Basics of Standard Solution : Preparations, Concentration and Dilution

ES 542 Laboratory guidance and safety
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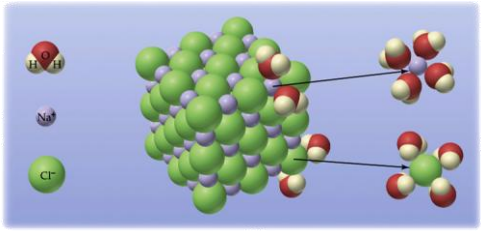
Definitions

- A solution is a homogeneous mixture
- A solute is dissolved in a solvent.
  - solute is the substance being dissolved
  - solvent is the liquid in which the solute is dissolved
  - an *aqueous* solution has water as solvent
- A saturated solution is one where the concentration is at a maximum - no more solute is able to dissolve.
  - A saturated solution represents an equilibrium: the rate of dissolving is equal to the rate of crystallization. The salt continues to dissolve, but crystallizes at the same rate so that there "appears" to be nothing happening.

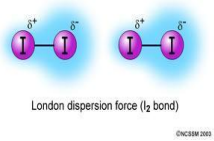
Dissolution of Solid Solute

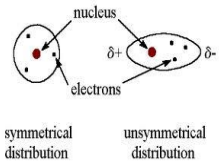
What are the driving forces which cause solutes to dissolve to form solutions?

1. **Covalent solutes dissolve by H-bonding to water or and covalent solutes that are non polar dissolve by London Dispersion Forces (LDF)**
2. **Ionic solutes dissolve by dissociation into their ions.**



London dispersion forces (LDF, also known as **dispersion forces**, **London forces**, **instantaneous dipole–induced dipole forces**, or loosely **van der Waals forces**) are a type of force acting between atoms and molecules. They are part of the van der Waals forces.
The LDF is named after the German-American physicist Fritz London





Solution and Concentration

- 4 ways of expressing concentration

–**Molarity(M):** moles solute / Liter solution (moles/L or mmoles/ml)

–**Normality(N):** gram equivalent wt/ Liter solution

–Mass percent: (mass solute / mass of solution) * 100

–Molality* (m) - moles solute / Kg solvent

–Mole Fraction(χ_A) - moles solute / total moles solution

–Formality – Formula weight / Liter solution

*** Note that molality is the only concentration unit in which denominator contains only solvent information rather than solution.**

In normality calculations, the number of equivalents is the number of moles times the number of reacting units per molecule or atom.

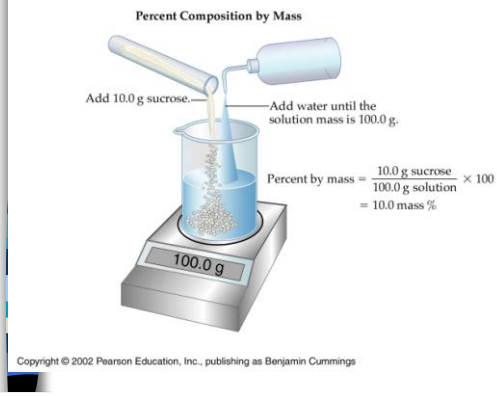
Reacting Units in Different Reactions

Reaction Type	Reacting Unit
Acid–base	H^+
Oxidation–reduction	Electron

©Gary Christian, Analytical Chemistry, 6th Ed. (Wiley)

% Concentration

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

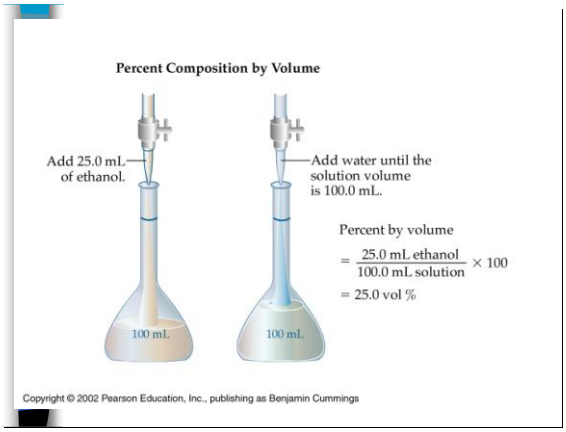


Examples

1. % V/V = 4.1 L / 55 L = 7.5% V/V
2. % W/V = 16 g / 50 mL = 32% W/V
3. % W/W = 1.7 g / 35.0 g = 4.9% W/W

More practice

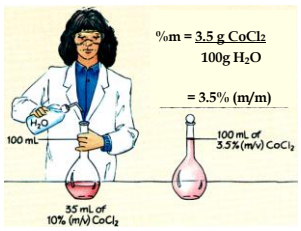
1. What is the % W/W of copper in an alloy when 10 g of Cu is mixed with 250 g of Zn?
2. What is approximate % V/V if 30 mL of pure ethanol is added to 250 mL of water?
3. What is the % W/W if 8.0 g copper is added to enough zinc to produce 100 g of an alloy



% Concentration: % Mass Example

3.5 g of $CoCl_2$ is dissolved in 100mL solution.

Assuming the density of the solution is 1.0 g/mL, what is concentration of the solution in % mass?



- ***Standard Solution:*** A reagent of a known concentration which is used in the analysis.

Density Calculations
How do we convert to Molarity

- Density = mass solute /unit volume
- Specific Gravity = D_{solute}/D_{H20}
- D_{H2O} = 1.00000 g/mL @ 4ºC
- D_{H2O} = 0.99821 g/mL @ 20ºC

The units ppm or ppb are used to express trace concentrations.

These are weigh or volume based, rather than mole based.

Table 5.2

Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million	ppm	mg/kg	mg/L	mL/L
(1 ppm = 10^{-4}%)		mg/g	mg/mL	nL/mL
Parts per billion	ppb	mg/kg	mg/L	nL/L
(1 ppb = 10^{-7}% = 10^{-3} ppm)		ng/g	ng/mL	pL/mL[a]
Milligram percent	mg%	mg/100 g	mg/100 mL	

[a]pL = picoliter = 10^{-12} L.

Expression of Analytical Results So Many Ways

- **Solid Samples:**
- %(wt/wt) = (wt analyte/wt sample)x 10^2 %
- pt(wt/wt) = (wt analyte/wt sample)x 10^3 ppt
- ppm(wt/wt) = (wt analyte/wt sample)x 10^6 ppm
- ppb(wt/wt) = (wt analyte/wt sample)x 10^9 ppb

Expression of Analytical Results So Many Ways

- **Liquid Samples**
- %(wt/vol) = (wt analyte/vol sample mL)x 10^2 %
- pt(wt/vol) = (wt analyte/vol sample mL)x 10^3 ppt
- ppm(wt/vol) = (wt analyte/vol sample mL)x 10^6 ppm
- ppb(wt/vol) = (wt analyte/vol sample,mL)x 10^9 ppb
- **Liquid Analyte**
- %(vol/vol) = (vol analyte/vol sample mL)x 10^2 %
- pt(vol/vol) = (vol analyte/vol sample mL)x 10^3 ppt
- ppm(vol/vol) = (vol analyte/vol sample mL)x 10^6 ppm
- ppb(vol/vol) = (vol analyte/vol sample,mL)x 10^9 ppb

The equivalents (based on charge) of cations and anions are equal.

Table 5.3

Major Electrolyte Composition of Normal Human Plasma[a]

Cations	meq/L	Anions	meq/L
Na^+	143	Cl^-	104
K^+	4.5	HCO^{3-}	29
Ca^{2+}	5	Protein	16
Mg^{2+}	2.5	HPO_4^-	2
		SO_4^{2-}	1
		Organic acids	3
Total	155	Total	155

[a]Reproduced from Joseph S. Annino, *Clinical Chemistry,* 3rd ed., by Boston: LIttle, Brown, 1964.

Reporting Concentrations as Different Chemical Species

- We may express results in any form of the analyte.
- Example:
- Water Hardness due to calcium ion is expressed as ppm $CaCO_3$.
- Chloride present in AgCl derived from a salt mixture of NaCl and KCl.

Volumetric Analysis - Principles

- "**Titrimetry**" – determination of **analyte** by reaction with measured amount of standard reagent
- "Standard Solution" (**titrant**) – reagent of known concentration
- "**Titration**" – slow addition of titrant to analyte solution from a volumetric vessel (buret)
- "**Equivalence Point**" – reached when amount of added titrant is chemically equivalent to amount of analyte present in the sample.
- "**End Point**" – the occurrence of an observable physical change indicating that the equivalence point is reached. Might differ from Eq.Pt.!

- Titration- What are the requirements?

1. Reaction must be stoichiometric
2. Reaction should be rapid
3. No side reactions
4. Marked change in some property of the solution when reaction is complete
5. Equivalence point
6. Reaction should be quantitative

Standard Solutions

- "Primary Standard " –
  - highly purified compound used as a reference material
- Properties:
- High purity
- Stable in air
- Independent of relative humidity
- Readily available
- Reasonable solubility
- Large formula weight

Standard Solutions

- "Secondary Standard"
  - do not meet requirements for a primary standard but are available with sufficient purity and properties to be generally acceptable
- Desirable properties of a Standard Solution:
- Prepared from primary standard
- Stable
- Reacts rapidly and completely with analyte
- Reacts selectively with analyte

Volumetric Analysis - Principles Examples of Standard Materials

- **Primary**
- Potassium Acid Phthalate
- $KHC_8H_4O_4$ (FW 204.23)
- Benzoic Acid
- C_6H_5COOH (FW 122.12)
- Na_2CO_3 , $KH(IO_3)_2$
- Arsenious Oxide (As_2O_3)
- Sodium Oxalate ($Na_2C_2O_4$)
- KI , $K_2Cr_2O_7$, Fe(pure)

- **Secondary**
- NaOH , KOH , $Ba(OH)_2$
- HCl , HNO_3 , $HClO_4$
- Sulfamic Acid (HSO_3NH_2)
- $KMnO_4$, $Na_2S_2O_3$
- $Ce(HSO_4)_4$ (FW 632.6)

Volumetric Analysis-Principles

- **Standardization** – involves establishing the concentration of a "standard solution"
- **Direct method:**
- dissolve carefully weighed quantity of primary standard; dilute to known volume
- **Indirect methods:**
- Titrate weighed quantity of primary standard
- Titrate weighed quantity of secondary standard
- Titrate measured volume of other standard solution

Molar concentration

- is able to compare the amount of solute dissolved in a certain volume of solution.
- Molar concentration (mol/L) or also called Molarity (M)

= Moles of solute (n)/Volume of solution (**V MUST be in litres**)

- **is the number of moles of solute in one litre of a solution. We use "M" to denote molar concentration and it has the units of"moles/L".**
- **C = n / V**
- **n = C x V**

Concentration: Molarity Example

If 0.435 g of $KMnO_4$ is dissolved in enough water to give 250. mL of solution, what is the molarity of $KMnO_4$?

As is almost always the case, the first step is to convert the mass of material to moles.

$$0.435\ g\ KMnO_4 \cdot \frac{1\ mol\ KMnO_4}{158.0\ g\ KMnO_4} = 0.00275\ mol\ KMnO_4$$

Now that the number of moles of substance is known, this can be combined with the volume of solution – which must be in liters – to give the molarity. Because 250. mL is equivalent to 0.250 L .

$$\text{Molarity } KMnO_4 = \frac{0.00275\ mol\ KMnO_4}{0.250\ L\ solution} = 0.0110\ M$$

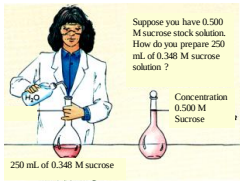
Dilution

When a solution is diluted, solvent is added to lower its concentration.

The amount of solute remains constant before and after the dilution:

moles BEFORE = moles AFTER

$$C_1V_1 = C_2V_2$$



A bottle of 0.500 M standard sucrose stock solution is in the lab.

Give precise instructions to your assistant on how to use the stock solution to prepare 250.0 mL of a 0.348 M sucrose solution.

Dilutions
Preparing the Right Concentration

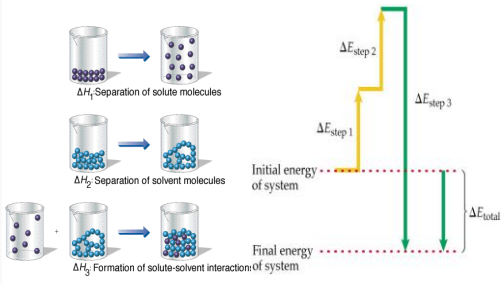
- The millimoles taken for dilution will be the same as the millimoles in the diluted solution.
- $M_{stock} x\ mL_{stock} = M_{diluted} x\ mL_{diluted}$

3 Stages of Solution Process

- **Separation of Solute**
  - must overcome IMF or ion-ion attractions in solute
  - requires energy, ENDOTHERMIC (+ ΔH)
- **Separation of Solvent**
  - must overcome IMF of solvent particles
  - requires energy, ENDOTHERMIC (+ ΔH)
- **Interaction of Solute & Solvent**
  - attractive bonds form between solute particles and solvent particles
  - "Solvation" or "Hydration" (where water = solvent)
  - releases energy, EXOTHERMIC (- ΔH)

Dissolution at the molecular level?

- **Consider the dissolution of NaOH in H_2O**



Factors Affecting Solubility

1. Nature of Solute / Solvent. - **Like dissolves like (IMF)**

2. Temperature -

i) Solids/Liquids- Solubility increases with Temperature

Increase K.E. increases motion and collision between solute / solvent.

ii) gas - Solubility decreases with Temperature

Increase K.E. result in gas escaping to atmosphere.

3. Pressure Factor -

i) Solids/Liquids - Very little effect

Solids and Liquids are already close together, extra pressure will not increase solubility.

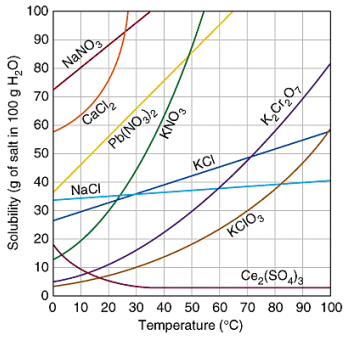
ii) gas - Solubility increases with Pressure.

Increase pressure squeezes gas solute into solvent.

Solubilities of Solids vs Temperature

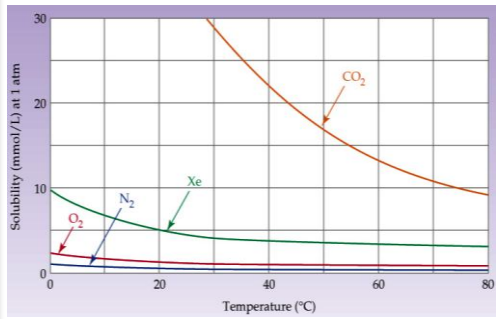
Solubilities of several ionic solid as a function of temperature. MOST salts have greater solubility in hot water.

A few salts have negative heat of solution, (exothermic process) and they become less soluble with increasing temperature.



Temperature & the Solubility of Gases

The solubility of gases DECREASES at higher temperatures



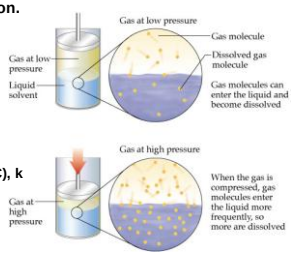
Henry's Law

The effect of partial pressure on solubility of gases

At pressure of few atmosphere or less, solubility of gas solute follows Henry Law which states that the amount of solute gas dissolved in solution is directly proportional to the amount of pressure above the solution.

$$c = k P$$

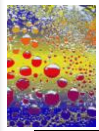
c = solubility of the gas (M)
k = Henry's Law Constant
P = partial pressure of gas



Henry's Law Constants (25°C), k

N_2	$8.42 \cdot 10^{-7}$ M/mmHg
O_2	$1.66 \cdot 10^{-6}$ M/mmHg
CO_2	$4.48 \cdot 10^{-5}$ M/mmHg

Henry's Law & Soft Drinks



- Soft drinks contain "carbonated water" – water with dissolved carbon dioxide gas.
- The drinks are bottled with a CO_2 pressure greater than 1 atm.
- When the bottle is opened, the pressure of CO_2 decreases and the solubility of CO_2 also decreases, according to Henry's Law.
- Therefore, bubbles of CO_2 escape from solution.

Henry's Law Application

- The solubility of pure N_2 (g) at 25ºC and 1.00 atm pressure is 6.8×10^{-4} mol/L. What is the solubility of N_2 under atmospheric conditions if the partial pressure of N_2 is 0.78 atm?

Step 1: Use the first set of data to find "k" for N_2 at 25°C

$$k = \frac{c}{P} = \frac{6.8x10^{-4} M}{1.00\ atm} = 6.8x10^{-4} M\ atm^{-1}$$

Step 2: Use this constant to find the solubility (concentration) when P is 0.78 atm:

$$c = kP = (6.8x10^{-4} M\ atm^{-1})(0.78\ atm) = 5.3x10^{-4} M$$

Colligative Properties

Dissolving solute in pure liquid will change all physical properties of liquid, Density, Vapor Pressure, Boiling Point, Freezing Point, Osmotic Pressure

Colligative Properties are properties of a liquid that change when a solute is added.

The magnitude of the change depends on the number of solute particles in the solution, NOT on the identity of the solute particles.

Molarity learning check

1. **How many moles of H_2SO_4 are there in 250mL of a 0.8M sulphuric acid solution?**
2. If 20g of NaOH is dissolved in sufficient water to produce 500 mL of solution, calculate the molar concentration in molarity.

Questions

1. **What is the molarity of the solution formed by dissolving 80 g of sodium hydroxide (NaOH) in 500 cm^3 of water?** (A,'s: **Na=23, O=16, H=1**) Ans = 4 M
2. **What is the molarity of the solution formed by dissolving 9.8 g of sulphuric acid (H_2SO_4) in 1000 cm^3 of water?** (A,'s: **H=1, S=32, O=16**) Ans = 0.1 M
3. **What mass (g) of hydrogen chloride (HCl) is needed to make up 500cm^3 of a solution of concentration 0.2mol/dm^3?** (A,'s: **H=1, Cl=35.5**) Ans = 3.65g

TYPICAL CONCENTRATIONS OF CONCENTRATED ACIDS AND BASES
(as written on the labels of their containers)

ACID/BASE NAME	WT%	DENSITY (sp. gr) (g/ml)	MOLARITY
Acetic acid	99.7%	1.05 g/ml	17.4
Ammonium hydroxide (aqueous ammonia)	28%	0.89 g/ml	14.6
Hydrochloric acid	37%	1.18 g/ml	12.0
Nitric acid (HNO_3)	70%	1.40 g/ml	15.6
Phosphoric acid	85%	1.69 g/ml	14.7
Sulfuric acid	96%	1.84 g/ml	18.0

Problem: Make one liter of a 1 Molar (1M) aqueous solution of H_2SO_4.

Electric balance

- Choose optimum one depending on your purpose.
- Put reagent dish and reset the weight .
  (tare: weight of container)

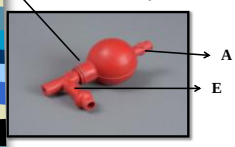
•Keep the level
•Use clean and dry spoon.
•Do not return the reagent once taken out.
•Keep clean (wipe around the balance every time you use)

pH meter

- Maintain the electrode properly.
- Fill the internal solution. Do not dry the electrode.
- Dip it in water when you don`t use.
- Calibrate every time you use, with a proper set of "fresh" standard solutions. Usually pH 4 & pH 7.
- Open the side cap when measurement has to be done.

Pipette

- **Use transfer pipette if accuracy required.**
- **Never suck from your mouth. Use safety pipette.**



- **Release air by pressing A.**
- **Take up the solution and press S.**
- **Press E to eject.**

How to use micropipette

- **Adjust the amount with the upper black dial.**
- **Press the white top lightly to the first stop point.**
- **Immerse tip and release the top slowly.**
- **Press top to the full to eject the solution.**