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BASICS OF SOLUTION CHEMISTRY

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Introduction to Solutions, Suspensions and Colloids

A solution is a homogeneous liquid formed by the addition of solutes to a solvent (solute + solvent = homogeneous solution); a suspension is a heterogeneous fluid containing solid particles that are sufficiently large for sedimentation. An example of a suspension would be sand in water. A colloid is a substance microscopically dispersed evenly throughout another substance. An example of a colloid is milk. Suspensions will eventually settle over time while colloids do not settle because particles suspended in colloids are smaller (particle sizes are 0.1 nm to 1.0 μm).

The behaviour of solutions depends on the type of solutes involved and their proportions, relative to the solvent. Laboratory work involves the calculation of concentrations, either when preparing a solution of a given concentration for an experiment or when expressing data in terms of solute concentration. This chapter will give you the basic idea of solutes, solvents and solutions and examples of calculations in the laboratory.

Solutes can affect the properties of solutions in many ways. They are *electrolytic dissociation (if solutes are electrolytes), osmotic effects and ideal/non- ideal behaviour.* Electrolytic dissociation occurs when a substance dissociates to give ions. A strong electrolyte such as NaCl is completely dissociated whereas a weak electrolyte such as ethanoic (acetic) acid will be only partially dissociated, depending on the pH and temperature of the solution. This is because NaCl is a salt whereas ethanoic acid is a weak acid; salts are completely ionised if they are soluble in a solvent.

Osmotic effects are the result of solute particles lowering the effective concentration of the solvent (water). These effects are particularly relevant to biological systems since membranes are more permeable to water than to most solutes. Water moves across biological membranes from the solution with the higher effective water concentration to that with the lower effective water concentration (osmosis).

Non-ideal behaviour occurs because real solutions do not necessarily conform to the theoretical relationships predicted for dilute solutions that show the so-called ideal behaviour. It is often necessary to take into account the non- ideal behaviour of real solutions, especially at high solute concentrations.

Classification of solvents can be done on the basis of physical and chemical properties and solute- solvent interaction.

Types of Solvents

1. Non polar solvents (hexane, benzene, toluene, diethyl ether, chloroform, DCM, ethyl acetate)
2. Polar solvents (water, DMSO, DCM, DMF, acetonitrile, methanol, ethanol, pyridine, acetone, THF)
3. Protic solvents (water, chloroform, methanol, ethanol)
4. Dipolar aprotic solvents (DMSO, DMF, pyridine, acetone, THF)

DCM - dicloromethane; DMSO- dimethyl sulphoxide;
DMF- dimethyl formamide; THF - tetrahydrofuran

Types of solute- solvent interactions include:

1. Ion- ion
2. Ion- dipole
3. Dipole-dipole (H-bonding included)
4. Dipole-induced dipole
5. Ion-induced dipole
6. Induced dipole-induced dipole (dispersion forces- van der Waals/ London forces)

Solvents are also classified according to the following:

1. Bulk physical properties: Liquid range (melting/boiling point), polarity (dielectric constant, dipole moment, refractive index) and others
2. Chemical properties: Acid-base properties (Brønsted, Lewis description), redox properties
3. Empirical parameters: effect on spectra, reaction equilibria or kinetics
4. Mixed classification

Dissolution of Solutes - Solubility

Solubility is the property of a solute that can be a solid, liquid or gas to dissolve in a solvent to form a homogeneous solution of the solute in the solvent. The solubility of a substance depends on the solvent used, temperature and pressure. Most often, the solvent is a liquid, which can be a pure substance or a mixture.

Solutes can dissolve in solvents in different ways:

- completely soluble (e.g. sodium chloride in water) or fully miscible (e.g. ethanol and water)
- sparingly soluble (e.g. silver chloride in water), and
- insoluble i.e. poorly or very poorly soluble compounds (e.g. calcium carbonate in water).

Solubility may be expressed in units of concentration or molar concentration-molarity, molality, mole fraction and other units.

Solubility of Ionic Compounds

Ionic compounds are soluble in water. In the water molecule, oxygen has a partial negative charge because it is more electronegative than hydrogen while hydrogen has a partial positive charge. Thus the water molecule is a dipole. Ionic compounds dissolve in water, because of the attraction between the positive ion (cation) and negative end of the dipole and negative ion (anion) and the positive end of the dipole of water. For example in NaCl, Na^+ attracts the partially negative oxygen while Cl^- attracts the partially positive hydrogen in H_2O- *ion dipole interaction.*

Solubility products (K_{sp}) give a quantitative explanation.

	K_{sp} ($mol^2\ dm^{-6}$)	
$CaSO_4$	2×10^{-4}	*partially soluble*
$BaSO_4$	1×10^{-10}	*sparingly soluble*
$SrSO_4$	4×10^{-7}	*sparingly soluble*

Solubility of Organic Compounds

The principle, *like dissolves like;* is the usual guide to solubility of organic compounds. This indicates that a solute will dissolve best in a solvent that is chemically similar to itself. This is a very simple idea, but is a useful rule of thumb. The overall solvation capacity of a solvent depends primarily on its polarity. For example, a very polar or hydrophilic (or 'water liking') solute such as urea is very soluble in highly polar water, less soluble in fairly polar methanol, and practically insoluble in non-polar solvents such as benzene. In contrast, a non-polar or lipophilic solute such as naphthalene is insoluble in water, fairly soluble in methanol, and highly soluble in non-polar solvents such as benzene.

Another example is petroleum jelly, which will dissolve in gasoline, because both petroleum jelly and gasoline are non-polar hydrocarbons. At the same time, it will not dissolve in ethanol or water, since the polarity of these solvents is too high. Sugar is not soluble in gasoline, because sugar is polar while gasoline is non-polar. The solubility is favoured by entropy of mixing and depends on enthalpy of dissolution and the hydrophobic effect. Synthetic chemists often exploit differences in solubility to separate and purify compounds from reaction mixtures.

Solubility is commonly expressed as a concentration (g of solute per dm^3 (L) of solvent, molarity, molality). The maximum equilibrium amount of solute that can dissolve per amount of solvent is the solubility of that solute in that solvent under the specified conditions. The advantage of expressing solubility in this manner is its simplicity, while the disadvantage is that it can strongly depend on the temperature and the presence of other species in the solvent (e.g. the common ion effect).

Solubility of Gases in Liquids

Solubility of gases in solvents is given by Henry's law, according to which the solubility of a gas in a solvent, G(sol) is directly proportional to the partial pressure of that gas p_G above the solvent. This relationship is written as:

$$G(sol) = K_H \, p_G$$

where, K_H is a temperature-dependent constant called Henry's constant; e.g. K_H for oxygen gas in water at 298 K is 1.3×10^{-3} mol dm^{-3} atm^{-1}.

The lowest level of oxygen gas dissolved in water that will support life is about 1.3×10^{-4} mol dm^{-3} (mol L^{-1}). At the normal atmospheric pressure of oxygen is there adequate oxygen to support life in water?

Let us calculate the solubility of oxygen in water under atmospheric conditions. Oxygen gas is about 21% of the atmospheric gases. Therefore the partial pressure of oxygen gas is 0.21 atm.

The solubility of oxygen gas in water

$$= 1.3 \times 10^{-3} \text{ mol dm}^{-3} \text{atm}^{-1} \times 0.21 \text{ atm} = 2.73 \times 10^{-4} \text{ mol dm}^{-3}$$

This is adequate to sustain life in water !

If the partial pressure of oxygen in the atmosphere is 0.21 atm., the highest level of oxygen dissolved is 2.73×10^{-4} mol dm^{-3}. Henry's law is valid for gases that do not form species (i.e. undergo *speciation)* on dissolution.

In addition, we also have *solid solutions*, e.g. an alloy such as brass; the components of brass are Cu and Zn. Here Zn is dissolved into Cu (base metal) without forming separate phases. The term solid solution is often used in the field of metallurgy.

Preparation of Solutions

Solutions are usually prepared with respect to their molar concentrations (e.g. mol dm^{-3}):

$$\text{Concentration} = \frac{\text{amount of moles}}{\text{volume}}$$

It is important to recognise clearly the units involved and to prepare the solution accordingly: for molar concentrations you will need the relative molecular mass of the chemical, so that you can calculate the mass of substance required.

You may also find that the concentration of a solution is expressed in terms of percentage; e.g. sodium carbonate (10% w/v). The symbol 'w' indicates weight of solute and 'v' is the volume of solution. The solution is prepared from sodium carbonate (10 g) dissolved in water and the solution made up to 100 cm^3 with water. The resulting solution is a general-purpose dilute aqueous solution of sodium carbonate used for neutralising acid. We will further discuss concentration in later sections.

This brings us to the discussion on the two levels of accuracy required for preparing solutions. Solutions of chemicals used in qualitative and preparative procedures, where the concentration of chemicals need not be known to more than one or two decimal places, are called *general-purpose solutions*. Solutions used in quantitative analytical procedures where the concentrations need to be known to an accuracy of four decimal places (e.g. 0.0001 mol dm^{-3}) are known as *analytical solutions*.

Examples of general-purpose solutions include solutions used in extraction and washing processes, e.g. hydrochloric acid (0.1 mol dm^{-3}), sodium hydroxide (2 M) and the 10% (w/v) sodium carbonate solution. It also includes solutions of chemicals used in preparative experiments, where the techniques of purification (distillation, recrystallization, filtration, etc.) any way introduce losses of substances that make accuracy meaningless.

Analytical solutions are used in volumetric procedures (titrations) and gravimetric analysis where the concentrations of standard solutions of reagents and compounds to be analysed need to be accurately known. They are also used in spectroscopy (e.g. quantitative UV- visible spectroscopy, atomic absorption spectroscopy and flame photometry), electrochemical measurements (pH titrations, conductance measurements and polarography) and chromatographic methods.

The procedures for weighing (i.e. the type of balance used) and the glassware used in the preparation of solutions differ according to the level of accuracy required. The levels of accuracy required for preparation of a solution are indicated in the protocol or by the nature of the experiment. The phrase, 'accurately weighed' means weighing to four decimal places on an analytical balance, together with a quantitative transfer. Volumes quoted as 250.00 cm^3, 100.00 cm^3, 25.00 cm^3 indicate the use of volumetric flasks and pipettes. Volumes given in μL imply the use of pipettes or syringes.

Quantities and Concentrations

Concentration is a way of expressing the relative amounts of solute and solvent. The SI unit of concentration of a solute is mol m^{-3}. This is not convenient when dealing with solutions in the laboratory. A common unit of volume used is the liter (L) or dm^3 which is a non-SI unit. It can be converted to the SI unit of volume (m^3) using the relationship, $1\ L = 10^{-3}\ m^3$. The concentration of a solute is shown by square brackets, e.g. $[Cl^-]$. We will learn how to prepare solutions later.

There are a number of ways of expressing the concentration. They are molarity, molality and normality. In addition, per cent composition (% w/w), per cent concentration (% w/v and v/v) and parts per million (ppm) are also used.

Molarity

This term refers to the molar concentration, [C], expressed as moles of solute per dm^3 (liter) volume of solution - mol dm^{-3} (mol L^{-1}). This is not an SI unit, but it's use continues because scientists are familiar with the term and also the laboratory glassware is calibrated in cm^3 (mL) and dm^3 (L). This makes the preparation of molar (M) and millimolar (mM) solutions relatively straightforward.

$$[C] = \frac{\text{mass of solute}/M_r}{\text{volume of solution}}$$

where M_r is the relative molecular mass of solute.

If we require 200 cm^3 (0.2 dm^3) of an aqueous solution of anhydrous sodium carbonate (Na_2CO_3, M_r= 105.98 g mol^{-1}) at a concentration of 0.2 mol dm^{-3}, we can calculate the amount of anhydrous Na_2CO_3 required.

Substituting the given values, we have

$$[0.2] = \frac{\text{mass of solute}/105.98}{0.2}$$

$$\textit{mass of solute} = 0.2 \times 0.2 \times 105.98 = 4.2392\ g$$

Similarly, we can calculate the concentration of a solution containing a known amount of solute; e.g. 0.1060 g of Na_2CO_3 dissolved in water and made up to 50 cm^3 (0.05 dm^3) will give:

$$[Na_2CO_3] = \frac{0.1060\ g\ /\ 105.98\ g\ mol^{-1}}{0.05\ dm^3} = 0.02\ mol\ dm^{-3}$$

Molality

The concentration of solute relative to *mass* of solvent is expressed as molality. It is a temperature independent way of expressing solute concentration. It is seldom used except when we are interested in the osmotic properties (e.g. pressure) of a solution; e.g. a 0.05 molal solution of Na_2CO_3 contains Na_2CO_3 per 1 kg of water.

Normality

A 1 normal (1 N) solution is one that contains one *equivalent mass* of a substance per dm^3 (L) of solution.

$$normality = \frac{mass\ of\ substance\ per\ litre}{equivalent\ mass}$$

Equivalence and normality are outdated terms; today the term, normality is replaced by *moles of charge*, i.e., cmol. However, the term equivalence is still used in certain cases, e.g. in the study of quality of irrigation water. The water quality characteristic, *Sodium adsorption ratio* (SAR) is given by:

$$\text{SAR} = \frac{Na^+}{\sqrt{Ca^{2+} + Mg^{2+}}}\ \text{mmol dm}^{-3}$$

where $[Na^+]$, $[Ca^{2+}]$ and $[Mg^{2+}]$ represent concentrations of Na^+, Ca^{2+} and Mg^{2+} respectively expressed in milli-equivalents per dm^3 (or cmmol dm^{-3}).

This is a measure of the suitability of water for use in agricultural irrigation. In general, the higher the sodium adsorption ratio, the less suitable the water is for irrigation. If irrigation water with a high SAR is applied to a soil for years, the sodium in the water can displace the calcium and magnesium in the soil. This will cause a decrease in the ability of the soil to form stable aggregates and a loss of soil structure. This will also lead to a decrease in infiltration and permeability of the soil to water, leading to problems with crop production. The magnitude of an equivalent mass (equivalent weight) can be identified from the balanced equation for the reaction under consideration. Remember that the equivalent mass can change, depending on the reaction.

In the reaction, $HCl + NaOH \longrightarrow NaCl + H_2O$,
we know that 1 mol of HCl reacts with 1 mol of NaOH; thus the equivalent mass of HCl is $M_r = 36.5$ and the equivalent mass of NaOH is also its $M_r = 40$.

In the reaction, $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$,
since 1 mol of H_2SO_4 reacts with 2 mol of NaOH, the equivalent mass of H_2SO_4 is $M_r/2 = 98/2 = 49$, while the equivalent mass of NaOH is still $M_r = 40$.

In the reaction, $5FeSO_4 + KMnO_4 \longrightarrow Fe_2(SO_4)_3 + 2MnSO_4$, since the half- reaction, $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ involves $5e^-$, the equivalent mass of $KMnO_4$ is $M_r/5 = 158/5 = 31.6$. Since the corresponding half- reaction for the oxidation, $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ involves one electron, the equivalent mass of $FeSO_4$ is still $M_r = 152$.

However, for the reaction, $H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + CO_2 + H_2O$, since the reaction is 1:1, the equivalent masses of H_2SO_4 and Na_2CO_3 are their M_r values, 98 and 106, respectively. Because of this possible confusion, the concept of equivalent mass (weight) is seldom used. The use of normality is also now obsolete.

Percent composition (% w/w)

This is the mass (in g) of solute per 100 g solution. A 10% w/w NaOH solution contains 10 g NaOH and 90 g water (= 90 cm^3 water, assuming a density of 1 g cm^{-3}) to give 100 g of solution. It is easy to prepare such a solution; all we need is to weigh each component and mix them together. For water, we can use an appropriate volume (= mass) using a measuring cylinder. Therefore this has an advantage of being easy to prepare.

Similar terms are parts per thousand, i.e. mg g^{-1}, and parts per million, i.e. $\mu g\ g^{-1}$, about which will be discussed in detail later.

A 5% w/v KOH solution contains 5 g KOH in 100 cm^3 of solution. A 5% v/v glycerol solution would contain 5 cm^3 of glycerol in 100 cm^3 of solution. Note that when water is the solvent, this is often not specified in the expression; e.g. a 10% v/v ethanol solution contains 10 cm^3 of ethanol and the solution is made up to 100 cm^3 by adding water.

The terms w/w or w/v are mainly used for solutes whose molecular mass is unknown (e.g. polymers) or for mixtures of certain type of substance (e.g. total salt in sea water). When you use the per cent terms, you must always specify how the solution was prepared (i.e. by using the term w/w, w/v or v/v).

Parts per million (ppm) Concentration

The term ppm originally described a solution that contained a mass (in g) in a million (10^6) g of solvent; it is a weight per weight (w/w) expression. However, in the present day applications, it has become a weight per volume (w/v) concentration term because the solvent is often water (where density is unity and 1 ml= 1 g). It is not an SI unit for concentration like mol dm^{-3}. It is widely used in quantitative analysis such as flame photometry, atomic absorption spectrophotometry (AAS) and gas chromatography.

$$\begin{aligned}1\text{ ppm} &= 1\text{ g in }10^6\text{ g} \approx 1\text{ g in }10^6\text{ cm}^3\text{ (for water 1 cm}^3 \approx 1\text{ g)}\\ &= 1\text{ g in }10^3 \times (10^3\text{ cm}^3)\text{ water} = 1\text{ g in }10^3\text{ dm}^3\text{ (or L) OR}\\ &= 1\text{ mg in 1 dm}^3 = 1\text{ mg dm}^{-3}\text{ (mg L}^{-1}) = 1\ \mu\text{g cm}^{-3}\ (\mu\text{g mL}^{-1})\end{aligned}$$

When we handle very dilute aqueous solutions, we use the term *parts per billion (ppb)*.

$$\begin{aligned}1\text{ ppb} &= 1\text{ g in }10^9\text{ g} \approx 1\text{ mg in }10^3\text{ dm}^3 = 1\ \mu\text{g in 1 dm}^3\\ &= 1\ \mu\text{g dm}^{-3}\ (\mu\text{g L}^{-1}) = 1\text{ ng cm}^{-3}\text{ (ng mL}^{-1})\end{aligned}$$

When ppm is used, it is always essential to indicate the species; e.g. 50 ppm of NO_3^- is the same as 11.3 ppm of NO_3-N.

Let us practice some of the basic ideas that we have studied. Consider the following examples:

- We will convert ppm to mol dm^{-3} (or mol L^{-1}). Let us calculate the molarity of 50 ppm $MgSO_4.7H_2O$ (M_r= 246.475).

$$\begin{aligned}50\text{ ppm} &= 50\text{ mg dm}^{-3} = 50 \times 10^{-3}\text{ g dm}^{-3}\\ &= \frac{50 \times 10^{-3}\text{ g}}{246.475\text{ g mol}^{-1}}\text{ dm}^{-3}\\ &= 0.2\text{ mol dm}^{-3}\end{aligned}$$

- We will also convert mol dm^{-3} (or mol L^{-1}) to ppm. Let us calculate Ni^{2+} ppm in $5\text{x}10^{-3}$ M (mol dm^{-3}) solution of $NiSO_4.7H_2O$ (M_r = 280.86).

$$\begin{aligned}5 \times 10^{-3}\text{ mol dm}^{-3} &= 5 \times 10^{-3}\text{ mol} \times 58.69\text{ g mol}^{-1}\text{ dm}^{-3}\text{ Ni}\\ &= 293.5 \times 10^{-3} \times 10^3\text{ mg dm}^{-3}\text{ (ppm) Ni}\end{aligned}$$

- We will convert parts per million (ppm) concentration to per cent concentration (% w/v) and then to molar concentration.

Let us calculate the weight of solute required to prepare a solution of a given concentration. Suppose you are asked to prepare 250.00 cm^3 of an aqueous solution of 10 ppm sodium ions from anhydrous sodium carbonate.

$$10\,ppm = 10 \times 10^{-3}\,g\,dm^{-3} Na^+ = 10^{-2} g\,dm^{-3} \frac{1}{23\,g\,mol^{-1}} Na^+$$

$$= \frac{10^{-2}}{23} mol\,dm^{-3} Na^+$$

$$= \frac{10^{-2}}{23} \times \frac{1}{2}\,mol\,dm^{-3} Na_2CO_3 = \frac{10^{-2}}{23 \times 2} \times 105.98\,g\,dm^{-3} = 0.0230\,g\,dm^{-3}$$

The weight of Na_2CO_3 required to prepare 250.00 cm^3 of 10 ppm Na^+ solution is:

$$= 0.0230 \times \frac{250}{1000}\,g = 0.00575\,g$$

When you practise this type of calculations, you can simplify it as follows:

$$10 \times 10^{-3} g\,dm^{-3} Na^+ = 10^{-2} \times \frac{1}{2} \times \frac{105.98}{23} g\,dm^{-3} Na_2CO_3 = 0.0230\,g\,dm^{-3}$$

$$= 0.0230 \times \frac{250}{1000}\,g\,Na_2CO_3\,in\,250.00\,cm^3 = 0.00575\,g\,in\,250.00\,cm^3$$

- Let us convert per cent composition (% w/w or % w/v) to molar concentration. Suppose you are asked to calculate the molar concentration of concentrated sulphuric acid; e.g. if you were supplied with a bottle that read 98% H_2SO_4, density is 1.80 g cm^{-3}; $M_r = 98$.

The molarity (or molar concentration) of conc. H_2SO_4 will be

$$\frac{98\,g}{98\,g\,mol^{-1}} \times \frac{1}{100\,g} \times 1.80\,g\,cm^{-3} = .018\,mol \times (10^{-1}dm)^{-3} = 18\,mol\,dm^{-3},$$

if the percent composition is by weight (w/w).

If the percent composition is by weight and volume (w/v), the molarity will be totally different.

$$\frac{98\,g}{98\,g\,mol^{-1}} \times \frac{1}{0.1\,dm^3} = 10\,mol\,dm^{-3}$$

Therefore, it is important to establish whether the percent composition is by weight only (w/w) or by weight and volume (w/v).

Concentration units: ppmv and mg/m^3

The term ppm is an acronym for parts per million. In the context of concentration of airborne gaseous pollutant, it stands for volumes of gaseous pollutant X per million volumes of air. In such cases, it is very important to use the terms ppmv or ppm by volume rather than simply ppm. Concentrations of some airborne gaseous pollutant may be expressed as ppbv or ppb by volume, meaning volumes of gaseous pollutant per billion volumes of air. Airborne pollutant concentration limits are usually expressed as parts per million by volume (i.e., ppmv) for gases and vapors, and mg/m^3 for dusts, aerosols and mists.

Quite often you will find the hazardous concentration limit of an airborne gaseous pollutant expressed as either *ppmv* or *mg/m*^{3} or both. There is a simple mathematical method of converting one to the other for gaseous substances. However, for non-gaseous pollutants such as dusts, mists or aerosols, it would be very difficult, if not impossible, to convert *mg/m*^{3} to *ppmv.*

Converting Atmospheric Pollutant Concentrations

From mg/m*^{3} *to ppmv

The conversion factor depends on the temperature at which you want the conversion (usually about 20 to 25 °C). At an ambient pressure of 1 atmosphere, the general equation can be derived as follows:

$$mg\,/\,m^3 = 10^{-3}\,g \times \frac{8.314\,J\,K^{-1}\,mol^{-1} \times (T\,K)}{1.01325 \times 10^5\,N\,m^{-2}\,(M\,g\,mol^{-1})}\,/\,m^3$$

$$from\ V = \frac{m}{d};\ d = \frac{PM}{RT}$$

$$mg\,/\,m^3 = \frac{(T\ K)}{(12.187)(M)}\,cm^3\,/\,m^3\ (cm^3\,/\,10^6\,cm^3 = ppmv)$$

The general equation to convert mg m^{-3} value to ppmv is:

$$ppmv = (mg\,/\,m^3)(273.15 + {}^{o}C)\,/(12.187)(M)$$

Where ppmv = ppm by volume (i.e., volume of gaseous pollutant per 10^6 volumes of ambient air)

mg/m^3 = milligrams of gaseous pollutant per cubic meter of ambient air
M = molecular weight of the gaseous pollutant
°C = ambient air temperature in degrees Celsius

As an example, for gaseous pollutant NO_x, convert 20 mg/m^3 to ppmv at 25 °C:

$$\text{ppmv} = (20)(273.15 + 25) / (12.187)(46.01) = 10.6$$

where: 46.01 = molecular weight of NO_2 (i.e., NO_x expressed as nitrogen dioxide)

From ppmv to mg/m3

Yet again, the conversion factor depends on the temperature at which you want the conversion (usually about 20 to 25 °C).

$$\text{ppmv} = \text{volume per } 10^6 \text{ volumes of air}$$

$$= \text{cm}^3/10^6\,\text{cm}^3 = \text{cm}^3/\text{m}^3 \qquad (10^6\,\text{cm}^3 = \text{m}^3)$$

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

$$\text{From the ideal gas equation, } PV = nRT, P = \frac{mRT}{MV} \text{ where density, } d = \frac{PM}{RT}$$

$$\text{density} = \frac{1.01325 \times 10^5\,\text{N m}^{-2} \times (M)\,\text{g mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1} \times (T\,\text{K})} = \frac{(12.187)(M) \times 10^3}{T}\,\text{g m}^{-3}$$

$$\text{ppmv} = \frac{(10^3)(12.187)(M) \times 10^3}{T} \times 10^{-6}\,\text{mg}/\text{m}^3$$

$$= \frac{(12.187)(M)}{T}\,\text{mg}/\text{m}^3$$

The general equation to convert ppmv value to mg m^{-3} is:

$$mg/m^3 = (ppmv)(12.187)(M)/(273.15 + {}^\circ C)$$

where, mg/m^3 = milligrams of gaseous pollutant per cubic meter of ambient air
ppmv = ppm by volume (i.e., volume of gaseous pollutant per 10^6 volumes of ambient air)
M = molecular weight of the gaseous pollutant
°C = ambient air temperature in degrees Celsius

As an example, for gaseous pollutant NO_x, convert 20 ppmv to mg/m^3 at 25 °C:

$$mg/m^3 = (20)(12.187)(46.01) / (273.15 + 25) = 37.6$$

where: 46.01 = molecular weight of NO_2 (i.e., NO_x expressed as nitrogen dioxide).

Preparation of Analytical Solutions

In analytical work we prepare two types of solutions:

- standard solutions, and
- stock solutions

A standard solution is one in which the solute, which is a *primary standard substance,* is weighed out to an accuracy of 4 decimal places (±0.1 mg), is dissolved in distilled water and the solution is made up to the mark in a volumetric flask. A 'primary standard substance' is typically a reagent which can be weighed easily and is so pure that its weight is truly representative of the number of moles of substance contained. It is extremely pure, stable, has no waters of hydration, and has a high molecular weight. Examples of primary standards are potassium bromate ($KBrO_3$) for standardization of sodium thiosulphate solution and potassium hydrogen phthalate (KHP) for standardization of aqueous base. Conversely, a secondary standard is a standard that is prepared in the laboratory for a specific analysis. It is usually standardized against a primary standard.

A stock solution is one from which dilutions are made. A stock solution is prepared by weighing the solute accurately using an analytical balance and quantitatively transferring it to the volumetric flask and making up to the mark. The stock solution needs to be standardised against a standard solution.

Suppose you have to prepare 250.00 cm^3 of 0.1 M ammonium ferrous sulphate, $(NH_4)_2FeSO_4.6H_2O$ (M_r= 392.14), which is to be used to determine the concentration of a solution of a potassium permanganate, $KMnO_4$.

The weight of ammonium ferrous sulphate required to prepare 0.1 M solution,

$$= 0.1 \times 392.14 \times \frac{250}{1000}\ g = 9.8035\ g$$

It is almost impossible to weigh exactly 9.8035 g of ammonium ferrous sulphate to prepare a 0.1 M solution. However, we can weigh out approximately between 9.8000 g and 9.8200 g accurately. From this we can calculate the exact concentration of ammonium ferrous sulphate. Suppose you weighed 9.8175 g and prepared the solution in a 250.00 cm^3 volumetric flask as described before. The concentration would be,

$$= \frac{9.8175\ g}{392.14\ g\ mol^{-1}} \times \frac{1}{0.25\ dm^3} = 0.1001\ mol\ dm^{-3}$$

You should remember that ammonium ferrous sulphate is not a primary standard substance. Therefore the solution has to be standardised against a solution of a primary standard substance.

Dilution

Dilution of solutions is an important part of our laboratory activities. This may involve either making a single dilution or preparing a dilution series.

Suppose we need to dilute 0.01 M (mol dm^{-3}) solution of cadmium nitrate, $Cd(NO_3)_2.4H_2O$ to 0.5 mM (mmol dm^{-3}). Let us calculate the volume of 0.01 M solution required for dilution, using the relationship, $[C_1]V_1 = [C_2]V_2$ where $[C_1]$ and $[C_2]$ are the initial and final concentrations of acid and V_1 and V_2 are their respective volumes,

$$0.01\, mol\, dm^{-3} \times V_1 = 0.5 \times 10^{-3} mol\, dm^{-3} \times 100\, cm^3$$

$$V_1 = 5.00\, cm^3$$

This relationship can be considered as equating the amounts of cadmium nitrate (or cadmium) as follows:

$$0.01\, mol\, dm^{-3} \times 10^{-3} \times V_1 = 0.5 \times 10^{-3} mol\, dm^{-3} \times 10^{-3} \times 100\, cm^3$$

The method of dilution involves the transfer of 5.00 cm^3 of 0.01 M solution to a 100.00 cm^3 volumetric flask and making up to the mark with distilled water. Add the last few drops from a Pasteur pipette until the lower meniscus touches the calibration mark. Mix thoroughly, by repeatedly inverting (holding the stopper firmly) the volumetric flask.

We must remember to express the concentrations in the same units.

For general-purpose work, where a higher degree of accuracy is not required, it may be acceptable to use conical flasks and beakers instead of volumetric flasks and use measuring cylinders for volume measurements.
Suppose we need to prepare 100 cm^3 each of the following:

- 100 ppm solution
- 10 ppm solution
- 1 ppm solution

from a 1000 ppm standard metal ion solution.

To prepare 100 cm^3 of 100 ppm solution,

- 10 cm^3 of standard (1000 ppm) solution is transferred to a 100 cm^3 volumetric flask, and
- the solution is made up to mark with distilled water.

Similarly, 100 cm^3 of 10 ppm solution can be prepared by transferring 10 cm^3 of 100 ppm solution prepared previously to a 100 cm^3 volumetric flask and making up to the mark with distilled water.

Finally, 100 cm^3 of 1 ppm solution can be prepared by transferring 10 cm^3 of 10 ppm solution to a 100 cm^3 volumetric flask and making up to the mark with distilled water. These processes can be best described by the following diagram:

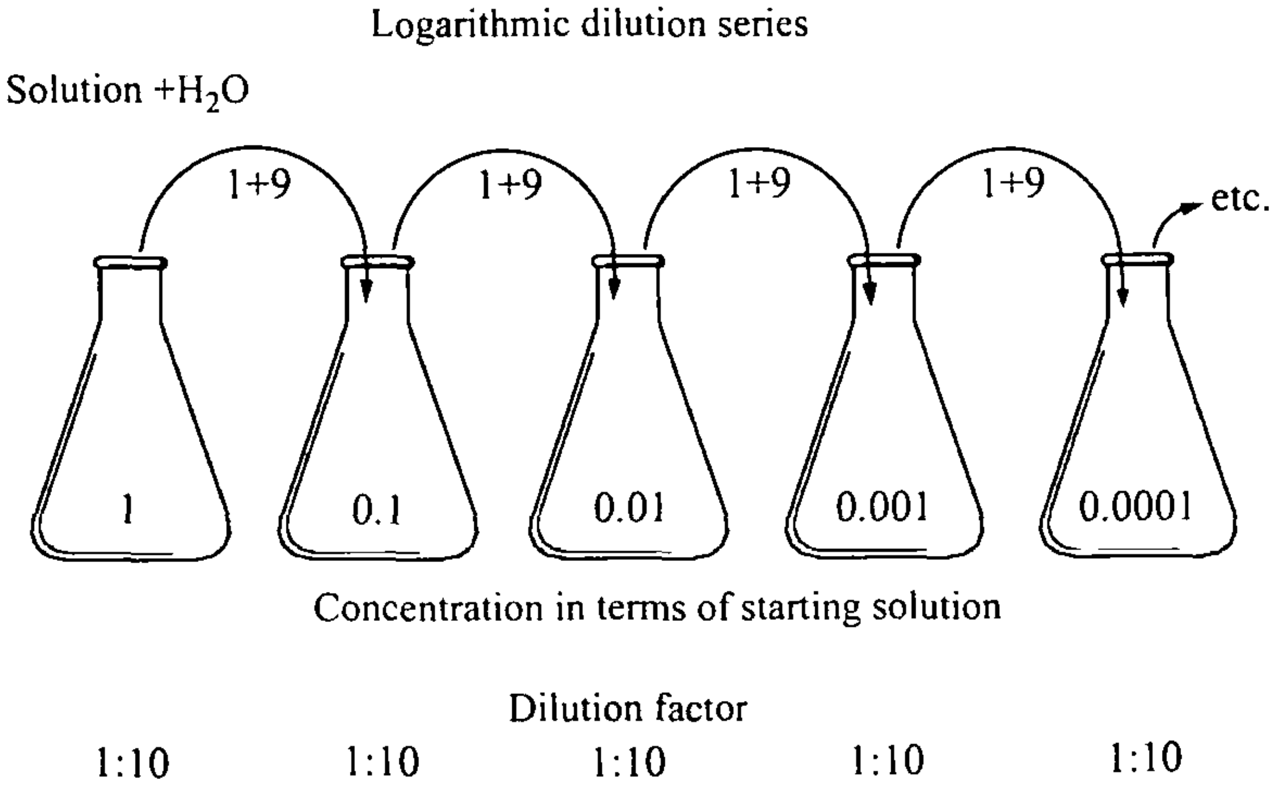

Figure 1. Logarithmic dilution series

Similarly dilution can be by a factor of 2, as shown in Fig. 2. However, you must remember that this process introduces an error (systematic error) at every step of the dilution process.

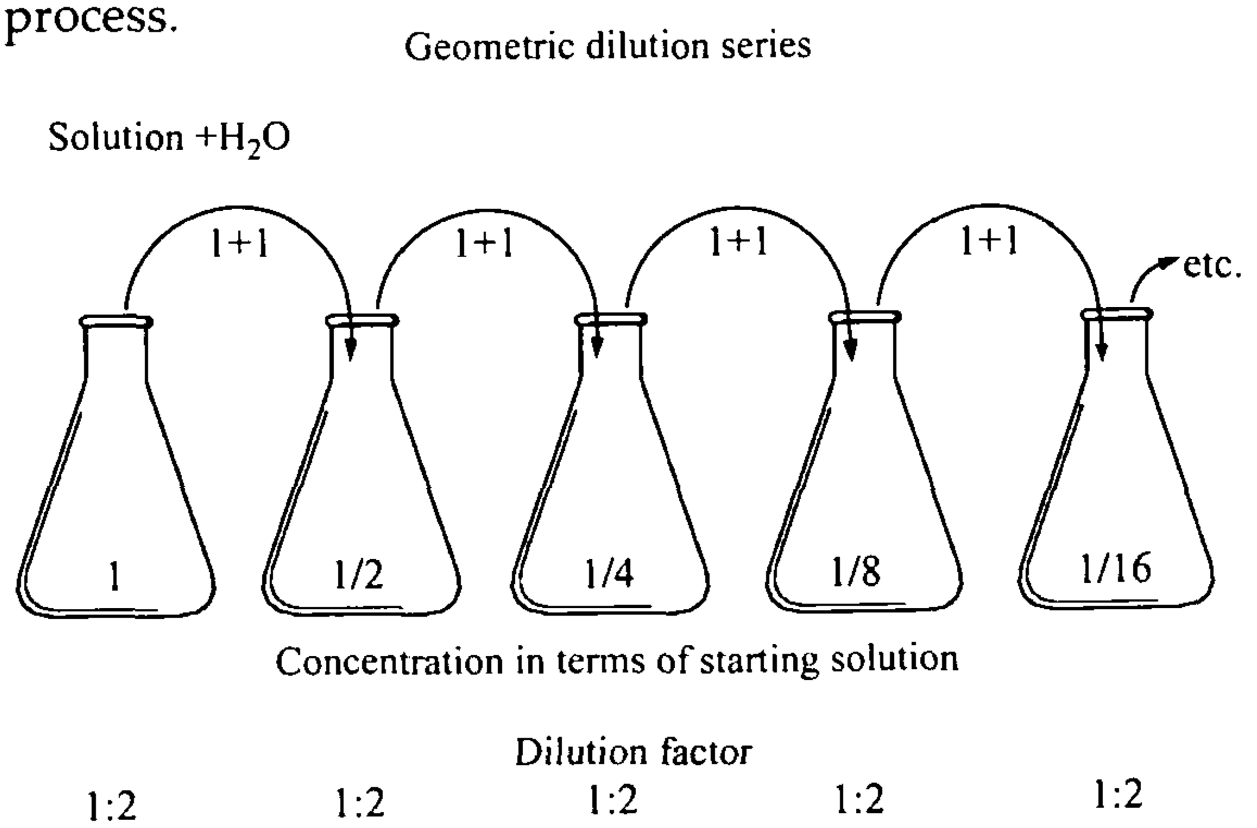

Figure 2. Geometric dilution series

Dilution series is used in many procedures including the preparation of standard curves for the calibration of analytical instruments such as atomic absorption spectrophotometer (AAS). The most common approach is the preparation of a linear dilution series where the concentrations are separated by an equal amount; e.g. a series of solutions containing cadmium at 0, 0.2, 0.4, 0.6, 0.8, 1.0 mmol dm^{-3} may be used to prepare a calibration curve for atomic absorption spectroscopy.

Using the relationship, $[C_1]V_1 = [C_2]V_2$, we can calculate the volume of 0.01 mol dm^{-3} $Cd(NO_3)_2.4H_2O$ required to prepare the dilution series. Let us do one calculation, for the preparation of 50 cm^3 of $0.2\text{x}10^{-3}$ mol dm^{-3} solution.

Suppose we need 50 cm^3 of solution or have volumetric flasks of 50 cm^3 capacity. Then, i.e. we have to transfer 1.00 cm^3 (V_1) of the Cd^{2+} stock solution to a 50.00 cm^3 volumetric flask and make up to the mark with distilled water to obtain 0.2 mmol dm^{-3} solution. Similarly, we can prepare 0.4, 0.6, 0.8 and 1.0 mmol dm^{-3} solution as given in the table below.

Cd concentration / mmol dm^{-3}		0	0.2	0.4	0.6	0.8	1.0
Volume/ cm^3	0.01 M Cd^{2+} stock solution	0	1.00	2.00	3.00	4.00	5.00
	Distilled water	50	49.00	48.00	47.00	46.00	45.00

We prepare dilute acids by appropriately diluting concentrated acids. Suppose we have to prepare 500 cm^3 of 5 M H_2SO_4; we can calculate the volume of conc. H_2SO_4 required to prepare 5 M acid by dilution.

Using the relationship, $[C_1]V_1 = [C_2]V_2$,

$$18 \times V_1 = 5 \times 100 \quad V_1 = 28\, cm^3.$$

or preferably equating the amounts,

$$18 \times 10^{-3} \times V_1 = 5 \times 10^{-3} \times 100; \quad V_1 = 28\, cm^3.$$

i.e. 28 cm^3 of conc. sulphuric acid is needed to prepare 100 cm^3 5 M acid.

To dilute concentrated acids (especially sulphuric), the conc. acid must be added to water. Thus 5 M sulphuric acid can be prepared by adding 28 cm^3 of conc. sulphuric acid into a measuring cylinder containing enough distilled water and making up to 100 cm^3. You can do similar exercises to prepare dilute acids as and when required.

It is not easy to measure volumes very accurately and more so using a measuring cylinder. We can prepare only approximately 5 M sulphuric acid by the method described previously. If we need to know the exact molar concentration, we have to titrate a known volume of appropriately diluted acid against a standard solution of a base such as anhydrous sodium carbonate (M_r= 105.98), which is a primary substance.

References and Further Reading

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