PHARMACEUTICAL ANALYTICAL CHEMISTRY

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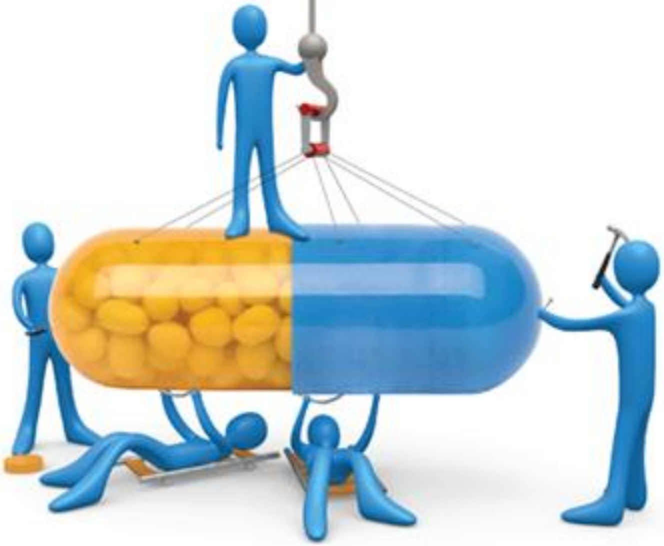
Stoichiometric Calculations



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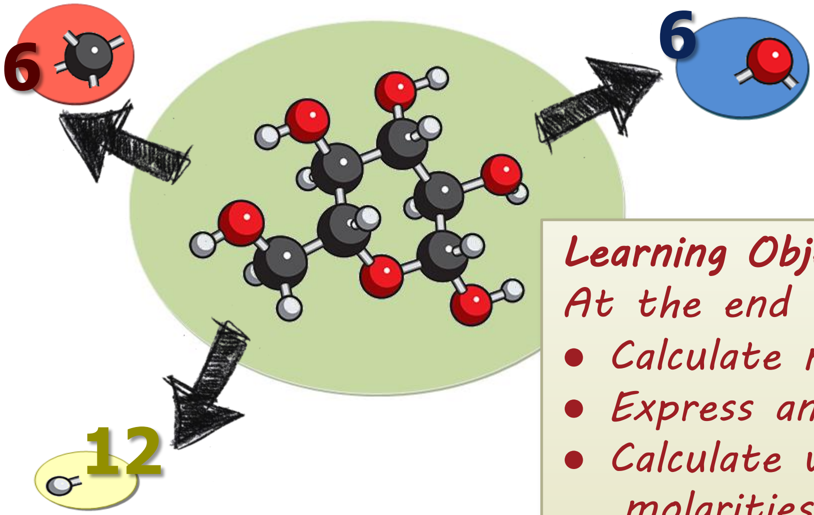
First Semester, 2022/2023

Stoichiometric Calculations

Chapter 5



Learning Objectives

At the end of this chapter, the student will be able to

- *Calculate molarities and moles*
- *Express analytical results*
- *Calculate weight and percent analyted from molarities, volumes, and reaction ratios*
- *Formulate weight relationships for gravimetric analysis*
- *List the requirements for a titration and the main four classes of titrations*

Molar Mass

It is the mass of one mole of substance, it is called:

molar mass, molar weight, formula weight, M.m., M.wt. or f.wt., molecular mass or weight (if analyte is molecule or molecular ion) and atomic mass or weight (if analyte is atom or atomic ion).

Its unit is (g/mol) or (mg/mmol)

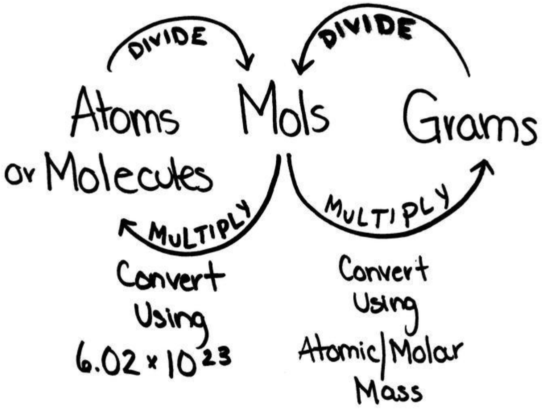
Mole

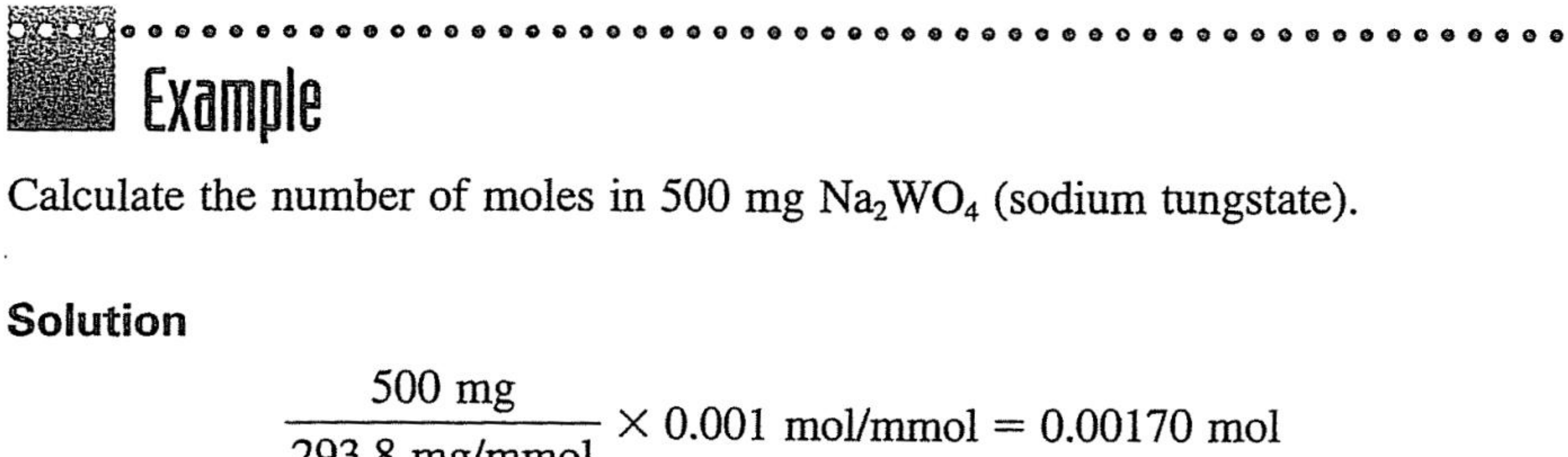
1 **Mole of molecules ≡** avogadro's num. of molecules
(avogadro's num. = 6.022×10^{23})

also **moles of substance =**

mass of substance ÷ M.wt

e.g. 36 g of H_2O contains 36/18=2 mol





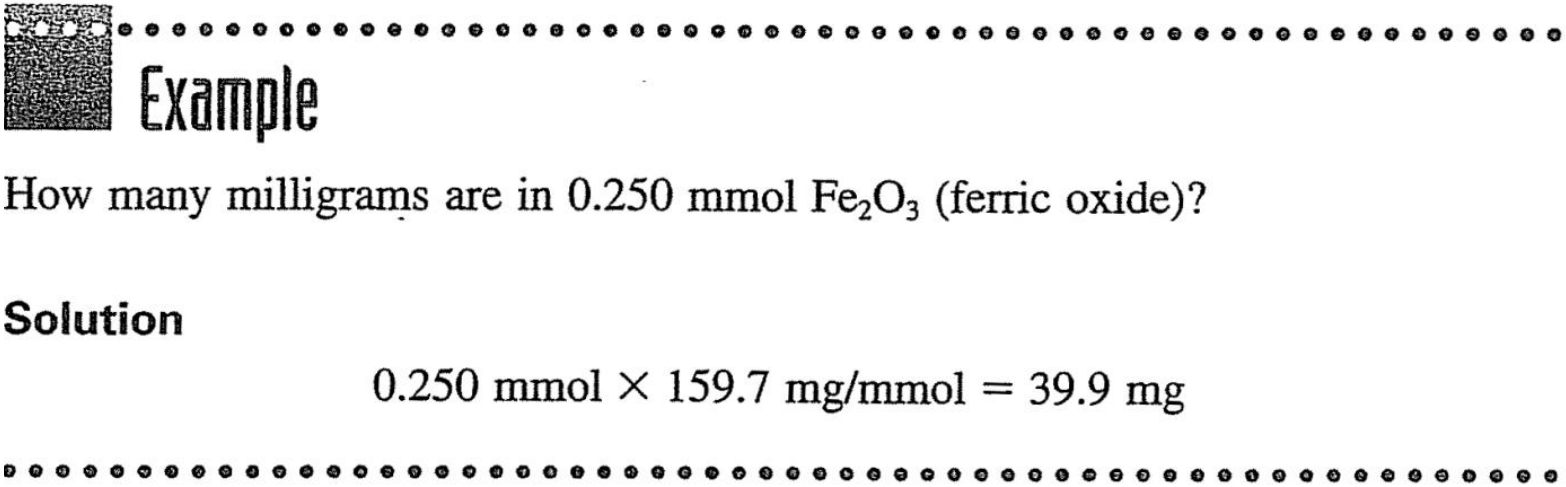
Example

Calculate the number of moles in 500 mg Na_2WO_4 (sodium tungstate).

Solution

$$\frac{500\ \text{mg}}{293.8\ \text{mg/mmol}} \times 0.001\ \text{mol/mmol} = 0.00170\ \text{mol}$$

$$\frac{1\ \text{mol}}{1000\ \text{mmol}}$$



Example

How many milligrams are in 0.250 mmol Fe_2O_3 (ferric oxide)?

Solution

$$0.250\ \text{mmol} \times 159.7\ \text{mg/mmol} = 39.9\ \text{mg}$$

Example

(a) How many glucose molecules are in 5.23 g of $C_6H_{12}O_6$?
(molar mass is 180.0 g/mol)

(b) How many oxygen atoms are in this sample?

Answer

(a) Firstly, calculate the number of moles then calculate the number of molecules from the number of moles

$$\text{moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{5.23}{180} = 0.0291\,\text{mol}$$

$$\text{number of molecules} = \text{number of moles} \times \text{Avogadro's no.}$$

$$= 0.0291 \times 6.022\text{x}10^{23} = 1.75 \times 10^{22}$$

(b) Each molecule of glucose has **6** atoms of oxygen, therefore

$$\text{number of oxygen atoms} = 6 \times \text{number of glucose moelcules}$$

$$= 6 \times 1.75 \times 10^{22} = 1.05 \times 10^{23}$$

Mole and Stoichiometry

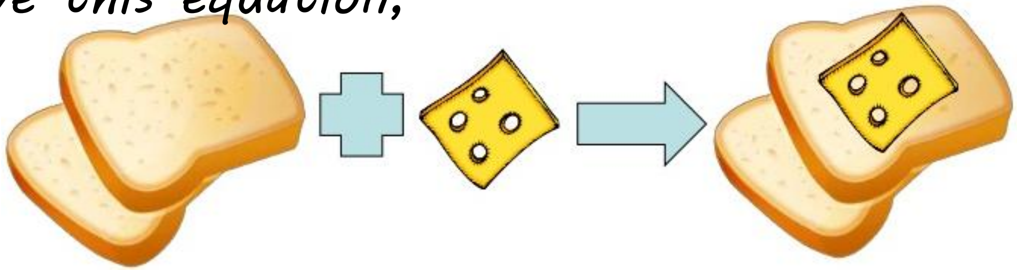
Stoichiometry is

the ratio between substances in the balance chemical equation

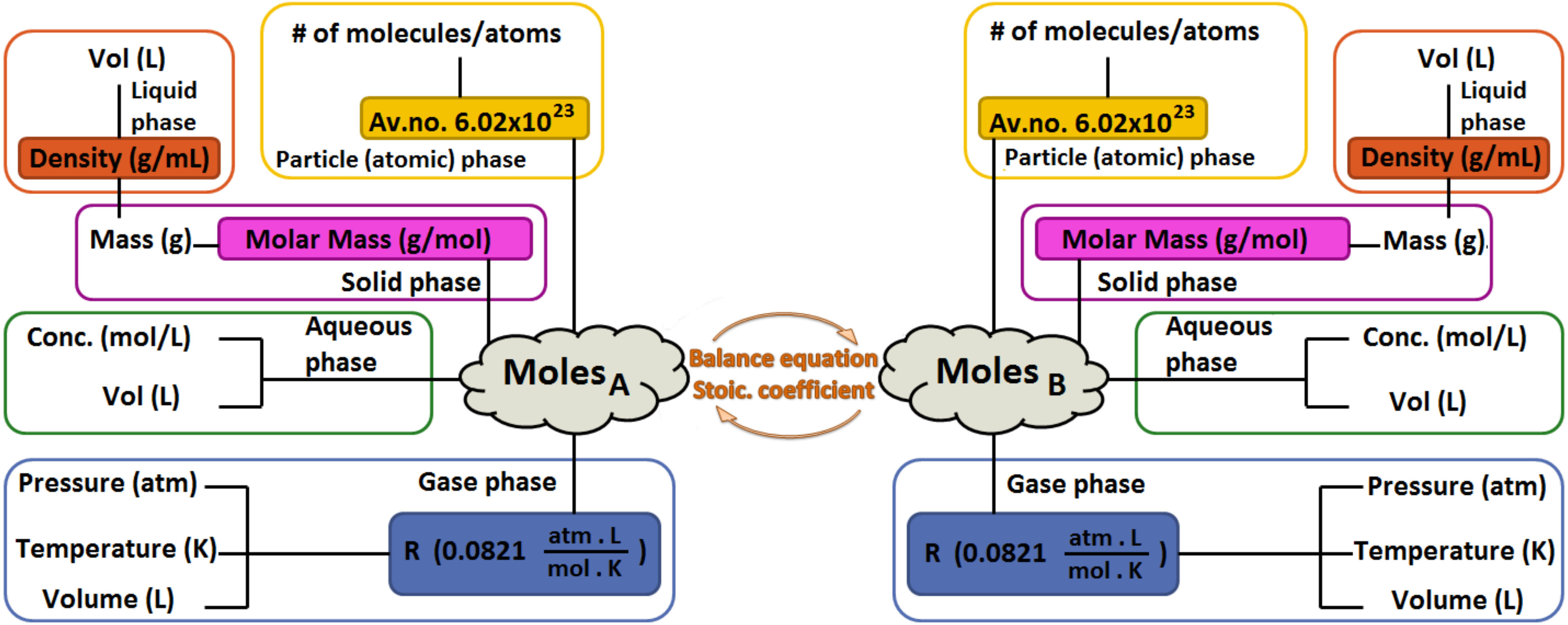
e.g. $Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^{-}$, the ratio between $Ca(OH)_2:Ca^{2+}:OH^{-}$ is 1:1:2

Q. If we have 5 moles of $Ca(OH)_2$, how many moles of OH will produce?

Q. If you have this equation,



so how many sandwich could you make by 10 slices of bread and 10 slices of cheese?



Vol (L)
Liquid phase
Density (g/mL)

# of molecules/atoms
Av.no. 6.02×10^{23}
Particle (atomic) phase

Mass (g)
Molar Mass (g/mol)
Solid phase

Conc. (mol/L)
Vol (L)
Aqueous phase

Moles$_A$

Balance equation
Stoic. coefficient

Moles$_B$

Pressure (atm)
Temperature (K)
Volume (L)
Gase phase
R $(0.0821 \frac{atm \cdot L}{mol \cdot K})$

# of molecules/atoms
Av.no. 6.02×10^{23}
Particle (atomic) phase

Vol (L)
Liquid phase
Density (g/mL)

Molar Mass (g/mol)
Mass (g)
Solid phase

Aqueous phase
Conc. (mol/L)
Vol (L)

Gase phase
R $(0.0821 \frac{atm \cdot L}{mol \cdot K})$
Pressure (atm)
Temperature (K)
Volume (L)

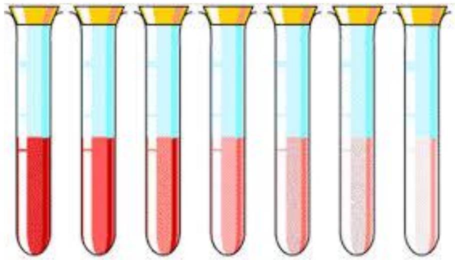
$$\text{Moles of A} = \frac{\text{mass of A}}{\text{Molar mass of A}} \text{(this is used generally if A is solid substance)}$$

$$\text{Moles of A} = \text{Molar concentration of A} \times \text{Volume of solution (this is used generally if A is solute substance in a solution)}$$

$$\text{Moles of A} = \frac{\text{Pressure} \times \text{Volume}}{\text{R(constant)} \times \text{Temperature}} \text{(this is used generally if A is gaseous substance)}$$

$$\text{Moles of A} = \frac{\text{Number of A particles}}{\text{Avogadro's Number (constant)}} \text{(this is used generally if number of A is known)}$$

Concentration



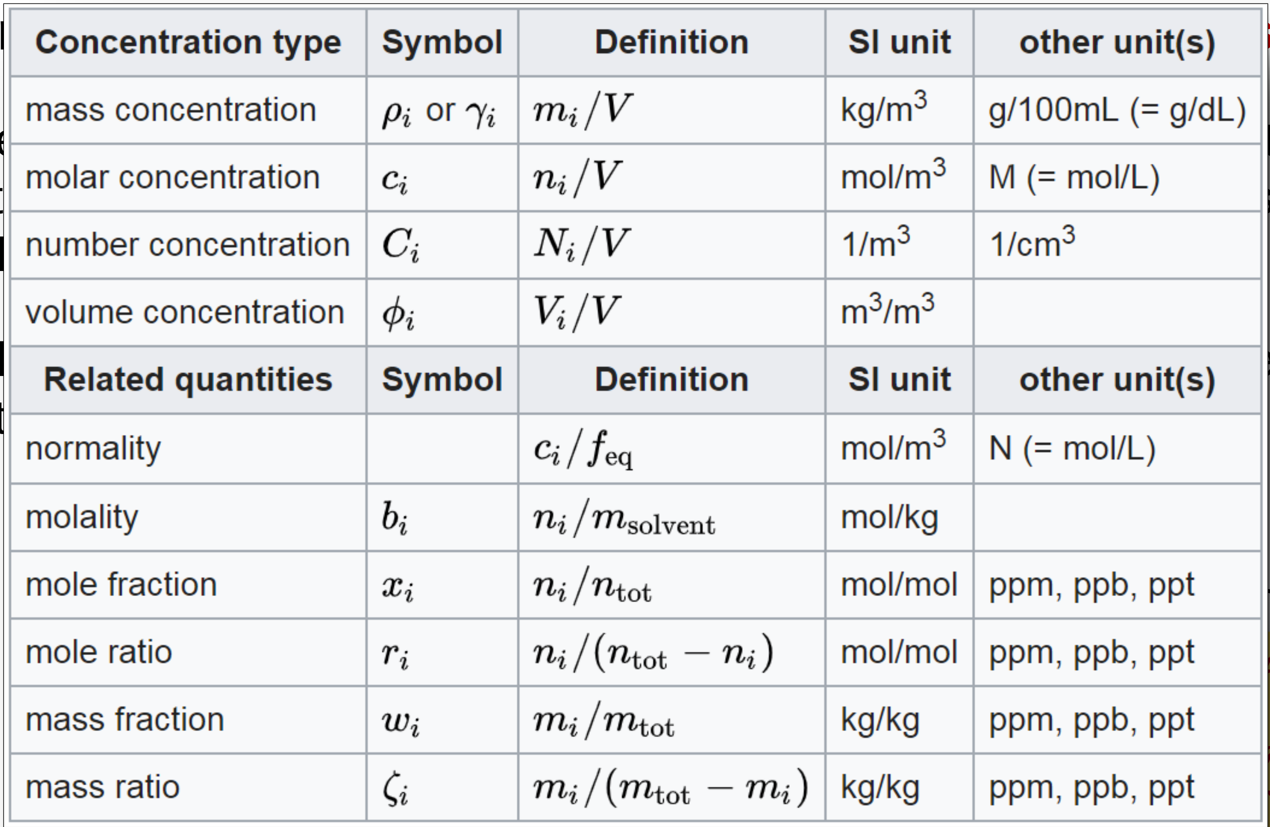
Concent **space”**

We refe tration by
“Analyt s called
“Sampl

The most l e molar
concentrat

Molarity **of solution**]

n (L)



Concentration type	**Symbol**	**Definition**	**SI unit**	**other unit(s)**
mass concentration	ρ_i or γ_i	m_i/V	kg/m^3	g/100mL (= g/dL)
molar concentration	c_i	n_i/V	mol/m^3	M (= mol/L)
number concentration	C_i	N_i/V	$1/m^3$	$1/cm^3$
volume concentration	ϕ_i	V_i/V	m^3/m^3	
Related quantities	**Symbol**	**Definition**	**SI unit**	**other unit(s)**
normality		c_i/f_{eq}	mol/m^3	N (= mol/L)
molality	b_i	$n_i/m_{solvent}$	mol/kg	
mole fraction	x_i	n_i/n_{tot}	mol/mol	ppm, ppb, ppt
mole ratio	r_i	$n_i/(n_{tot} - n_i)$	mol/mol	ppm, ppb, ppt
mass fraction	w_i	m_i/m_{tot}	kg/kg	ppm, ppb, ppt
mass ratio	ζ_i	$m_i/(m_{tot} - m_i)$	kg/kg	ppm, ppb, ppt

the volume is
temperature,
rity unit is
e dependent.

Q. Calculate the molarity of Cl^- in a solution made by dissolving 20 g of $BaCl_2$ in 360 mL water? (M.wt of $BaCl_2$ is 208 g/mol)

Concentration

Solution Preparation steps

(a) An amount of solute is weighed out on an analytical balance and then

(b) A portion of the solvent is added to the volumetric flask.

(c) The mixture is swirled until *all* of the solute is dissolved.

(d) Additional solvent is added up to the mark on the volumetric flask.

Example

A solution is prepared by dissolving 1.26 g $AgNO_3$ in a 250-mL volumetric flask and diluting to volume. Calculate the molarity of the silver nitrate solution. How many millimoles $AgNO_3$ were dissolved? (M.wt. $AgNO_3$ is 169.9 g/mol)

Solution

$$M = \frac{1.26\ \text{g}/169.9\ \text{g/mol}}{0.250\ \text{L}} = 0.0297\ \text{mol/L (or 0.0297 mmol/mL)}$$

Then,

$$\text{Millimoles} = (0.0297\ \text{mmol/mL})(250\ \text{mL}) = 7.42\ \text{mmol}$$

Remember, the units in a calculation must combine to give the proper units in the answer

Example

How many grams Na_2SO_4 should be weighed out to prepare 500 mL of a 0.100 M solution? (M.wt. Na_2SO_4 is 142 g/mol)

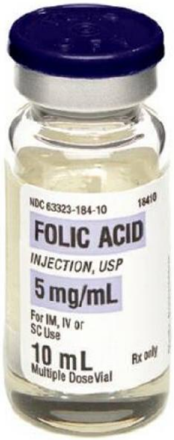
Solution

$$500\ \text{mL} \times 0.100\ \text{mmol/mL} = 50.0\ \text{mmol}$$

$$50.0\ \text{mmol} \times 142\ \text{mg/mmol} \times 0.001\ \text{g/mg} = 7.10\ \text{g}$$

M.wt. (g/mol) ≡ M.wt. (mg/mmol)

Concentration Units

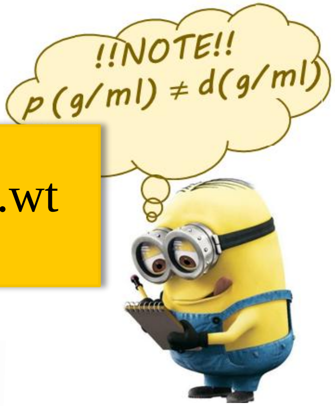


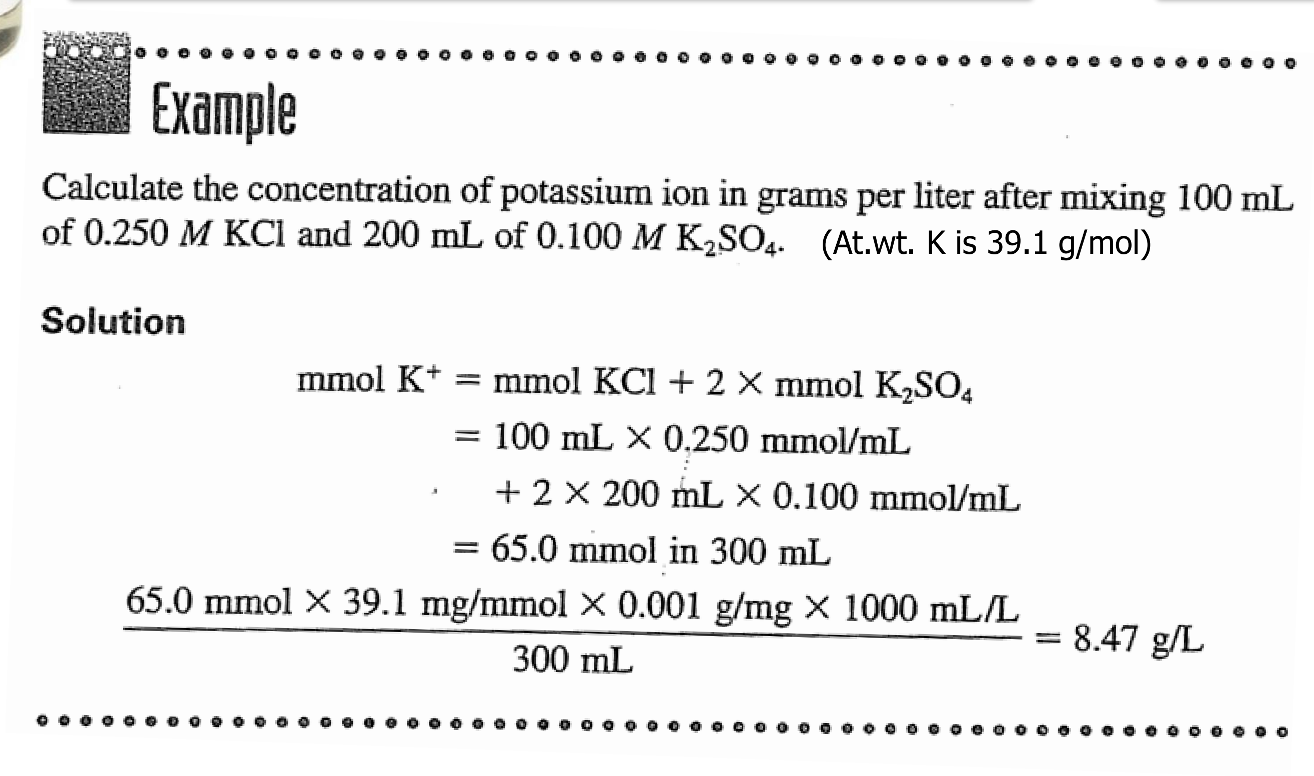
For solutions also we can use the unit of **g/L (≡mg/mL)** or **g/mL** or **mg/L** to express the **mass of solute per volume of solution** (mass concentration ***p***)

$$\text{concentration (g/L)} = \frac{\text{mass of solute (g)}}{\text{volume of solution (L)}}$$

or

$$M \times M.wt$$





Example

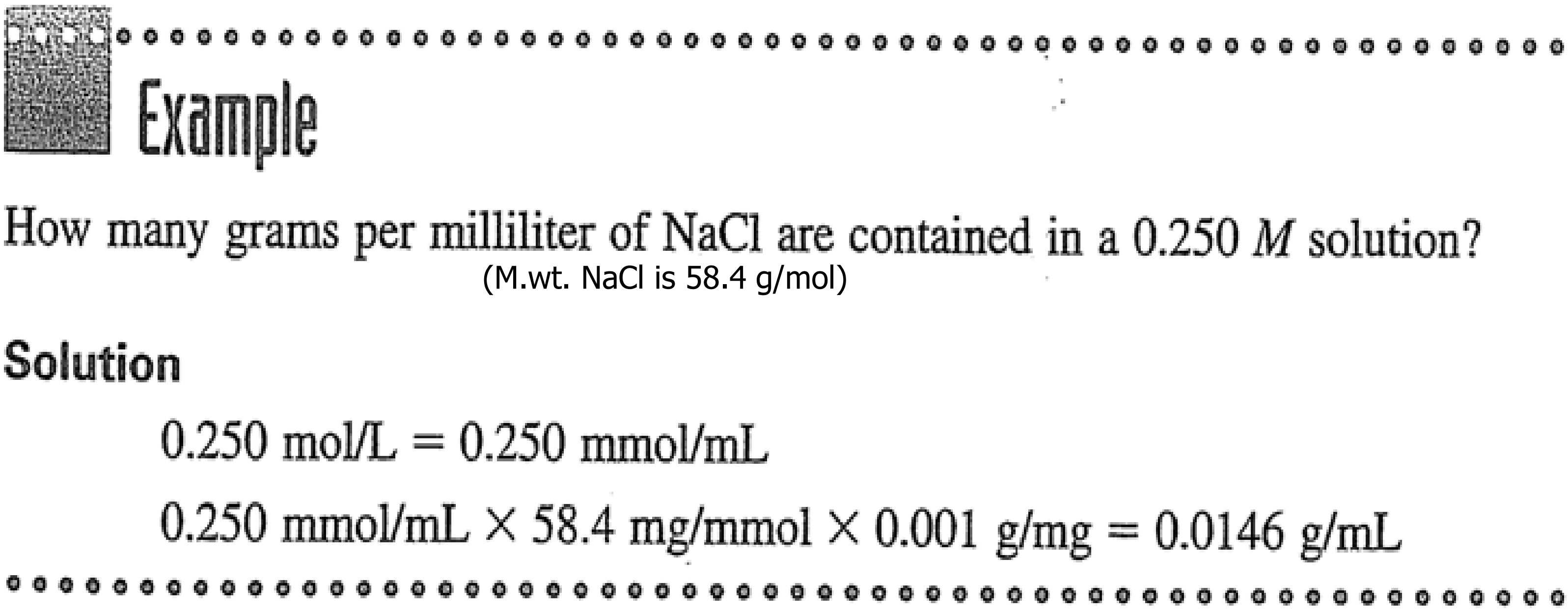
Calculate the concentration of potassium ion in grams per liter after mixing 100 mL of 0.250 *M* KCl and 200 mL of 0.100 *M* K_2SO_4. (At.wt. K is 39.1 g/mol)

Solution

$$\begin{aligned}\text{mmol } K^+ &= \text{mmol KCl} + 2 \times \text{mmol } K_2SO_4\\ &= 100 \text{ mL} \times 0.250 \text{ mmol/mL}\\ &\quad + 2 \times 200 \text{ mL} \times 0.100 \text{ mmol/mL}\\ &= 65.0 \text{ mmol in } 300 \text{ mL}\end{aligned}$$

$$\frac{65.0 \text{ mmol} \times 39.1 \text{ mg/mmol} \times 0.001 \text{ g/mg} \times 1000 \text{ mL/L}}{300 \text{ mL}} = 8.47 \text{ g/L}$$

Concentration Units



Example

How many grams per milliliter of NaCl are contained in a 0.250 *M* solution?

(M.wt. NaCl is 58.4 g/mol)

Solution

0.250 mol/L = 0.250 mmol/mL

0.250 mmol/mL × 58.4 mg/mmol × 0.001 g/mg = 0.0146 g/mL

Concentration Units

Normality (N) unit

Although molarity is widely used in chemistry, some chemists use a unit of concentration in quantitative analysis called **normality (N).**

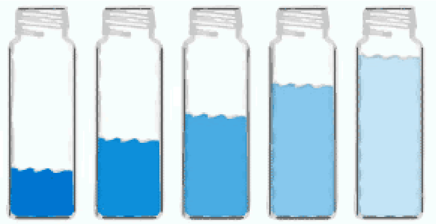
A **one-normal solution** contains **one equivalent per liter**. An equivalent represents the mass of material providing Avogadro’s number of reacting units. A reacting unit is a proton or an electron. **The number of equivalents is given by the number of moles multiplied by the number of reacting units per molecule or atom**; the equivalent weight is the formula weight divided by the number of reacting units **(n)**.

Molality (*m*) unit

- A one-molal solution contains one mole per 1000 g of solvent.

$$\text{Molality (m)} = \frac{\text{No. of moles (mol)}}{\text{Mass of Solvent (kg)}}$$

Dilution



Dilution is a process in which we decrease the concentration of a substance from high concentration (initial) to lower concentration (final) by adding more solvent.

Number of moles is not changed, only the concentration and volume are changed, therefore

$$\textbf{Moles}_{\text{initial}} = \textbf{Moles}_{\text{final}}$$

$$(\textbf{Conc. x Vol})_i = (\textbf{Conc. x Vol})_f$$

Example

What will be the volume of 0.2M NaCl solution that should be taken to prepare 5L of 0.004M NaCl solution?

Answer

Initial: Conc. = 0.2M, Vol.=??
Final: Conc. = 0.004M, Vol.=5L
$(M.V)_i=(MV)_f$ ⇨ $0.2xV_i = 0.004x5$ ⇨ $V_i = (0.004x5)/0.2 = 0.1$ L

Dilution

Dilution steps

(a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration.

(b) The measured volume of stock solution is transferred to a second volumetric flask.

(c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].

Dilution

Example

You wish to prepare a calibration curve for the spectrophotometric determination of permanganate. You have a stock 0.100 M solution of $KMnO_4$ and a series of 100-mL volumetric flasks. What volumes of the stock solution will you have to pipet into the flasks to prepare standards of 1.00, 2.00, 5.00, and 10.0×10^{-3} M $KMnO_4$ solutions?

Solution

A 100-mL solution of 1.00×10^{-3} M $KMnO_4$ will contain

$$100 \text{ mL} \times 1.00 \times 10^{-3} \text{ mmol/mL} = 0.100 \text{ mmol } KMnO_4$$

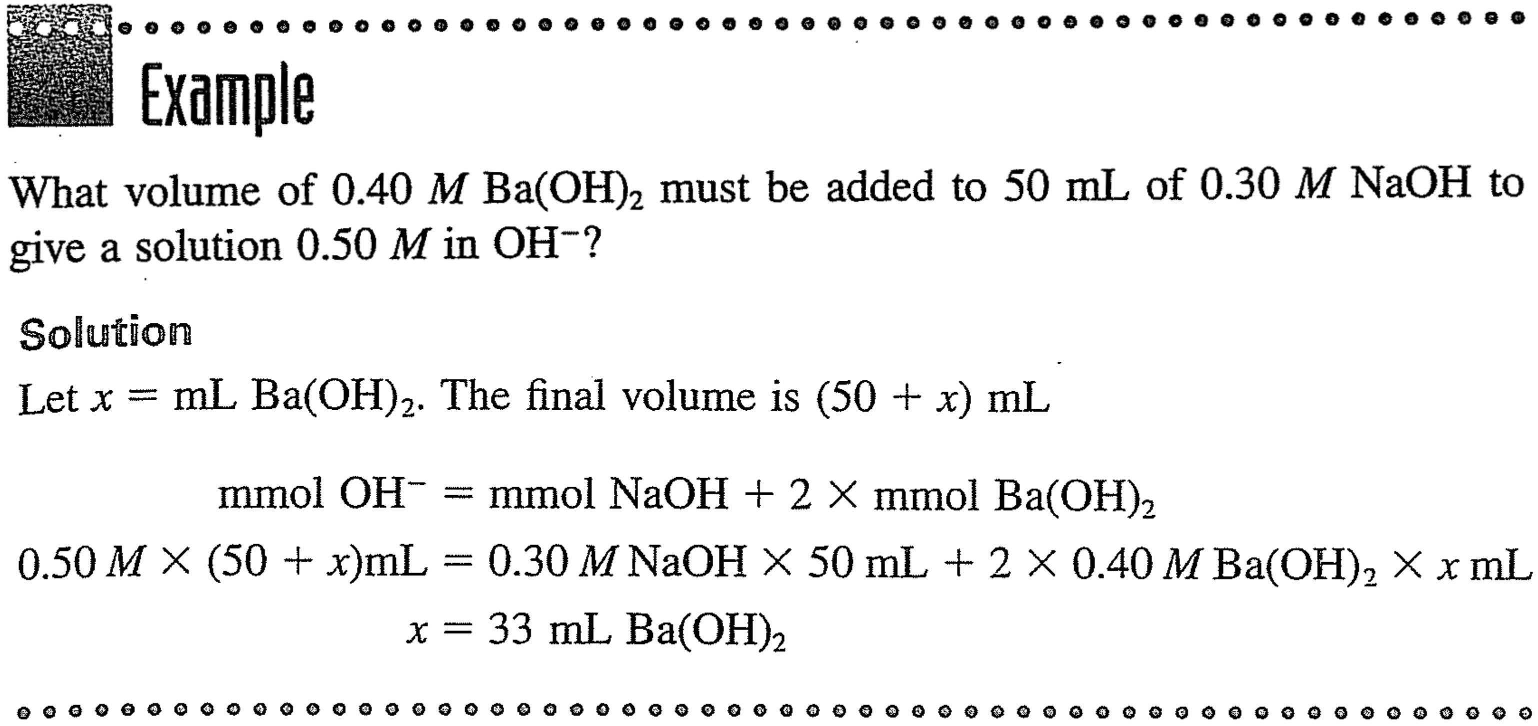
We must pipet this amount from the stock solution.

$$0.100 \text{ mmol/mL} \times x \text{ mL} = 0.100 \text{ mmol}$$
$$x = 1.00 \text{ mL stock solution}$$

Similarly, for the other solutions we will need 2.00, 5.00, and 10.0 mL of the stock solution, which will be diluted to 100 mL.

What is the difference between Standard solution, Stock solution, and Working solution!!

Dilution



Example

What volume of 0.40 M $Ba(OH)_2$ must be added to 50 mL of 0.30 M NaOH to give a solution 0.50 M in OH^-?

Solution

Let x = mL $Ba(OH)_2$. The final volume is $(50 + x)$ mL

$$\text{mmol OH}^- = \text{mmol NaOH} + 2 \times \text{mmol Ba(OH)}_2$$

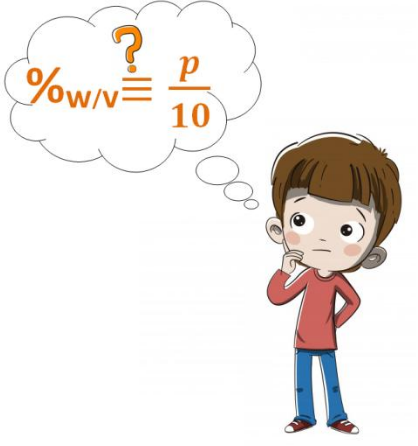
$$0.50\,M \times (50 + x)\text{mL} = 0.30\,M\ \text{NaOH} \times 50\ \text{mL} + 2 \times 0.40\,M\ \text{Ba(OH)}_2 \times x\ \text{mL}$$

$$x = 33\ \text{mL Ba(OH)}_2$$

Concentration units

Percentage unit (%)

Percentage unit is a concentration unit generally used for solid media. It could be expressed as



$$\%_{w/w} = \frac{\text{mass of solute (g)}}{\text{mass of sample (g)}} \times 100$$

$$\%_{w/v} = \frac{\text{mass of solute (g)}}{\text{volume of sample (mL)}} \times 100$$

$$\%_{v/v} = \frac{\text{volume of solute (mL)}}{\text{volume of sample (mL)}} \times 100$$

The units here does not cancel each other, note that the numerator unit is (g) of solute while the denominator unit is (g) of sample

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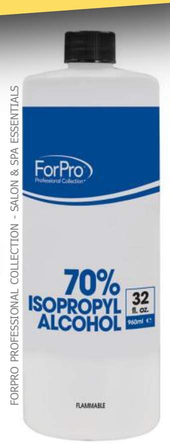


Q. What is the percentage concentration ($\%_{w/w}$) of NaCl in a solution made by dissolving 20.0 g NaCl in 200 mL water?

Q. Calculate the Na $\%_{w/w}$ in the above solution? (M.wt. NaCl is 58.5 g/mol and At.wt. for Na is 23 g/mol)

Q. What is the molar concentration (M) of Glucose solution that has %w/w of 15%? (M.wt. for glucose is 180 g/mol) (hint: assume solute will not affect $V_{solution}$)

Concentration units

Example

Calculate the molarity of concentrated HCl solution that have a density of 1.188 g/mL and have % concentration of 36% w/w? (M.wt. HCl = 36.5 g/mol)

Answer

$$\text{Molarity of HCl concentrated} = \frac{\text{mole of HCl}}{\text{volume of solution (L)}}$$

$$\text{1L of the solution has a mass of 1188 g, Density} = \frac{\text{mass}}{\text{volume}}$$

$$\Rightarrow \text{mass} = \text{Density} \times \text{volume} \Rightarrow \text{mass} = 1.188\text{g/mL} \times 1000\text{ mL} = 1188\text{ g}$$

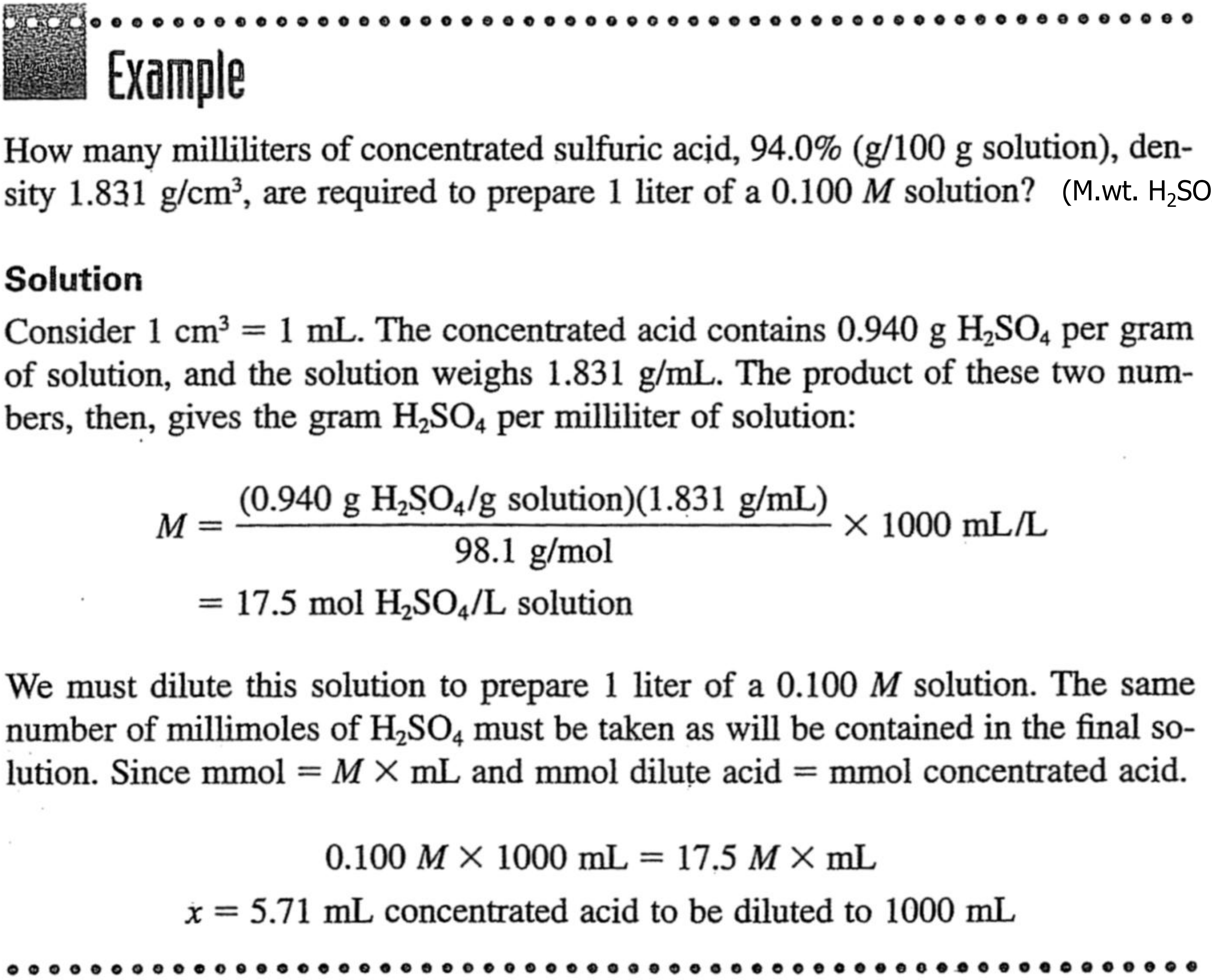
$$\text{this mass of solution has 36\% of HCl, so mass of HCl} = 1188 \times \frac{36}{100} = 427.68\text{ g HCl}$$

$$\text{this mass of HCl contains no. of moles equal to } \frac{\text{mass HCl}}{\text{M.wt. HCl}} = \frac{427.68\text{ g}}{36.5\text{ g/mol}} = 11.72\text{ mol HCl}$$

$$\text{So 1L of the solution contains 11.72 mol HCl, then } M_{HCl} = \frac{\text{mol HCl}}{\text{volume of solution (L)}} = \frac{11.72}{1} = 11.72\text{M}$$

$$\text{in other words, } \boxed{M_{HCl} = \frac{1000 \times D \times \%_{w/w}}{\text{M.wt.}}} = \frac{1000 \times 1.188 \times 0.36}{36.5} = 11.72\text{ M}$$

Dilution



Example

How many milliliters of concentrated sulfuric acid, 94.0% (g/100 g solution), density 1.831 g/cm³, are required to prepare 1 liter of a 0.100 *M* solution? (M.wt. H_2SO_4 is 98.1 g/mol)

Solution

Consider 1 cm³ = 1 mL. The concentrated acid contains 0.940 g H_2SO_4 per gram of solution, and the solution weighs 1.831 g/mL. The product of these two numbers, then, gives the gram H_2SO_4 per milliliter of solution:

$$M = \frac{(0.940 \text{ g } H_2SO_4/\text{g solution})(1.831 \text{ g/mL})}{98.1 \text{ g/mol}} \times 1000 \text{ mL/L}$$

$$= 17.5 \text{ mol } H_2SO_4/\text{L solution}$$

We must dilute this solution to prepare 1 liter of a 0.100 *M* solution. The same number of millimoles of H_2SO_4 must be taken as will be contained in the final solution. Since mmol = *M* × mL and mmol dilute acid = mmol concentrated acid.

$$0.100\ M \times 1000 \text{ mL} = 17.5\ M \times \text{mL}$$

$$x = 5.71 \text{ mL concentrated acid to be diluted to 1000 mL}$$

Concentration units

Mainly used for trace analysis

Part Per Million (ppm) and Part Per Billion (ppb) Units

These units could be used either if the solute was present in solid, liquid or gas medium

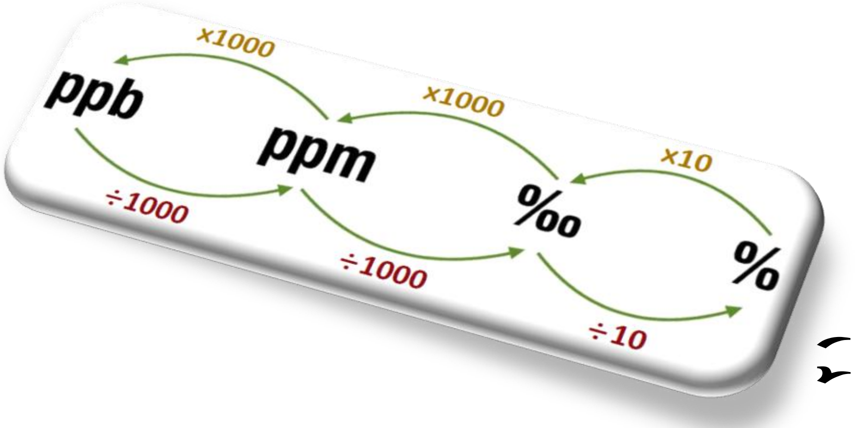
‰ = [mass of substance (g) / mass of solution (g)] x $\mathbf{10^3}$

ppm = [mass of substance (g) / mass of solution (g)] x $\mathbf{10^6}$

ppb = [mass of substance (g) / mass of solution (g)] x $\mathbf{10^9}$

ppt = [mass of substance (g) / mass of solution (g)] x $\mathbf{10^{12}}$

- we can convert **molarity** to **ppm** if we knew the density of the solution.

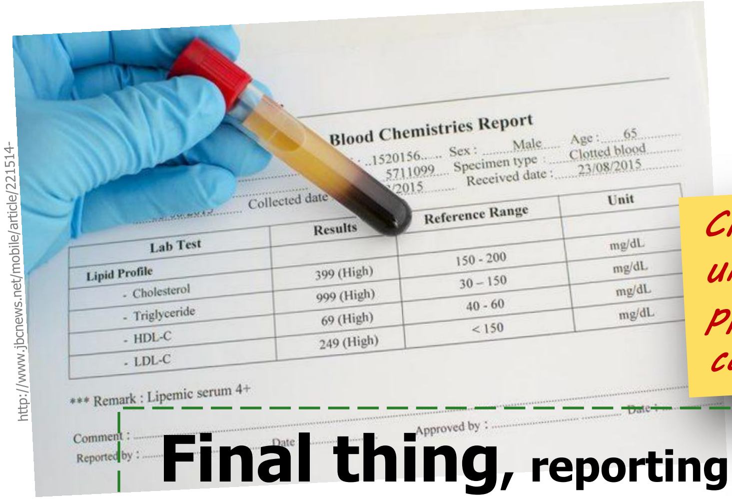


Concentration units

Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million	ppm	mg/kg	mg/L	μL/L
(1 ppm = 10^{-4}%)		μg/g	μg/mL	nL/mL
Parts per billion	ppb	μg/kg	μg/L	nL/L
(1 ppb = 10^{-7}% = 10^{-3} ppm)		ng/g	ng/mL	pL/mL[a]
Milligram percent	mg%	mg/100 g	mg/100 mL	

[a] pL = picoliter = 10^{-12} L.



Blood Chemistries Report

..1520156.... Sex : Male Age : 65

5711099 Specimen type : Clotted blood

/2015 Received date : 23/08/2015

Collected date

Lab Test	Results	Reference Range	Unit
Lipid Profile	399 (High)	150 - 200	mg/dL
- Cholesterol	999 (High)	30 – 150	mg/dL
- Triglyceride	69 (High)	40 - 60	mg/dL
- HDL-C	249 (High)	< 150	mg/dL
- LDL-C			

*** Remark : Lipemic serum 4+

Comment :

Reported by : Date Approved by : Date :

http://www.jbcnews.net/mobile/article/221514-

For dilute aqueous solutions, wt/wt ≈ wt/vol because the density of water is near 1.000 mg/ml

Clinical chemists sometimes prefer to use the unit milligram percent (mg%) rather than ppm for small concentrations and usually it called milligrams per deciliter (mg/dL)

Final thing, reporting concentrations as different chemical species!

We may express results in any form of the analyte. This is often done to facilitate the interpretation by other professionals. For example, water hardness due to calcium ion is expressed as ppm $CaCO_3$.

Concentration units

Example

A 2.6-g sample of plant tissue was analyzed and found to contain 3.6 μg zinc. What is the concentration of zinc in the plant in ppm? In ppb?

Solution

$$\frac{3.6\ \mu g}{2.6\ g} = 1.4\ \mu g/g \equiv 1.4\ ppm$$

$$\frac{3.6 \times 10^3\ ng}{2.6\ g} = 1.4 \times 10^3\ ng/g \equiv 1400\ ppb$$

One ppm is equal to 1000 ppb. $\boxed{\text{One ppb is equal to } 10^{-7}\%.}$

Example

(a) Calculate the molar concentrations of 1.00 ppm (1 mg/L) solutions each of Li^+ and Pb^{2+}. (b) What weight of $Pb(NO_3)_2$ will have to be dissolved in 1 liter of water to prepare a 100 ppm (100 mg/L) Pb^{2+} solution?

At.wt Li = 6.94 g/mol, Pb = 207 g/mol.
M.wt $Pb(NO_3)_2$ = 283.2 g/mol

Solution

■ **(a)** $M_{Li} = 1.44 \times 10^{-4}$ mol/L
$M_{Pb} = 4.83 \times 10^{-6}$ mol/L
(b) 0.137 g $Pb(NO_3)_2$

CLASSICAL CHEMICAL ANALYSIS

Chemical analysis is mainly employ the use of a balanced chemical reaction.

In **Volumetric** or titrimetric analyses, the test substance **Analyte** (the substance that we need to determine its concentration) reacts with an added reagent of known concentration (standard solution). This standard solution is typically delivered gradually from a burette, and called **Titrant**. Analyte concentration could be calculated from the chemical relation between these two reactants.

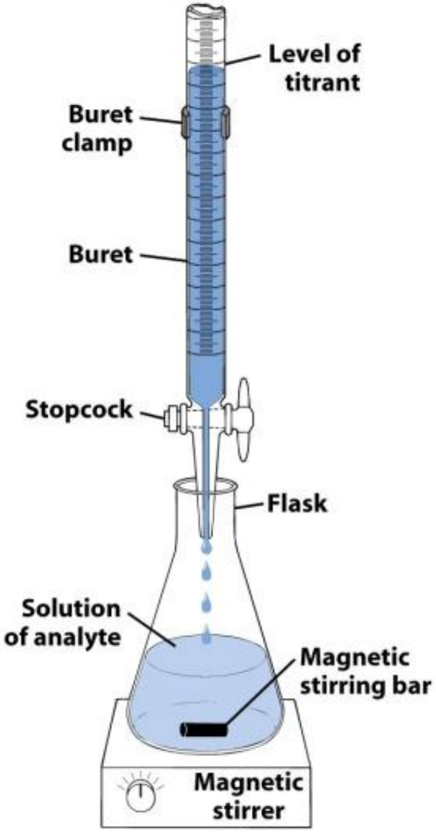
In **Gravimetric** analyses, the **Analyte** is converted to a **Precipitated Product** according to a balanced chemical reaction. Analyte concentration could be calculated from the chemical relation between the analyte reactant and the precipitated product as indicated from the balanced chemical equation.

TITRATION

The requirements of a titration are as follows:

1. The reaction must be stoichiometric. That is, there must be a well-defined and known reaction between the analyte and the titrant.
2. The reaction should be rapid and quantitative. That is, the equilibrium of the reaction should be far to the product side so that a sufficiently sharp change will occur at the end point to obtain the desired accuracy.
3. There should be no side reactions; the reaction should be specific.
4. There should be a marked change in some property of the solution when the reaction is complete. An indicator is generally added to monitor this change.

The point at which an equivalent or stoichiometric amount of titrant is added is called the equivalence point. The point at which the reaction is observed to be complete is called the end point, that is, when a change in some property of the solution is detected.



STANDARD SOLUTIONS

A standard solution is prepared by dissolving an accurately weighed quantity of a **highly pure material called a primary standard** and diluting to an accurately known volume in a volumetric flask. Alternatively, if the material is not sufficiently pure, a solution is prepared to give approximately the desired concentration, then this solution **standardized** by titrating against weighed quantity of a primary standard. A solution standardized by titrating a primary standard is itself **a secondary standard**.

A primary standard should fulfill these requirements:

1. It should be highly pure (100.00%), with accurately known impurity.
2. It should be stable to drying temperatures, and indefinitely at room temperature.
3. It should be readily and relatively inexpensively available.
4. Although not essential, it should have a high formula weight.
5. It should possess the properties required for a titration listed above. In particular, the equilibrium of the reaction should be far to the right so that a sharp end point will be obtained.

CLASSIFICATION OF TITRATION METHODS

1. **Acid–Base.** The end points of these titrations are easy to detect, either by means of an indicator or by following the change in pH with a pH meter.
2. **Precipitation.** Titrant forms an insoluble product with the analyte. Again, indicators can be used to detect the end point, or the potential of the solution can be monitored electrically.
3. **Complexometric.** Titrant is a reagent that forms a water-soluble complex with the analyte, a metal ion. The titrant is often a chelating agent like Ethylenediaminetetraacetic acid (EDTA). Indicators can be used to form a highly colored complex with the metal ion.
4. **Reduction–Oxidation.** These “redox” titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa. Appropriate indicators for these titrations are available; various electrometric means to detect the end point may also be used.

Volumetric Calculations

A 0.4671-g sample containing sodium bicarbonate was dissolved and titrated with standard 0.1067 *M* hydrochloric acid solution, requiring 40.72 mL. The reaction is

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

Calculate the percent sodium bicarbonate in the sample.

$NaHCO_3$ 84.01 g/mol

Solution 78.14% $NaHCO_3$

A 0.2638-g soda ash sample is analyzed by titrating the sodium carbonate with the standard 0.1288 *M* hydrochloride solution, requiring 38.27 mL. The reaction is

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

Calculate the percent sodium carbonate in the sample.

Na_2CO_3 105.99 g/mol

Solution 99.02% Na_2CO_3

Volumetric Calculations

How many milliliters of 0.25 *M* solution of H_2SO_4 will react with 10 mL of a 0.25 *M* solution of NaOH?

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

Solution 5.0 mL H_2SO_4

The iron(II) in an acidified solution is titrated with a 0.0206 *M* solution of potassium permanganate:

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

If the titration required 40.2 mL, how many milligrams iron are in the solution?

Fe 55.8 g/mol

Solution 231 mg Fe

Volumetric Calculations

Aluminum is determined by titrating with EDTA:

$$Al^{3+} + H_2Y^{2-} \rightarrow AlY^{-} + 2H^{+}$$

A 1.00-g sample requires 20.5 mL EDTA for titration. The EDTA was standardized by titrating 25.0 mL of a 0.100 *M* $CaCl_2$ solution, requiring 30.0 mL EDTA. Calculate the percent Al_2O_3 in the sample.

Al_2O_3 101.96 g/mol

Solution 8.71% Al_2O_3

Volumetric Calculations

Pure $Na_2C_2O_4$ plus $KHC_2O_4 \cdot H_2C_2O_4$ (three replaceable protons, KH_3A_2) are mixed in such a proportion that each gram of the mixture will react with equal volumes of 0.100 *M* $KMnO_4$ and 0.100 *M* NaOH. What is the proportion?

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

$$H^+ + NaOH \rightarrow Na^+ + H_2O$$

Na_2A	134 g/mol
KH_3A_2	218 g/mol

A is C_2O_4

Solution 3.38 g Na_2A/g KH_3A_2

Back Titration

- Sometimes it is not possible to use direct titration methods. The reaction between the standard (analyte) and the titrant can be too slow, or there can be a problem with end point determination.
- In such situations we can often use a technique called back titration.
- In back titration we use two reagents - one, that reacts with the original analyte in the sample (lets call it A), and second (lets call it B), that reacts with the remaining quantities of the first reagent.
- How do we proceed? We add precisely measured amount of reagent A to the sample and once the reaction ends we titrate excess reagent A left with standard of reagent B.
- Knowing initial amount of reagent A and amount that was left after the reaction (from titration) we can easily calculate how much reagent A was used for the first reaction.

A

- *Transfer exact volume of the sample (if it's a solution) to erlenmeyer flask.*
- *If the sample is solid, then transfer exact mass of it to the flask and add solvent to dissolve it.*

B

- *Add exact volume of the reacting standard solution. Be sure that the added amount of reacting standard is sufficient to vanish the analyte in the sample and an excess of it is still remained in the reaction mixture.*

C

- *Titrate the remaining amount of reacting standard in the reaction mixture by a titrant standard solution*

Volumetric Calculations

A 0.200-g sample of pyrolusite is analyzed for manganese content as follows. Add 50.0 mL of a 0.100 *M* solution of ferrous ammonium sulfate to reduce the MnO_2 to Mn^{2+}. After reduction is complete, the excess ferrous ion is titrated in acid solution with 0.0200 *M* $KMnO_4$, requiring 15.0 mL. Calculate the percentage of manganese in the sample as Mn_3O_4 (the manganese may or may not exist in this form, but we can make the calculations on the assumption that it does).

$$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$$

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

Mn_3O_4 228.8 mg/mmol

Solution 66.7% Mn_3O_4

Gravimetric Calculations

Calculate the weight of barium and the weight of Cl present in 25.0 g $BaCl_2$.

fw $BaCl_2$ 208.2

fw Cl 35.45

Solution 8.51 g Cl

Aluminum in an ore sample is determined by dissolving it and then precipitating with base as $Al(OH)_3$ and igniting to Al_2O_3, which is weighed. What weight of aluminum was in the sample if the ignited precipitate weighed 0.2385 g?

fw Al_2O_3 101.96

fw Al 26.982

Solution 0.1262_3 g Al

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