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Quantitative Chemical Analysis
Eighth Edition

Chapter 1

Chemical Measurements

SI Units

Table 1-1   Fundamental SI units

Quantity	Unit (symbol)	Definition
Length	meter (m)	One meter is the distance light travels in a vacuum during $\frac{1}{299\,792\,458}$ of a second.
Mass	kilogram (kg)	One kilogram is the mass of the prototype kilogram kept at Sèvres, France.
Time	second (s)	One second is the duration of 9 192 631 770 periods of the radiation corresponding to a certain atomic transition of ^{133}Cs.
Electric current	ampere (A)	One ampere of current produces a force of 2×10^{-7} newtons per meter of length when maintained in two straight, parallel conductors of infinite length and negligible cross section, separated by 1 meter in a vacuum.
Temperature	kelvin (K)	Temperature is defined such that the triple point of water (at which solid, liquid, and gaseous water are in equilibrium) is 273.16 K, and the temperature of absolute zero is 0 K.
Luminous intensity	candela (cd)	Candela is a measure of luminous intensity visible to the human eye.
Amount of substance	mole (mol)	One mole is the number of particles equal to the number of atoms in exactly 0.012 kg of ^{12}C (approximately 6.022 141 5 $\times 10^{23}$).
Plane angle	radian (rad)	There are 2π radians in a circle.
Solid angle	steradian (sr)	There are 4π steradians in a sphere.

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Using Prefixes as Multipliers

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
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Converting Between Units

Table 1-4   Conversion factors

Quantity	Unit	Symbol	SI equivalent[a]
Volume	liter	L	$*10^{-3}m^3$
	milliliter	mL	$*10^{-6}m^3$
Length	angstrom	Å	$*10^{-10}m$
	inch	in.	$*0.025\ 4$ m
Mass	pound	lb	$*0.453\ 592\ 37$ kg
	metric ton		$*1\ 000$ kg
Force	dyne	dyn	$*10^{-5}N$
Pressure	bar	bar	$*10^5Pa$
	atmosphere	atm	$*101\ 325$ Pa
	torr (= 1 mm Hg)	Torr	133.322 Pa
	pound/in.^{2}	psi	6 894.76 Pa
Energy	erg	erg	$*10^{-7}J$
	electron volt	eV	$1.602\ 176\ 53 \times 10^{-19}J$
	calorie, thermochemical	cal	$*4.184$ J
	Calorie (with a capital C)	Cal	$*1000$ cal $= 4.184$ kJ
	British thermal unit	Btu	1 055.06 J
Power	horsepower		745.700 W
Temperature	centigrade (= Celsius)	°C	$*K - 273.15$
	Fahrenheit	°F	$*1.8(K - 273.15) + 32$

*a . An asterisk (*) indicates that the conversion is exact (by definition).*

$$given\ unit \times \frac{desired\ unit}{given\ unit} = desired\ unit$$

The speed of sound in air is about 343 m/s. What is this speed in miles per hour?

conversion units

meters to miles: 1 mi = 1609 m

seconds to hours: 1 min = 60 s & 1 hour = 60 min

$$343\ \frac{m}{s} \times \frac{1\ mi}{1609\ m} \times \frac{60\ s}{1\ \min} \times \frac{60\ \min}{1\ hour} = 767\ \frac{mi}{hour}$$

Chemical Concentrations

● Solutions are defined as homogeneous mixtures of two or more pure substances.

● The **solvent** is present in greatest abundance.

● All other substances are **solutes.**

The ***concentration*** of a solution is the amount of solute present in a given quantity of solvent or solution.

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Molarity (*M*): the concentration of solution is measured as the number of moles of solute per liter of solution.

$$M \ = \ \text{molarity} \ = \ \frac{\text{moles of solute}}{\text{liters of solution}} = \ \frac{mol}{L} \ = \ \frac{mmol}{mL}$$

$$0.10 \ M \ HCl \ = \ 0.10 \ \frac{mol \ HCl}{L} \ = \ \frac{0.10 \ mmol \ HCl}{mL}$$

$$moles \ = \ M\left(\frac{mol}{L}\right) \times \ V(L)$$

$$mmol \ = \ M\left(\frac{mmol}{mL}\right) \times \ V(mL)$$

$$mass(g) \ = \ number \ of \ moles \ \times \ molar \ mass(g/mol)$$

Molality (m)

$$m = \frac{\text{mol of solute}}{\text{kg of solvent}}$$

● Since volume is temperature-dependent, *molarity* can change with temperature.

● Since both moles and mass do not change with temperature, *molality* (unlike *molarity*) is *not* temperature-dependent.

Percent Composition

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

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

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$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$\text{Specific gravity} = \frac{\text{density of a substance}}{\text{density of water at } 4^\circ C}$$

The density of water at 4⁰C is close to 1 g/mL, so specific gravity is nearly the same as density.

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Example 1) An aqueous solution of HCl (36.5 g/mol) contains 36.0% HCl by mass and has a density of 1.10 g/mL. Calculate
  (a) molarity and (b) molality of HCl

Suppose you have 100 g solution — Abdul-Wahab El-Rjoob

100 g solution contains 36.0 g HCl and 64.0 g H_2O

$$n_{HCl} = \frac{36.0 \text{ g}}{36.5 \text{ g/mol}} = 0.986 \text{ mol}$$

$$V_{solution} = \frac{100 g}{1.10 \text{ g/mL}} = 90.9 \text{ mL} = 0.0909 \text{ L}$$

$$M_{HCl} = \frac{0.986 \text{ } mol}{0.0909 \text{ } L} = 10.8 \text{ } mol/L$$

$$m_{HCl} = \frac{0.986 \text{ mol}}{0.0640 \text{ kg}} = 15.4 \text{ mol/kg}$$

Parts per Million (ppm) and Parts per Billion (ppb)

$$ppm = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 10^6$$

also, $1 \text{ ppm} = \frac{1 \text{ mg solute}}{\text{kg solution}} \approx \frac{1 \text{ mg solute}}{1 \text{ L solution}}$ if $d_{solution} \approx d_{water} = 1 \text{ g/mL}$

$$1 \text{ ppm} = \frac{1 \text{ mg solute}}{1 \text{ L solution}} = \frac{1 \text{ } \mu g \text{ solute}}{1 \text{ mL solution}}$$

$$ppb = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 10^9$$

also, $1 \ ppb = \dfrac{1 \ \mu g \ \text{solute}}{kg \ \text{solution}} \approx \dfrac{1 \ \mu g \ \text{solute}}{1 \ L \ \text{solution}}$ if $d_{\text{solution}} \approx d_{\text{water}} = 1 \ g/mL$

$1 \ ppb = \dfrac{\mu g \ \text{solute}}{L \ \text{solution}} = \dfrac{ng \ \text{solute}}{mL \ \text{solution}}$

Preparing Solutions

Example 1) **How many grams of $CuSO_4.5H_2O$ (249.68 g/mol) should be dissolved in a volume of 500.0 mL to make 8.00 mM Cu^{2+}?**

$$8.00 \times 10^{-3} \ \frac{mol}{L} \times 0.500 \ L \times 249.68 \ \frac{g}{mol} = 0.999 \ g$$

Dilution is the procedure for preparing a less concentrated solution from a more concentrated solution. Abdul-Wahab El-Rjoob

Moles of solute before dilution (i)	=	Moles of solute after dilution (f)
M_iV_i	=	M_fV_f

Q) How would you prepare 60.0 mL of 0.200 M HNO_3 from a stock solution of 4.00 M HNO_3?

$$V_i = \frac{M_f V_f}{M_i} = \frac{0.200 \ M \ x \ 60.0 \ mL}{4.00 \ M} = 3 \, mL$$

$3 \, mL$ of acid $+ \ 57 \, mL$ of water $= \ 60 \, mL$ of solution

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Stoichiometry Calculations for Gravimetric Analysis

Chemical analysis based on weighing a final product is called **gravimetric analysis**.

Analyte → insoluble form → dry or ignite ppt. → weigh the ppt.

Example page 21: In a gravimetric analysis, we need enough product to weigh accurately. Each tablet provides approximately 15 mg of Fe (55.845 g/mol). How many tablets should we analyze to provide 0.25 g of Fe_2O_3 (159.69 g/mol) product?

$$g \ Fe = 0.25 \ g \ Fe_2O_3 \ \times \frac{1 \ mol \ Fe_2O_3}{159.69 \ g \ Fe_2O_3} \times \frac{2 \ mol \ Fe}{1 \ mol \ Fe_2O_3}$$

$$\times \frac{55.845 \ g \ Fe}{1 \ mol \ Fe} = 0.18 \ g \ Fe$$

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

What mass of 3.0 wt% H_2O_2 (34.01 g/mol) solution is required to provide a 50% excess of reagent for reaction (1-5) with 12 dietary iron tablets?

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \qquad (1\text{-}5)$$

g Fe^{2+} = 12 × 0.015 g = 0.18

mol Fe^{2+} = (0.18 g Fe^{2+}) / (55.845 g Fe^{2+}/mol Fe^{2+}) = 3.2×10^{-3}

moles H_2O_2 = 1/2 × 3.2×10^{-3} × 1.5 = 2.4×10^{-3}

g H_2O_2 = 2.4×10^{-3} mol × 34.01 g/mol = 0.082 g

g H_2O_2 solution = 0.082 g ÷ 0.030 g H_2O_2/g solution = 2.7

Introduction to Titration

● Procedures in which we measure the volume of a standard reagent needed to react with analyte (the substance being measured) are called **volumetric analysis**.

● A ***standard reagent*** is one whose concentration is known.

● In a *titration* a solution of accurately known concentration (titrant) is added gradually to another solution of unknown concentration

(analyte) until the chemical reaction between the two solutions is complete.

● *Equivalence point* – the point at which the reaction is complete.

● *End point* – is marked by a sudden change in a physical property of the solution.   Abdul-Wahab El-Rjoob

$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$
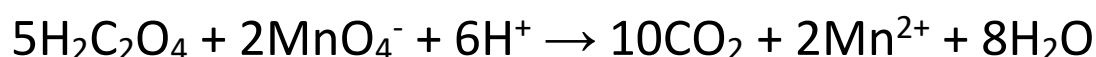
5 moles   2 moles

Methods of determining end point:

1) detecting a sudden change in the voltage or current between a pair of electrodes.

2) monitoring absorption of light by reactants or products.

3) observing an indicator color change.

Indicator – a substance having a physical property (usually color) that changes abruptly near the equivalence point of a chemical reaction.

● **Titration error** is the difference between the observed end point and the true equivalence point in a titration.

● **Titration error** can be estimated with **a blank titration**, in which we carry out the same procedure without analyte.

● **Blank titration** is one in which a solution containing reagents except analyte is titrated. The volume of titrant needed in the blank titration should be subtracted from the volume needed to titrate unknown.

● **Primary standard** is a reagent that is pure enough (99.9% or better) and stable enough to be used directly after weighing. It should not decompose under ordinary storage, and it should be stable when dried by heat or vacuum.

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Examples of Primary standards:

KHP: A Primary standard acid.

Na_2CO_3: A Primary standard base.

$Na_2C_2O_4$ (sodium oxalate) is a commercially available Primary standard for generating oxalic acid to standardize permanganate solution (page 9).

● **Standardization**: Process of determining the concentration of a reagent by reaction with a known quantity of a second reagent.

● **Direct titration**: one in which the analyte is treated with titrant and the volume of titrant required for complete reaction is measured.

● **Back titration**: one in which a known excess of one standard reagent is added to react with analyte. The excess reagent is titrated with a second standard reagent.

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● **A back titration is useful**

‒ When its end point is clearer than the end point of the direct titration

— Or when an excess of the first reagent is required for complete reaction with analyte.

● **Gravimetric titration**: A titration in which the mass of titrant is measured, instead of the volume. Titrant can be delivered from a pipette. Titrant concentration is expressed as mol of reagent/kg of titrant solution. Gravimetric titration can be more accurate and precise than volumetric titrations.

Example **1**: A 0.5662-g sample of an ionic compound containing an unknown metal is dissolved in water and treated with an excess of $AgNO_3$. If 1.0882 g of AgCl (143.4 g/mol) precipitate forms, what is the percent by mass of Cl (35.45 g/mol) in the original compound?

$$moles\ AgCl = \frac{1.0882\ g}{143.4\ g/mol} = 7.589\times10^{-3}\ moles\ AgCl \equiv moles\ Cl$$

$$mass\ Cl = 7.589\times10^{-3}\ moles\ Cl \times \frac{35.45\ g\ Cl}{1\ mol\ Cl} = 0.2690\ g$$

$$\%Cl = \frac{0.2690\ g}{0.5662\ g} \times 100\% = 47.51\%$$

Q1) You have 505 mL of a 0.150 *M* HCl solution and you want to dilute it to exactly 0.100 *M*. How much water would you add?

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Q2) A 46.2-mL, 0.568 *M* calcium nitrate [Ca(NO₃)₂] solution is mixed with 80.5 mL of 1.396 *M* calcium nitrate solution. Calculate the concentration of the final solution. (**Answer = 1.09 *M***)

Q1) A solution is prepared by dissolving 23.7 g of $CaCl_2$ (111.0 g/mol) in 375 g of water. The density of the resulting solution is 1.05 g/mL. The concentration of $CaCl_2$ is _____% by mass.

A) 5.94   B) 6.32   C) 0.0632   D) 0.0594   E) 6.24

Q2) The concentration of nitrate ion in a solution that contains 0.900 *M* aluminum nitrate[(Al(NO₃)₃] is _____ *M*.
A) 0.900   B) 0.450   C) 0.300   **D**) 2.70   E) 1.80

Example 2) A 100-g sample of mineral water (مياه) (معدنية) was found to contain 2.50 mg of sodium. Calculate the concentration of sodium in units of **(a) ppm and (b) ppb**

Mass of solution ≈ mass of solvent

$$\text{ppm of Na} = \frac{2.50\times10^{-3}\ \text{g}}{100\ \text{g}} \times 10^6 = 25.0\ \text{ppm}$$

$$\text{ppb of Na} = \frac{2.50\times10^{-3}\ \text{g}}{100\ \text{g}} \times 10^9 = 2.50\times10^4\ \text{ppb}$$

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Example 3) The concentration of an aqueous solution of glucose (180 g/mol) is 0.500 mol/L and its density is 1.05 g/mL. Calculate the *molality* of the glucose.

1 L of solution contains 0.500 mol (90.0 g) of glucose

The mass of 1 L solution = V × density = 10^3 mL × 1.05 g/mL = 1050 g
Mass of water (solvent) = 1050 – 90.0 = 960 g

$$m_{glucose} = \frac{0.500 \ mol \ glucose}{0.960 \ kg \ H_2O} = 0.521 \ mol/kg$$

Example 4) The *molality* of a solution of glucose (180 g/mol) in water is 1.00 mol/kg and its density is 1.07 g/mL. Calculate the *molarity* of the glucose in this solution.

m = 1 mol/kg
mass of 1 mole of glucose = 180 g
mass of solvent (water) = 1000 g
mass of solution = 180 + 1000 = 1180 g

$$V_{solution} = \frac{mass \ of \ solution}{density \ of \ solution} = \frac{1180 \ g}{1.07 \ g/mL} = 1103 \ mL = 1.103 \ L$$

$$M = \frac{1.00 \ mol}{1.103 \ L} = 0.907 \ mol/L$$

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$Q1$) The concentration of lead nitrate $(Pb(NO_3)_2)$ in a 0.726 M solution is _____ molal. The density of the solution is 1.202 g/mL.
A) 0.476   B) 1.928   **C) 0.755**   D) 0.819   E) 0.650
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$Q2$) A solution is prepared by dissolving 23.7 g of $CaCl_2$ (111 g/mol) in 375 g of water. The density of the resulting solution is 1.05 g/mL. The concentration of Cl^- (35.45 g/mol) in this solution is _____ M.
A) 0.214   B) 0.562   **C) 1.12**   D) 1.20   E) 6.64×10^{-2}

$Q3$) The molarity of urea in a solution of 16 g of urea (MW = 60.0 g/mol) in 39 g of H_2O is _____ M. The density of the solution is 1.3 g/mL.
A) 0.11   B) 3.7   C) 6.8   **D) 6.3**   E) 0.16

$Q4$) What is the molarity of sodium chloride in solution that is 13.0% by mass sodium chloride and that has a density of 1.10 g/mL?
A) 143   **B) 2.45**   C) 2.56   D) 2.23   E) 1.43×10^{-2}

$Q5$) What mass of K_2CO_3 is needed to prepare 200. mL of a solution having a potassium ion concentration of 0.150 M?
 A) 10.4 g   B) 4.15 g   C) 13.8 g   D) 2.07 g   E) 1.49 g

$Q6$) The density of a 5.24 M $NaHCO_3$ (84.0 g/mol) solution is 1.19 g/mL. Its molality is_____.
A) 6.99 m B) 7.27 m C) 9.97 m D) 6.71 m

$Q7$) What is the concentration in **ppm** of a 1.5 x 10^{-3} **molal** solution of NaCl (58.5 g/mol)?
A) 1.5 ppm   B) 8.8 ppm   C) 88 ppm   D) 150 ppm

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