

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- Course name: Analytical chemistry/ second year
- 4hrs per week divided on two groups, covering 15 weeks,
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- Examination: 2 main exams

  Theory 12marks
- Practical (6 marks)
- Quizzes, activities (2.0 marks)
- Final exam 30(22.5 theory, 7.5 prac).
- Total marks: (50%)

Course book content by weeks:

1. Introduction on analytical chemistry, electrolytes, acids and bases, conjugate acids and bases, units of weight and concentrations,
2. Mole, millimole , molarity and normality examples
3. Percentage concentration, ppm examples,
4. Chemical equilibrium: le chatelier’s principle
5. Theory of neutralization, salts and their types, ionization of week acids and bases , PKa, PKb, kw, examples
6. Ph , buffer solutions their properties, acidic buffer solutions , alkaline buffers, examples, adding acids or bases to the buffer solutions.

7- Titrimetric analysis: classification of titrimtric analyses, acid- base titration reactions, acid- base indicators

8- More on acid base indicators, titration strong acid with strong base, strong acid with weak base, weak acid with the weak base.

9-Precipitation titrations: the formation of second precipitate, the Mohr method.

10-The formation of colored method: Volhard method, adsorption methods (fajan method)

11-Introduction to electrochemistry, Oxidation reduction reactions:, oxidation/ reduction titrations

12-Complex metric titrations: introduction, titration using EDTA.

13-Idometric titration, Gravimetric analysis

14-Chromatography, introduction to chromatographic separations

Analytical chemistry

- **Analytical chemistry is the branch of chemistry that deals with separation, identification and determination of the component in the sample.**

- **Analytical chemistry can be divided into two categories :**

1-Qualitative analysis

- Deals with the identification of one or more of the components in the sample . For example, screening an athlete’s urine for the presence of a performance-enhancing drug.

2- Quantitative analysis

- Deals with the determination of the amount of matter that present in the sample. For example measuring the concentration of glucose in blood.

Electrolytes

- Electrolytes are solutes that produce ions when dissolved in water creating an electrically conducting medium.
- The ability of ions in the solution to move nearly independently , permits them to carry positive or negative electrical charges from one place to another. Hence the solution conducts an electrical current.

The classification of the Electrolyte:

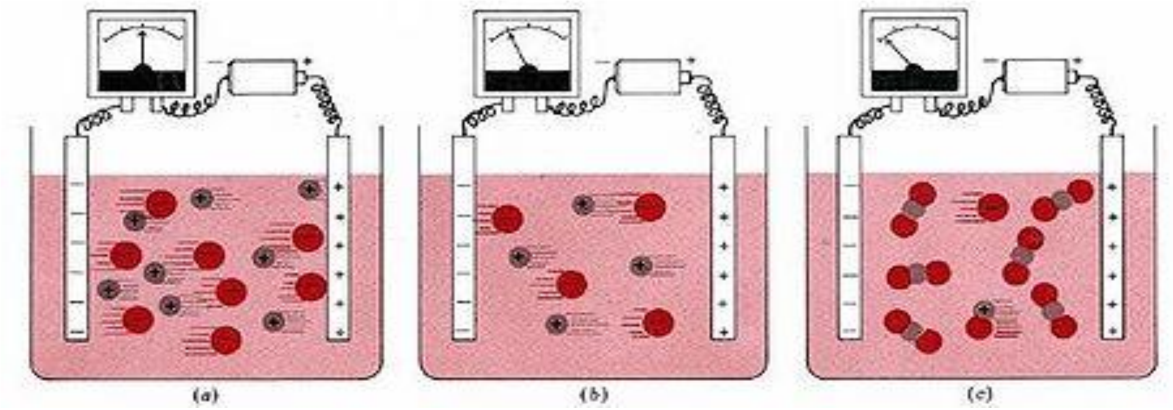
- Strong electrolytes : are considered to ionize completely when dissolved in water such as :

H_2SO_4, HCl. HI, HBr

They conduct very well because they provide a plentiful supply of ions in solution.

- Weak Electrolytes are partially ionized in the solvent such as:

  H_2CO_3, H_3BO_3, H_3PO_4, H_2S and Most organic acids



The larger the concentration of ions, the better the solution conducts.

Nonelectrolytes

Materials that are soluble in water but do not dissociate and no increase in conductivity is observed, such as :

ethanol – C2H5OH

- Problem: which of the solutions conduct electricity more?
- 1 x 10 $^{-2}$ M NaCl or 1 x 10^{-5}

Acid and Bases

- According to Bronsted – Lowry view in 1923:

- **Acid** is any substance that donates a proton,

- **Base** is any substance that can accept a proton

- A substance cannot act as an acid without the presence of a base to accept the proton, and *vice versa.* The solvent in many cases acts like proton acceptor or donor.

- water is an **amphiprotic** solvent, because it shows both acidic and basic properties depending on the solute. Examples are water, ammonia, and ethanol.

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

acid1 *base2* *base1* *acid2*

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

base1 acid2 acid1 base2

Conjugate acids and bases

- The term *conjugate*
- means “connected with", the implication being that any species and its conjugate species are related by the gain or loss of one proton.
- *When any acid gives up a proton the base is formed*

$$\textbf{acid1} \rightleftharpoons \textbf{base1 + proton}$$

acid1 and base1 are a conjugate acid/base pair.

Every base produces a conjugate acid as a result of accepting a proton

$$\textbf{base2 + proton} \rightleftharpoons \textbf{acid2}$$

In acid base reaction

$$\textbf{acid1 + base2} \rightleftharpoons \textbf{base1 + acid2}$$

Examples of Conjugate acids and Bases

- $HNO_3 + H_2O \rightarrow NO_3^- + H_3O^+$

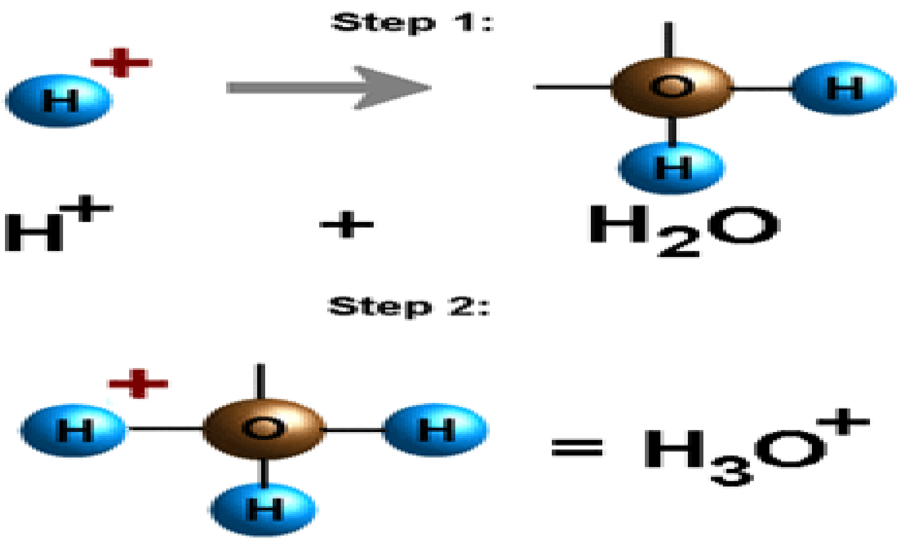
  acid1 base2 base1 acid2

$NH_3 + H_2O \rightleftharpoons NH4^+ + OH^-$

base1 acid2 acid1 base2

substance	acid	conjugate base
hydrochloric acid	HCl	Cl^-
acetic acid	CH_3COOH	CH_3COO^-
nitric acid	HNO_3	NO_3^-
ammonium ion	NH^{+4}	NH_3

Hydronium ion. (H_3O^+)

- 

- The H_3O^+ ion, formed by capture of a hydrogen ion by a water molecule. A strong covalent bond is formed between the hydrogen ion and water oxygen; all hydrogen ions in aqueous solution are bound inside hydronium ions.
- For simplicity, it will some times be mentioned as H^+

More about conjugate acids and bases

Strongest acid	$HClO_4 + H_2O$	$\rightarrow$	$H_3O^+ + ClO_4^-$	*Weakest base*
↑	$HCl + H_2O$	$\rightarrow$	$H_3O^+ + Cl^-$	↓
	$H_3PO_4 + H_2O$	$\rightarrow$	$H_3O^+ + H_2PO_4^-$	
	$HC_2H_3O_2 + H_2O$	$\rightarrow$	$H_3O^+ + C_2H_3O_2^-$	
	$NH_4^+ + H_2O$	$\rightarrow$	$H_3O^+ + NH_3$	
Weakest acid				*Strongest base*

This table shows that acids become weaker from the top to the bottom of the list, but their conjugate base will be stronger from the top to the bottom

The stronger an acid, the weaker its conjugate base,

the stronger a base, the weaker its conjugate acid.

- **Strong acid**

  Strong acid is an acid that ionizes completely in an aqueous solution

  Will release **all** of its H^+ ions, Example hydrochloric acid:

$$HCl \rightleftharpoons H^+ + Cl$$

- **Weak acid**

  Weak acid is an acid that does not ionize completely ,when dissolved in water for example: acetic acid:

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

Units of weight and concentration

- Scientists through out the world have agreed on a standardized system of units known as the **International System of Units (SI)**
- In analytical chemistry for mass measurements, units of kilograms(Kg), grams(g), milligrams(mg), micrograms (µg) are used
- For Volumes of liquids , liters(L), milliliters(mL) and microliters(µL) are used
- For small or large measured quantities, prefixes are used with base units , example 50 x 10^{-6} g is equal to 50µg

Measurement	Unit	Symbol
mass	kilogram	kg
volume	liter	L
distance	meter	m
temperature	kelvin	K
time	second	s
current	ampere	A
amount of substance	mole	mol

Common Prefixes for Exponential Notation

Exponential	Prefix	Symbol
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

The mole(mol)

- **It is a fundamental chemical unit used to measure the quantity of a substance. A mole** is defined as the number of ^{12}C atoms in exactly 12 g of ^{12}C. The mole is equal to **6.02×10^{23}** particles (atoms, ions, molecules,) and called **Avogadro's number**
- A mole is similar to a term dozen except much larger. If you have a dozen carrots, you have twelve of them. Similarly, if you have a mole of carrots, you have 6.022×10^{23} carrots.
- It is one of the base units in the International System of Units(IS), and has the unit symbol **mol**

- We also need a bridge between these numbers, which we are unable to measure directly, and the weights of substances, which we do measure and observe. The *mole concept* provides this bridge, and is central to all of quantitative chemistry.
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- Due to their tiny size, atoms and molecules cannot be counted by direct observation. But much as we do when "counting" beans in a jar, we can estimate the number of particles in a sample of an element or compound if we have some idea of the volume occupied by each particle and the volume of the container.
- The number depends both on the **formula** of the substance and on the **weight** of the sample.

1856-1766

Just How Large is Avogadro's Number?

- A mole of marbles would cover the United States 70 miles deep.
- There are more atoms in a glass of water than there are glasses of water in the ocean.

Amount of water in the oceans (liters)

Population of the Earth

602,200,000,000,000,000,000,000

Distance from the Earth to the Sun (centimeters)

Average college tuition (U.S. dollars)

Calcium has an atomic mass of 40 atomic mass units (**amu**). So, 40 grams of calcium makes one mole,

55.85g Fe = 6.022 x 10^{23} atoms Fe = 1 mole

32.07g S = 6.022 x 10^{23} atoms S = 1 mole

Molar mass (Mm)

- Molar mass of the substance is the mass in grams of 1 mole of that substance. So Mm are calculated by summing the atomic masses of all the atoms appearing in a chemical formula. For example

Mm NaCl (sodium chloride) = 23+ 35.5 = 58.5 g/ mol

Thus 1 mole of NaCl has the mass of 58.5 g

Mm glucose $C_6H_{12}O_6$ =

12.0 x 6 + 1.0x 12+ 16 x 6 = 180.0 g/mol

A mole of glucose has the mass of 180.0 g

- Molecular formula
  - identifies the number of each type of atom in a molecule.

  Hexane's molecular formula is C_6H_{14}

- Structural formula

  shows the structure of the molecule. Ex.:

  the chemical compound n-hexan has the structural formula $CH_3CH_2CH_2CH_2CH_2CH_3$, which shows that it has 6 carbon atoms arranged in a straight chain, and 14 hydrogen atoms.

$$\text{Number of moles (mol)} = \frac{\text{Mass (g)}}{\text{Molar Mass (g mol}^{-1}\text{)}}$$

PROBLEM:

Silver (Ag) is used in jewellery and tableware ,

How many grams of Ag are in 0.03 mol of Ag?

solution: Mass = mol x Mm

$$0.03 \text{ mol} \times \frac{107.9 \text{ g}}{\text{mol}} = 3.237 \text{ g}$$

- How many moles are present in 4.60 g of silicon?
- Atomic weight Si is 28.086

- How many g of Si are present in 9.0 mol of Si?

- 252.81 g Si

- What is the mass in grams of 2.5 mol of the element aluminum Al?
- Mole = mass / molar mass
- 2.5 = g / 26.98
- Mol = 2.5 x 26.98
- 67.45 g

- How many moles of Copper, are in 5 g of copper Cu? Mm of Cu 63.55 g/mol

millimole

Millimole are 1/1000 of the mole

moles = 1000 x Millimoles (mmole)

- 1 mole = 1000 millimole

Introduction to the Concentration

- In general, Concentration refers to the amount of solute contained in a certain amount of solution

Different methods to calculate concentration :

- **1- Molarity**
- **2-Normality**
- **3-Molality**
- **4-Percentage**
- **5- Part per million**

Methods for the expression of the concentrations

- **Molarity** M :
- Molarity is the number of moles of solute dissolved in one litre of solution. The units, therefore are **moles per litre;** specifically **moles of solute** per **litre of solution**

- $$\text{Molarity} = \frac{\text{moles of solute}}{\text{litre of solution}}$$

Example: If 5.00 g of NaOH are dissolved in 5000 mL of water, what is the molarity of the solution?

- One of our first steps is to convert the amount of NaOH given in grams into moles:
- $$\frac{5.00\text{g NaOH}}{1} \times \frac{1 \text{ mole}}{(22.9 + 16.00 + 1.008)\text{g}} = 0.125 \text{ moles}$$

Now we simply use the definition of molarity: moles/liters to get the answer

- $$\text{Molarity} = \frac{0.125 \text{ moles}}{5.00 \text{ L}} = 0.025 \text{ mol/L}$$
- So the molarity (M) of the solution is 0.025 mol/L.

- **PROBLEM:** How many grams of solute are in 1.75L of 0.460M sodium monohydrogen phosphate?

Step1: number of moles?

M = mol / (V)L

$$1.75\text{L} \times \frac{0.460\text{mol}}{1\ \text{L}} = 0.805\text{mol } Na_2HPO_4$$

step2: mol = mass / Mm

$$0.805\ \text{mol } Na_2HPO_4 \times \frac{141.96\text{g } Na_2HPO_4}{\text{mol } Na_2HPO_4}$$

114.277g

Describe the preparation of 4.00L of 0.200M KOH.

Solution,

Calculate how much weight from KOH you need?

M= mol/L

0.200 = mol / 4.00

Mol = 0.200 x 4.00

Mol = 0.8

Mm(KOH) = 39 x 1+ 16x1+ 1x1 = 56g/mol

Mol = mass(g) / Mm

mass= mol x Mm

mass = 0.8 x 56 = 44.8 g

Dissolve 44.8 g of KOH and dilute to 4 L

- What is the molarity of a solution prepared by dissolving 15.0 g of NaOH in amount of water to make a total of 225 mL of solution?

- ***. How many water you have to add to 450 ml of a solution 0.3 M to obtain a concentration 0.25 M ?***

Normality N

- Normality is similar to molarity, but uses equivalents, not moles of the substance. **It is expressed as number of equivalent weights of the solute in a liter of solution.**

- The number of equivalents, n, is based on a reaction unit, which is that part of a chemical species involved in a reaction . **Normality is the only concentration unit that is reaction dependent**

Equivalent weight = Mm/ n

- In a precipitation reaction, for example, the reaction unit is the charge of the cation or anion involved in the reaction; thus

$$Pb^{2+}(aq) + 2I^{-}(aq) \longrightarrow PbI_2(s)$$

n = 2 for Pb^{2+} and n = 1 for I^{-}

- In the acid base reaction the reaction unit is the number of H^+ ions donated by an acid or accepted by a base, example

$$H_2SO_4\,(aq) + 2NH_3(aq) \longrightarrow 2NH_4^+(aq) + SO_4^{2-}(aq)$$

$n = 2$ for H_2SO_4 and $n = 1$ for NH3.

- The normality of a solution is simply a **multiple of the molarity** of the solution.

$$N = n \times M$$

$$2M\ H_3PO_4 = 6\ N\ H_3PO_4$$

Generally, the normality of a solution is just one, two or three times the molarity.

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How many grams of sodium hydroxide would you need to dilute to a liter to make a 1N NaOH solution?

- Molar mass= 40

- equivalent mass ?

Calculate the equivalent weight and normality for a solution of 6.0 M H_3PO_4 given the following reactions:

(a) $H_3PO_4 + 3OH^- \longrightarrow PO_4^{3-} + 3H2O$

(b) $H_3PO_4 + 2NH_3 \longrightarrow HPO_4^{2-} + 2NH_4^+$)

SOLUTION

For phosphoric acid, the number of equivalents is the number of H^+ ions donated to the base. For the reactions in (a) and (b) equivalents are 3 and 2, respectively. Thus, the calculated equivalent weights and normalities are

a- EW =Mm/n

97.994 / 3 = 32.665

N = n x M = 3 x 6.0 = 18 N

b- EW =Mm/n

97.994 / 2 = 48.997

N = n x M = 2 x 6.0 = 12 N

By using the solvent's mass in place of its volume, the resulting concentration becomes independent of temperature

Molality ... ram of solvent (*m*

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

- Calculate the molality when 75.0 grams of $MgCl_2$ is dissolved in 500.0 g of solvent.

$$\frac{75.0\ \text{g}}{95.2\ \text{g/mol}} = 0.788\ \text{mol}$$

$$\frac{0.788\ \text{mol}}{0.500\ \text{kg}} = 1.58\ \text{m}$$

38.5 grams of NaCl is dissolved in 1.00 kg of solvent. What is the molality?

If you have a 0.25 M solution of benzene with a density of 15 g/L, calculate the molality of the solution

A 4 g sugar cube (Sucrose: $C_{12}H_{22}O_{11}$) is dissolved in a 350 ml teacup of 80 °C water. What is the molality of the sugar solution?

Given: Density of water at 80° = 0.975 g/ml

Step 1 - Determine number of moles of sucrose in 4 g

Solute is 4 g of $C_{12}H_{22}O_{11}$

$C_{12}H_{22}O_{11}$ = (12)(12) + (1)(22) + (16)(11)

$C_{12}H_{22}O_{11}$ = 342 g/mol

mol = mass/ Mm

4 g /(342 g/mol) = 0.0117 mol

Step 2 - Determine mass of solvent in kg.

density = mass/volume

mass = density x volume

mass = 0.975 g/ml x 350 ml

mass = 341.25 g

mass = 0.341 kg

Step 3 - Determine molality of the sugar solution.

molality = $mol_{solute} / m_{solvent}$

molality = 0.0117 mol / 0.341 kg

molality = 0.034 mol/kg

Percentage Concentrations

- **Weight percent (% w/w), volume percent (% v/v) and weight-to-volume percent** (% w/v) express concentration as units of solute per 100 units of sample.
- **Volume Percent:**

It is usually used when the solution is made by **mixing two liquids**.

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

- Weight percent(W/W) = $\frac{\text{weight of solute}}{\text{Wt of solution}} \times 100$

$$\text{Weight- Volume percent (W/V)} = \frac{\text{weight of solute (g)}}{\text{Volume of solution, mL}} \times 100$$

- The denominator in each of these expressions refers to the solution rather than solvent

- Example a solution in which a solute has a concentration of 23% w/v contains 23 g of solute per 100 mL of solution.

- weight/volume percent or mass/volume percent measures the amount of solute in grams but measures the amount of solution in milliliters. An example would be a 5%(w/v) NaCl solution. It contains 5 g of NaCl for every 100. mL of solution.
- Because of the different units in the numerator and denominator, this type of concentration is not a true percentage. It is used as a quick and easy concentration unit because volumes are easier to measure than weights and because the density of dilute solutions is generally close to 1 g/mL. Thus, the volume of a solution in mL is very nearly numerically equal to the mass of the solution in grams.
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- Milk is about 12% v/v water.
- This means there are 12 ml milk for every 100 ml of water.

- Determine the percent composition by mass of a 100 g salt solution which contains 20 g salt.

- Solution:
  20 g NaCl / 100 g solution x 100 = 20% NaCl solution

Question:

What is the weight percent of glucose in a solution made by dissolving 4.6 g of glucose in 145.2 g of water?

Analysis:

To get weight percent we need the weight of the solute and the total weight of the solution.

Determine total weight of solution:

4.6 g glucose
+ 145.2 g water
149.8 g solution

Calculate percent:

Weight % glucose =

$$\frac{4.6 \text{ g glucose}}{149.8 \text{ g solution}} \times 100 = 3.1\% \text{ glucose}$$

Parts per million (ppm) and parts per billion (ppb)

They are mass ratios of grams of solute to one million or one billion grams of sample, respectively. For example, a steel that is 450 ppm in Mn contains 450 μg of Mn for every gram of steel. If we approximate the density of an aqueous solution as 1.00 g/mL, then solution concentrations can

be expressed in parts per million or parts per billion using the following relationships

$$\text{ppm} = \frac{\text{mg}}{\text{liter}} = \frac{\mu\text{g}}{\text{mL}}$$

$$\text{ppb} = \frac{\mu\text{g}}{\text{liter}} = \frac{\text{ng}}{\text{mL}}$$

For gases a part per million usually is a volume ratio. Thus, a helium

concentration of 6.3 ppm means that one liter of air contains 6.3 mL of He.

Parts per million

- For very dilute solutions, it is convenient to express concentrations in terms of parts per million (ppm)

- $$\text{ppm} = \frac{\text{mg solute}}{\text{V(L) solution}} = \frac{\mu\text{g solute}}{\text{V(mL) solution}}$$

$\mu g = 10^{-6}$ g

150mL of an aqueous sodium chloride solution contains 0.0045g NaCl. Calculate the concentration of NaCl in parts per million (ppm).

- ppm = mass solute (mg) ÷ volume solution (L)

- mass NaCl = 0.0045g = 0.0045 x 1000mg = 4.5mg
  volume solution = 150mL = 150 ÷ 1000 = 0.150L

- concentration of NaCl = 4.5mg ÷ 0.150L = 30mg/L = 30ppm

A solution has a concentration of 1.25g/L.
What is its concentration in ppm?

- Convert the mass in grams to a mass in milligrams:
  1.25g = 1.25 x 1000mg = 1250mg
- Re-write the concentration in mg/L = 1250 mg/L = 1250ppm

A student is provided with 500mL of 600ppm solution of sucrose. What volume of this solution in millilitres contains 0.15g of sucrose?

- ppm = mass solute (mg) ÷ volume solution (L)
- Re-arrange this equation to find volume of solution:
  volume solution (L) = mass solute (mg) ÷ ppm
- Substitute in the values:
  volume solution (L) = (0.15g x 1000mg/g) ÷ 600 = 0.25L
- Convert litres to millilitres: volume solution = 0.25L x 1000mL/L = 250 mL
-

2.0L of an aqueous solution of potassium chloride contains 80.0g of KCl. What is the weight/volume percentage concentration of this solution in g/100mL?

- Convert the units (mass in grams, volume in mL):
  mass KCl = 80.0g
  volume of solution = 2.0L = 2.0 x 10^3mL = 2000mL
- Calculate w/v (%) = mass solute (g) ÷ volume solution (mL) x 100
  w/v (%) = 80.0 ÷ 2000mL x 100 = 4g/100mL (%)