Chapter 1
Chemical Measurements

Overview

1-1 SI Units

1-2 Chemical Concentrations

1-3 Preparing Solutions

1-4 Stoichiometry Calculations for Gravimetric Analysis

SI Units

SI base units include the following:

- meter (m)
- kilogram (kg)
- second (s)
- ampere (A)
- kelvin (K)
- mole (mol)

Derived SI Units

Other quantities can be derived in terms of base SI units. See Table 1-2.

- force (newton, N), $Kg{\cdot}m / s^2$
- pressure (pascal, Pa), N / m^2
- energy (joule, J), $N{\cdot}m$

Prefixes

TABLE 1-3 **Prefixes**

Prefix	Symbol	Factor	Prefix	Symbol	Factor
yotta Y		10^{24} deci		d	10^{-1}
zetta Z		10^{21} centi		c	10^{-2}
exa E		10^{18} milli		m	10^{-3}
peta P		10^{15} micro		μ 10	$^{-6}$
tera T		10^{12} nano		n	10^{-9}
giga G		10^{9} pico		p	10^{-12}
mega M		10^{6} femto	f		10^{-15}
kilo k		10^{3} atto		a	10^{-18}
hecto h		10^{2} zepto		z	10^{-21}
deca da		10^{1} yocto		y	10^{-24}

Table 1.3
Memorize these prefixes with their abbreviations and powers of ten.

Using Prefixes in Calculations

- In calculations, units should be carried along with the numbers.
- Prefixes such as kilo- and milli- are used to denote multiples of units.
- Prefixes can be used to simplify conversions between units.

Example:

Express 19.3 mPa in terms of atm

19.3 mPa can be written as 19.3×10^{-3} Pa

$$19.3\times10^{-3}\ \text{Pa}\ \times\frac{1.00\ \text{atm}}{101325\ \text{Pa}}=1.90\times10^{-7}\ \text{atm}$$

Concentrations

- **Molarity** (moles of solute per liter of solution), M
- **Molality** (moles of solute per kilogram of solvent), m
- **Formal concentration** (formula units per liter), F
- **Percent composition** (w/w, v/v or w/v), %
- **Parts per million,** ppm
- **Parts per billion,** ppb

% Composition (w/w or v/v)

$$\text{Weight percent} = \frac{\text{mass of solute}}{\text{mass of total solution or mixture}} \times 100$$

$$\text{Volume percent} = \frac{\text{volume of solute}}{\text{volume of total solution}} \times 100$$

95% (w/w) ethanol contains 95 g of ethanol for every 100 g of solution.

ppm, Parts per Million

$$\text{ppm} = \frac{\text{mass of substance}}{\text{mass of sample}} \times 10^6$$

$$\text{ppb} = \frac{\text{mass of substance}}{\text{mass of sample}} \times 10^9$$

- **Shortcut:** ppm is also mg/L or μg/mL if the density of the solution is 1.0 g/mL.
- An aqueous solution that is 1 000 ppm in Cu contains 1 000 mg Cu per liter of solution.
- It also contains 1000 μg per mL of solution.

ppm, Parts per Million

EXAMPLE **Converting Parts per Billion into Molarity**

Normal alkanes are hydrocarbons with the formula C_nH_{2n+2}. Plants selectively synthesize alkanes with an odd number of carbon atoms. The concentration of $C_{29}H_{60}$ in summer rainwater collected in Hannover, Germany, is 34 ppb. Find the molarity of $C_{29}H_{60}$ and express the answer with a prefix from Table 1-3.

Solution A concentration of 34 ppb means there are 34 ng of $C_{29}H_{60}$ per gram of rainwater, which is nearly the same as 34 ng/mL because the density of rainwater is close to 1.00 g/mL. To find the molarity, we need to know how many grams of $C_{29}H_{60}$ are contained in a liter. Multiplying nanograms and milliliters by 1 000 gives 34 μg of $C_{29}H_{60}$ per liter of rainwater:

$$\frac{34\ \cancel{\text{ng}}\ C_{29}H_{60}}{\cancel{\text{mL}}}\left(\frac{1\,000\ \cancel{\text{mL}}/\text{L}}{1\,000\ \cancel{\text{ng}}/\mu\text{g}}\right) = \frac{34\ \mu\text{g}\ C_{29}H_{60}}{\text{L}}$$

The molecular mass of $C_{29}H_{60}$ is $29 \times 12.011 + 60 \times 1.008 = 408.8$ g/mol, so the molarity is

$$\text{Molarity of } C_{29}H_{60} \text{ in rainwater} = \frac{34 \times 10^{-6}\ \cancel{\text{g}}/\text{L}}{408.8\ \cancel{\text{g}}/\text{mol}} = 8.3 \times 10^{-8}\ \text{M}$$

An appropriate prefix from Table 1-3 would be nano (n), which is a multiple of 10^{-9}:

$$8.3 \times 10^{-8}\ \cancel{\text{M}}\left(\frac{1\ \text{nM}}{10^{-9}\ \cancel{\text{M}}}\right) = 83\ \text{nM}$$

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Making Solutions

- To calculate quantities of reagents needed to prepare solutions, use the relation

$$(M_{conc})(V_{conc}) = (M_{dil})(V_{dil})$$

- Equates moles of reagent removed from a stock solution to moles delivered into a new solution.

Making Solutions

- How many **moles** of $CuCl_2 \cdot 5H_2O$ are needed to make 500 mL of a solution that is 1 000.0 ppm in Cu?

- **grams** of $CuCl_2 \cdot 5H_2O$?

- **milliliters** of 10 000 ppm $CuCl_2 \cdot 5H_2O$ solution?

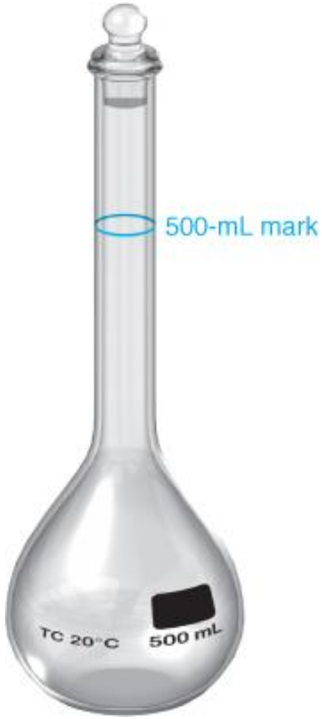
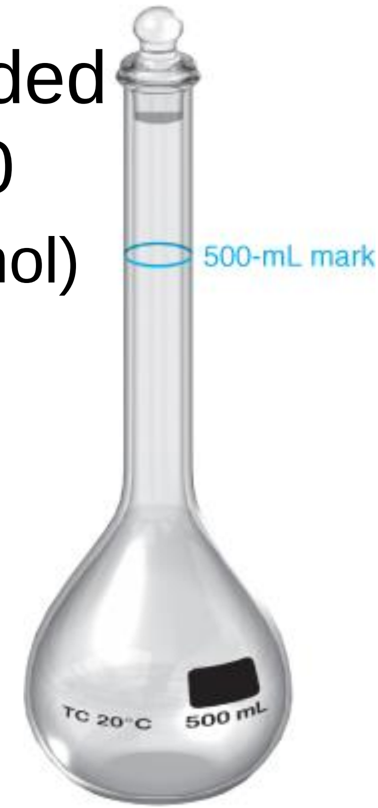


Figure 1-4

Making Solutions

- How many grams of $CuCl_2 \cdot 5H_2O$ are needed to make 500 mL of a solution that is 1 000 ppm in Cu? (MM of $CuCl_2 \cdot 5H_2O$ is 224.53 g/mol)



- First calculate the grams of Cu required
  - (500-mL) $\times$ (1000 μg/mL) = 5.0 $\times$ 10^5 μg Cu
  - 5.0 $\times$ 10^5 μg Cu = (5.0 $\times$ 10^5)(10^{-6})g Cu
  - 5.0 $\times$ 10^{-1}g Cu

$$\left(5.0 \text{ x } 10^{-1}\text{ g Cu}\right) \times \left(\frac{224.53\text{ g } CuCl_2 \cdot 5H_2O\text{ / mol}}{63.546\text{ g Cu /mol}}\right) = \mathbf{1.76_7\, g\, CuCl_2 \cdot 5H_2O}$$

Making Solutions

- How many **milliliters** of $CuCl_2{\cdot}5H_2O$ are needed to make 500 mL of a solution that is 1 000.0 ppm in Cu?

- **moles** of $CuCl_2{\cdot}5H_2O$ solution?

$$(M_{conc})(V_{conc}) = (M_{dil})(V_{dil})$$

$$(10\ 000\ \text{ppm})(V_{conc}) = (1\ 000\ \text{ppm})(500\ \text{mL})$$

$$V_{conc} = (1\ 000\ \text{ppm})(500\ \text{mL}) / (10\ 000\ \text{ppm})$$

$$V_{conc} = 50\ \text{mL}$$

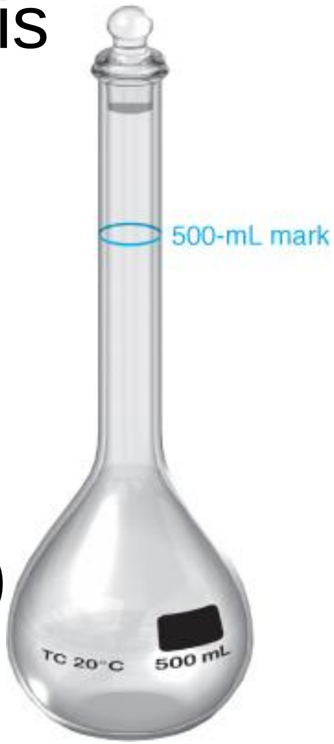


Figure 1-4

Place 50 mL of 10 000 ppm $CuCl_2$ stock solution in the 500 mL flask and fill to the 500 mL mark!

Making Solutions

- How many milliliters of concentrated HCl are needed to make 500 mL of a solution that is 0.250 M in HCl?

$$(M_{conc})(V_{conc}) = (M_{dil})(V_{dil})$$

- Need to know molarity of concentrated HCl.

Figure 1-4

Concentrated HCl is 37.2% (w/w) HCl and has a density of 1.188 g/cm^3

Making Solutions

- How many milliliters of concentrated HCl are needed to make 500 mL of a solution that is 0.250 M in HCl?

$$M_{\text{conc. HCl}} = ?$$

$$(M_{\text{conc}})(V_{\text{conc}}) = (M_{\text{dil}})(V_{\text{dil}})$$

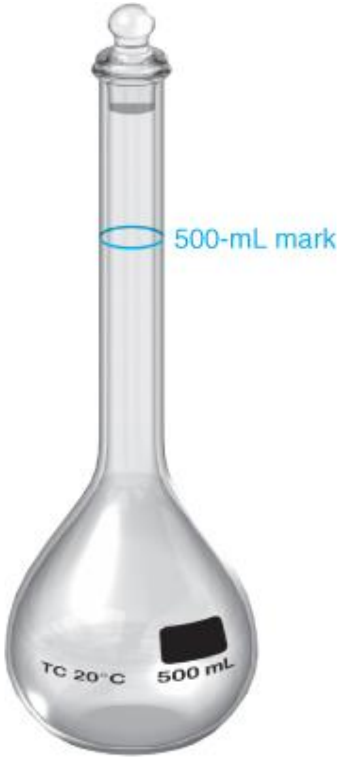


Figure 1-4

Molarity of the Conc. HCl Solution

$c = 37.2\% = 37.2\ \mathrm{gHCl} / 100\ \mathrm{g_{soln}}$

$MM = 36.46\ \mathrm{g/mol}$

$\rho = 1.188\ \mathrm{g/cm^3}$

$$\left.\begin{matrix} \\ \\ \\ \end{matrix}\right\} \begin{matrix}\text{desired units} \\ \dfrac{\text{mol HCl}}{\text{L soln}}\end{matrix}$$

$$\frac{37.2\ \mathrm{g}\ \cancel{\mathrm{HCl}}}{100\ \cancel{\mathrm{g_{soln}}}} \times \frac{1\ \mathrm{mol\ HCl}}{36.46\ \cancel{\mathrm{g\ HCl}}} \times \frac{1.188\ \cancel{\mathrm{g_{soln}}}}{1.000\ \cancel{\mathrm{cm^3_{soln}}}} \times \frac{1000\ \cancel{\mathrm{cm^3_{soln}}}}{1\ \mathrm{L}}$$

$$= 12.1\ \mathrm{mol/L}$$

Making Solutions

- How many **milliliters** of concentrated HCl are needed to make 500 mL of a solution that is 0.250 M in HCl?

$$M_{\text{conc. HCl}} = 12.1\ \text{M}$$

$$(\text{M}_{\text{conc}})(V_{\text{conc}}) = (\text{M}_{\text{dil}})(V_{\text{dil}})$$

$$(12.1\text{M})(V_{\text{conc}}) = (0.250\ \text{M})(500\ \text{mL})$$

$$V_{\text{conc}} = (0.250\ \text{M})(500\ \text{mL} / (12.1\ \text{M})$$

$$V_{\text{conc}} = 10.3_3\ \text{mL}$$

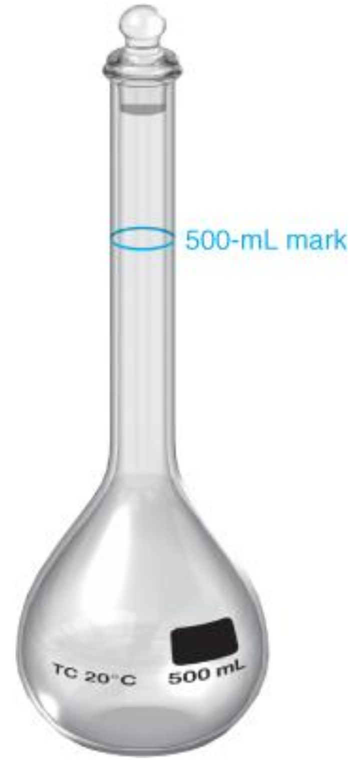


Figure 1-4

Stoichiometry

- Use stoichiometry relationships to calculate required masses or volumes of reagents for chemical reactions.
- From the mass of product of a reaction, you should be able to compute how much reactant was consumed.

Stoichiometry

Iron from a dietary supplement tablet can be measured gravimetrically by dissolving the tablet and then converting the dissolved iron into solid Fe_2O_3. The mass of Fe_2O_3 tells us the mass of iron in the original tablet.

Here are the steps in the procedure:

Step 1 Tablets containing iron(II) fumarate ($Fe^{2+}C_4H_2O_4^{2-}$) and inert binder are mixed with 150 mL of 0.100 M HCl to dissolve the Fe^{2+}. The mixture is filtered to remove insoluble binder.

Step 2 Iron(II) in the clear liquid is oxidized to iron(III) with excess hydrogen peroxide:

$$\underset{\substack{\text{Iron(II)}\\\text{(ferrous ion)}}}{2Fe^{2+}} + \underset{\substack{\text{Hydrogen peroxide}\\\text{FM 34.01}}}{H_2O_2} + 2H^+ \rightarrow \underset{\substack{\text{Iron(III)}\\\text{(ferric ion)}}}{2Fe^{3+}} + 2H_2O \qquad \textbf{(1-7)}$$

Step 3 Ammonium hydroxide is added to precipitate hydrous iron(III) oxide, which is a gel. The gel is filtered and heated in a furnace to convert it to pure solid Fe_2O_3.

$$Fe^{3+} + \underset{\text{Hydroxide}}{3OH^-} + (x-1)H_2O \longrightarrow \underset{\text{Hydrous iron(III) oxide}}{FeOOH \cdot xH_2O(s)} \xrightarrow{900°C} \underset{\substack{\text{Iron(III) oxide}\\\text{FM 159.69}}}{Fe_2O_3(s)} \qquad \textbf{(1-8)}$$

Stoichiometry

EXAMPLE **How Many Tablets Should We Analyze?**

In a gravimetric analysis, we need enough product to weigh accurately. Each tablet provides ~15 mg of iron. How many tablets should we analyze to provide 0.25 g of Fe_2O_3 product?

Solution We can answer the question if we know how many grams of iron are in 0.25 g of Fe_2O_3. The formula mass of Fe_2O_3 is 159.69 g/mol, so 0.25 g is equal to

$$\text{mol } Fe_2O_3 = \frac{0.25 \cancel{\text{g}}}{159.69 \cancel{\text{g}}/\text{mol}} = 1.6 \times 10^{-3} \text{ mol}$$

Each mol of Fe_2O_3 has 2 mol of Fe, so 0.25 g of Fe_2O_3 contains

$$1.6 \times 10^{-3} \cancel{\text{mol } Fe_2O_3} \times \frac{2 \text{ mol Fe}}{1 \cancel{\text{mol } Fe_2O_3}} = 3.2 \times 10^{-3} \text{ mol Fe}$$

The mass of Fe is

$$3.2 \times 10^{-3} \cancel{\text{mol Fe}} \times \frac{55.845 \text{ g Fe}}{\cancel{\text{mol Fe}}} = 0.18 \text{ g Fe}$$

If each tablet contains 15 mg Fe, the number of tablets required is

$$\text{Number of tablets} = \frac{0.18 \cancel{\text{g Fe}}}{0.015 \cancel{\text{g Fe}}/\text{tablet}} = 12 \text{ tablets}$$

Limiting Reagent

- The **limiting reagent** in a chemical reaction is the one that is consumed first.
- Once the limiting reagent is gone, the reaction ceases.

Example: For the reaction: $A + 2B \rightarrow P$

0.751 moles of A are mixed with 1.43 moles of B.

- What is the limiting reagent and how much excess reagent remains unreacted?

Limiting Reagent

Solution:

	A	+	2B	→	P
I.	0.751		1.43		0
F.	?		?		

If A is the L.R., how much B is required to completely consume A?

$$0.751 \text{ mol A} \times \left(\frac{2 \text{ mol B}}{1 \text{ mol A}} \right) = \mathbf{1.502 \ \ mol\ B\ required}$$

However, we only have 1.43 mol B, so B must be the L.R.

Limiting Reagent

Solution:

	A	+	2B	$\rightarrow$	P
Initial	0.751		1.43		0
Final	?		0		

If B is the L.R., how much is required to completely consume A?

$$0.1.43\ \text{mol B} \times \left(\frac{1\ \text{mol A}}{2\ \text{mol B}}\right) = \mathbf{0.715\ \ mol\ \ A}\ \ \text{react withB.}$$

So, 0.751 mol A – 0.715 mol A = 0.036 mol A remain after the reaction is complete. All of B is consumed.

Limiting Reagent

EXAMPLE **Limiting Reagent**

Reaction 1-9 requires one mole of oxalate for each mole of calcium.

$$\underset{}{Ca^{2+}} + \underset{\text{Oxalate}}{C_2O_4^{2-}} \rightarrow \underset{\text{Calcium oxalate}}{Ca(C_2O_4)\cdot H_2O(s)} \qquad (1\text{-}9)$$

If you mix 1.00 g of $CaCl_2$ (FM 110.98) with 1.15 g of $Na_2C_2O_4$ (FM 134.00) in water, which is the limiting reagent? What fraction of the nonlimiting reagent is left over?

Solution The available moles of each reagent are

$$\frac{1.00\text{ g }CaCl_2}{110.98\text{ g/mol}} = 9.01\text{ mmol }Ca^{2+} \qquad \frac{1.15\text{ g }Na_2C_2O_4}{134.00\text{ g/mol}} = 8.58\text{ mmol }C_2O_4^{2-}$$

The reaction requires 1 mol Ca^{2+} for 1 mol $C_2O_4^{2-}$, so oxalate will be used up first. The Ca^{2+} remaining is $9.01 - 8.58 = 0.43$ mmol. The fraction of unreacted Ca^{2+} is (0.43 mmol/9.01 mmol) = 4.8%

TEST YOURSELF The reaction $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$ requires 5 mol $H_2C_2O_4$ for 2 mol MnO_4^-. If you mix 1.15 g $Na_2C_2O_4$ (FM 134.00) with 0.60 g $KMnO_4$ (FM 158.03) and excess aqueous acid, which reactant is limiting? How much CO_2 is produced?