

Methods of chemical analysis

- Qualitative analysis.
- Quantitative analysis.
- Traditional analysis.

Qualitative analysis :

- The determination of the components of an unknown sample. Recognition of chemical species by means of color, reaction producing a color, reaction producing a precipitate, the reaction involving a change of a physical parameter.
- Colored ions are: Cu^{2+} (blue), Cr^{3+} (green), $\text{CrO}_4^{=}$ (yellow), $\text{Cr}_2\text{O}_7^{=}$ (orange), MnO_4^- (violet), $\text{MnO}_4^{=}$ (green), Ni^{2+} (green), Co^{2+} (pink, or blue), Mn^{2+} (pink), and generally ions of transition metals.

Precipitates (slight soluble compounds): sulphurs of heavy metals (like As, Sb, Hg, Cu, Pb, Cd, Sn, Bi, Zn, Ni, Co, Mn), BaSO_4 , Hg_2Cl_2 , AgCl , PbCl_2 , Ag_2CrO_4 , many hydroxides of heavy metals.

Solubility :

- When you add a chemical substance to water it could do two things:
- It could dissolve this is a soluble substance. It might there and not dissolve it is insoluble.

Quantitative Analysis :

- The determination of the quantity of the components in a sample.

Classical methods :

- **Gravimetric Method:** They include mass is measured.
- **Volumetric Method:** They volume is measured or used to determine an amount of sample via concentration.
- **Instrumental Method:** They use an instrumental technique to assay the amount of sample.
- **Such as:**
- **Electro analytical:** Based upon electron-transfer.

- **Spectroscopy:** Including mass spectrometry.
- **Separation:** Including the HPLC Technique and Columns of separation.

Methods of expressing the concentration of solution:

- **Solution:** Is a homogenous mixture of 2 or more substances.
- **Solute:** Is the substance present in the smaller amount.
- **Solvent:** Is the substance present in the larger amount.
- **Concentration:** Of a solution is a measure of the amount of solute that is dissolved in a given quantity of solvent.
- **dilute solution:** Is the one that contains a small amount of solute.
- **Concentrated solutions:** Solution contains a large amount of solute.

Express concentrations:

- **Solids substances :**

Concentration: the general measurement unit stating the amount of solute present in a known amount of solution.

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}}$$

Molarity (M): The number of moles of solute per liter of solution.

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$\text{— Molarity} = \frac{\text{weight of substance(g)}}{\text{Gram molecular weight}} \times \frac{1000}{\text{Volume in ml}}$$

$$W = \frac{M \times \text{MWt} \times \text{Vml}}{1000}$$

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Example 1 \ calculate the molarity of sodium hydroxide (3 g) dissolved in (100 ml) distill water?

Example 2 \ How many grams of sodium carbonate required to prepare (2 M) dissolved in (250 ml) distill water?

Normality:

Normality (N): The number of equivalents of solute per liter of solution.

$$\text{Normality (N)} = \frac{\text{NO. of gram equivalent of solute}}{\text{Volume of solution in liters}}$$

$$N = \frac{X}{V \text{ in liters}}$$

Where :

X = No. of grams equivalents of solute.

It is calculated by the following relation:

$$X = \frac{\text{Weight of solute in gram (W)}}{\text{Equivalent weight (EW)}}$$

$$N = \frac{W_g}{\text{eq wt}} \times \frac{1000}{V \text{ ml}}$$

$$\text{eq. wt} = \frac{MWt}{n}$$

Example 3 \ Find the normality of solution prepared by dissolving (10 g) of NaOH in (500 ml) of distilling water?

Example 4 \ How many grams of sodium carbonate required to prepare (2 N) dissolved in (250 ml) distill water?

Liquid substance:

— 1- Molarity :

$$— M = \frac{D \times P \times 1000}{MWt}$$

2- Normality :

$$— N = \frac{D \times P \times 1000}{eqWt}$$

— D: Density.

P: Percentage.

A relationship exists between normality and molarity :

$$N = n \times M$$

— **Example 5** \ \ prepare the standard solution (0.2 N) H₂SO₄ dissolved in (100 ml) distill water?

— **Example 6** \ \ prepare the standard solution (2 M) HCl dissolved in (100 ml) distill water?

Dilution :

water is added volume increases a concentration of solute decreases.

$$C_1 \times V_1 = C_2 \times V_2$$

Where :

C₁ = Concentration of concentrated solution.

V₁ = Volume of concentrated solution.

C₂ = Concentration of dilute solution.

V₂ = Volume of a dilute solution.

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Example 7 \ A laboratory procedure calls for (250 ml) of an approximately (0.1 M) solution of NH_3 . Describe how you would prepare this solution using a stock solution of concentrated NH_3 (14.8 M)?

Answer :

$$\begin{aligned}(M_1 \times V_1)_{\text{concentrated}} &= (M_2 \times V_2)_{\text{diluted}} \\ 14.8 \text{ M} \times V_1 &= 0.1 \text{ M} \times 250 \text{ ml} \\ V_1 &= 1.68 \text{ ml}\end{aligned}$$

We can measure the appropriate amount of concentrated NH_3 using a graduated cylinder, transfer the NH_3 to a volumetric flask, and add sufficient water to bring the total solution volume to approximately (250 ml).

Parts Per Million (ppm) and part per Billion (ppb)

Parts Per Million (ppm): Is the units are often expressed as milligrams of solute per liter of solution.

$$C_{ppm} = \frac{W_g}{V_{ml}} \times 10^6$$

$$\text{ppm} = \frac{W_{\text{mg}}}{V_L}$$

part per Billion (ppb): Is the units are often expressed as micrograms of solute per liter of solution.

$$C_{ppb} = \frac{W_g}{V_{ml}} \times 10^9$$

$$\text{ppb} = \frac{W_{\mu\text{g}}}{V_L}$$

A relationship exists between part per million and molarity :

$$C_{ppm} = \frac{W_g}{V_{ml}} \times 10^6$$

$$w = \frac{\text{ppm} \times V_{ml}}{10^6}$$

$$M = \frac{\text{ppm} \times V_{ml} \times 1000}{10^6 \times MWt \times V_{ml}}$$

$$M = \frac{\text{ppm}}{1000 \times MWt}$$

$$M \times MWt = \frac{\text{ppm}}{1000}$$

$$\text{ppm} = M \times MWt \times 1000$$

$$M = \frac{\text{ppm}}{MWt \times 1000}$$

Example 8 || What is the molarity of K^+ in a solution that contains 63.3 ppm of $K_3Fe(CN)_6$ (329.3 g/mol)?

Answer :

$$M = \frac{\text{ppm}}{MW_t \times 1000}$$

$$M_{K_3Fe(CN)_6} = \frac{63.3}{329.3 \times 1000} = 1.922 \times 10^{-4} M$$

$$M_{K^+} = 1.922 \times 10^{-4} \times 3 = 5.77 \times 10^{-4}$$

Weight, Volume, and Weight-to-Volume Ratios

1. volume percent (% v/v) :

volume percent (% v/v) : Milliliters of solute per 100 mL of solution.

$$\text{Volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100\%$$

Solution = solvent + solute

Example 9 \\ What is the percent by volume concentration of a solution in which (75 ml) of ethanol is diluted to a volume of (250 ml)?

Example 10 \\ What volume of acetic acid is present in a bottle containing (350 ml) of a solution which measures (5%) concentration?

2. weight percent (% w/w) :

weight percent (% w/w) : Grams of solute per 100 g of solution.

$$\text{Weight} = \frac{\text{Weight of solute}}{\text{Weight of solution}} \times 100 \%$$

Example 11 \\ Calculate the percent by mass in which (41.0 g) of NaCl is dissolved in (331 g) of water?

3. weight-to-volume percent (% w/v) :

weight-to-volume percent (% w/v) : Grams of solute per 100 mL of solution.

$$\text{Weight} = \frac{\text{Weight of solute}}{\text{Volume of solution}} \times 100\%$$

parts per thousand (ppt) = $\times 10^3$

parts per million (ppm) = $\times 10^6$

Parts per billion (ppb) = $\times 10^9$

p-Functions :

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

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

Example 12 Calculate the p-value for each ion in a solution that is 2×10^{-3} M in NaCl and 5.4×10^{-4} M in HCl.

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

To obtain pNa, we write:

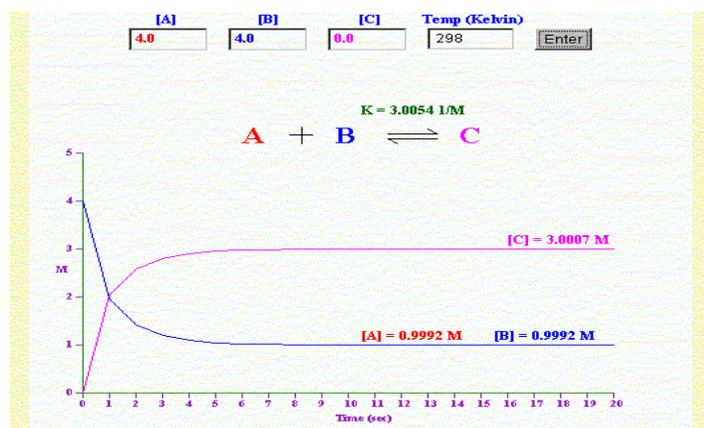
$$pNa = -\log (2.00 \times 10^{-3}) = -\log 2.00 \times 10^{-3} = 2.699$$

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

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

Equilibrium Constant

Equilibrium Position



Equilibrium Expression equilibrium Constant, K_{eq} :



$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

The concentrations are at the **equilibrium** position.

The K_{eq} is constant for a given temperature regardless of the initial concentrations.

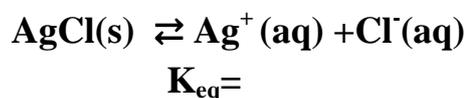
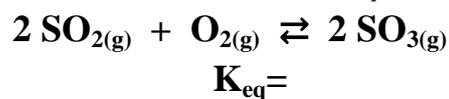
$K_{eq} > 1$, products favored in equilibrium

$K_{eq} < 1$, reactants favored in equilibrium

K_{eq} is not expressed with units.

Rules for K_{eq} of Heterogeneous Equilibrium (more than one phase)

- Only gases and solutes concentrations appear in the equilibrium expressions.
- Pure liquids and solids do not affect the K_{eq} because they do not change.



Example 13 \\ Calculate the K_{eq} , given equilibrium concentrations:



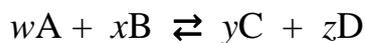
At equilibrium at $10^\circ C$, $[N_2O_4] = 0.0045 M$ and $[NO_2] = 0.030 M$.

Calculate the K_{eq} .

Answer:

$$K_{eq} = 0.20$$

Expression for Equilibrium Constant Consider the following equilibrium system:

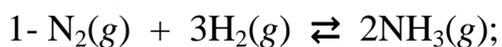


$$K_c = \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

- The numerical value of K_c is calculated using the concentrations of reactants and products that exist at equilibrium.

Expressions for Equilibrium Constants

Examples 14 \\



$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

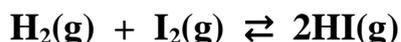


$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Calculating Equilibrium Constant :

Example 15 :

1.000 mole of H₂ gas and 1.000 moles of I₂ vapor are introduced into a (5.00 L) sealed flask. The mixture is heated to a certain temperature and the following reaction occurs until equilibrium is established.



At equilibrium, the mixture is found to contain 1.580 mole of HI. (a) What are the concentrations of H₂, I₂ and HI at equilibrium? (b) Calculate the equilibrium constant K_c. Calculating Equilibrium Constant for reaction: H₂(g) + I₂(g) ⇌ 2HI(g)

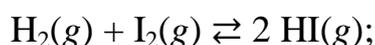
	H ₂ (g)	+	I ₂ (g)	⇌	2 HI(g)
Initial [], M:	0.200		0.200		0.000
Change in [], M:	-0.158		-0.158		+ 0.316
Equilibrium [], M	0.042		0.042		0.316

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.316)^2}{(0.042)^2}$$

$$K_C = 56.6$$

Relationships between chemical equations and the expressions of equilibrium constants:

The expression of equilibrium constant depends on how the equilibrium equation is written. For example, for the following equilibrium:



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

- For the reverse reaction:



$$K_c' = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 1/K_c$$

- And for the reaction: $\text{HI}(g) \rightleftharpoons \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{I}_2(g);$

$$K_c'' = \sqrt{\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}} = \sqrt{K_c'}$$

Expression and Values of Equilibrium Constant Using Partial Pressures :

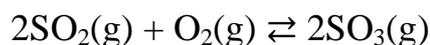
- Consider the following reaction involving gases:



$$K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2(P_{\text{O}_2})}$$

The Relationship between K_c and K_p :

Consider the reaction:



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \quad \text{and} \quad K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2(P_{\text{O}_2})}$$

- Assuming ideal behavior :
- where $PV = nRT$ and $P = (n/V) RT = [M] RT$
- and $P_{\text{SO}_3} = [\text{SO}_3] RT$; $P_{\text{SO}_2} = [\text{SO}_2] RT$; $P_{\text{O}_2} = [\text{O}_2] RT$

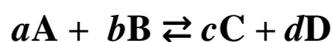
$$K_p = \frac{[\text{SO}_3]^2 (RT)^2}{[\text{SO}_2]^2 (RT)^2 [\text{O}_2] (RT)} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} (RT)^{-1} = K_c (RT)^{-1}$$

Relationship between K_c and K_p :

For reaction: $\text{PCl}_5(g) \rightarrow \text{PCl}_3(g) + \text{Cl}_2(g)$

$$K_p = \frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})} = \frac{[\text{PCl}_3](RT) \times [\text{Cl}_2](RT)}{[\text{PCl}_5](RT)}$$
$$= \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}(RT)^1 = K_c(RT)^1$$

In general, for reactions involving gases such that :



where A, B, C, and D are all gases, and a , b , c , and d are their respective coefficients:

$$K_p = K_c(RT)^{\text{Dn}}$$

$$\text{and Dn} = (c + d) - (a + b)$$

(In heterogeneous systems, only the coefficients of the gaseous species are counted.)

For other reactions:

1. $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$; $K_p = K_c(RT)^{-1}$
2. $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$; $K_p = K_c$
3. $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$; $K_p = K_c(RT)^{-2}$