

Lecture One- Pharmacy collage first
Year-Analytical chemistry
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**What are formula weights and
molecular weights?**

SOME IMPORTANT UNITS OF MEASUREMENT

Scientists throughout the world have adopted a standardized system of units known as the **International System of Units (SI)**. This system is based on the seven fundamental base units shown in Table 4-1. Numerous other useful units, such as volts, hertz, coulombs, and joules, are derived from these base units.

SI Base Units		
Physical Quantity	Name of Unit	Abbreviation
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	cd

formula weights(FW) of a compounds is the sum of atomic weight in atomic mass unit (amu).of all atoms in the compounds formula.

This term used for both ionic and molecular compounds.

molecular weight(MW): the sum of atomic weights of all atoms in molecular compound expressed in atomic mass units (amu). Used only for covalent compounds

The Mole

The mole (abbreviated mol) is the SI unit for the amount of a chemical species. It is always associated with a chemical formula and represents Avogadro's number (6.022×10^{23}) of particles represented by that formula.

The molar mass (.M) of a substance is the mass in grams of 1 mol of that substance. Molar masses are calculated by summing the atomic masses of all the atoms appearing in a chemical formula.

For example Molar masses for $\text{CH}_2\text{O}=30.0\text{g/mol}$. And for glucose is 180.0 g/mol ($\text{C}_6\text{H}_{12}\text{O}_6$)

The Millimole

Sometimes it is more convenient to make calculations with millimoles (mmol) rather than moles; the millimole is $1/1000$ of a mole. The mass in grams of a millimole, the millimolar mass (mM), is likewise $1/1000$ of the molar mass.

Example: 4-1 (page 74)

How many moles and millimoles of benzoic acid (M.wt= 122.1 g/mol) are contained in 2.00 g of the pure acid?

EXAMPLE 4-2

How many grams of Na⁺ (22.99 g/mol) are contained in 25.0 g of Na₂SO₄ (142.0 g/mol)?

If we use HBz to represent benzoic acid, we can write that 1 mol of HBz has a mass of 122.1 g. Thus,

$$\begin{aligned} \text{amount of HBz} = n_{\text{HBz}} &= 2.00 \text{ g} \cancel{\text{HBz}} \times \frac{1 \text{ mol HBz}}{122.1 \text{ g} \cancel{\text{HBz}}} && (4-1) \\ &= 0.0164 \text{ mol HBz} \end{aligned}$$

To obtain the number of millimoles, we divide by the millimolar mass (0.1221 g/mmol). That is,

$$\text{amount HBz} = 2.00 \text{ g} \cancel{\text{HBz}} \times \frac{1 \text{ mmol HBz}}{0.1221 \text{ g} \cancel{\text{HBz}}} = 16.4 \text{ mmol HBz}$$

SOLUTIONS AND THEIR **CONCENTRATIONS**

1-Molar Concentration

The molar concentration C_x of a solution of a chemical species X is the number of moles of that species that is contained in 1 L of the solution (not 1 L of the solvent).

The unit of molar concentration is molarity, M , which has the dimensions of mol L^{-1} .

Molarity also expresses the number of millimoles of a solute per milliliter of solution.

$$c_X = \frac{\text{no. mol solute}}{\text{no. L solution}} = \frac{\text{no. mmol solute}}{\text{no. mL solution}} \quad (4-2)$$

EXAMPLE 4-3

Calculate the molar concentration of ethanol in an aqueous solution that contains 2.30 g of $\text{C}_2\text{H}_5\text{OH}$ (46.07 g/mol) in 3.50 L of solution.

Because molarity is the number of moles of solute per liter of solution, both of these quantities will be needed. The number of liters is given as 3.50, so all we need to do is convert the number of grams of ethanol to the corresponding number of moles.

$$\begin{aligned} \text{amount } \text{C}_2\text{H}_5\text{OH} = n_{\text{C}_2\text{H}_5\text{OH}} &= 2.30 \text{ g } \cancel{\text{C}_2\text{H}_5\text{OH}} \times \frac{1 \text{ mol } \text{C}_2\text{H}_5\text{OH}}{46.07 \text{ g } \cancel{\text{C}_2\text{H}_5\text{OH}}} \\ &= 0.04992 \text{ mol } \text{C}_2\text{H}_5\text{OH} \end{aligned}$$

To obtain the molar concentration, $c_{\text{C}_2\text{H}_5\text{OH}}$, we divide by the volume. Thus,

$$\begin{aligned} c_{\text{C}_2\text{H}_5\text{OH}} &= \frac{2.30 \text{ g } \cancel{\text{C}_2\text{H}_5\text{OH}} \times \frac{1 \text{ mol } \text{C}_2\text{H}_5\text{OH}}{46.07 \text{ g } \cancel{\text{C}_2\text{H}_5\text{OH}}}}{3.50 \text{ L}} \\ &= 0.0143 \text{ mol } \text{C}_2\text{H}_5\text{OH}/\text{L} = 0.0143 \text{ M} \end{aligned}$$

Analytical molarity is the total number of moles of a solute, regardless of its chemical state, in 1 L of solution. The analytical molarity describes how a solution of a given molarity can be prepared.

solution can be prepared. For example, a sulfuric acid solution that has an analytical concentration of 1.0 M can be prepared by dissolving 1.0 mol, or 98 g, of H_2SO_4 in water and diluting to exactly 1.0 L.

Equilibrium molarity is the molar concentration of a particular species in a solution.

solvent. For example, the species molarity of H_2SO_4 in a solution with an analytical concentration of 1.0 M is 0.0 M because the sulfuric acid is entirely dissociated into a mixture of H^+ , HSO_4^- , and SO_4^{2-} ions; essentially no H_2SO_4 molecules as such are present in this solution. The equilibrium concentrations and thus the species molarity of these three ions are 1.01, 0.99, and 0.01 M, respectively.

Equilibrium molar concentrations are often symbolized by placing square brackets around the chemical formula for the species, so for our solution of H_2SO_4 with an analytical concentration of 1.0 M, we can write





EXAMPLE 4-4

Calculate the analytical and equilibrium molar concentrations of the solute species in an aqueous solution that contains 285 mg of trichloroacetic acid, Cl_3CCOOH (163.4 g/mol), in 10.0 mL (the acid is 73% ionized in water).

$$\begin{aligned}
 \text{amount HA} = n_{\text{HA}} &= 285 \text{ mg HA} \times \frac{1 \text{ g HA}}{1000 \text{ mg HA}} \times \frac{1 \text{ mol HA}}{163.4 \text{ g HA}} \\
 &= 1.744 \times 10^{-3} \text{ mol HA}
 \end{aligned}$$

The analytical molar concentration, c_{HA} , is then

$$c_{\text{HA}} = \frac{1.744 \times 10^{-3} \text{ mol HA}}{10.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.174 \frac{\text{mol HA}}{\text{L}} = 0.174 \text{ M}$$

In this solution, 73% of the HA dissociates, giving H^+ and A^- :



The species molarity of HA is then 27% of c_{HA} . Thus,

$$\begin{aligned}
 [\text{HA}] &= c_{\text{HA}} \times (100 - 73)/100 = 0.174 \times 0.27 = 0.047 \text{ mol/L} \\
 &= 0.047 \text{ M}
 \end{aligned}$$

The species molarity of A^- is equal to 73% of the analytical concentration of HA. That is,

$$[\text{A}^-] = \frac{73 \text{ mol A}^-}{100 \text{ mol HA}} \times 0.174 \frac{\text{mol HA}}{\text{L}} = 0.127 \text{ M}$$

Because 1 mole of H^+ is formed for each mole of A^- , we can also write

$$[\text{H}^+] = [\text{A}^-] = 0.127 \text{ M}$$

EXAMPLE 4-5

Describe the preparation of 2.00 L of 0.108 M BaCl_2 from $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (244.3 g/mol).

Percent Concentration

Chemists frequently express concentrations in terms of percent (parts per hundred). Unfortunately, this practice can be a source of ambiguity because percent composition of a solution can be expressed in several ways. Three common methods are:

$$\text{weight percent (w/w)} = \frac{\text{weight solute}}{\text{weight solution}} \times 100\%$$

$$\text{volume percent (v/v)} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

$$\text{weight/volume percent (w/v)} = \frac{\text{weight solute, g}}{\text{volume solution, mL}} \times 100\%$$

Parts per Million and Parts per Billion

For very dilute solutions, parts per million (ppm) is a convenient way to express concentration:

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

$$c_{\text{ppm}} = \frac{\text{mass solute (mg)}}{\text{volume solution (L)}}$$

approximately 1.00 g/mL, 1 ppm =
1.00 mg/L. That is,

$$\begin{aligned} c_{\text{ppb}} &= \frac{\text{mass solute (g)}}{\text{mass solution (g)}} \times 10^9 \text{ ppb} \\ &= 1.00 \mu\text{g/L} \end{aligned}$$

EXAMPLE 4-7

What is the molarity of K^+ in a solution that contains 63.3 ppm of $\text{K}_3\text{Fe}(\text{CN})_6$ (329.3 g/mol)?

Because the solution is so dilute, it is reasonable to assume that its density is 1.00 g/mL. Therefore, according to Equation 4-2,

$$63.3 \text{ ppm } \text{K}_3\text{Fe}(\text{CN})_6 = 63.3 \text{ mg } \text{K}_3\text{Fe}(\text{CN})_6/\text{L}$$

$$\begin{aligned} \frac{\text{no. mol } \text{K}_3\text{Fe}(\text{CN})_6}{\text{L}} &= \frac{63.3 \text{ mg } \text{K}_3\text{Fe}(\text{CN})_6}{\text{L}} \times \frac{1 \text{ g } \text{K}_3\text{Fe}(\text{CN})_6}{1000 \text{ mg } \text{K}_3\text{Fe}(\text{CN})_6} \\ &\quad \times \frac{1 \text{ mol } \text{K}_3\text{Fe}(\text{CN})_6}{329.3 \text{ g } \text{K}_3\text{Fe}(\text{CN})_6} \\ &= 1.922 \times 10^{-4} \frac{\text{mol}}{\text{L}} = 1.922 \times 10^{-4} \text{ M} \end{aligned}$$

$$\begin{aligned} [\text{K}^+] &= \frac{1.922 \times 10^{-4} \text{ mol } \text{K}_3\text{Fe}(\text{CN})_6}{\text{L}} \times \frac{3 \text{ mol } \text{K}^+}{1 \text{ mol } \text{K}_3\text{Fe}(\text{CN})_6} \\ &= 5.77 \times 10^{-4} \frac{\text{mol } \text{K}^+}{\text{L}} = 5.77 \times 10^{-4} \text{ M} \end{aligned}$$

Solution-Diluent Volume Ratios

The composition of a dilute solution is sometimes specified in terms of the volume of a more concentrated solution and the volume of solvent used in diluting it. The volume of the former is separated from that of the latter by a colon. Thus, a 1:4 HCl solution contains four volumes of water for each volume of concentrated hydrochloric acid. This method of notation is frequently ambiguous in that the concentration of the original solution is not always obvious to the reader. Moreover, under some circumstances 1:4 means dilute one volume with three volumes. Because of such uncertainties, you should avoid using solution-diluent ratios.

p-Functions

Scientists frequently express the concentration of a species in terms of its **p-function**, or **p-value**. The p-value is the negative logarithm (to the base 10) of the molar concentration of that species. Thus, for the species X,

$$pX = -\log [X]$$

▶ The most well known p-function is pH, which is the negative logarithm of $[H^+]$.

$$pX = -\log [X]$$

EXAMPLE 4-8

Calculate the p-value for each ion in a solution that is 2.00×10^{-3} M in NaCl and 5.4×10^{-4} M in HCl.

$$pH = -\log [H^+] = -\log (5.4 \times 10^{-4}) = 3.27$$

To obtain pNa, we write

$$pNa = -\log (2.00 \times 10^{-3}) = -\log 2.00 \times 10^{-3} = 2.699$$

The total Cl^- concentration is given by the sum of the concentrations of the two solutes:

$$\begin{aligned} [Cl^-] &= 2.00 \times 10^{-3} \text{ M} + 5.4 \times 10^{-4} \text{ M} \\ &= 2.00 \times 10^{-3} \text{ M} + 0.54 \times 10^{-3} \text{ M} = 2.54 \times 10^{-3} \text{ M} \end{aligned}$$

$$pCl = -\log 2.54 \times 10^{-3} = 2.595$$

EXAMPLE 4-9

Calculate the molar concentration of Ag^+ in a solution that has a pAg of 6.372.

$$\text{pAg} = -\log [\text{Ag}^+] = 6.372$$

$$\log [\text{Ag}^+] = -6.372$$

$$[\text{Ag}^+] = 4.246 \times 10^{-7} \approx 4.25 \times 10^{-7}$$

Density and Specific Gravity of Solutions

Density expresses the mass of a substance per unit volume. In SI units, density is expressed in units of kg/L or, alternatively, g/mL .

Specific gravity is the ratio of the mass of a substance to the mass of an equal volume of water.

EXAMPLE 4-10

Calculate the molar concentration of HNO_3 (63.0 g/mol) in a solution that has a specific gravity of 1.42 and is 70.5% HNO_3 (w/w).

$$\frac{\text{g HNO}_3}{\text{L reagent}} = \frac{1.42 \text{ kg reagent}}{\text{L reagent}} \times \frac{10^3 \text{ g reagent}}{\text{kg reagent}} \times \frac{70.5 \text{ g HNO}_3}{100 \text{ g reagent}} = \frac{1001 \text{ g HNO}_3}{\text{L reagent}}$$

Then

$$c_{\text{HNO}_3} = \frac{1001 \text{ g HNO}_3}{\text{L reagent}} \times \frac{1 \text{ mol HNO}_3}{63.0 \text{ g HNO}_3} = \frac{15.9 \text{ mol HNO}_3}{\text{L reagent}} \approx 16 \text{ M}$$

TABLE 4-3

Specific Gravities of Commercial Concentrated Acids and Bases

Reagent	Concentration, % (w/w)	Specific Gravi
Acetic acid	99.7	1.05
Ammonia	29.0	0.90
Hydrochloric acid	37.2	1.19
Hydrofluoric acid	49.5	1.15
Nitric acid	70.5	1.42
Perchloric acid	71.0	1.67
Phosphoric acid	86.0	1.71
Sulfuric acid	96.5	1.84

Describe the preparation of 100 mL of 6.0 M HCl from a concentrated solution that has a specific gravity of 1.18 and is 37% (w/w) HCl (36.5 g/mol).

Proceeding as in Example 4-10, we first calculate the molarity of the concentrated reagent. We then calculate the number of moles of acid that we need for the diluted solution. Finally, we divide the second figure by the first to obtain the volume of concentrated acid required. Thus, to obtain the molarity of the concentrated reagent, we write

$$c_{\text{HCl}} = \frac{1.18 \times 10^3 \text{ g reagent}}{\text{L reagent}} \times \frac{37 \text{ g HCl}}{100 \text{ g reagent}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} = 12.0 \text{ M}$$

The number of moles HCl required is given by

$$\text{no. mol HCl} = 100 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{6.0 \text{ mol HCl}}{\text{L}} = 0.600 \text{ mol HCl}$$

Finally, to obtain the volume of concentrated reagent, we write

$$\begin{aligned} \text{vol concd reagent} &= 0.600 \text{ mol HCl} \times \frac{1 \text{ L reagent}}{12.0 \text{ mol HCl}} \\ &= 0.0500 \text{ L or } 50.0 \text{ mL} \end{aligned}$$

Thus dilute 50 mL of the concentrated reagent to 600 mL.

► Equation 4-4 can be used with L and mol/L or mL and mmol/mL. Thus,

$$L_{\text{concd}} \times \frac{\text{mol}_{\text{concd}}}{L_{\text{concd}}} = L_{\text{dil}} \times \frac{\text{mol}_{\text{dil}}}{L_{\text{dil}}}$$

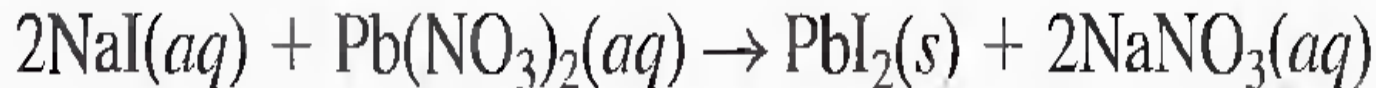
$$\text{mL}_{\text{concd}} \times \frac{\text{mmol}_{\text{concd}}}{\text{mL}_{\text{concd}}} = \text{mL}_{\text{dil}} \times \frac{\text{mmol}_{\text{dil}}}{\text{mL}_{\text{dil}}}$$

CHEMICAL STOICHIOMETRY

The **stoichiometry** of a reaction is the relationship among the number of moles of reactants and products as shown by a balanced equation.

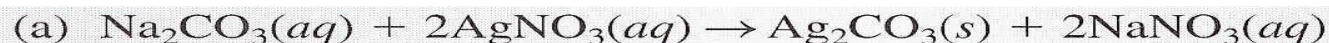
Stoichiometric Calculations

A balanced chemical equation gives the combining ratios, or stoichiometry-in units of moles-of reacting substances and their products. Thus, the equation



EXAMPLE 4-12

(a) What mass of AgNO_3 (169.9 g/mol) is needed to convert 2.33 g of Na_2CO_3 (106.0 g/mol) to Ag_2CO_3 ? (b) What mass of Ag_2CO_3 (275.7 g/mol) will be formed?



Step 1. no. mol $\text{Na}_2\text{CO}_3 = n_{\text{Na}_2\text{CO}_3} = 2.33 \text{ g Na}_2\text{CO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{106.0 \text{ g Na}_2\text{CO}_3}$
 $= 0.02198 \text{ mol Na}_2\text{CO}_3$

Step 2. The balanced equation reveals that

$$\text{no. mol AgNO}_3 = n_{\text{AgNO}_3} = 0.02198 \text{ mol Na}_2\text{CO}_3 \times \frac{2 \text{ mol AgNO}_3}{1 \text{ mol Na}_2\text{CO}_3}$$

$$= 0.04396 \text{ mol AgNO}_3$$

Here the stoichiometric factor is (2 mol AgNO_3)/(1 mol Na_2CO_3).

Step 3. mass $\text{AgNO}_3 = 0.04396 \text{ mol AgNO}_3 \times \frac{169.9 \text{ g AgNO}_3}{\text{mol AgNO}_3}$
 $= 7.47 \text{ g AgNO}_3$

(b) no. mol $\text{Ag}_2\text{CO}_3 = \text{no. mol Na}_2\text{CO}_3 = 0.02198 \text{ mol}$
 mass $\text{Ag}_2\text{CO}_3 = 0.02198 \text{ mol Ag}_2\text{CO}_3 \times \frac{275.7 \text{ g Ag}_2\text{CO}_3}{\text{mol Ag}_2\text{CO}_3}$
 $= 6.06 \text{ g Ag}_2\text{CO}_3$

EXAMPLE 4-13

What mass of Ag_2CO_3 (275.7 g/mol) is formed when 25.0 mL of 0.200 M AgNO_3 are mixed with 50.0 mL of 0.0800 M Na_2CO_3 ?

Mixing these two solutions will result in one (and only one) of three possible outcomes, specifically:

- (a) An excess of AgNO_3 will remain after reaction is complete.
- (b) An excess of Na_2CO_3 will remain after reaction is complete.
- (c) An excess of neither reagent will exist (that is, the number of moles of Na_2CO_3 is exactly equal to twice the number of moles of AgNO_3).

As a first step, we must establish which of these situations applies by calculating the amounts of reactants (in chemical units) available at the outset.

Initial amounts are

$$\begin{aligned} \text{amount AgNO}_3 &= n_{\text{AgNO}_3} = 25.0 \text{ mL AgNO}_3 \times \frac{1 \text{ L AgNO}_3}{1000 \text{ mL AgNO}_3} \\ &\times \frac{0.200 \text{ mol AgNO}_3}{\text{L AgNO}_3} = 5.00 \times 10^{-3} \text{ mol AgNO}_3 \end{aligned}$$

$$\begin{aligned} \text{no. mol Na}_2\text{CO}_3 &= n_{\text{Na}_2\text{CO}_3} = 50.0 \text{ mL Na}_2\text{CO}_3 \times \frac{1 \text{ L Na}_2\text{CO}_3}{1000 \text{ mL Na}_2\text{CO}_3} \\ &\times \frac{0.0800 \text{ mol Na}_2\text{CO}_3}{\text{L Na}_2\text{CO}_3} = 4.00 \times 10^{-3} \text{ mol Na}_2\text{CO}_3 \end{aligned}$$

Because each CO_3^{2-} ion reacts with two Ag^+ ions, $2 \times 4.00 \times 10^{-3} = 8.00 \times 10^{-3}$ mol AgNO_3 is required to react with the Na_2CO_3 . Since we have insufficient AgNO_3 , situation (b) prevails and the amount of Ag_2CO_3 produced will be limited by the amount of AgNO_3 available. Thus,

$$\begin{aligned} \text{mass Ag}_2\text{CO}_3 &= 5.00 \times 10^{-3} \text{ mol AgNO}_3 \times \frac{1 \text{ mol Ag}_2\text{CO}_3}{2 \text{ mol AgNO}_3} \times \frac{275.7 \text{ g Ag}_2\text{CO}_3}{\text{mol Ag}_2\text{CO}_3} \\ &= 0.689 \text{ g Ag}_2\text{CO}_3 \end{aligned}$$

What will be the analytical molar Na_2CO_3 concentration in the solution produced when 25.0 mL of 0.200 M AgNO_3 are mixed with 50.0 mL of 0.0800 M Na_2CO_3 ?

We have seen in the previous example that formation of 5.00×10^{-3} mol of AgNO_3 will require 2.50×10^{-3} mol of Na_2CO_3 . The number of moles of unreacted Na_2CO_3 is then given by

$$\begin{aligned}n_{\text{Na}_2\text{CO}_3} &= 4.00 \times 10^{-3} \text{ mol Na}_2\text{CO}_3 - \\ &\quad 5.00 \times 10^{-3} \text{ mol AgNO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol AgNO}_3} \\ &= 1.50 \times 10^{-3} \text{ mol Na}_2\text{CO}_3\end{aligned}$$

By definition the molarity is the number of moles of $\text{Na}_2\text{CO}_3/\text{L}$. Thus,

$$c_{\text{Na}_2\text{CO}_3} = \frac{1.50 \times 10^{-3} \text{ mol Na}_2\text{CO}_3}{(50.0 + 25.0) \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.0200 \text{ M Na}_2\text{CO}_3$$

Thanks

CHAPTER 4

Calculations Used in Analytical Chemistry

Fundamentals of
Analytical Chemistry

EIGHTH EDITION