

LECTURE – 2

1.5.4 Converting Weight, Volume, and Weight – to – Volume Ratios

Weight percent (% w/w), **volume percent** (% v/v) and **weight-to-volume percent** (% w/v) express concentration as units of solute per 100 units of sample. A solution in which a solute has a concentration of 23% w/v contains 23 g of solute per 100 mL of solution.

Parts per million (ppm) and **parts per billion** (ppb) are mass ratios of grams of solute to one million or one billion grams of sample, respectively. For example, a steel that is 450 ppm in Mn contains 450 μg of Mn for every gram of steel. If we approximate the density of an aqueous solution as 1.00 g/mL, then solution concentrations can be expressed in parts per million or parts per billion using the following relationships.

$$\text{ppm} = \frac{\text{mg}}{\text{liter}} = \frac{\mu\text{g}}{\text{mL}}$$
$$\text{ppb} = \frac{\mu\text{g}}{\text{liter}} = \frac{\text{ng}}{\text{mL}}$$

For gases a part per million usually is a volume ratio. Thus, a helium concentration of 6.3 ppm means that one liter of air contains 6.3 μL of He.

1.5.5 Converting Between Concentration Units

The units of concentration most frequently encountered in analytical chemistry are molarity, weight percent, volume percent, weight-to-volume percent, parts per million, and parts per billion. By recognizing the general definition of concentration given in equation 2.1, it is easy to convert between concentration units.

Example 1.2

A concentrated solution of aqueous ammonia is 28.0% w/w NH_3 and has a density of 0.899 g/mL. What is the molar concentration of NH_3 in this solution?

SOLUTION

$$\frac{28.0 \text{ g NH}_3}{100 \text{ g solution}} \times \frac{0.899 \text{ g solution}}{\text{mL solution}} \times \frac{1 \text{ mole NH}_3}{17.04 \text{ g NH}_3} \times \frac{1000 \text{ mL}}{\text{liter}} = 14.8 \text{ M}$$

Example 1.3

The maximum allowed concentration of chloride in a municipal drinking water supply is 2.50×10^2 ppm Cl^- . When the supply of water exceeds this limit, it often has a distinctive salty taste. What is this concentration in moles Cl^- /liter?

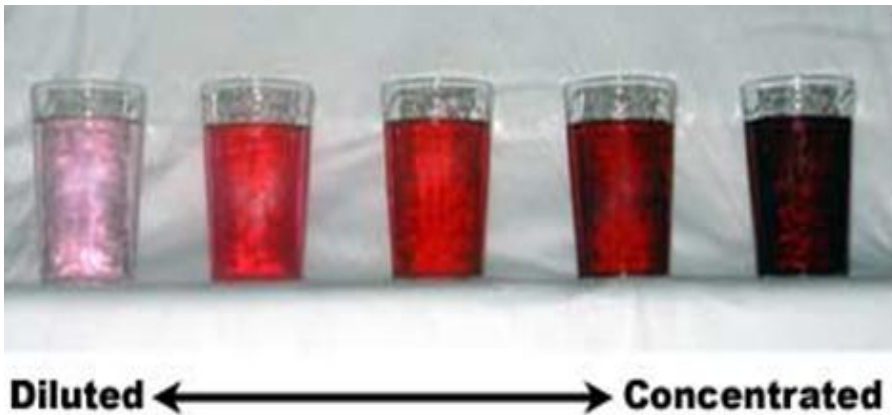
SOLUTION

$$\frac{2.50 \times 10^2 \text{ mg Cl}^-}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mole Cl}^-}{35.453 \text{ g Cl}^-} = 7.05 \times 10^{-3} \text{ M}$$

Concentration of Solutions

Remember:

- Solution – A mixture of a solute and a solvent
- Solvent – The liquid in which the solute is dissolved
- Solute – The substance that is dissolved in the solvent
- Dilute Solution – contains a small amount of solute per solvent
- Concentrated Solution – contains a large amount of solute per solvent
- Concentration – the amount of solute that is dissolved in a specific volume of solution
- In some solutions concentration can be indicated by colour intensity.
- The less intense the colour – dilute solution
- The more intense the colour – concentrated solution



1. % Weight per weight (% w/w)

- Mass per 100g
- Example:
 - 12% w/w means that there is 12g per 100g
 - Concentrated acid/base
 - % iron in iron tablets
- **Q: In a 125g solution, there is 22.5g of HCl. Express this concentration as %w/w.**
A: $22.5 \div 125 \times 100 = 18\% \text{ w/w}$

2. % Weight per volume (%w/v)

- Mass per 100cm³
- Example:
 - 30% w/v means that there is 30g per 100cm³
 - Saline solution – 0.91% w/v NaCl
- **Q: A 1.4% solution of CaCl₂ is required for an experiment. If you need 250cm³ of this solution, how much CaCl₂ should be weighed out?**
A: $1.4 \times 2.5 = 3.5\text{g}$

3. % Volume per volume (%v/v)

- Volume per 100cm³
- Example:
 - 9% v/v contains 9cm³ per 100cm³
 - Concentration of alcohol in beverages
- **Q: Wine contains 14% v/v. If a person consumes a 40cm³ glass of wine, how much alcohol do they consume?**
A: $14 \div 100 \times 40 = 5.6\text{cm}^3$

4. Parts per million (ppm)

- Number of milligrams per litre
- 1 ppm = 1mg per L (*remember 1000mg = 1g*)
- Used for very dilute solutions
- Example:
 - Concentrations of pollutants in water
- **Q: A sample of water is found to contain 0.003g of lead in a 250cm³ sample. What is the concentration of lead in ppm?**
A: $0.003 \times 4 \times 1000 = 12\text{ppm}$

5. Molarity

- Number of moles per litre
- Most common method of expressing concentration
- 1M = 1 mol/litre = 1 mol l⁻¹
- A 1 Molar solution contains one mole of solute dissolved in 1 litre of solution

Q: A solution is labelled 0.15M HCl. How many grams of HCl are present in 1 litre?

A: M_r of HCl = 36.5g
1M solution contains 36.5g / l
0.15M solution = 36.5 x 0.15 = 5.475g

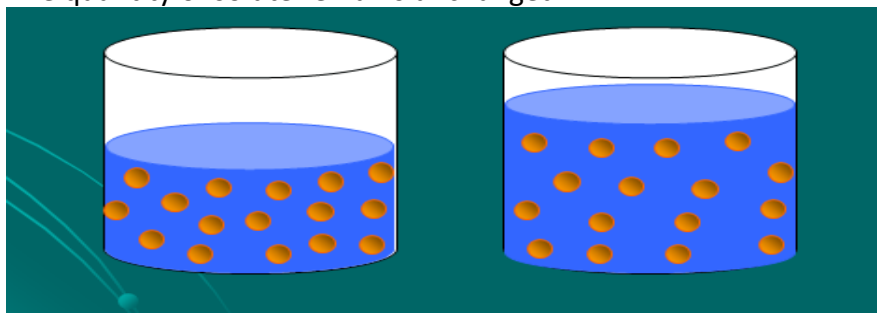
Q: A solution contains 4.9g H₂SO₄ in 100cm³.

Calculate the concentration in mol/l.

A: M_r of H₂SO₄ = 98g
 $4.9 \div 98 = 0.05\text{mol}$ in 100cm³
 $0.05 \times 10 = 0.5\text{mol/l}$

Effect of Dilution on Concentration

- When a solution is diluted, more solvent is added.
- The quantity of solute remains unchanged.



- To calculate the effect of dilution on concentration:

$$\frac{V_{\text{dil}} \times M_{\text{dil}}}{1000} = \frac{V_{\text{conc}} \times M_{\text{conc}}}{1000}$$

- **Q: What volume of 18M HCl would be required to prepare 250cm³ of 0.5M HCl?**

$$\text{A: } \frac{V_{\text{dil}} \times M_{\text{dil}}}{1000} = \frac{V_{\text{conc}} \times M_{\text{conc}}}{1000}$$

$$\frac{V_{\text{conc}} \times 18}{1000} = \frac{250 \times 0.5}{1000}$$

$$V_{\text{conc}} = \frac{250 \times 0.5}{18}$$

$$V_{\text{conc}} = 6.94\text{cm}^3$$

1.6 P – Function

Sometimes it is inconvenient to use the concentration units in Table 2.4. For example, during a reaction a reactant's concentration may change by many orders of magnitude. If we are interested in viewing the progress of the reaction graphically, we might wish to plot the reactant's concentration as a function of time or as a function of the volume of a reagent being added to the reaction. Such is the case in Figure 2.1, where the molar concentration of H⁺ is plotted (*y*-axis on left side of figure) as a function of the volume of NaOH added to a solution of HCl. The initial [H⁺] is 0.10 M, and its concentration after adding 75 mL of NaOH is 5.0 × 10⁻¹³ M. We can easily follow changes in the [H⁺] over the first 14 additions of NaOH. For the last ten additions of NaOH, however, changes in the [H⁺] are too small to be seen.

When working with concentrations that span many orders of magnitude, it is often more convenient to express the concentration as a **p-function**. The p-function of a number *X* is written as p*X* and is defined as

$$pX = -\log(X)$$

Thus, the pH of a solution that is 0.10 M H⁺ is

$$\text{pH} = -\log[\text{H}^+] = -\log(0.10) = 1.00$$

and the pH of 5.0 × 10⁻¹³ M H⁺ is

$$\text{pH} = -\log[\text{H}^+] = -\log(5.0 \times 10^{-13}) = 12.30$$

Figure 1.2 shows how plotting PH in place of [H⁺] provides more detail about how the concentration of H⁺ changes following the addition of NaOH.

Example 1.4

What is pNa for a solution of 1.76×10^{-3} M Na_3PO_4 ?

SOLUTION

Since each mole of Na_3PO_4 contains three moles of Na^+ , the concentration of Na^+ is

$$[\text{Na}^+] = \frac{3 \text{ mol Na}^+}{\text{mol Na}_3\text{PO}_4} \times 1.76 \times 10^{-3} \text{ M} = 5.28 \times 10^{-3} \text{ M}$$

and pNa is

$$\text{pNa} = -\log[\text{Na}^+] = -\log(5.28 \times 10^{-3}) = 2.277$$

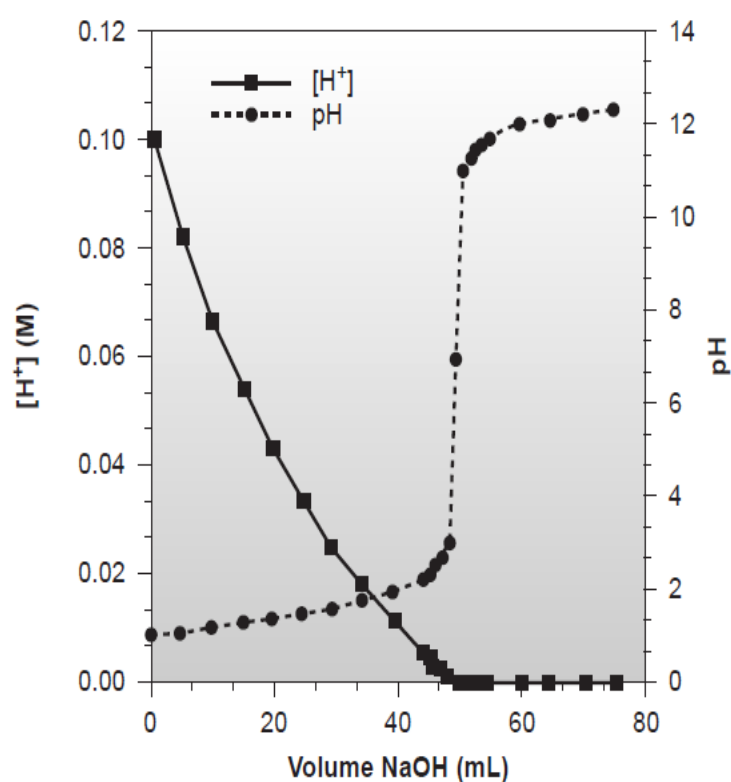


Figure 1.2 Graph of $[\text{H}^+]$ versus volume of NaOH and PH versus volume of NaOH for reaction of 0.10M HCl with 0.10M NaOH.

Example 1.5

What is the $[\text{H}^+]$ in a solution that has a pH of 5.16?

SOLUTION

The concentration of H^+ is

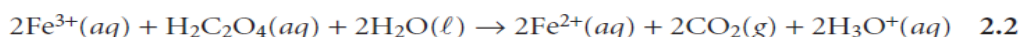
$$\text{pH} = -\log[\text{H}^+] = 5.16$$

$$\log[\text{H}^+] = -5.16$$

$$[\text{H}^+] = \text{antilog}(-5.16) = 10^{-5.16} = 6.9 \times 10^{-6} \text{ M}$$

1.7 Stoichiometric Calculation

A balanced chemical reaction indicates the quantitative relationships between the moles of reactants and products. These stoichiometric relationships provide the basis for many analytical calculations. Consider, for example, the problem of determining the amount of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, in rhubarb. One method for this analysis uses the following reaction in which we oxidize oxalic acid to CO_2 .



The balanced chemical reaction provides the stoichiometric relationship between the moles of Fe^{3+} used and the moles of oxalic acid in the sample being analyzed—specifically, one mole of oxalic acid reacts with two moles of Fe^{3+} . As shown in Example 2.6, the balanced chemical reaction can be used to determine the amount of oxalic acid in a sample, provided that information about the number of moles of Fe^{3+} is known.

Example 1.6

- The amount of oxalic acid in a sample of rhubarb was determined by reacting with Fe^{3+} as outlined in reaction 2.2. In a typical analysis, the oxalic acid in 10.62 g of rhubarb was extracted with a suitable solvent. The complete oxidation of the oxalic acid to CO_2 required 36.44 mL of 0.0130 M Fe^{3+} . What is the weight percent of oxalic acid in the sample of rhubarb?

SOLUTION

We begin by calculating the moles of Fe^{3+} used in the reaction

$$\frac{0.0130 \text{ mol Fe}^{3+}}{\text{L}} \times 0.03644 \text{ L} = 4.737 \times 10^{-4} \text{ mol Fe}^{3+}$$

The moles of oxalic acid reacting with the Fe^{3+} , therefore, is

$$4.737 \times 10^{-4} \text{ mol Fe}^{3+} \times \frac{1 \text{ mol C}_2\text{H}_2\text{O}_4}{2 \text{ mol Fe}^{3+}} = 2.369 \times 10^{-4} \text{ mol C}_2\text{H}_2\text{O}_4$$

Converting moles of oxalic acid to grams of oxalic acid

$$2.369 \times 10^{-4} \text{ mol C}_2\text{H}_2\text{O}_4 \times \frac{90.03 \text{ g C}_2\text{H}_2\text{O}_4}{\text{mol C}_2\text{H}_2\text{O}_4} = 2.132 \times 10^{-2} \text{ g oxalic acid}$$

and converting to weight percent gives the concentration of oxalic acid in the sample of rhubarb as

$$\frac{2.132 \times 10^{-2} \text{ g C}_2\text{H}_2\text{O}_4}{10.62 \text{ g rhubarb}} \times 100 = 0.201\% \text{ w/w C}_2\text{H}_2\text{O}_4$$

1.8 Preparing Solutions

Preparing a solution of known concentration is perhaps the most common activity in any analytical lab. The method for measuring out the solute and solvent depend on the desired concentration units, and how exact the solution's concentration needs to be known. Pipets and volumetric flasks are used when a solution's concentration must be exact; graduated cylinders, beakers, and reagent bottles suffice when concentrations need only be approximate. Two methods for preparing solutions are described in this section.

1.8.1 Preparing Stock Solutions

A **stock solution** is prepared by weighing out an appropriate portion of a pure solid or by measuring out an appropriate volume of a pure liquid and diluting to a known volume. Exactly how this is done depends on the required concentration units. For example, to prepare a solution with a desired molarity you would weigh out an appropriate mass of the reagent, dissolve it in a portion of solvent, and bring to the desired volume.

To prepare a solution where the solute's concentration is given as a volume percent, you would measure out an appropriate volume of solute and add sufficient solvent to obtain the desired total volume .

Example 1.7

Describe how you would prepare the following three solutions: (a) 500 mL of approximately 0.20 M NaOH using solid NaOH; (b) 1 L of 150.0 ppm Cu²⁺ using Cu metal; and (c) 2 L of 4% v/v acetic acid using concentrated glacial acetic acid.

SOLUTION

- (a) Since the concentration only needs to be known to two significant figures, the mass of NaOH and volume of solution do not need to be measured exactly. The desired mass of NaOH is

$$\frac{0.20 \text{ mol}}{\text{L}} \times \frac{40.0 \text{ g}}{\text{mol}} \times 0.50 \text{ L} = 4.0 \text{ g}$$

To prepare the solution we place 4.0 g of NaOH, weighed to the nearest tenth of a gram, in a bottle or beaker and add approximately 500 mL of water.

- (b) Since the concentration of Cu²⁺ needs to be exact, the mass of Cu metal and the final solution volume must be measured exactly. The desired mass of Cu metal is

$$\frac{150.0 \text{ mg}}{\text{L}} \times 1.000 \text{ L} = 150.0 \text{ mg} = 0.1500 \text{ g}$$

To prepare the solution we measure out exactly 0.1500 g of Cu into a small beaker. To dissolve the Cu we add a small portion of concentrated HNO₃ and gently heat until it completely dissolves. The resulting solution is poured into a 1-L volumetric flask. The beaker is rinsed repeatedly with small portions of water, which are added to the volumetric flask. This process, which is called a **quantitative transfer**, ensures that the Cu²⁺ is completely transferred to the volumetric flask. Finally, additional water is added to the volumetric flask's calibration mark.

- (c) The concentration of this solution is only approximate, so volumes do not need to be measured exactly. The necessary volume of glacial acetic acid is

$$\frac{4 \text{ mL CH}_3\text{COOH}}{100 \text{ mL}} \times 2000 \text{ mL} = 80 \text{ mL CH}_3\text{COOH}$$

To prepare the solution we use a graduated cylinder to transfer 80 mL of glacial acetic acid to a container that holds approximately 2 L, and we then add sufficient water to bring the solution to the desired volume.

1.8.2 Preparing Solutions by Dilution

Solutions with small concentrations are often prepared by diluting a more concentrated stock solution. A known volume of the stock solution is transferred to a new container and brought to a new volume. Since the total amount of solute is the same before and after **dilution**, we know that

$$C_o \times V_o = C_d \times V_d$$

where C_o is the concentration of the stock solution, V_o is the volume of the stock solution being diluted, C_d is the concentration of the dilute solution, and V_d is the volume of the dilute solution. Again, the type of glassware used to measure V_o and V_d depends on how exact the solution's concentration must be known

Example 1.8

A laboratory procedure calls for 250 mL of an approximately 0.10 M solution of NH_3 . Describe how you would prepare this solution using a stock solution of concentrated NH_3 (14.8 M).

SOLUTION

Substituting known volumes in equation 2.4

$$14.8 \text{ M} \times V_o = 0.10 \text{ M} \times 0.25 \text{ L}$$

and solving for V_o gives $1.69 \times 10^{-3} \text{ L}$, or 1.7 mL. Since we are trying to make a solution that is approximately 0.10 M NH_3 , we can measure the appropriate amount of concentrated NH_3 using a graduated cylinder, transfer the NH_3 to a beaker, and add sufficient water to bring the total solution volume to approximately 250 mL.

Example 1.9

- A sample of an ore was analyzed for Cu^{2+} as follows. A 1.25-g sample of the ore was dissolved in acid and diluted to volume in a 250-mL volumetric flask. A 20-mL portion of the resulting solution was transferred by pipet to a 50-mL volumetric flask and diluted to volume. An analysis showed that the concentration of Cu^{2+} in the final solution was 4.62 ppm. What is the weight percent of Cu in the original ore?

SOLUTION

Substituting known volumes (with significant figures appropriate for pipets and volumetric flasks) into equation 2.4

$$(\text{ppm Cu}^{2+})_o \times 20.00 \text{ mL} = 4.62 \text{ ppm} \times 50.00 \text{ mL}$$

and solving for $(\text{ppm Cu}^{2+})_o$ gives the original solution concentration as 11.55 ppm. To calculate the grams of Cu^{2+} we multiply this concentration by the total volume

$$\frac{11.55 \text{ } \mu\text{g Cu}^{2+}}{\text{mL}} \times 250.0 \text{ mL} \times \frac{1 \text{ g}}{10^6 \text{ } \mu\text{g}} = 2.888 \times 10^{-3} \text{ g Cu}^{2+}$$

The weight percent Cu is then given by

$$\frac{2.888 \times 10^{-3} \text{ g Cu}^{2+}}{1.25 \text{ g sample}} \times 100 = 0.231\% \text{ w/w Cu}$$

1.9 Basic Tools and Operations of Analytical Chemistry

1.9.1 Basic Equipment

Measurements are made using appropriate equipment or instruments. The array of equipment and instrumentation used in analytical chemistry is impressive, ranging from the simple and inexpensive, to the complex and costly.

1.9.2 Equipments for Measuring Mass (Analytical Balance)

An object's mass is measured using a **balance**. The most common type of balance is an in which the balance pan is placed over an electromagnet. Another type of analytical balance is the **mechanical balances** which are replaced by the electronic balances. **electronic balance electronic balance.**



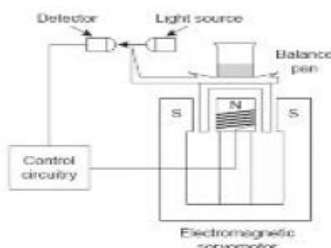
electronic balance



electronic balance



(a)



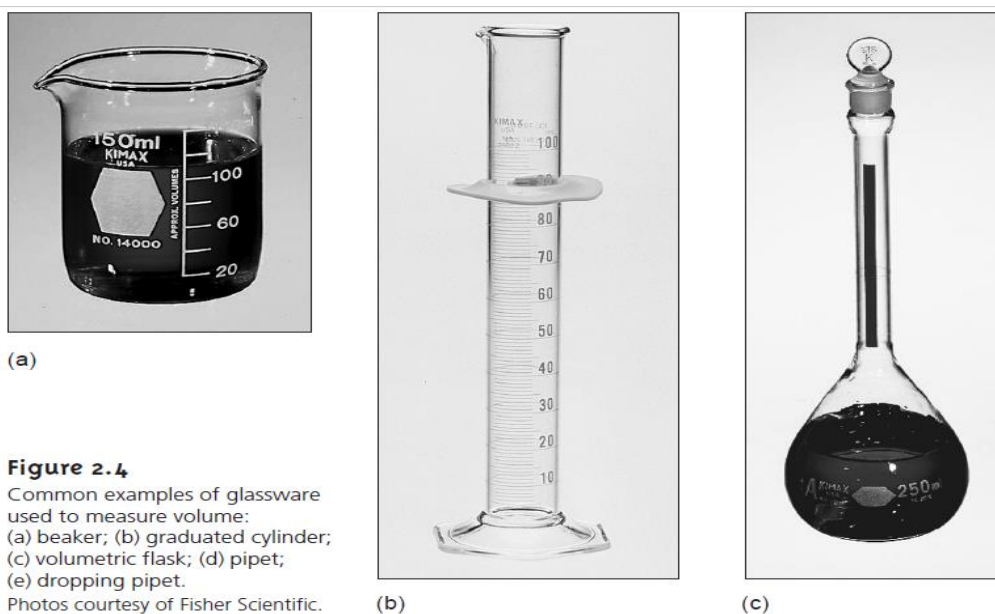
(b)

Figure 2.2
 (a) Photo of a typical electronic balance.
 (b) Schematic diagram of electronic balance; adding a sample moves the balance pan down, allowing more light to reach the detector. The control circuitry directs the electromagnetic servomotor to generate an opposing force, raising the sample up until the original intensity of light at the detector is restored.
 Photo courtesy of Fisher Scientific.

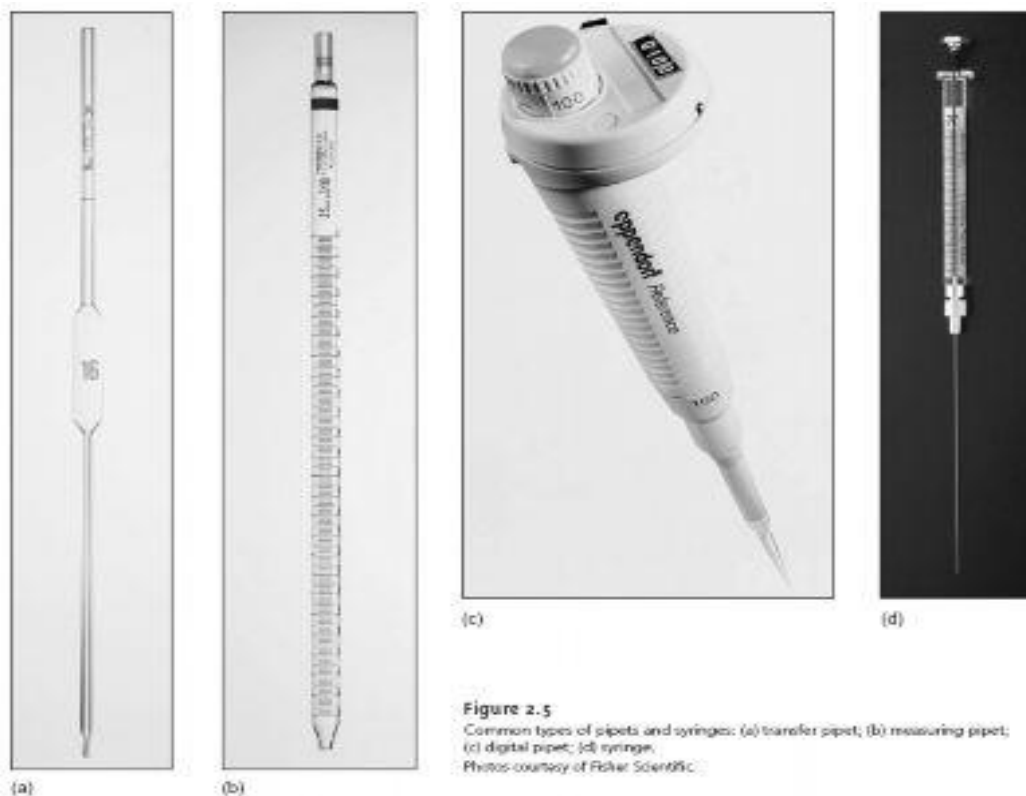
1.9.2 Equipment for Measuring Volume

Analytical chemists use a variety of glassware to measure volume. The type of glassware used depends on how exact the volume needs to be.

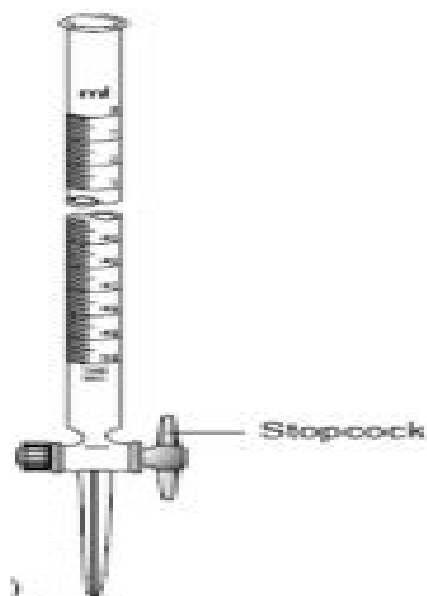
Volumetric flask is designed to contain a specified volume of solution at a stated temperature, usually 20 °C.



Pipette is used to deliver a specified volume of solution. Several different styles of



Burette is volumetric glassware used to deliver variable, but known volumes of solution. A burette is a long, narrow tube with graduated markings, and a stopcock for dispensing the solution.



1.9.3 Equipment for Drying

Reagents, precipitates, and glassware are conveniently dried in an oven at 110°C. Many materials need to be dried prior to their analysis to remove residual moisture.

Depending on the material, heating to a temperature of 110–140 °C is usually sufficient. Other materials need to be heated to much higher temperatures to initiate thermal decomposition. Both processes can be accomplished using a **laboratory oven** capable of providing the required temperature. Commercial laboratory ovens are used when the maximum desired temperature is 160–325 °C (depending on the model). Higher temperatures, up to 1700° C, can be achieved using a muffle **furnace**.

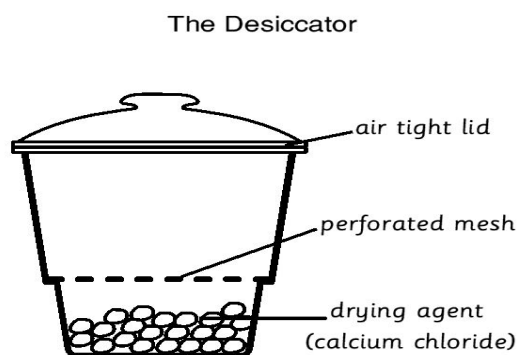


Conventional laboratory oven used for drying materials.



Example of a muffle furnace used for heating samples to maximum temperatures of 1100–1700 °C.

After drying or decomposing a sample, it should be cooled to room temperature in a desiccator to avoid the readsorption of moisture. A **desiccator** is a closed container that isolates the sample from the atmosphere. A drying agent, called a **desiccant**, is placed in the bottom of the container. Typical desiccants include calcium chloride and silica gel.



(a)

(a) Ordinary desiccator.

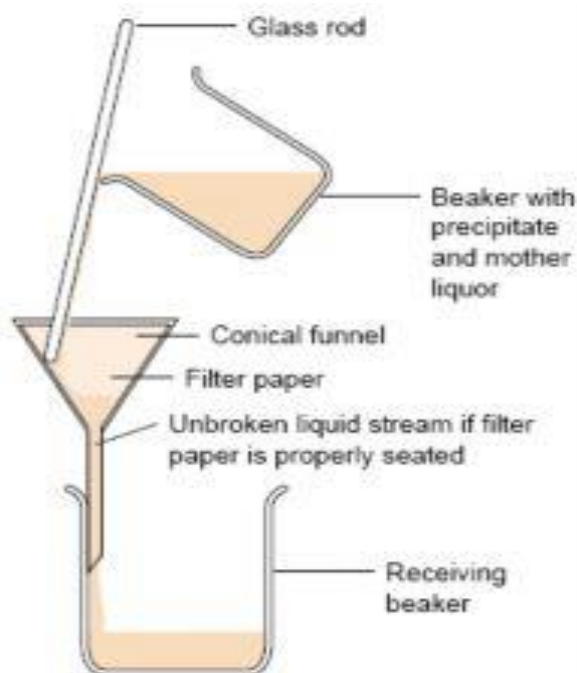


(b)

(b) Vacuum desiccator

1.9.4 Filtration

In *gravimetric analysis*, the mass of product from a reaction is measured to determine how much unknown was present. Precipitates from gravimetric analyses are collected by filtration. Liquid from which a substance precipitates or crystallizes is called the **mother liquor**. Liquid that passes through the filter is called **filtrate**.



Filtering a precipitate.

The conical funnel is supported by a metal ring attached to a ring stand, neither of which is shown.

Folding filter paper for a conical funnel.

- Fold the paper in half.
- Then fold it in half again.
- Tear off a corner to allow better seating of the paper in the funnel.
- Open the side that was not torn when fitting the paper in the funnel.

