A-3 The Mole4

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(MWt) 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, the molar mass of formaldehyde, CH₂O, is

$$\mathcal{M}_{CH_{2}O} = \frac{1 \text{ mol} \cdot C}{\text{mol} CH_{2}O} \times \frac{12.0g}{\text{mol} \cdot C} + \frac{2 \text{ mol} \cdot H}{\text{mol} CH_{2}O} \times \frac{1.0 \text{ g}}{\text{mol} \cdot H} + \frac{1 \text{ mol} \cdot O}{\text{mol} CH_{2}O} \times \frac{16.0 \text{ g}}{\text{mol} \cdot O}$$
$$= 30.0 \text{ g/mol} CH_{2}O$$

sive. But because the mass of the is only 1/81 that of Earth and the eration due to gravity is only 1/61 on Earth, the weight of the suits c Moon was only 1/6 of their weigh Earth. The mass of the suits, how was identical in both locations.

and that of glucose, $C_6H_{12}O_6$, is

 $\mathcal{M}_{C_{6}H_{12}O_{6}} = \frac{6 \text{ mol C}}{\text{mol } C_{6}H_{12}O_{6}} \times \frac{12.0 \text{ g}}{\text{mol C}} + \frac{12 \text{ mol H}}{\text{mol } C_{6}H_{12}O_{6}} \times \frac{1.0 \text{ g}}{\text{mol H}} + \frac{6 \text{ mol O}}{\text{mol } C_{6}H_{12}O_{6}} \times \frac{16.0 \text{ g}}{\text{mol O}} = 180.0 \text{ g/mol } C_{6}H_{12}O_{6}$

Thus, 1 mol of formaldehyde has a mass of 30.0 g and 1 mol of glucose has a mass

EXAM PIE 4-1 How many moles and millimoles of benzoic acid (MWt = 122.1 g/mol) are contained in 2.00 g of the pure acid

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

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

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

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

EXAMPLE 4-2 How many grams of Na⁺ (MWt 22.99 g/mol) are contained in 25.0 g of Na₂S0₄ (g/mol 142.0) The chemical formula tells us that 1mol of Na₂SO₄ contains 2 mol of Na⁺ That is :

amount Na⁺ =
$$n_{\text{Na}^+}$$
 = no. mol-Na₂SO₄ × $\frac{2 \text{ mol Na}^+}{\text{mol-Na}_2SO_4}$

To obtain the number of moles of Na2SO4 we proceed as in Example 4-1:

amount Na₂SO₄ =
$$n_{\text{Na}_2\text{SO}_4} = 25.0 \text{ g} \cdot \text{Na}_2\text{SO}_4 \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142.0 \text{ g} \cdot \text{Na}_2\text{SO}_4}$$

Combining this equation with the first leads to

amount Na⁺ =
$$n_{Na^+} = 25.0 \text{ g} \cdot Na_2 SO_4 \times \frac{1 \text{ mol} \cdot Na_2 SO_4}{142.0 \text{ g} \cdot Na_2 SO_4} \times \frac{2 \text{ mol} \cdot Na^+}{\text{mol} \cdot Na_2 SO_4}$$

To obtain the mass of sodium in 25.0 g of Na_2SO_4 , we multiply the number of moles of Na^+ by the molar mass of Na^+ , or 22.99 g. That is,

mass Na⁺ = no. mol-Na⁺
$$\times \frac{22.99 \text{ g Na^+}}{\text{mol-Na^+}}$$

Substituting the previous equation gives the number of grams of Na+:

 $\max \operatorname{Na^{+}} = 25.0 \operatorname{g} \operatorname{Na_2SO_4} \times \frac{1 \operatorname{mol} \operatorname{Na_2SO_4}}{142.0 \operatorname{g} \operatorname{Na_2SO_4}} \times \frac{2 \operatorname{mol} \operatorname{Na^{+}}}{\operatorname{mol} \operatorname{Na_2SO_4}} \times \frac{22.99 \operatorname{g} \operatorname{Na^{+}}}{\operatorname{mol} \operatorname{Na_2SO_4}} = 8.10 \operatorname{g} \operatorname{Na^{+}}$

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Concentration of Solutions

Chemists express the concentration of species in solution in several ways. The most important \Im ways are described in this section Molar Concentration

The molar concentration Cx of a solution of a chemical species X is the number of moles of that species that is contained in 1L 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

 $c_{\rm X} = \frac{\text{no. mol solute}}{\text{no. L solution}} = \frac{\text{no. mmol solute}}{\text{no. mL solution}}$

EXAMPLE 4-3

Calculate the molar concentration of ethanol in an aqueous solution that contains 2.30 g of C_2H_5OH (46.07g / 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

amount $C_2H_5OH = n_{C_2H_5OH} = 2.30 \text{ g} \cdot C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g} \cdot C_2H_5OH}$ = 0.04992 mol C_2H_5OH

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

$$c_{C_2H_5OH} = \frac{2.30 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH}}{3.50 \text{ L}}$$
$$= 0.0143 \text{ mol } C_2H_5OH/L = 0.0143 \text{ M}$$

Analytical Molarity

The number of moles of a solute in 1L of the solution (or the total number of millimoles in 1mL). That is, the analytical molarity specifies a recipe by which the 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-The equilibrium molarity expresses the molar concentration of a particular species in a solution at equilibrium. To state the species molarity, it is necessary to know how the solute behaves when it is dissolved in a solvent

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).

As in Example 4-3, we calculate the number of moles of Cl_3CCOOH , which we designate as HA, and divide by the volume of the solution, 10.0 mL, or 0.01000 L. Thus,

amount HA =
$$n_{\text{HA}} = 285 \text{ mg-HA} \times \frac{1 \text{ g-HA}}{1000 \text{ mg-HA}} \times \frac{1 \text{ mol HA}}{163.4 \text{ g-HA}}$$

= $1.744 \times 10^{-3} \text{ mol HA}$

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

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

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

$$HA \rightleftharpoons H^+ + A^-$$

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

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

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

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

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

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

EXAMPLE 4-5

Describe the preparation of 2.00 L of 0.108 M $BaCl_2$ from $BaCl_2 \cdot 2H_2O$ (244.3 g/mol).

To determine the number of grams of solute to be dissolved and diluted to 2.00 L, we note that 1 mol of the dihydrate yields 1 mol of BaCl₂. Therefore, to produce this solution we will need

$$2.00 \, \mathcal{L} \times \frac{0.108 \text{ mol } \text{BaCl}_2 \cdot 2\text{H}_2\text{O}}{\mathcal{L}} = 0.216 \text{ mol } \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$$

The mass of BaCl₂ · 2H₂O is then

$$0.216 \text{ mol } \text{BaCl}_2 \cdot 2\text{H}_2\text{O} \times \frac{244.3 \text{ g } \text{BaCl}_2 \cdot 2\text{H}_2\text{O}}{\text{mol } \text{BaCl}_2 \cdot 2\text{H}_2\text{O}} = 52.8 \text{ g } \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$$

Dissolve 52.8 g of BaCl₂ · 2H₂O in water and dilute to 2.00 L.

Describe the preparation of 500 mL of 0.0740 M Cl⁻ solution from solid BaCl₂ · 2H₂O (244.3 g/mol).

 $\begin{array}{l} \text{mass } \text{BaCl}_2 \cdot 2\text{H}_2\text{O} = \frac{0.0740 \text{ mol} \cdot \text{Cl}^-}{\textit{\textit{E}}} \times 0.500 \textit{\textit{E}} \times \frac{1 \text{ mol} \cdot \text{BaCl}_2 \cdot 2\text{H}_2\text{O}}{2 \text{ mol} \cdot \text{Cl}} \\ \times \frac{244.3 \text{ g} \cdot \text{BaCl}_2 \cdot 2\text{H}_2\text{O}}{\text{mol} \cdot \text{BaCl}_2 \cdot 2\text{H}_2\text{O}} = 4.52 \text{ g} \cdot \text{BaCl}_2 \cdot 2\text{H}_2\text{O} \end{array}$

Dissolve 4.52 g of BaCl₂ · 2H₂O in water and dilute to 0.500 L or 500 mL.

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

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

 Weight percent would be more properly called mass percent and abbreviated m/m. The term "weight percent" is so widely used in the chemical literature, however, that we will use it throughout this text.

Weight percent is frequently employed to express the concentration of commercial aqueous reagents. For example, nitric acid is sold as a 70% solution, which means that the reagent contains 70 g of HNO₃ per 100 g of solution (see Example 4-10)

Volume percent is commonly used to specify the concentration of a solution prepared by diluting a pure liquid compound with another liquid. For example, a 5% aqueous solution of methanol usually describes a solution prepared by diluting 5.0mL of pure methanol with enough water to give 100 Ml

Weight/volume percent is often employed to indicate the composition of dilute aqueous solutions of solid reagents. For example, 5% aqueous silver nitrate often refers to a solution prepared by dissolving 5 g of silver nitrate in sufficient water to give 100 mL of solution

Parts per Million and Parts per Billion

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

Concentration

A handy rule in calculating parts per million is to remember that for dilute aqueous solutions whose densities are approximately 1.00 g/mL, 1ppm=1.0 mg/L that is :-

$$c_{\rm ppm} = \frac{\rm mass of solute}{\rm mass of solution} \times 10^{6} \,\rm ppm \qquad c_{\rm ppm} = \frac{\rm mass solute (mg)}{\rm volume solution (L)} \qquad (4-3)$$
$$c_{\rm ppb} = \frac{\rm mass solute (g)}{\rm mass solution (g)} \times 10^{9} \,\rm ppb$$
$$= 1.00 \,\mu g/L$$

EXAMPLE 4-7

What is the molarity of K^+ in a solution that contains 63.3 ppm of $K_3Fe(CN)_6$ (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,

$$63.3 \text{ ppm } \text{K}_{3}\text{Fe}(\text{CN})_{6} = 63.3 \text{ mg } \text{K}_{3}\text{Fe}(\text{CN})_{6}/\text{L}$$

$$\frac{\text{no. mol } \text{K}_{3}\text{Fe}(\text{CN})_{6}}{\text{L}} = \frac{63.3 \text{ mg } \text{K}_{3}\text{Fe}(\text{CN})_{6}}{\text{L}} \times \frac{1 \text{ g } \text{K}_{3}\text{Fe}(\text{CN})_{6}}{1000 \text{ mg } \text{K}_{3}\text{Fe}(\text{CN})_{6}}$$

$$\times \frac{1 \text{ mol } \text{K}_{3}\text{Fe}(\text{CN})_{6}}{329.3 \text{ g } \text{K}_{3}\text{Fe}(\text{CN})_{6}}$$

$$= 1.922 \times 10^{-4} \frac{\text{mol}}{\text{L}} = 1.922 \times 10^{-4} \text{ M}$$

$$[\text{K}^{+}] = \frac{1.922 \times 10^{-4} \text{ mol } \text{K}_{3}\text{Fe}(\text{CN})_{6}}{\text{L}} \times \frac{3 \text{ mol } \text{K}^{+}}{1 \text{ mol } \text{K}_{3}\text{Fe}(\text{CN})_{6}}$$

$$= 5.77 \times 10^{-4} \frac{\text{mol } \text{K}^{+}}{\text{L}} = 5.77 \times 10^{-4} \text{ M}$$

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

$$P^{X} = -\log [X]$$

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:

 $[Cl⁻] = 2.00 \times 10^{-3} \text{ M} + 5.4 \times 10^{-4} \text{ M}$ = 2.00 × 10⁻³ M + 0.54 × 10⁻³ M = 2.54 × 10⁻³ M pCl = -log 2.54 × 10⁻³ = 2.595

EXAMPLE 4-9

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

$$pAg = -log [Ag^+] = 6.372$$

 $log [Ag^+] = -6.372$
 $[Ag^+] = 4.246 \times 10^{-7} \approx 4.25 \times 10^{-7}$

The density

of a substance is its mass per unit volume, whereas its specific gravity is the ratio of its mass to the mass of an equal volume of water at 4°C. Density has units of kilograms per liter or grams per milliliter in the metric system.

Calculate the molar concentration of HNO₃ (63.0 g/mol) in a solution that has a specific gravity of 1.42 and is 70.5% HNO₃ (w/w).

Let us first calculate the grams of acid per liter of concentrated solution

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

Then

$$c_{\rm HNO_3} = \frac{1001 \text{ g HNO}_3}{\text{L reagent}} \times \frac{1 \text{ mol HNO}_3}{63.0 \text{ g HNO}_3} = \frac{15.9 \text{ mol HNO}_3}{\text{L reagent}} \approx 16 \text{ M}$$

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

$$c_{\rm HCI} = \frac{1.18 \times 10^3 \,\text{g-reagent}}{\text{L reagent}} \times \frac{37 \,\text{g-HC1}}{100 \,\text{g-reagent}} \times \frac{1 \,\text{mol HCl}}{36.5 \,\text{g-HC1}} = 12.0 \,\text{M}$$

The number of moles HCl required is given by

no. mol HCl = 100 mł ×
$$\frac{1 L}{1000 ml}$$
 × $\frac{6.0 \text{ mol HCl}}{L}$ = 0.600 mol HCl

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

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

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

The solution to Example 4-11 is based on the following useful relationship, which we will be using countless times:

$$V_{\rm concd} \times c_{\rm concd} = V_{\rm dil} \times c_{\rm dil} \tag{4-4}$$

Stoichiometry is defined as the quantitative relationship among reacting chemical species. This section provides a brief review of stoichiometry and its applications to chemical calculations

- (a) What mass of AgNO₃ (169.9 g/mol) is needed to convert 2.33 g of Na₂CO₃ (106.0 g/mol) to Ag₂CO₃? (b) What mass of Ag₂CO₃ (275.7 g/mol) will be formed?
- (a) $Na_2CO_3(aq) + 2AgNO_3(aq) \rightarrow Ag_2CO_3(s) + 2NaNO_3(aq)$

Step 1. no. mol Na₂CO₃ =
$$n_{\text{Na}_2\text{CO}_3} = 2.33 \text{ g-Na_2CO_3} \times \frac{1 \text{ mol Na}_2\text{CO}_3}{106.0 \text{ g-Na}_2\text{CO}_3}$$

= 0.02198 mol Na₂CO₃

Step 2. The balanced equation reveals that

no. mol AgNO₃ =
$$n_{AgNO_3}$$
 = 0.02198 mol Na₂CO₃ × $\frac{2 \text{ mol AgNO}_3}{1 \text{ mol Na}_2CO_3}$
= 0.04396 mol AgNO₃

Here the stoichiometric factor is (2 mol AgNO₃)/(1 mol Na₂CO₃).

Step 3. mass AgNO₃ = 0.04396 mol AgNO₃ $\times \frac{169.9 \text{ g AgNO_3}}{\text{mol AgNO_3}}$ = 7.47 g AgNO₃

(b) no. mol Ag₂CO₃ = no. mol Na₂CO₃ = 0.02198 mol
mass Ag₂CO₃ = 0.02198 mol Ag₂CO₃ ×
$$\frac{275.7 \text{ g Ag}_2\text{CO}_3}{\text{mol} \text{-Ag}_2\text{CO}_3}$$

= 6.06 g Ag₂CO₃

What mass of Ag₂CO₃ (275.7 g/mol) is formed when 25.0 mL of 0.200 M AgNO₃ are mixed with 50.0 mL of 0.0800 M Na₂CO₃?

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

- (a) An excess of AgNO3 will remain after reaction is complete.
- (b) An excess of Na₂CO₃ will remain after reaction is complete.
- (c) An excess of neither reagent will exist (that is, the number of moles of Na₂CO₃ is exactly equal to twice the number of moles of AgNO₃).

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

amount AgNO₃ =
$$n_{AgNO_3} = 25.0 \text{ mL-AgNO_3} \times \frac{1 \text{ L-AgNO_3}}{1000 \text{ mL-AgNO_3}}$$

 $\times \frac{0.200 \text{ mol AgNO_3}}{\text{ L-AgNO_3}} = 5.00 \times 10^{-3} \text{ mol AgNO_3}$
no. mol Na₂CO₃ = $n_{Na_2CO_3} = 50.0 \text{ mL-Na_2CO_3} \times \frac{1 \text{ L-Na_2CO_3}}{1000 \text{ mL-Na_2CO_3}}$
 $\times \frac{0.0800 \text{ mol Na_2CO_3}}{\text{ L-Na_2CO_3}} = 4.00 \times 10^{-3} \text{ mol Na_2CO_3}$

Because each $CO_3^{2^-}$ ion reacts with two Ag⁺ ions, $2 \times 4.00 \times 10^{-3} = 8.00 \times 10^{-3}$ mol AgNO₃ is required to react with the Na₂CO₃. Since we have insufficient AgNO₃, situation (b) prevails and the amount of Ag₂CO₃ produced will be limited by the amount of AgNO₃ available. Thus,

$$\max Ag_2CO_3 = 5.00 \times 10^{-3} \text{ mol} \text{ AgNO}_3 \times \frac{1 \text{ mol} \text{ Ag}_2CO_3}{2 \text{ mol} \text{ AgNO}_3} \times \frac{275.7 \text{ g} \text{ Ag}_2CO_3}{\text{ mol} \text{ Ag}_2CO_3}$$

= 0.689 g Ag_2CO_3

What will be the analytical molar Na₂CO₃ concentration in the solution produce when 25.0 mL of 0.200 M AgNO₃ are mixed with 50.0 mL of 0.0800 M Na₂CO₃ We have seen in the previous example that formation of 5.00×10^{-3} mol c AgNO₃ will require 2.50×10^{-3} mol of Na₂CO₃. The number of moles of unre acted Na₂CO₃ is then given by

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

By definition the molarity is the number of moles of Na₂CO₃/L. Thus,

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