ANALYTICAL CHEMISTRY

LECTURE-1

BY

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Analytical Chemistry

- **ANALYTICAL CHEMISTRY:** It is a chemistry branch deals with the study on the identification of material composition and the determination of the amount of each component presented by an expression of concentration directly or indirectly (after separation).

- It is divided in to two main parts:

1- QUALITATIVE ANALYSIS:

It is process of many steps that through which material, compounds or elements or elements forming certain material or a mixture of materials can be identified at liquid, gas or solid phases. This process is the first step in analysis.

2-QUANTITATIVE ANALYSIS:

It is a process deals with the determination of elements or other components that form the analyzed material (compound or mixture). It tell us what is the amount of the components of the materials or their Components. Quantitative analysis can not be preceded without processing qualitative analysis.

Analytes: Are the components of a sample that are to be determined. •

Matrix: All other constituents in a sample except for the analytes. •

Classifying Analytical Techniques:

1- Classical Techniques

2- Instrument Techniques

Classical Techniques

- **Mass, volume, and charge** are the most common signals for classical techniques, and the corresponding techniques are:

- 1- **Volumetric techniques** (Titrimetric analysis): The analyte reacts with a measured volume of reagent of known concentration, in a process called titration.

- **2- Gravimetric techniques:** usually involves the selective separation of the analyte by precipitation, followed by the very non-selective measurement of mass (of the precipitate).

- **3- Coulometeric techniques.**

INSTRUMENTAL TECHNIQUES

- Determination of materials or their components can be performed using instruments that their measurements of certain properties such as conductivity, turbidity, potentiometry, color, refractive index, absorption at UV or visible region etc…provided these measurements depend on and relate to the concentration of the material or its components directly or indirectly.

INSTRUMENTAL TECHNIQUES

- **1- Spectroscopic methods:-** measuring the interaction between the analyte and electromagnetic radiation (or the production of radiation by an analyte).

- **2- Electroanalytic methods:-** measure an electrical property (i.e., potential, current, resistance, amperes, etc.) chemically related to the amount of analyte.

- A - Using of Conductivitimeter to measure the conductivity of sample solution which is changing with variation in the component concentration.

- B - Using of potentiometer to measure the potential of an electrode which is in equilibrium with the sample solution.

- C - Using of UV-visible spectrometer to measure the absorbance of radiation at a wave length that relate to the component directly or to the compound formed by its reaction with a reagent.

STEPS OF CHEMICAL ANALYSIS:

- There are a general steps for any analysis process, a modifications in these steps depend on nature, size, the accuracy required, availability of reagents chemicals equipment's and apparatus

- **STEP 1:** **CHOICE OF THE METHOD:**

- The selected method should be suitable to the nature of the sample, number of samples and accuracy required. Some samples like archaeological or forensic samples need a nondestructive method to keep the samples without destruction.

- **STEP 2: SAMPLING:**

  Sampling is a very important criterion. It is the fraction of the material with which he plans to work. It is truly representative the whole of it. If the material is big many samples are selected and collected.

STEP 3: PREPARING OF LABORATORY SAMPLE:

The field sample is treated to prepare the laboratory sample required for the analysis.

1. Producing a homogenized sample by crashing, grinding and mixing.

2. Decreasing the size of the material sample granules.

3. Turning the sample into a phase and formula can be attacked by reagent.

4. Care should be taken to avoid the interferences or any other factors affecting the estimation such as contamination.

- **STEP 4:** MEASURE THE QUANTITY OF THE SAMPLE:
- If the sample is solid certain weight of the dried homogenized sample is taken using calibrated balance. If it is liquid certain volume is taken.

- **STEP 5:** DISSOLUTION OF THE MEASURED SAMPLE:
- A suitable solvent is selected to dissolve the sample completely and within short time. The sample should not interfere in the analysis. Water is a magic solvent for almost all the inorganic materials and some of the organic materials. Organic materials require organic solvents like alcohols, carbontetrachloride and chloroform. Fusion is used for melting samples do not dissolve in solvents.

- **STEP 6:** **SEPARATION OF THE INTERFERING SUBSTANCES.**

- To measure the sample freely from interferences by other components certain steps should be taken such as separation or using masking agents.

- **STEP 7:** **COMPLETION OF THE ANALYSIS**

- This step concern with the measurement of the substance or component under consideration precisely using a suitable method by precipitation or color formation, titration etc.

- **STEP 8:** CALCULATIONS AND DATA ANALYSIS:

- From the numeric results obtained by measurements the final result is calculated using the weight of the analyzed sample. The final results may e evaluated by statistic analysis.

METHODS OF EXPRESSION OF CONCENTRATION

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

- concentration $= \dfrac{amount\ of\ solute}{amount\ of\ solution}$

• 1- Molarity

Number of grams molecular weight (moles) of solute per liter of
 solution.

$$M= \frac{number\ of\ moles}{V\ (Liter)}$$

$$M= \frac{n}{V\ (Liter)}$$

$$M= \frac{number\ of\ millimoles}{V\ mL}$$ **Units: mole/L, mmole/mL**

$$n= \frac{Wt}{M.Wt}$$

$$M= \frac{Wt}{M.Wt} \times \frac{1000}{mL}$$

- **Ex: How many grams of 0.125 M AgNO3 used to prepare 500ml of its solution.**

- **(M.Wt= 169.9 g/mole)**

- $M = \dfrac{Wt}{M.Wt} \times \dfrac{1000}{VmL} \Rightarrow 0.125 = \dfrac{Wt}{169.9} \times \dfrac{1000}{500}$

- $Wt = \dfrac{M \times M.WT \times VmL}{1000}$

- $Wt = \dfrac{0.125 \times 169.9 \times 500}{1000} = 10.619 \text{ g}$

- **Ex: Calculate the Molarity (M) of solution result from dissolving 20 g of Sodium hydroxide in 2 Litters of solution. Na = 23 , O = 16 , H = 1**

- $M = \dfrac{n}{V\,(Liter)}$ $NaOH\ M.Wt = 23 + 16 + 1 = 40 g/mole$

- $n = \dfrac{Wt}{M.Wt} = \dfrac{20}{40} = 0.5\ mole \Rightarrow M = \dfrac{0.5}{2} = 0.25 M$

or: $M = \dfrac{Wt}{M.Wt} \times \dfrac{1000}{mL}$ $\Rightarrow M = \dfrac{20}{40} \times \dfrac{1000}{2000} = 0.25 M$

or: $M = \dfrac{Wt}{M.Wt} \times \dfrac{1}{vl}$ $\Rightarrow M = \dfrac{20}{40} \times \dfrac{1}{2} = 0.25 M$

- Q: A sample of water is found to contain 0.003g of lead in a 250cm^3 sample. What is the concentration of lead in ppm?
  A: 0.003 x 4 x 1000 = 12ppm

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 H$_2$SO$_4$ in 100cm^3.
Calculate the concentration in mol/l.
A: M$_r$ of H$_2$SO$_4$ = 98g
4.9 ÷ 98 = 0.05mol in 100cm^3
0.05 x 10 = 0.5mol/l

2-Normality:

Number of gram equivalent weight of solute per liter of solution

$$N = \frac{number\ of\ equivelant}{V\ (Liter)} \qquad N = \frac{no.\ of\ eq}{V\ (Liter)}$$

$$no.\ of\ eq = \frac{Wt}{EW}$$ **Wt: weight of solute, EW: equivalent weight of solute**

$$N = \frac{no.\ of\ meq}{V\ mL}$$ **VmL: volume of solution in mL**

$$N = \frac{Wt}{EW} \times \frac{1000}{mL}$$ **Units: eq/L, eq/mL**

Consequently, the following simple relationship exists between normality and molarity.

$$N = n \times M$$

Example 2.1 illustrates the relationship among chemical reactivity, equivalent weight, and normality.

- **Ex: How many grams of 0.2 N Sodium carbonate in 250 ml solution.**
 (M.Wt =106g / mole)

$$EW(\boldsymbol{salt}) = \frac{M.Wt}{no.of\ cations\ x\ oxidation\ number\ of\ cations}$$

EW (Na2CO3) = $\frac{106}{2x1}$ = 53 g/eq

N= $\frac{Wt}{EW}$ x $\frac{1000}{mL}$

0.2= $\frac{Wt}{53}$ x $\frac{1000}{250}$ $\Rightarrow$ Wt = $\frac{0.2x53x250}{1000}$ = 2.650 g

- **Ex: Calculate the normality (N) of solution result from dissolving 0.5 g of**
- **Cu(OH)2 in 100 mL of distilled water.**
- $\qquad$ Cu =63.5   O=16   H=1
- Cu(OH)2 $M.wt$ = $\mathbf{63.5+\ 2x16+2x1\ =97.5g/mol}$e

- $eq.wt(base) = \dfrac{M.Wt}{no.of\ OH\ ions\ ready\ to\ substituted}$

- $\dfrac{97.5}{2}$=48.75

- **N**$= \dfrac{Wt}{EW}$ **x** $\dfrac{1000}{mL}$ $\qquad \Rightarrow \dfrac{0.5}{48.75}$ **x** $\dfrac{1000}{100}$= 0.103 N

- **Example:** 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).

- • Solution: we calculate the number of moles of Cl_3CCOOH, which we symbolize, as HA, and divide by the volume of the solution, 10.0 mL, or 0.0100 L.

- Therefore,

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

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

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

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

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

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

The equilibrium concentration of HA is then 27% of c_{HA}. Thus,

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

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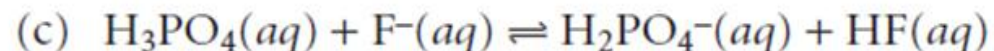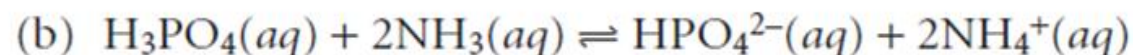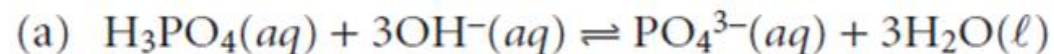
$$[H^+] = [A^-] = 0.127 \text{ M}$$

and

$$c_{HA} = [HA] + [A^-] = 0.047 + 0.127 = 0.174 \text{ M}$$

- **Example: Describe the preparation of 2.00 L of 0.10 M Na2CO3 (106g/mol) from the solid?**

- **mol Na_2CO_3 needed = 0.1mol/L x 2L= 0.2 mol**

- **mass Na_2CO_3 = 0.2 mol x 106 g/mol =21.2g**

- **Dissolve 21.2g of Na_2CO_3 in distilled water and dilute to 2L.**

EXAMPLE 2.1

- Calculate the equivalent weight and normality for a solution of 6.0 M H_3PO_4 given the following reactions:

(a) $H_3PO_4(aq) + 3OH^-(aq) \rightleftharpoons PO_4^{3-}(aq) + 3H_2O(\ell)$

(b) $H_3PO_4(aq) + 2NH_3(aq) \rightleftharpoons HPO_4^{2-}(aq) + 2NH_4^+(aq)$

(c) $H_3PO_4(aq) + F^-(aq) \rightleftharpoons H_2PO_4^-(aq) + HF(aq)$

SOLUTION

For phosphoric acid, the number of equivalents is the number of H^+ ions donated to the base. For the reactions in (a), (b), and (c) the number of equivalents are 3, 2, and 1, respectively. Thus, the calculated equivalent weights and normalities are

$$\text{(a)} \quad EW = \frac{FW}{n} = \frac{97.994}{3} = 32.665 \qquad N = n \times M = 3 \times 6.0 = 18 \, N$$

$$\text{(b)} \quad EW = \frac{FW}{n} = \frac{97.994}{2} = 48.997 \qquad N = n \times M = 2 \times 6.0 = 12 \, N$$

$$\text{(c)} \quad EW = \frac{FW}{n} = \frac{97.994}{1} = 97.994 \qquad N = n \times M = 1 \times 6.0 = 6.0 \, N$$

2B.3 Molality

Molality is used in thermodynamic calculations where a temperature independent unit of concentration is needed. Molarity, formality and normality are based on the volume of solution in which the solute is dissolved. Since density is a temperature dependent property a solution's volume, and thus its molar, formal and normal concentrations, will change as a function of its temperature. By using the solvent's mass in place of its volume, the resulting concentration becomes independent of temperature.

- **3-Formality**

  Number of gram formula weight of solute per liter of solution

$$F = \frac{number\ of\ formula\ weight}{V\ (Liter)}$$

$$F = \frac{no.of\ fw}{V\ (Liter)}$$

$$no.\ of\ fw = \frac{Wt}{fw}$$ **Wt: weight of solute, fW: formula weight of solute**

$$F = \frac{Wt}{fw} \times \frac{1000}{VmL}$$ **wt: weight of solute,   fw: formula weight**

Units: eq/L,   eq/mL

- **4- Percentage Ratio:**

A- Weight per Volume Percentage : No. of g of solute in 100mL of solution

$$\%W/V = \frac{Wt\ of\ solute}{V\ mL\ of\ solution} \times 100$$

B- Volume Percentage : No. of mL of solute in 100 mL of solution

$$\%V/V = \frac{VmL\ of\ solute}{V\ mL\ of\ solution} \times 100$$

C- Weight Percentage : No. of g of solute in 100 g of solution.

$$\%W/W = \frac{wt\ of\ solute}{wt\ of\ solution} \times 100$$

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

$$\frac{28.0 \text{ g } NH_3}{100 \text{ g solution}} \times \frac{0.899 \text{ g solution}}{\text{mL solution}} \times \frac{1 \text{ mole } NH_3}{17.04 \text{ g } NH_3} \times \frac{1000 \text{ mL}}{\text{liter}} = 14.8 \text{ M}$$

- 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

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

- **Ex: Calculate the percentage ratio for solution result from dissolving 5 g of Sodium hydroxide in 0.25 L of solution**

- $\%W/V = \dfrac{Wt\ of\ solute}{V\ mL\ of\ solution}$ **x 100** $= \dfrac{5}{250}$ **x 100 = 2%**

- **Ex: Calculate the percentage ratio for solution result from addition of 200 mL of Methanol to 400 mL distilled water.**

- $\%V/V = \dfrac{VmL\ of\ solute}{V\ mL\ of\ solution}$ **x 100** $= \dfrac{200}{200+400}$ **x 100 = 33.33%**

- **Ex: Calculate the No. of g of glucose solution in 800 mL industrial solution, if its percentage ratio is 15%**

- $\%W/V = \dfrac{Wt\ of\ solute}{V\ mL\ of\ solution} \times 100$

- $\%15 = \dfrac{Wt\ of\ glucose}{800} \times 100 = 120\ g$

- **Gram (g) = 1000 Milligram (mg)**
- **Milligram (mg) =1000 Microgram (µg)**
- **Microgram (µg) = 1000 Nanogram(ng)**
- **Liter (L) = 1000 Milliliter (mL)**
- **Milliliter (mL) = 1000 Microliter(µL)**
- **Microliter(µL) = 1000 Nanoliter(nL)**

- **5. Parts per thousandth (ppt)**

- $ppt = \dfrac{Wt\ of\ solute}{wt\ of\ solution} \times 10^3$ $= \dfrac{Wt\ (mg)}{wt\ (g)} = \dfrac{Wt\ (g)}{wt\ (kg)}$

- **6-Parts per million (ppm)**

- $ppm = \dfrac{Wt\ of\ solute}{wt\ of\ solution} \times 10^6$ $= = \dfrac{Wt\ (mg)}{wt\ (kg)}$

- **7-Parts per billion (ppb)**

- $ppb = \dfrac{Wt\ of\ solute}{wt\ of\ solution} \times 10^9$ $= \dfrac{Wt\ (ng)}{wt\ (g)} = \dfrac{Wt\ (ug)}{wt\ (g)}$

- $\dfrac{Wt\ (ug)}{wt\ (g)}$

Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million	ppm	mg/kg	mg/L	μL/L
(1 ppm = 10^{-4}%)		μg/g	μg/mL	nL/mL
Parts per billion	ppb	μg/kg	μg/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.

- **Example :-** A 2.6 g sample of plant tissue was analyzed and found to contain 3.6 ug zinc, what is the concentration of zinc in the plant in ppm? in ppb?

- **Ppm =** $\dfrac{Wt\ (ug)}{wt\ (g)} = \dfrac{3.6(ug)}{2.6\ (g)} = 1.4\dfrac{ug}{g} = 1.4\ ppm$

- **Ppb =** $\dfrac{Wt\ (ng)}{wt\ (g)} = \dfrac{3.6\ x10^3\ (ng)}{2.6\ (g)} = 1.4x10^3\dfrac{ng}{g} = 1400\ ppb$

Table 2.4 Common Units for Reporting Concentration

Name	Units[a]	Symbol
molarity	$\dfrac{\text{moles solute}}{\text{liters solution}}$	M
formality	$\dfrac{\text{number FWs solute}}{\text{liters solution}}$	F
normality	$\dfrac{\text{number EWs solute}}{\text{liters solution}}$	N
molality	$\dfrac{\text{moles solute}}{\text{kg solvent}}$	m
weight %	$\dfrac{\text{g solute}}{100 \text{ g solution}}$	% w/w
volume %	$\dfrac{\text{mL solute}}{100 \text{ mL solution}}$	% v/v
weight-to-volume %	$\dfrac{\text{g solute}}{100 \text{ mL solution}}$	% w/v
parts per million	$\dfrac{\text{g solute}}{10^6 \text{ g solution}}$	ppm
parts per billion	$\dfrac{\text{g solute}}{10^9 \text{ g solution}}$	ppb

[a]FW = formula weight; EW = equivalent weight.

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

- **Dilution**

- • Dilute solutions can be prepared from **concentrated solutions**. A volume of the concentrated solution is transferred to a fresh vessel and diluted to the desired final volume. The number of moles of reagent in V liters containing M moles per liter is the product **M.V = mol/L. L**, so we equate the number of moles in the concentrated (conc) and dilute (dil) solutions:

- •**Dilution Law:**

- **(Mconc x V conc) = (Mdil x Vdil)**

- **(N conc x V conc) = (Ndil x Vdil)**

- **We often must prepare to dilute solutions from more concentrated stock solutions. For example, we may prepare a dilute HCL solution from concentrated HCL to be used for titration. Or, we may have a stock standard solution from which we wish to prepare a series of more dilute standards. The millimoles of stock solution taken for dilution will be identical to the millimoles in the final diluted solution.**

- **Ex: Calculate the normality (N) of solution result from dilution 100mL of 0.25 N Nitric Acid to 250mL**.

- $N_1V_1 = N_2V_2$

- $0.25 \times 100 = N_2 \times 250$ $\Rightarrow$ $N_2 = 0.1N$

- **Example:- You wish to prepare a calibration curve for the spectrophotometric determination of permanganate. You have a stock 0.100 M solution of KMnO4 and a series of 100 mL volumetric flasks. What volumes of the stock solution will you have to pipet into the flasks to prepare standards of 1.00, 2.00, 5.00, and 10.0×10^{-3} M KMnO4 solutions.**

- **Solution-1: 1.0×10^{-3} M**

- $$(M1 \times V1)conc. = (M2 \times V2)dilu.$$

- **0.1 (mmol/ mL) x V1 = 1.0 x 10^{-3} (mmol/mL) X 100 mL**

- **V1 = 1. 0 mL stock solution (conc.),Also to prepare 2.0, 5.0, 10.0×10^{-3} M**

- • **Example:** 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 Cu^{2+} 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**

- $M= \dfrac{Wt}{M.Wt} \times \dfrac{1000}{mL}$

- $0.20 \text{ mol/L} = \dfrac{Wt}{40g/mol} \times \dfrac{1000}{500mL} = 4.0 \text{ g}$

- To prepare the solution we place 4.0 g of NaOH, 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**

- $wt = \dfrac{150\ mg}{L} \times 1.000\ L = 150.0\ mg = 0.1500\ g$

- 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.

- **(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**

$$\frac{4.0 \; mL \; of \; CH3COOH}{100mL} \text{x } 2000 \; mL = 800 \; mL \; CH3COOH$$

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.

- **Stock solution: A solution of known concentration from which other solutions are prepared. Quantitative transfer: The process of moving a sample from one container to another in a manner that ensures all material is transferred.**

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- • Example: The molarity of "concentrated" HCl is approximately 12.1 M. How many milliliters of this reagent should be diluted to 1.000 L to make 0.100 M HCl?

- • Solution: The dilution formula handles this problem directly:
- **M conc. Vconc = M$_c$dil . Vdil**
- (12.1 M).(x mL) = (0.100 M).(1 000 mL) → **x = 8.26 mL**
- **To make 0.100 M HCl, we would dilute 8.26 mL of concentrated HCl up to 1.000 L. The concentration will not be exactly 0.100 M, because the reagent is not exactly 12.1 M. A table inside the cover of this book gives volumes of common reagents required to make 1.0 M solutions.**

Chemical equilibrium

In a chemical reaction, **chemical equilibrium** is the state in which both the reactants and products are present in concentrations which have **no further change** with **time**, so that there is no observable change in the properties of the system.

A reaction is in chemical equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.

- **Chemical Reactions Divided into:**

- **1- Irreversible Reactions:**

- A chemical reaction that can occur in one direction reactions, so that the reactants are completely consumed in the reaction and shown by one arrow.

-                    $HCl + NaOH \longrightarrow NaCl + H_2O$

- **2- Reversible Reactions:**

- A chemical reaction that can occur in both directions (the forward and backward directions), so that the reactants are incompletely consumed in the reaction and shown by two arrows

$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$
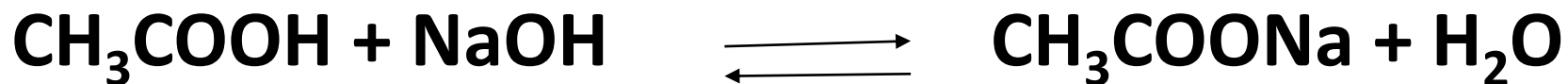
- Most of the reactions that are useful for chemical analysis proceed rapidly to a state of chemical equilibrium in which reactants and products exist in constant ratios. The knowledge of this ratio permits the chemists to decide whether the reaction is suitable for chemical analysis or not. Equilibrium constant expressions are algebraic equations that relate to the concentrations of reactants or products.
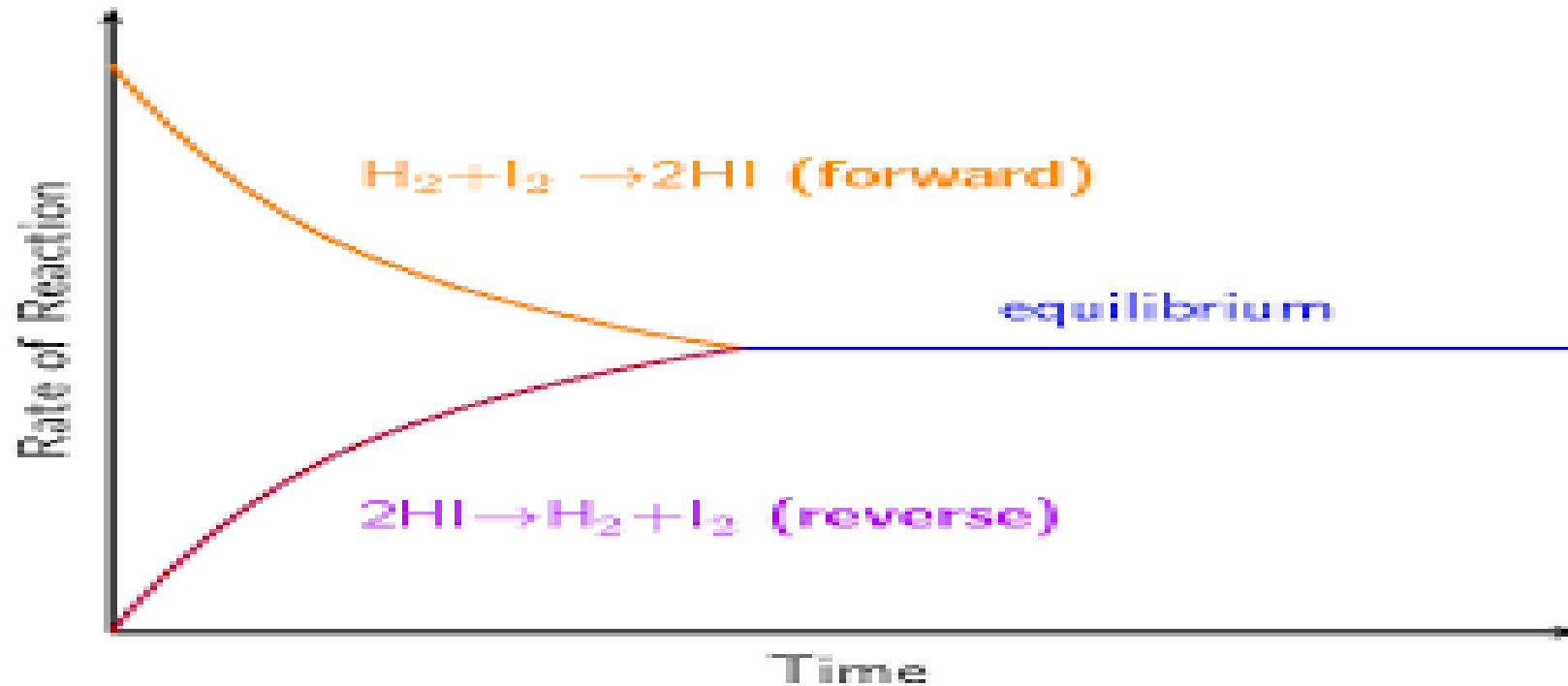
Volumetric analysis (titration analysis)

- These are the most useful and accurate analytical techniques, especially for millimole amounts of analyte. They are rapid and can be automated, and they can be applied to smaller amounts of analyte when combined with a sensitive instrumental technique for detecting the completion of the titration reaction, **for example,** pH measurement. In a titration, the test substance (analyte) in reacts with a reagent added from a burette as a solution of known concentration. This is referred to as a standard solution and is called the titrant. The volume of titrant required to just completely react with the analyte is measured. Since we know the concentration as well as the reaction between the analyte and the reagent, we can calculate the amount of analyte.

- **Classification of volumetric or titration methods:-**

- (1) **Neutralization (acid-base) titrations:** Many compounds, both inorganic and organic, are either acids or bases that can be titrated with a standard solution of a strong base or a strong acid. The endpoint of these titrations is easy to detect, either by means of an indicator or by following the change in pH with a pH meter.

- (2) **Precipitation titrations:** In the case of precipitation, the titrant forms an insoluble product with the analyte. An example is the titration of chloride ions with silver nitrate solution to form a silver chloride precipitate.

- (3) **Complexometric titrations (sometimes chelatometry)** is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in a solution.

- (4) **Reduction-Oxidation titrations:** These (redox) titrations involve the titration of an oxidizing agent with a reducing agent or vice versa . An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.

•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 species X,

  - pX = -log [X]

- As shown by the following examples, p-values offer the advantage of allowing concentrations that vary over ten or more orders of magnitude to be expressed in terms of small positive numbers.
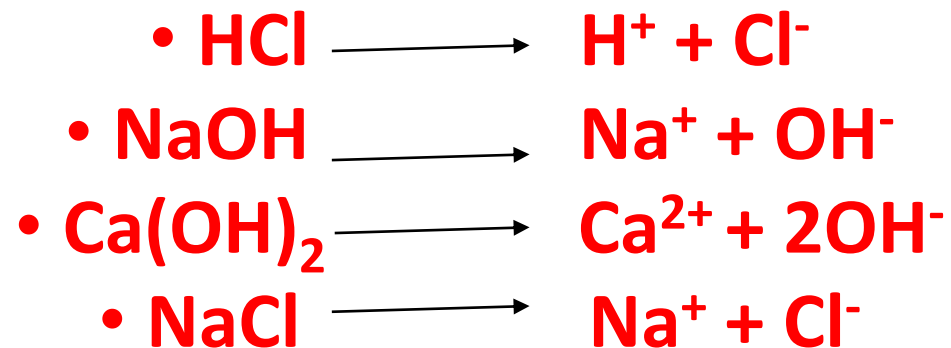
- **Example : Calculate the p-value for each ion in a solution that is 2.00 X 10^{-3} M in NaCl and 5.4 X 10^{-4} M in HCl.**

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

- pNa = -log (2.00×10^{-3}) = -log 2.00×10^{-3} = 2.699

- $[Cl\text{-}]$ = 2.00×10^{-3} M + 5.4×10^{-4} M

- = 2.00×10^{-3} M + 0.54×10^{-3} M = 2.54×10^{-3} M

- pCl = -log 2.54×10^{-3} M = 2.595

- **Example: Calculate the molar concentration of Ag^+ in a solution that has a pAg of 6.372.**

- Solution:

- pAg = -log $[Ag^+]$ = 6.372, log $[Ag^+]$ = -6.372, $[Ag^+]$ = 4.246×10^{-7} = 4.25×10^{-7}

- **Materials in its aquase solution classified into two types:**
- **Electrolytes   and non Electrolytes**
- All substances that dissociate in water into ions are called **electrolytes or ionic substance,** those do not dissociate are termed **non-electrolytes or nonionic substance.**
- • Aqueous solutions of electrolytes conduct an electric currant, but those of non- electrolytes do not. Electrolytes are classified as **Strong or Weak.**
- **A. Strong Electrolyte materials**
- Materials that totally ionized in their aqueous solutions are called strong electrolytes. These electrolytes are good electricity conductors, high solubility, such as strong acids and bases.

  - $HCl \longrightarrow H^+ + Cl^-$
  - $NaOH \longrightarrow Na^+ + OH^-$
  - $Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$
  - $NaCl \longrightarrow Na^+ + Cl^-$

- **B. Weak electrolyte materials**
- Materials that partially ionized in their aqueous solutions, reaching ionic equilibrium called weak electrolytes. These electrolytes are weak electricity conductors such as weak acids and bases.

$$HCN \rightleftharpoons H^+ + CN^-$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
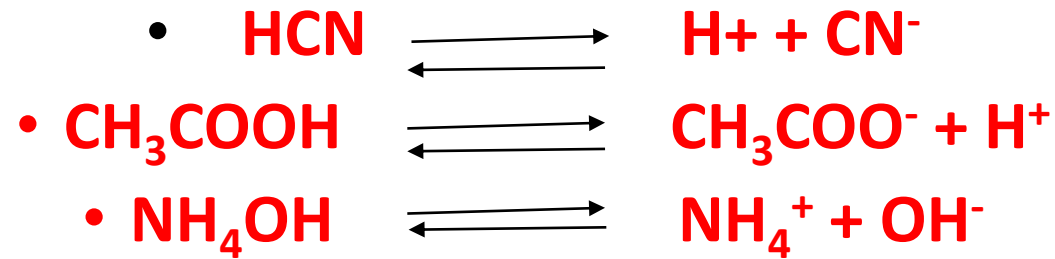
- **The dissociation or ionization of weak electrolytes is quantitatively described by equilibrium constant. Suppose the dissociation of AB.**
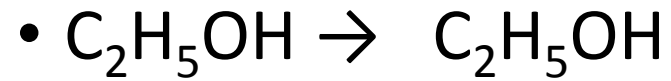
$$AB \rightleftharpoons A + B$$

- **The equilibrium constant Ke of the dissociation is generally written as:**

$$Ke = \frac{[A][B]}{[AB]}$$

- **NON ELECTROLYTE MATERIALS**
- These are the materials that do not release any ions in their aqueous solutions such as ethanol.
  - $C_2H_5OH \rightarrow C_2H_5OH$
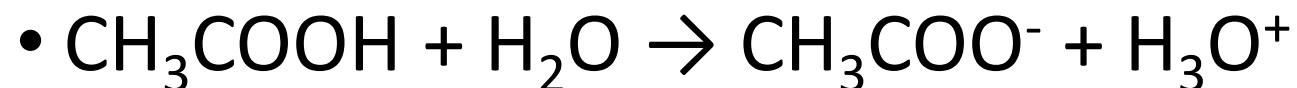 - Glucose $\rightarrow$ Glucose

- **ACIDS AND BASES**
- **1.Arrhenius concept**
- Acid is a material that ionized in water to give hydrogen ion.
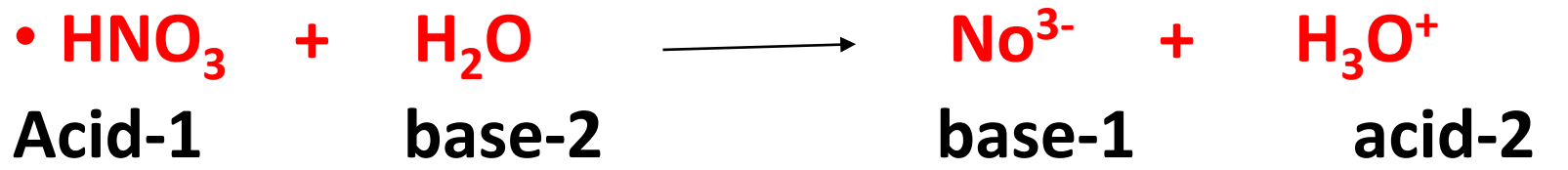- Base is a material that ionized in water to give hydroxide ion.
  - $HCl \rightarrow H+ + Cl^-$, $NaOH \rightarrow Na^+ + OH^-$
- 2.Bronsted and Lowry concept
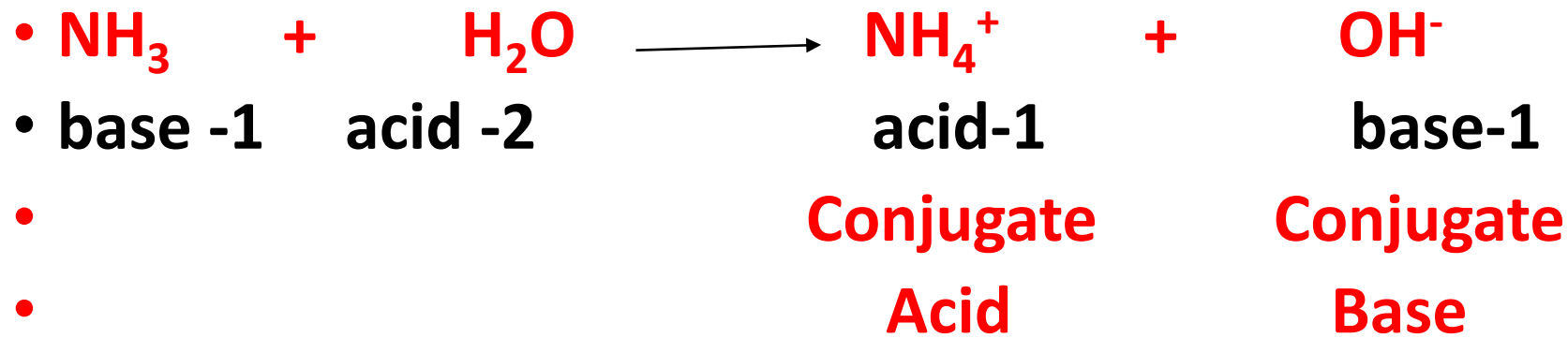- Acid is any substance that is capable of donating proton wherase base is any substance can accept a proten.
  - Acid $\rightarrow$ base + proton
  - $CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$
    acid-1   base-2   base-1   acid-2

- HNO_3 + H_2O $\longrightarrow$ NO^{3-} + H_3O^+

Acid-1   base-2   base-1   acid-2

-                                    Conjugate   Conjugate

-                                      Base   Acid

- NH_3 + H_2O $\longrightarrow$ NH_4^+ + OH^-

- base -1   acid -2   acid-1   base-1

-                                      Conjugate   Conjugate

-                                      Acid   Base

- water is amphprotic solvent because it exhibits both acidic and basic properties.

- After an acid has donate a proton the species that remains is capable of accepting proton to reform the original acid then every acid is paired with its corresponding base which is called as conjugate base.

• ION PRODUCT CONSTANT OF WATER
(Equilibrium Constant)

Aqueous solutions contain small amount of hydronium ion H_3O^+ and hydroxide ion OH^-

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
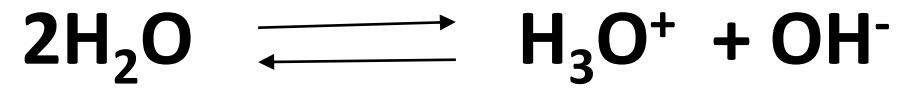
Water dissociates to H^+ and OH^- ions in aqueous solutions which are strongly contacted to water molecules. Applying mass product law gives the following equation.

$$k = \frac{[H_3O+]\,[OH-]}{[H_2O]_2}$$

The concentration of water is enormous (each one liter of water equal to 55.5 M) when compared with the concentration of hydrogen and hydroxide ions. As consequence water concentration can be considered as a constant.

- Kw = [H_3O+] [OH-] or Kw =[H^+][OH^-]

- H_2O $\longrightarrow$ H^+ + OH^-

- Kw = [H^+] . [OH^-]

- Kw = 1.0 x 10^{-14} mole/L

- [H+] . [OH-] = K [H_2O] = Kw (ion product constant of water) by using water concentration as one, Kw approximation value is:

- 1.01x10^{-14} or 1.0x10^{-14} at 25 ^oC. Kw increasing with the increase in temperature (at 50 ^oC = 5.47 x 10^{-14} and at 100 ^oC = 49x10^{-14}).

- Kw = ion product constant of water = $[H^+][OH^-] = 1.0 \times 10^{-14}$
- in case of pure water.
  - $[H^+] = [OH^-]$
  - $[H^+] = [OH^-] = 10^{-7}$ mole/L = M
- **By taking the logarithm of this equation**
- **Kw= [H+] [OH-]**
- **-log Kw= -log $[H^+]$ $[OH^-]$**
- **-log Kw= -log $[H^+]$ –log $[OH^-]$**
- **pKw = pH + pOH = 14**
- **if pH < 7 then the solution acidic.**
- **if pH > 7 then the solution is basic.**
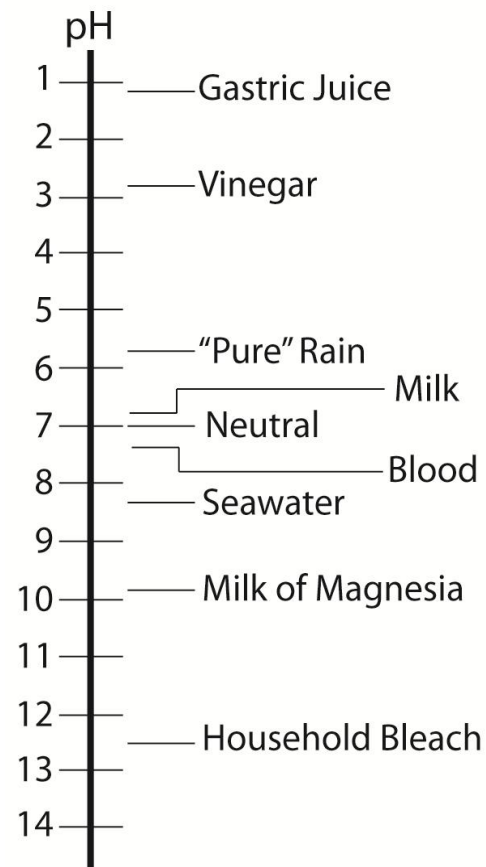- **If pH = 7 then the solution is equilibrium.**

Figure 6.2: *Scale showing the pH value for representative solutions. Milk of Magnesia is a saturated solution of $Mg(OH)_2$.*

- **Ex2: Calculate the pH and pOH values of a solution in which the hydronium ion concentration is 2.0 x 10^{-3} M.**
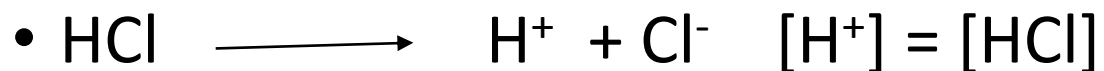
- $[H^+]$ = $[H_3O^+]$ = 2.0 x 10^{-3} mole/L

- pH = -log [H] = -log [2.0 x 10^{-3}]

- = 2.699

- pOH= 14- pH = 14 – 2.699 = 11.301

• EQUILIBRIUM CONSTANTS FOR PAIR ACIDS AND BASES

• Calculation of hydronium and hydroxide ions for strong, acids and bases and weak acids and bases.

• **1-Strong acids**

• The strong Acids will completely ionize in its aqueous solution, and shown by one arrow.

• HCl $\longrightarrow$ H^+ + Cl^- $[H^+]$ = $[HCl]$

• Ex. Calculate [H+] and pH of 0.01 M HCl solution

•   HCl $\longrightarrow$ H+ + Cl-

• before ionization   0.01   0   0

• after ionization   0   0.01   0.01

• [H+] = 0.01 M

• pH = -log $[H^+]$ = -log 0.01 = 2

- Ex: Calculate pH and pOH for 0.15 M H_2SO_4

- $H_2SO_4 \longrightarrow 2H^+ + SO^{4-}$
- before ionization   0.015   0   0
- after ionization   0   2 x 0.15   0.15
- $[H^+] = 2 \times 0.15 = 0.3$ M
- pH = -log $[H^+]$ = -log 0.3 = 0.523
- Kw = PH + pOH =14
- pOH = 14 — 0.523 = 13.477

- **2- Week acids**

- The Weak Acids will incompletely ionize (partial ionization) in its aqueous solution, and shown by two reverse arrows. So Ionic equilibrium in is occurring.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
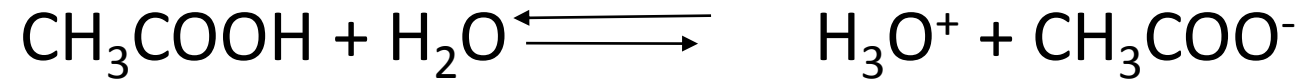
$$ka = \frac{[H_3O^+]\,[CH\,COO^-]}{[CH\,COOH]\,[H_2O]}$$

Ka is a reaction between the ionized part of the acid and the unionized part of the acid, **Ka** is a constant provided temperature and pressure are constant, called acid ionization or dissociation constant.

$$kb = \frac{Kw}{Ka}$$ **for Conjugate Base**

- **Ex. Calculate [H⁺] of 0.1 M CH₃COOH at 25 °C (Ka = 1.8x10⁻⁵)**

$$CH_3COOH \quad \longrightarrow \quad CH_3COO- \ + H^+$$

Before ionization   0.1   0   0

After ionization   0.1 - x   x   x

$$ka = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

Ka = 1.8 x 10⁻⁵ = $\dfrac{x.x}{0.1-x}$

1.8 x 10⁻⁵ = $\dfrac{x2}{0.1}$ X is small value and hence it is neglected

x2 = 1.8 x 10⁻⁶   so x =$\sqrt{1.8x10-6}$

x = 1.342 x 10⁻³ mole/L

CALCULATION OF HYDROXID ION CONCENTRATION

1. Strong bases

The strong Bases will completely ionize in its aqueous solution. and shown by one arrow.

$NaOH \rightarrow Na^+ + OH^-$

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$

Ex 1: Calculate the hydronium and hydroxide ion concentrations in 0.2M aqueous NaOH solution?

$NaOH \rightarrow Na^+ + OH^-$

0.2   0   0

0   0.2   0.2

$[OH-] = 0.2 \ M$

$[H^+] = \dfrac{Kw}{[OH]} = \dfrac{1X\ 10^{-14}}{0.2} = 5X\ 10^{-14}$

- Q: Calculate pOH and pH for 0.15 M Ca(OH)$_2$

- (homework)

- **2. Week bases:**

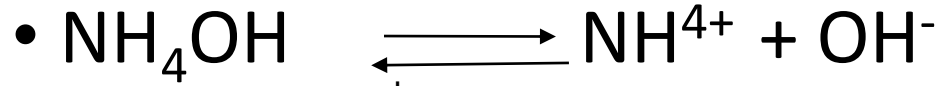- The Weak Bases will incompletely ionize (partial ionization) in its aqueous solution, shown by two arrows. So the Ionic equilibrium is occurring.

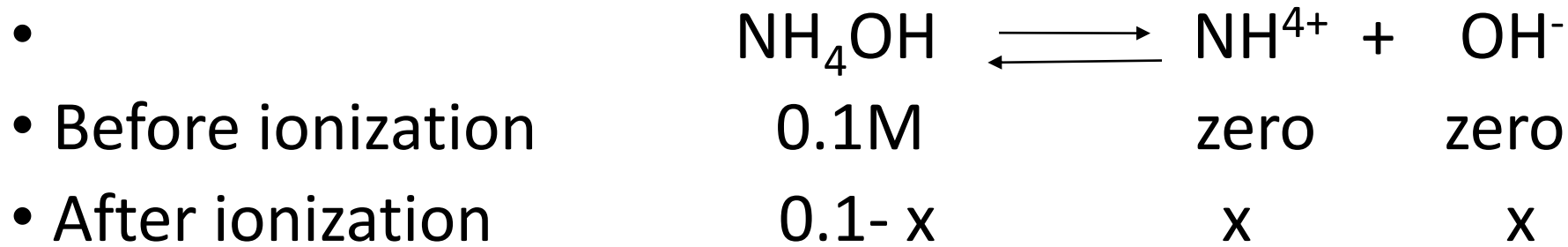- NH$_3$ + H$_2$O $\rightleftharpoons$ NH$_4$OH $\rightleftharpoons$ NH^{4+} + OH$^-$

- $kb = \dfrac{[NH^{4^+}] [OH^-]}{[NH_4OH]}$ base   Conjugate Acid
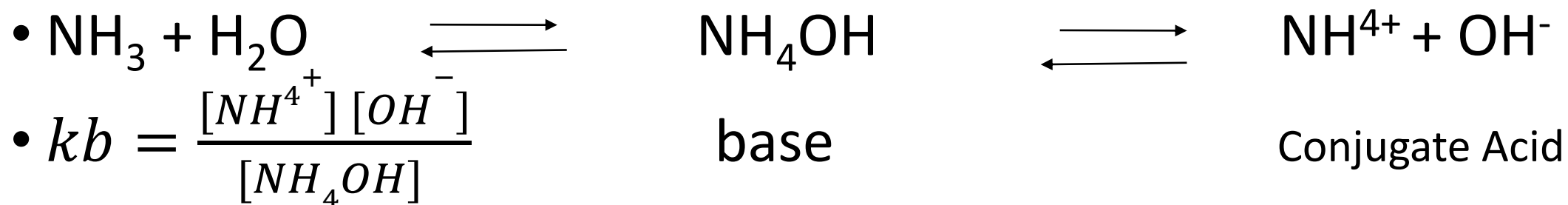
- POH = -log [OH]   Kb is base ionization constant

- $ka = \dfrac{Kw}{Kb}$ **for Conjugate Acid**

- **Ex: Calculate [OH⁻], pH and pOH of 0.1M ammonia solution at 25 °C if Kb =1.8 x 10⁻⁵.**

- $NH_4OH \rightleftharpoons NH^{4+} + OH^-$

- $kb = \dfrac{[NH^{4+}][OH^-]}{[NH_4OH]}$

- $\qquad\qquad NH_4OH \rightleftharpoons NH^{4+} + OH^-$

- Before ionization $\qquad$ 0.1M $\qquad$ zero $\quad$ zero

- After ionization $\qquad$ 0.1- x $\qquad$ x $\qquad$ x

- $kb = \dfrac{x.x}{0.1-x} = 1.8\text{x}10^{-5}$ $\qquad$ x is ignored

- X = [OH⁻] = 1.342 x 10⁻³

- pOH = -log[OH-] = -log 1.342 x10⁻³ = 2.872

- pH = 14- pOH = 14 − 2.872 = 11.128

- **Ex: Calculate [H+], pH and pOH of 0.001M Acetic acid solution at 25 oC if Ka =1.8 x 10-5.**

- $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
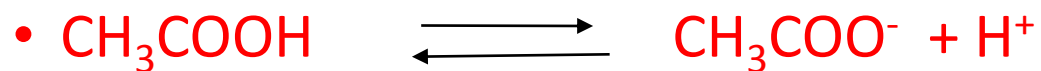
- $ka = \dfrac{[H_3O^+][CH\,COO^-]}{[CH_3COOH]}$
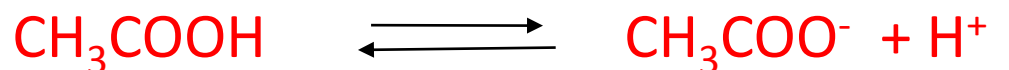
	CH_3COOH	$\rightleftharpoons$	CH_3COO^-	$+ H^+$
Before ionization	0.001		zero	zero
After ionization	0.001 - x		x	x

$1.8x10^{-5} = \dfrac{x.x}{0.001-x} = 1.8x10^{-5}$ **x is ignored**

$1.8 \times 10^{-5} = \dfrac{x2}{0.001}$ So $X^2 = 1.8x10^{-5} \times 0.001 = 1.8 \times 10^{-8}$

x = 2.621 × 10⁻⁴

pH = -log [H] = -log 2.621 × 10⁻⁴

$\qquad$ = 2.582

pOH = 14 – pH

$\qquad$ = 14 - 2.582 = 11. 418

Classification of solutions

Solutions are classified into:

According to the concentration of solute in solution as follows;

1. **Saturated solution:** the solution in which the solute is in a dynamic equilibrium state with a solution at a certain temperature. i.e. **dissolve the amount of solute= amount precipitated of it**. The concentration of saturated solution at a certain temperature is represented by the solubility of the solute in a solvent at that temperature. e.g. 37g NaCl /100 mL H2O at 0°C.

2. Unsatu**rated solution:** the solution in which the amount of solute is less than is needed for saturation, thus, no dynamic equilibrium exists between the solute and solvent e.g. 20g of NaCl in 100 mL of water at 0°C.

3- Supersaturated solutions: the solutions that contain more solute than ordinary required for saturation, at 0°C. Sodium acetate dissolves in water to extent of 119g/100 mL, but its solubility increases with increasing temperature.

Solubility of precipitates

• Solubility is the amount of solute needed to give a saturated solution with a given amount of solvent. Thus, the solubility of NaCl in water at 0°C is 37g/100mL. Usually solute's solubility changes with temperature. For example at 100°C the solubility of NaCl is 39.1g/100mL of H_2O.this means that we should always specify the temperature when stating the solubility.

- Reactions that yield products of limited solubility find application in three important analytical processes:

- **1. The separation** of an analyte as a precipitate from soluble substances that would otherwise interfere with ultimate measurement.

- **2. Gravimetric analysis,** in which the precipitate is formed whose weight is chemically related to the amount of analyte.

- **3. Titrimetric analysis,** based on the determination of volume of a standard reagent required precipitating the analyte essentially completely.

- The success of each of these applications requires that the solids produced have a **relatively low solubility,** be **reasonably pure**, and have a suitable **particle size.**

PRECIPITATION TITRATION

Precipitation Reaction:

- Reactions occurring in solution may produce substances that are insoluble in the solution and thus eventually settle to the bottom or "precipitate" out.

- Typically precipitation reactions occurs in aqueous solutions between ions (i.e., the reactants are electrolytes). Often only one pair of ions actually reacts or precipitates while the other pair remains in the solution unchanged.

Precipitation Titrations

A reaction in which the analyte and titrant form an **insoluble precipitate** also can form the basis for a titration. We call this type of titration a **precipitation titration**.

The meaning of ANALYTE is a chemical substance that is the subject of chemical analysis.

The meaning of TITRANT is a substance (such as a reagent solution of precisely known concentration) that is added in titration.

Precipitation= Reaction that results in the formation of an insoluble product (precipitate)

Precipitate= insoluble solid that separates from solution

Metathesis/ double-displacement reaction
= reaction that involves the exchange of parts between two compounds

Example: Precipitation of Lead Iodide

$Pb(NO_3)_2$ (*aq*) + 2NaI (*aq*) $\longrightarrow$ PbI_2 (*s*) + 2NaNO$_3$ (*aq*)

$\uparrow$
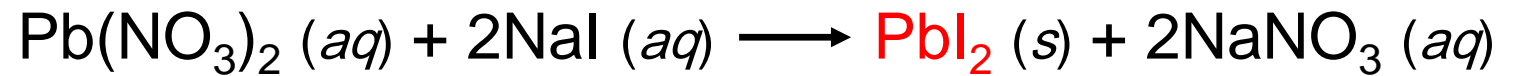
Yellow precipitate
(insoluble)

PbI_2

PRECIPITATION TITRATION

Precipitation Reactions

A precipitation reaction occurs when two or more soluble species combine to form an insoluble product that we call a precipitate. The 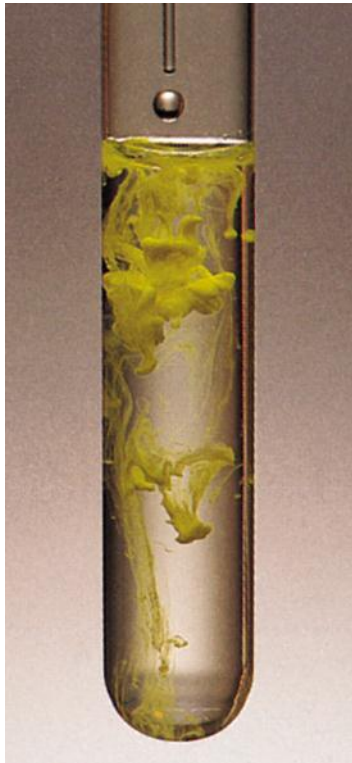most common precipitation reaction is a **metathesis reaction**, in which two soluble ionic compounds exchange parts. When a solution of **lead nitrate** is added to a solution of **potassium chloride**, for example, a precipitate of lead chloride forms. We usually write the balanced reaction as a **net ionic equation**, in which only the precipitate and those ions involved in the reaction are included.

Precipitation Reactions

Precipitation is the formation of a solid in a solution

solid formed is called the **precipitate**

A precipitation reaction occurs when water solutions of two different ionic compounds are mixed and an insoluble solid separates out of the solution.

$$KCl + AgNO_3 \longleftrightarrow AgCl + KNO_3$$

Cl- solution   Precipitating   White

agent   precipitate

The precipitate is itself ionic; the **cation** comes from one solution and the **anion** from another.

- **Solubility product (Ksp):**
- The **solubility product constant, Ksp**, is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute dissolves in solution. **The more soluble a substance is, the higher the Ksp value it has**.

- When a compound is referred to as insoluble, its **not completely insoluble** but is **slightly soluble**. When substances have a limited solubility and their solubility is exceeded, the ions of the dissolved portions exist in equilibrium with a solid material. So-called "insoluble" compounds generally exhibit this property.

- The precipitate will have a definite solubility (i.e., a definite amount that will dissolve) in g/dm^{-3} or mol/dm^{-3} at a given temperature (a saturated solution). A small amount of un-dissolved compound usually exists in equilibrium in the aqueous phase (e.g., on the order of 0.1%) and its concentration is constant. It is difficult to measure the un-dissociated molecule, and we are interested in the ionized form, presence of any un-dissociated species can generally be neglected.

$$AgCl \longrightarrow Ag^+ + Cl^-$$

$$Keq = \frac{\{Prouct\}}{\{Reactant\}}$$

$$Keq = \frac{\{Ag^+\}\{Cl^-\}}{\{AgCl\}}$$

Since the concentration of a solid is a constant value that does not depend on temperature, pressure, or the presence of the solution in contact with it and can be neglected, , we simplify the above equation to.

$$[Ag^+] [Cl^-] = K_{eq} [AgCl] = constant$$

- **This constant called constant of solubility product:**

$$K_{sp} = K_{eq} = [Ag^+] [Cl^-]$$

Every substance that is poorly soluble in water has its own solubility product

Salt that has a **lower Ksp** value is the one that **precipitates first**, that is, if it has a **low Ksp value**, it indicates that the **solubility of the salt is lo**w.

Complexometric Titrations

Complexometry

A volumetric titration involves the formation of a soluble complex between a metal ion (as acceptor) and ligand (as donor) to form coordination bonds.

The metal ion is known as a Central metal atom.

The anion or neutral molecule is known as Ligand (L)

Metal ions are Lewis acid, accepting electron pairs from electro-donating ligands that are Lewis bases.

$Ag^+ +$:C–≡N: ⇋ $[:N≡C-Ag-C≡N:]^-$

 Lewis acid   Lewis base   complex ion

(electron pair acceptor)   (electron pair donor)
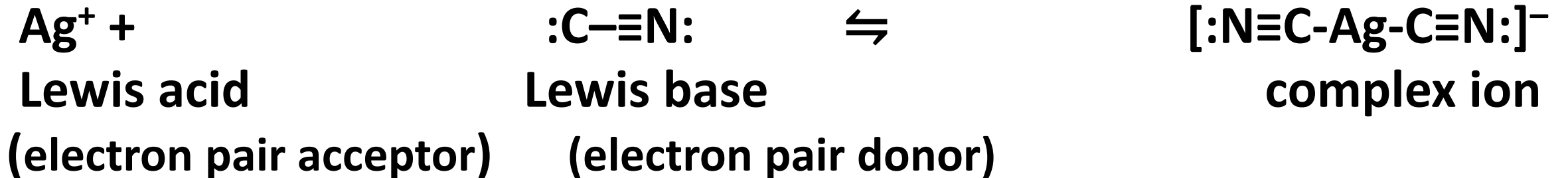
The formation of Complexes

Complexation reactions are important in many areas of science. Complexes play an essential role in many **chemical and biochemical processes**. For example, the hemoglobin molecule in blood holds the iron atom tightly because the nitrogen of the hemoglobin forms strong complexing bonds, that is nitrogen is a good complexer.

Complexation reactions are widely used in analytical chemistry. One of the first uses of these reactions was for titrating cations.

Complex ions (coordination compounds) are produce from reaction of many **metal ions (electrons accepter) with electron pair donors.**
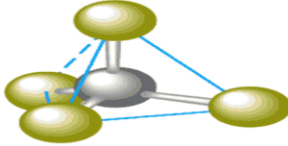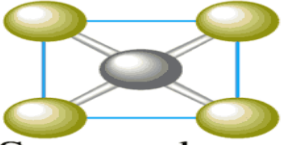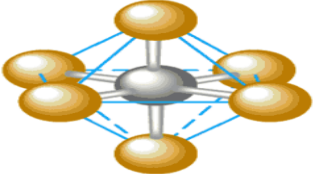
The donor species **(or called ligands)** must have at least one pair of unshared electrons for bond formation.

- Metals ions, especially **transition metals**, act as **Lewis acids**, because they accept electrons from **Lewis bases**

- • When metal cations combine with Lewis bases, the resulting species is called a complex ion or **coordination complexes**

- **COMPLEX= LIGAND + METAL ION**

$$\left[\begin{array}{c} \text{NH}_3 \\ \text{H}_3\text{N} \cdots \text{Co} \cdots \text{NH}_3 \\ \text{H}_3\text{N} \quad\quad \text{NH}_3 \\ \text{NH}_3 \end{array}\right]^{3+} (\text{Cl}^-)_3$$
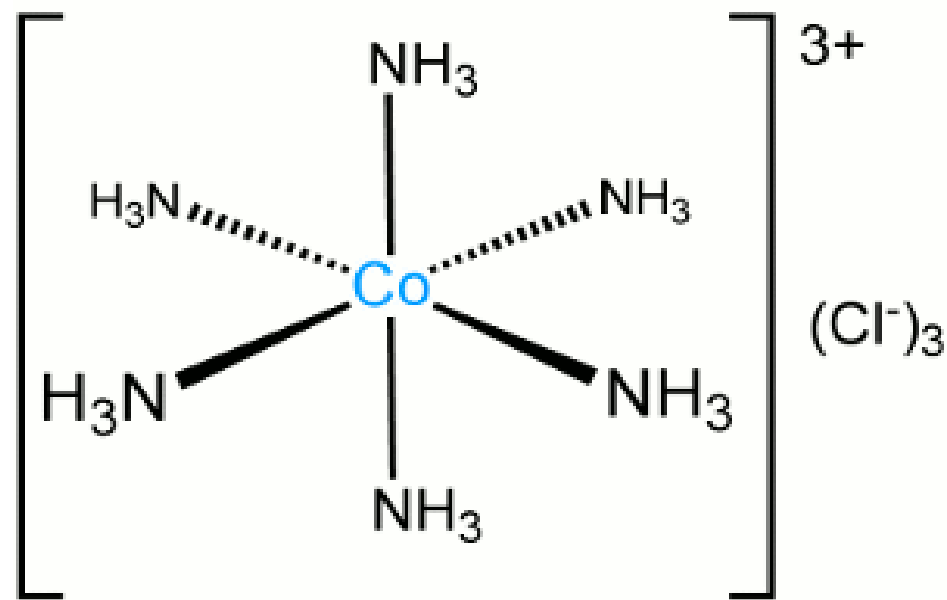
- **A ligand** is an **ion** or **molecule** that forms a **covalent bond** with a **cation or neutral metal** atom by **donating a pair** of electrons, which are then shared by the two. Ligands can be classified into **inorganic ligands** such as water, ammonia, and halide ions, and **organic ligands** such as 8-hydroxyquinoline.

- a) **anionic ligands : like , SCN$^-$, CN$^-$, OH$^-$,…….ect.**

- b) **molecular ligands : like , H$_2$O , NH$_3$, RNH$_2$, …..ect.**

- **[Ag(CN$^-$)$_2$], [Cu(NH$_3$)$_4$]$^{+2}$, [Zn(H$_2$O)$_4$]$^{+2}$**

- Species formed as a result of coordination can be classified as **positive**

- **or   neutral or negative** :

- Cu^{+2} + 4NH^{3+} → [Cu(NH$_3$)$_4$]$^{+2}$ ………………….. cationic complex

- Cu^{+2} + NH$_2$CH$_2$COO$^-$ → Cu(NH$_2$CH$_2$COO)$_2$ ….. neuteral complex

- Cu^{+2} + 4Cl$^-$ → CuCl$_4^{-2}$ …………………………. anionic complex

- **Coordination Number:-**
- The number of covalent bonds that a cation tends to form with electron donors is called the **coordination number**.
- **Common coordination numbers are 2, 4 and 6**

Coordination number	Geometry
2	Linear
4	Tetrahedral Square planar
6	Octahedral

- **Chelates:** are produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five or six-member heterocyclic ring and form a cyclic structure.

- The key difference between ligands and chelates is that ligands are the chemical species that are **donating or sharing** their electrons with a central atom through coordination bonds, whereas chelates are compounds containing a central atom bonded with surrounding ligands.

- **A ligand that has**:

- single donor group is called **unidentate**

- two donor groups is called **bidentate**

- three donor groups is called **tridentate**

- four donor groups is called **tetradentate**

- five donor groups is called **pentadentate**

- six donor groups is called **hexadentate**

- **Tetradentate and hexadentate ligands** are more satisfactory as titrants than ligands with a lesser number of donor groups **because their reactions with cations are more**

- A titration based on the formation of a coordination complex is known as a **complexometric titration**.

- **Complexometric titrations** are particularly useful for the determination of a mixture of different **metal ions** in solution.

• Chelation

• **Chelate** : It is a complex formed between the ligand containing two or more donor groups and metal to form ring structure. (heterocyclic rings or chelate rings).

• **Chelating agents:** organic molecules containing two or more donor groups which combine with metal to form complex having ring structure.

Chelates are usually insoluble in water but soluble in organic solvent.

Glycine

Cu^{2+} complex with glycine.
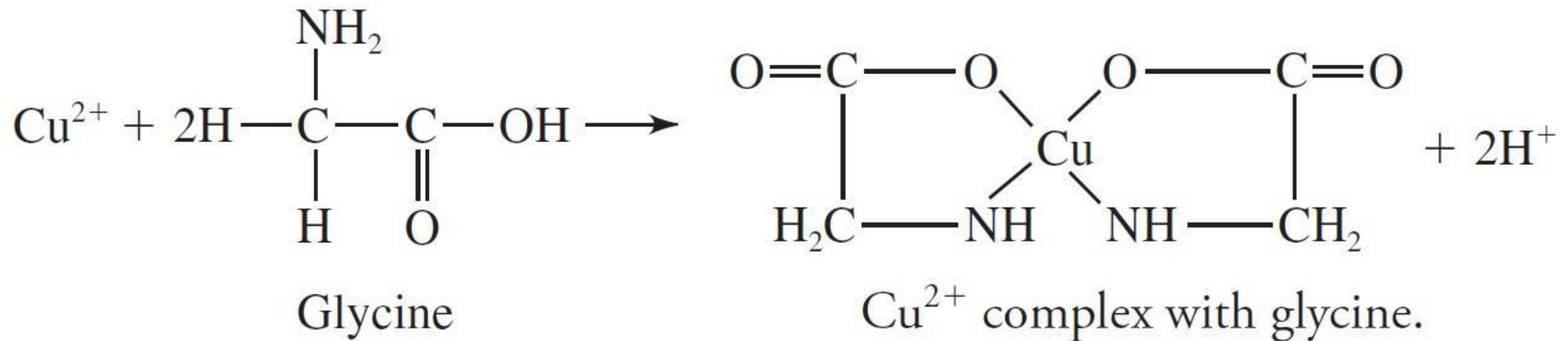
The following reaction between the metal ion Cd^{2+} and the **ligand** NH_3 is typical of a complexation reaction.

$$Cd^{2+} (aq) + 4{:}NH_3 (aq) \rightleftharpoons Cd({:}NH_3)_4^{2+} (aq) \qquad\qquad (6.4.35)$$
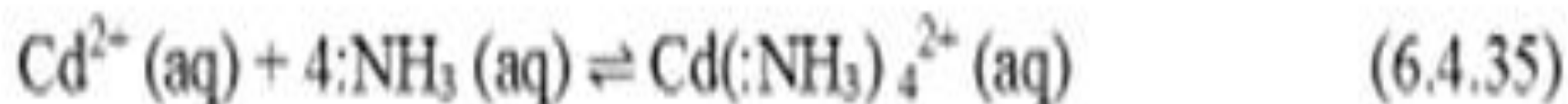
The product of this reaction is a **metal–ligand complex**. In writing this reaction we show ammonia as $:NH_3$, using a pair of dots to emphasize the pair of electrons it donates to Cd^{2+}. In subsequent reactions we will omit this notation.

Metal-Ligand Formation Constants

We characterize the formation of a metal–ligand complex by a **formation constant**, K_f. The complexation reaction between Cd^{2+} and NH_3, for example, has the following equilibrium constant.

$$K_f = \frac{[Cd(NH_3)_4^{2+}]}{[Cd^{2+}][NH_3]^4} = 5.5 \times 10^7 \qquad (6.4.36)$$

The reverse of reaction 6.4.35 is a dissociation reaction, which we characterize by a **dissociation constant**, K_d, that is the reciprocal of K_f.

Many complexation reactions occur in a stepwise fashion. For example, the reaction between Cd^{2+} and NH_3 involves four successive reactions.

$$Cd^{2+} (aq) + NH_3 (aq) \rightleftharpoons Cd(NH_3)^{2+}(aq) \qquad (6.4.37)$$
$$Cd(NH_3)^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH3)_2^{2+} (aq) \qquad (6.4.38)$$

$$Cd(NH_3)_2^{2+} (aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_3^{2+} (aq) \qquad (6.4.39)$$

$$Cd(NH3)_3^{2+} (aq) + NH_3 (aq) \rightleftharpoons Cd(NH3)_4^{2+} (aq) \qquad (6.4.40)$$

١٠

To avoid ambiguity, we divide formation constants into two categories. **Stepwise formation constants**, which we designate as K_i for the ith step, describe the successive addition of one ligand to the metal–ligand complex from the previous step. Thus, the equilibrium constants for reactions 6.4.37–6.4.40 are, respectively, K_1, K_2, K_3, and K_4. Overall, or **cumulative formation constants**, which we designate as β_i, describe the addition of i ligands to the free metal ion. The equilibrium constant in equation 6.4.36 is correctly identified as β_4, where

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 \qquad (6.4.41)$$

In general

$$B_i = K_1 \times K_2 \times \ldots \times K_i \qquad (6.4.42)$$

Stepwise and overall formation constants for selected metal–ligand complexes are in <u>Appendix 12</u>.

Metal-Ligand Complexation and Solubility

A formation constant characterizes the addition of one or more ligands to a free metal ion. To find the equilibrium constant for a complexation reaction involving a solid, we combine appropriate K_{sp} and K_f expressions. For example, the solubility of AgCl increases in the presence of excess chloride as the result of the following complexation reaction.

$$AgCl\ (s) + Cl^- (aq) \rightleftharpoons AgCl_2^- (aq) \qquad (6.4.43)$$
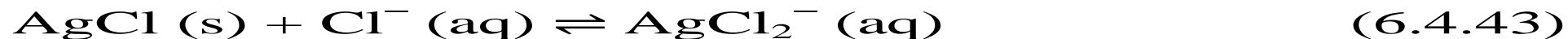
We can write this reaction as the sum of three other reactions with known equilibrium constants—the solubility of AgCl, described by its K_{sp}

$$AgCl(s) \rightleftharpoons Ag^+ (aq) + Cl^- (aq) \qquad (6.4.44)$$
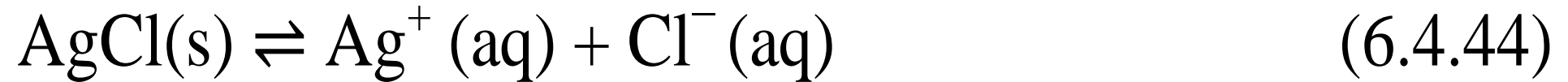
and the stepwise formation of $AgCl_2^-$, described by K_1 and K_2.

$$Ag^+ (aq) + Cl^- (aq) \rightleftharpoons AgCl (aq) \qquad (6.4.45)$$

$$AgCl (aq) + Cl^- (aq) \rightleftharpoons AgCl_2^- (aq) \qquad (6.4.46)$$
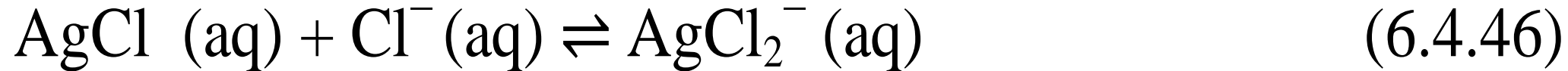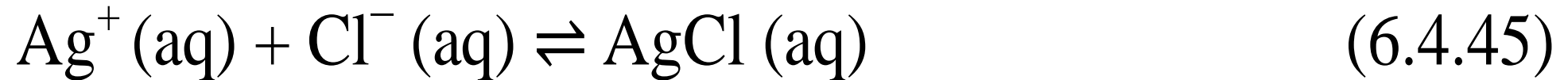
The equilibrium constant for reaction 6.4.43, therefore, is $K_{sp} \times K_1 \times K_2$.

Example 6.4

Determine the value of the equilibrium constant for the reaction

$$PbCl_2 \text{ (s)} \rightleftharpoons PbCl_2 \text{ (aq)} \hspace{3cm} (6.4.47)$$

Solution

We can write this reaction as the sum of three other reactions. The first of these reactions is the solubility of $PbCl_2(s)$, described by its K_{sp} reaction.

$$PbCl_2 \text{ (s)} \rightleftharpoons Pb^{2+} \text{ (aq)} + 2Cl^- \text{(aq)} \hspace{2cm} (6.4.48)$$

The remaining two reactions are the stepwise formation of $PbCl_2(aq)$, described by K_1 and K_2.

$$Pb^{2+} \text{ (aq)} + Cl^- \text{ (aq)} \rightleftharpoons PbCl^+ \text{ (aq)} \hspace{2cm} (6.4.49)$$

$$PbCl^+ \text{ (aq)} + Cl^- \text{ (aq)} \rightleftharpoons PbCl_2 \text{ (aq)} \hspace{2cm} (6.4.50)$$
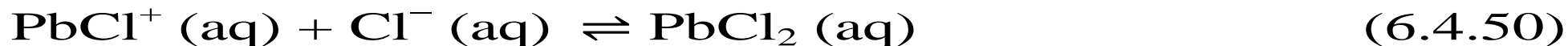
Using values for K_{sp}, K_1, and K_2 from Appendix 10 and Appendix 12, we find that the equilibrium constant is

$$K = K_{sp} \times K_1 \times K_2 = (1.7 \times 10^{-5}) \times 38.9 \times 1.62 = 1.1 \times 10^{-3} \hspace{1cm} (6.4.51)$$

Practice Exercise 6.3

What is the equilibrium constant for the following reaction? You will find appropriate equilibrium constants in Appendix 10 andAppendix 11.

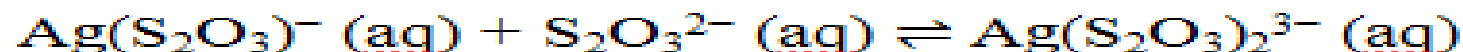$$AgBr \text{ (s)} + 2S_2O_3{}^{2-} \text{ (aq)} \rightleftharpoons Ag(S_2O_3)_2{}^{3-}\text{(aq)} + Br^-\text{(aq)} \qquad (6.4.52)$$

We can write the reaction as a sum of three other reactions. The first reaction is the solubility of $AgBr(s)$, which we characterize by its K_{sp}.

$$AgBr \text{ (s)} \rightleftharpoons Ag^+ \text{ (aq)} + Br^- \text{ (aq)}$$

The remaining two reactions are the stepwise formation of $Ag(S_2O_3)_2{}^{3-}$, which we characterize by K_1 and K_2.

$$Ag^+ \text{ (aq)} + S_2O_3{}^{2-} \text{ (aq)} \rightleftharpoons Ag(S_2O_3)^- \text{ (aq)}$$

$$Ag(S_2O_3)^- \text{ (aq)} + S_2O_3{}^{2-} \text{ (aq)} \rightleftharpoons Ag(S_2O_3)_2{}^{3-} \text{ (aq)}$$

Using values for K_{sp}, K_1, and K_2 from Appendix 10 and Appendix 11, we find that the equilibrium constant for our reaction is

$$K = K_{sp} \times K_1 \times K_2 = (5.0 \times 10^{-13})(6.6 \times 10^8)(7.1 \times 10^4) = 23$$

Composition of EDTA solution as a function of pH :

The most common echelon (or titrant) used in complexation titration is EDTA **(ethylenediaminetetraacetic acid).**

EDTA is a weak acid dissociate in four steps :

$H_4y + H_2O \longrightarrow H_3y^- + H_3O^+$

$H_3y^- + H_3O^+ \longrightarrow H_2y^{-2} + H_3O^+$

$H_2y^{-2} + H_3O^+ \longrightarrow Hy^{-3} + H_3O^+$

$Hy^{-3} + H_3O^+ \longrightarrow y^{-4} + H_3O^+$

These values refer to that the first two protons are lost much more readily than the remaining two.

$CT = [H_4y] + [H_3y^-] + [H_2y^{-2}] + [Hy^{-3}] + [y^{-4}]$

It found that EDTA values depend upon the pH of the solution, which is :

- a) when pH (3 - 6), H_2y^{-2} is predominant.

- b) when pH (6 -10), Hy^{-3} is predominant.

- c) at pH > 10 , y^{-4} is predominant .

- **EDTA** is hexadentate because each nitrogen atom has an unshared pair of electrons in addition to four acidic hydrogens, thus, the molecule has six potential sites for bonding with a metal ion.

- **the presence of hydrophilic groups such as COOH, SO$_3$H, NH$_2$, and OH,** when both acidic and basic groups are present, the complex will be soluble over a wide pH range.

- **When hydrophilic groups are absent,** the solubilities of both the chelating agent and the metal chelate will be low, but they will be soluble in organic solvents

• Plotting precipitation titration curves

- • Consider the titration of Cl^- with a standard solution of $AgNO_3$.

- • Titration curve prepared by plotting **pCl (-log[Cl^-])** against the volume of **$AgNO_3$** in a manner similar to acid-base titration.

- • **Before titration started** – only have Cl^-.

$$\textbf{pCl = - log[Cl^-]}$$

- • **Titration proceed –** part of Cl^- is removed from solution by precipitation as AgCl.

$$\textbf{pCl = -log [remaining Cl^-]}$$

- • **At equivalence point -** we have solution a saturated solution of AgCl. $[Cl-] = \sqrt{KSP}$

- • **Excess AgNO$_3$ added –** excess Ag$^+$. [Cl$^-$] is determine from the concentration of Ag$^+$ and Ksp.

- **[Cl$^-$] = Ksp/[Ag$^+$]**

- Plots of titration curves are normally sigmoidal curves consisting of pAg (or pAnalyte) versus volume of AgNO$_3$ solution added.

- A useful relationship can be derived by taking the negative logarithm of both sides of a solubility-product expression. Thus, for silver chloride,

- $Ksp = [\,Ag^+]\,[Cl^-]$
- $logKsp = -\mathrm{log}(\,[Ag^+]\,[Cl^-]\,)$
- $-logKsp = -\,\mathrm{log}\,[Ag^+] + (-\,log\,[Cl^-])$
- $pKsp = pAg^+ + pCl^-$

- **EX. Derive a titration curve for the titration of 50ml of 0.1M NaCl with 0.1M AgNO$_3$, KSP AgCl = 1.82x10^{-10} ?**
- Notes :
- 1) In precipitation titration we are using molar and formal conc. and we are not using normal conc.
- 2) Precipitation titration methods are used to determine halogen ions.
- 3) Precipitation titration curves are plotted as :
- 4) Precipitation titration curve is influenced by the concentrations. of Ag$^+$ and Cl$^-$
- 5) Precipitation titration curve is influenced by KSP value (completeness of reaction). when the KSP value is small the titration curve is perfect.

- Answewer of example :
- a) before adding AgNO3 :

  - NaCl → Na⁺ + Cl⁻

    0.1   0.1   0.1

- pCl = - log [Cl⁻] = - log 0.1 = 1
- pAg = zero

- b) after adding 10 mL of $AgNO_3$:

  NaCl   + $AgNO_3$ → AgCl + $NaNO_3$
  (50x0.1)   (10x0.1)   0
      5   1   0
      4   0   1
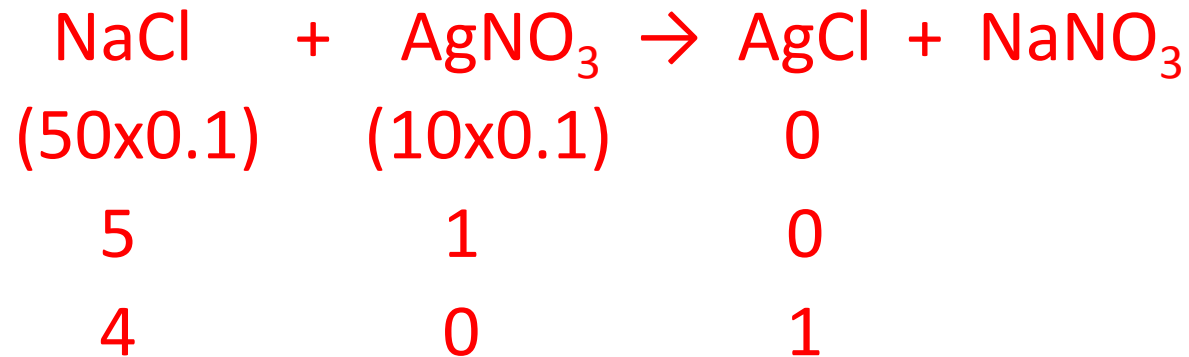
- $[Cl^-] = \dfrac{4}{60} = 6.7 \times 10^{-2}$
- $pCl = -\log 6.7 \times 10^{-2} = 1.17$
- $[Ag^+] = \dfrac{KSP}{[Cl^-]} = \dfrac{1.82 \times 10^{-10}}{6.7 \times 10^{-2}} = 2.7 \times 10^{-9}$
- $pAg = -\log 2.7 \times 10^{-9} = 8.57$
- c) when adding 49.95ml of $AgNO_3$:

  - $NaCl + AgNO_3 \rightarrow \quad AgCl + NaNO_3$

	(50x0.1)	(49.95x0.1)	0
	5	4.95	0
	0.05	0	0.05

- $[Cl-] = \dfrac{0.05}{99.95} = 5 \times 10^{-5}$
- $pCl = -\log 5 \times 10^{-5} = 4.3$
- $[Ag^+] = \dfrac{KSP}{[Cl^-]} = \dfrac{1.82 \times 10^{-10}}{5 \times 10^{-10}} = 0.36 \times 10^{-5}$ $pAg = -\log 0.36 \times 10^{-5},\ \ pAg = 5.44$
-

- d) at equivalent point , when adding 50ml of $AgNO_3$:

    - $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$

-                     (50x0.1)   (50x0.1)   0

-                         5   5   0

-                         0   0   5

- $[Ag^+] = [Cl^-] = 1.82x10^{-10}$

- $[Cl-]^2 = 1.82x10^{-10}$

- $[Ag^+] = [Cl^-] = 1.35x10^{-5}$

- pCl = pAg = 4.87

- e) after adding 52.5ml of AgNO3 :

  - $NaCl$ + $AgNO_3$ → $AgCl$ + $NaNO_3$
-              (50x0.1)   (52.5x0.1)   0
-                   5   5.25   0
-                   0   0.25   0.25

- $[Ag^+] = \dfrac{0.25}{102.5} = 2.4 \times 10^{-3}$
- $[Cl^-] = \dfrac{1.82 x 10^{-10}}{2.4 x 10^{-3}} =$
- pAg = 2.62
- pCl = 7.12

Factors affecting the solubility of precipitates

- **Solubility is important factor in gravimetric analysis which requires pure material. This means there is a need for washing the precipitate to remove impurities and obtain pure precipitate .**

1 - Nature of the precipitate: If the attraction between solvent molecules and solute ions is higher than that between solute ions in the crystal then the salt is soluble.

2 - Nature of solvent: Two properties of the solvent affecting the solubility of the solute, these are **polarity and dielectric value** . Solvent of more polarity means more attraction between solute ions and solvent molecules. The attraction at crystal surface decreases with higher electric constant of the solvent. Water as with high **polarity and dielectric constant value** is a good solvent for nearly all inorganicionic salts .Organic solvents such as chloroform, alcohols are good solvents for organic salts (non polar compounds) .

- 3 - Temperature : Higher temperature means higher solubility ; in water this solubility process in endothermic.

- 4 - Common ion effect: The ion that forms the precipitate is the common ion if the solvent contain these common ions. The solubility of the salts decreases compared with pure solvents. Other uncommon ions increases the solubility.

5 - pH value :The concentration of hydrogen ion and hydroxide ions affect the acidity of the solution and hence the solubility of sparingly soluble solute.

- Ex.1. If the solubility of AgBr= 2×10^{-5} g/100ml at 20°C, calculate Ksp value? (M.Wt=187.8 g/mole)

- The solubility should be calculated in unit of mole/liter

- Concentration   volume

- 2×10^{-5} 100 ml

-           x   1000 ml

$$X= \frac{2 x 10^{-5} x 1000}{100} = 2 \times 10^{-4} \text{ g / L}$$

Concentration mole/L= (solute weight (g)/L) / F. Wt

Or: Concentration mole/L= (solute weight (g)/L) / M.Wt

$$X= \frac{2 x 10^{-4}}{187.8} = 1.065 \times 10^{-6} \text{ mol/ L}$$

- This means that 1.065×10^{-6} mole of AgBr is dissolved in one liter of solution (available as ions). Therefore each liter of the solution contains:

- $[Ag^+] = 1.065 \times 10^{-6}$ mole/L

- $[Br^-] = 1.065 \times 10^{-6}$ mole/L 2×10^{-5}

- Or: M = mole/L

- M= $\dfrac{Wt}{M.Wt}$ x $\dfrac{1000}{VmL}$ = $\Rightarrow$ M= $\dfrac{2 X 10^{-5}}{187.8}$ x $\dfrac{1000}{100}$

- =1.065×10^{-6} mole/L

- Ksp can be calculated as follows:

- AgBr $\rightleftharpoons$ Ag^+ + Br^-

- Ksp = $[Ag^+][Br^-]$ = $1.065 X 10^{-6}$ mole/L x $1.065 X 10^{-6}$ mole/L

- = $1.134 X 10^{-12}$

# ANALYTICAL CHEMISTRY

LECTURE- 5
BY

Dr. ABBAS HASAN FARIS

Oxidation-Reduction Reactions

- An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

- Often called **"redox"** reactions

- • Electrons are transferred between the reactants

- One substance is **oxidized**, loses electrons

- **Reducing agent**

- Another substance is **reduced**, and gains electrons

- **Oxidizing agent**

- • Oxidation numbers change during the reaction

4.4 Oxidation-Reduction / Redox Reactions

$$Zn\ (s) + CuSO_4\ (aq) \longrightarrow ZnSO_4\ (aq) + Cu\ (s)$$
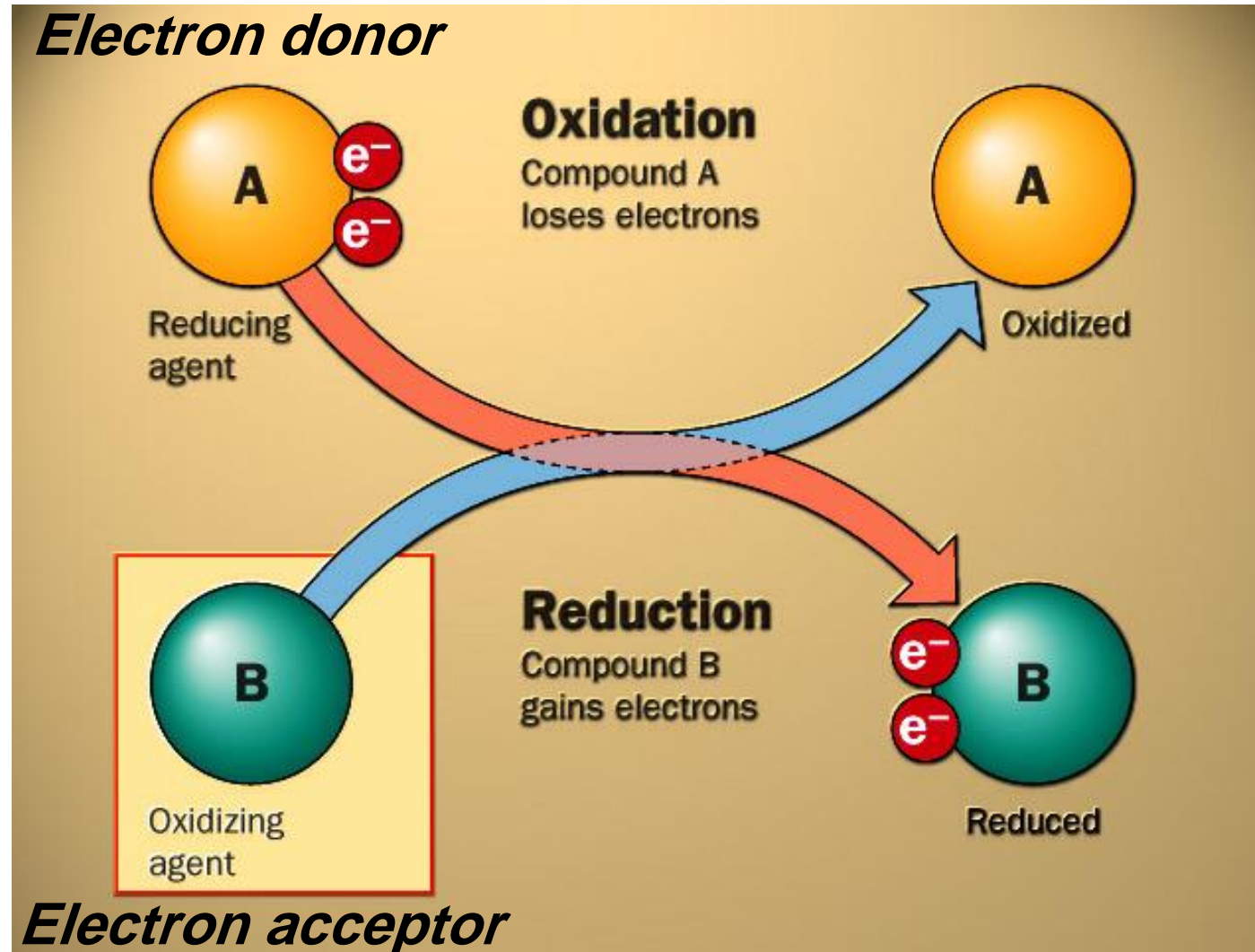
$Zn \longrightarrow Zn^{2+} + 2e^-$ Zn is oxidized   Zn is the **reducing agent**

$Cu^{2+} + 2e^- \longrightarrow Cu$ Cu^{2+} is reduced Cu^{2+} is the **oxidizing agent**

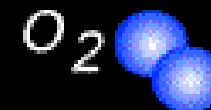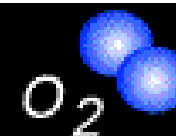Copper wire reacts with silver nitrate to form silver metal.
What is the oxidizing agent in the reaction?

$$Cu\ (s) + 2AgNO_3\ (aq) \longrightarrow Cu(NO_3)_2\ (aq) + 2Ag\ (s)$$

$Cu \longrightarrow Cu^{2+} + 2e^-$ Cu is oxidized   Cu is the **reducing agent**

$Ag^+ + 1e^- \longrightarrow Ag$ Ag^+ is reduced Ag^+ is the **oxidizing agent**

Chemical Equations are simple.
$$2H_2 + O_2 \rightarrow 2H_2O$$

$$\overset{0}{2H_2} + \overset{0}{O_2} \longrightarrow \overset{+1\ -2}{2H_2O}$$

$$4Fe + 3O_2$$

4
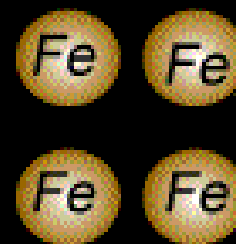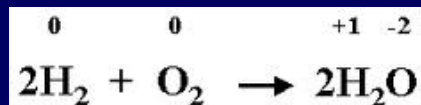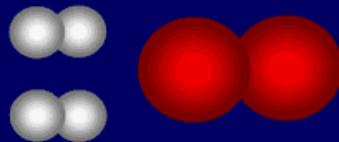
6.4.4 Oxidation–Reduction (Redox) Reactions

An oxidation–reduction reaction occurs when electrons move from one reactant to another reactant. As a result of this electron transfer, these reactants undergo a change in oxidation state. Those reactants that experience an increase in oxidation state undergo **oxidation**, and those experiencing a decrease in oxidation state undergo **reduction**. For example, in the following redox reaction between Fe^{3+} and oxalic acid, $H_2C_2O_4$, iron is reduced because its oxidation state changes from +3 to +2.

$$2Fe^{3+} (aq) + H_2C_2O_4 (aq) + 2H_2O(l) \rightleftharpoons 2Fe^{2+} (aq) + 2CO_2(g) + 2H_3O^+ (aq) \qquad (6.4.53)$$
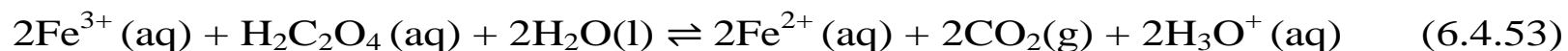
Oxalic acid, on the other hand, undergoes oxidation because the oxidation state for carbon increases from +3 in $H_2C_2O_4$ to +4 in CO_2.

We can divide a redox reaction, such as reaction 6.4.53, into separate **half-reactions** that show the oxidation and the reduction processes.

$$H_2C_2O_4 (aq) + 2H_2O (l) \rightleftharpoons 2CO_2(g) + 2H_3O^+(aq) + 2e- \qquad (6.4.54)$$

$$Fe^{3+} (aq) + e- \rightleftharpoons Fe^{2+} (aq) \qquad (6.4.55)$$
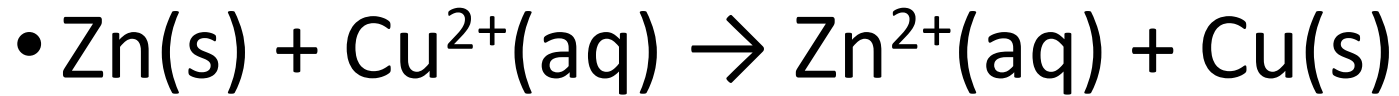
- **Example**
- $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$
- $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
- Zinc is **losing 2** electrons and **oxidized**.
- **Reducing agent**
- $Zn(s) \rightarrow Zn^{2+}(aq) + 2e\text{-}$
- Copper ions are **gaining the 2** electrons.
- **Oxidizing agent**
- $Cu^{2+}(aq) + 2e\text{-} \rightarrow Cu(s)$
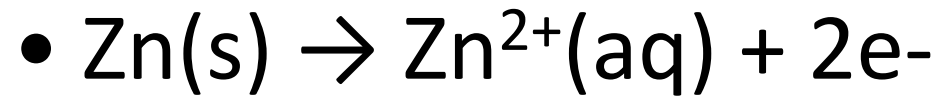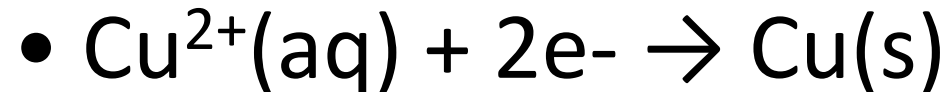
- Rules for assigning oxidation numbers
- **1. Elements (uncombined) are 0.**
- Al, N2, He, Zn, Ag, Br2, O2, O3
- **2. Oxidation numbers must sum to the overall charge of the species.**
- $(SO_4)^{2-}$ = -2 (O is usually -2 so....)
- ? + 4(-2) = -2
- Solve: ? - 8 = -2 ? = + 6 (S)

- Balancing redox reactions
- – Electrons (charge) must be balanced as well as number and types of atoms – Consider this net ionic reaction:
  - $Al(s) + Ni^{2+}(aq) \rightarrow Al^{3+}(aq) + Ni(s)$
- – The reaction appears balanced as far as the number and type of atoms are concerned, but look closely at the charge on each side.
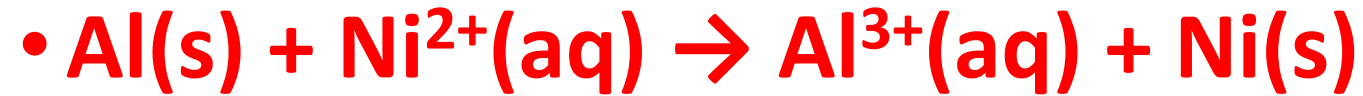
- **Al(s) + Ni^{2+}(aq) → Al^{3+}(aq) + Ni(s)**

- – Divide reaction into two half-reactions

- **Al(s) → Al^{3+}(aq) + 3e-**

- **Ni^{2+}(aq) + 2e- → Ni(s)**

- – Multiply by a common factor to equalize electrons (the number of electrons lost must equal number of electrons gained)

- **2 [Al(s) → Al^{3+}(aq) + 3e-]**

- **3 [Ni^{2+}(aq) + 2e- → Ni(s)]**

- Cancel electrons and write balanced net ionic reaction
  - $2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^-$
  - $3Ni^{2+}(aq) + 6e^- \rightarrow 3Ni(s)$

-

  - $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$
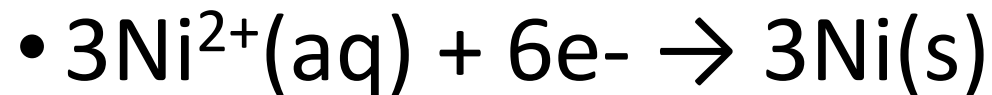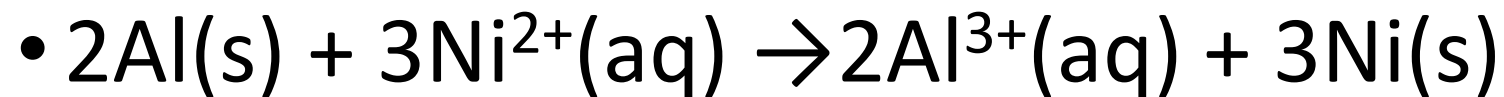
- **Reagent EDTA**

- **Disodium salt** of EDTA is a water-soluble chelating agent and is always preferred. It is non-hygroscopic and a very stable sequestering agent.

- **EDTA has the broadest general application because:**

1. It has a low price

2. The unique structure, which has six ligands atoms

3. It forms strainless five-membered rings

- The selectivity of EDTA can be increased by the following procedures: **Masking and demasking agent**

- • **Masking agents:** Protects some components of the analyte from reacting with EDTA. These reagents form complexes with interfering ions which are more stable than complexes formed with EDTA.

- **Masking agents:** A reagent added to prevent reaction of some metal ion with EDTA (block metal ions)
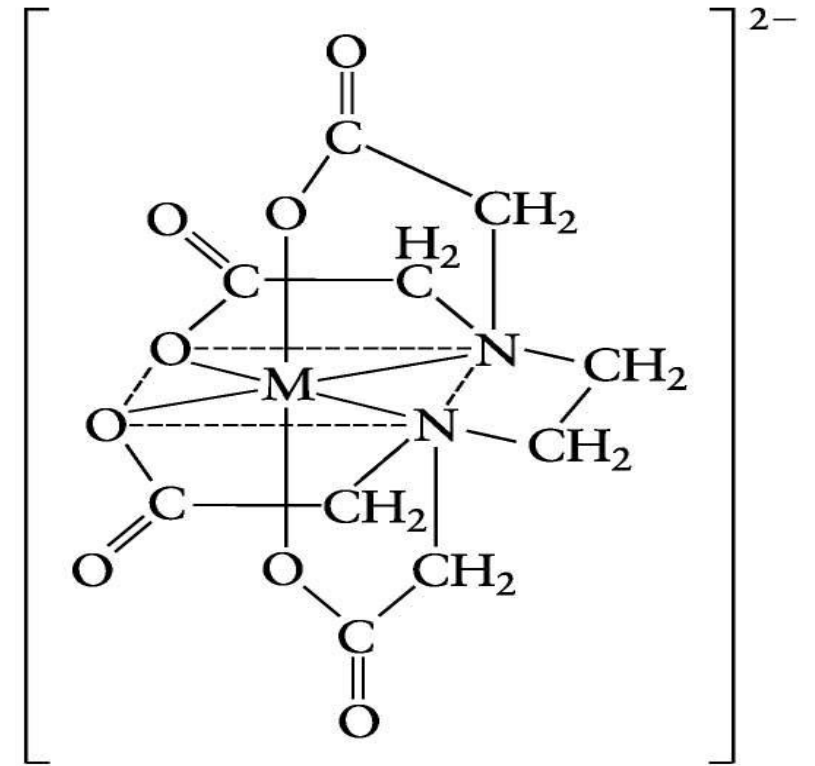
- • Examples of masking agent: (give examples of masking agent)

- **KCN:** It is used as masking agent for $Ag+$, Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, … etc.

  - $M^+ + 2CN^- \qquad [M(CN)_2]^-$
  - $M^+ + 4CN^- \longrightarrow [M(CN)4]^{2-}$

- **Triethanolamine:** It is used as masking agent for Fe^{3+}, Al^{3+} and $Sn2+$

- **Fluoride (e.g. NH_4F):** It is used as masking agent for **Fe^{3+}** and **Al^{3+}** to give $[FeF_6]^{3-}$ and $[AlF_6]^{3-}$

- **Iodide (KI):** It is used as masking agent for **Hg^{2+}** to give tetraiodo complex **(HgI_4)**

- • **Demasking agent:** Releasing masking agent from the analyte.
- **Reagents that release of a metal ion from a masking agent**
- **Example:**
- • Example of using masking and demasking agents in complexometry is the analysis of 3 metals, Cu, Cd, and Ca. The following method of analysis is followed
- Step 1: All metals are titrated
- Ca   Ca-EDTA
- Cd   +   EDTA   ⇌   Cd-EDTA
- Cu   Cu-EDTA
- **How can we determine a mixture of metals using complexometric titration?**
- Step 2: Only Ca titrated
- [Cu, Cd]   +   cyanide ion   →   [Cu-cyanide]complex] EDTA
-   [Cd-cyanide]complex] EDTA

- **Ca + cyanide** $\longrightarrow$ **ion no reaction** **EDTA** $\longrightarrow$ **Ca-EDTA**
- • Step 3: Cd and Ca are titrated
- [Cd-cyanide]complex + HCHO $\rightleftharpoons$ Cd^{2+} (free)

- **demasking agent**
- [Cu-cyanide]complex + HCHO   no reaction

- Cd   Cd-EDTA
-           + EDTA $\rightleftharpoons$
- Cu   Cu-EDTA

- Oxidation with H$_2$O$_2$ releases Cu^{2+} from [Cu$^+$ -Thiourea] complex.

Titration curves

• For derivation of the titration curve,

consider the titration of 50.0 mL of 0.1 M solution of Mg^{2+} (buffered at pH 10) with 0.1 M EDTA solution.

We calculate the concentration of Mg^{2+} (as pMg= -log(Mg) and plotted versus the volume added from ETDA

1) **pMg before the addition of EDTA**

Mg^{2+} = 0.1 M , so, pMg=-log (0.1)=1.0

At start of Titration when no titrant EDTA is added to the solution, only Mg^{2+} , will be present in the solution. The concentration of Mg^{2+} can be given as,

- **2) pMg after adding 10.0 mL EDTA, we will calculate the remaining unchelated Mg solution in the whole solution (60 ml)**

- Mg^{+2} + y^{-4} $\longrightarrow$ Mgy^{-2}

- 50×0.1 $\quad$ 10×0.1 $\qquad\qquad$ 0

- $\quad 5$ $\qquad\qquad$ 1 $\qquad\qquad\qquad$ 0

- $\quad 4$ $\qquad\qquad$ 0 $\qquad\qquad\qquad$ 4

- $M_{Mg}^{+2}\, unreacted = \dfrac{(50\times0.1)-(10\times0.1)}{50+10}$ = 0.067 M

- P_{Mg} = -log(0.067) =1.17

3) pMg after adding 25.0 mL EDTA, we will calculate the remaining unchelated Mg solution in the whole solution (75 ml)

$M_{Mg\ +\ 2}\, unreacted = \dfrac{(50\times0.1)\,(25\times0.1)}{50+25}$ = 0.033 M

P_{Mg} = -log(0.033) =1.48

- **4) pMg at the equivalence point**
- At this Point, 50 mL of EDTA have been added to completely react with Mg solution
- We will use the stability constant to calculate the pMg

$$Mg^{+2} + y^{-4} \longleftrightarrow MgY^{-2}$$
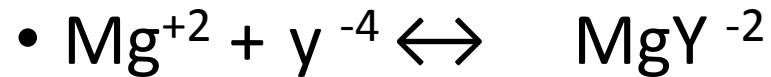
	50×0.1	50×0.1	0
	5	5	0
	0	0	5-a

- $K_{stab} = \dfrac{(MgY^{-2})}{(Mg^{2+})(Y^{-4})} = 5 \times 108$
- Concentration of MgY^{2-} is calculated as follows
- $M_{Mg}^{+2} = \dfrac{50 \times 0.1}{50+50}$ = 0.05 M
- $M_{MgY}^{-2} = \dfrac{50 \times 0.1}{50+50}$ = 0.05 — a

- Substitute at equation $K_{stab} = \dfrac{(0.05 - a)}{a^2} = 5 \times 10^8$

- **a, is neglected because it is very small relative to 0.05**

- **So,** $\dfrac{(0.05 - a)}{a^2}$ **a=(Mg^{+2}) =1.0×10^{-5}, P$_{Mg}$ = 5.0**

5) pMg, beyond the equivalence point:

By adding 60 mL of the 0.1 M EDTA

$$M_{MgY\,-2} = \frac{50*0.1}{50+60} - a$$

Neglect the term a

and then substitute (MgY^{2-}) of 5/110 M in K$_{stab}$ equation

- There will be an excess from EDTA

- $Y^{-4} = \dfrac{(60 \times 0.1)\,(50 \times 0.1)}{50+60} = 1/110$

- $\dfrac{5/110}{(1/110)\,\times (a)} = 5.0 \times 108$

- **a =1x10^8 M   And pMg=8.0**

The titration curve is plotted by using the previous data

Volume added (ml)EDTA   pMg

Oxidation-Reduction/ Redox Reactions

(electron transfer reactions)

Example: formation of MgO from Mg and O_2

Oxidation reaction: half-reaction involves lose e^-	*Reduction reaction:* half-reaction involves gain e^-
$2Mg \longrightarrow 2Mg^{2+} + 4e^-$	$O_2 + 4e^- \longrightarrow 2O^{2-}$

Half reaction: Reaction that shows e^- involved in redox reaction

$$2Mg + O_2 + 4e^- \longrightarrow 2Mg^{2+} + 2O^{2-} + 4e^-$$

$$2Mg + O_2 \longrightarrow 2MgO$$
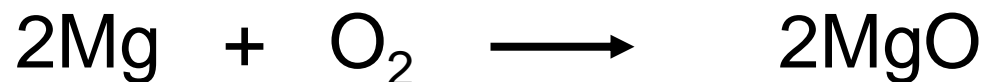
Oxidized

Reduced

Reducing Agent: donates electrons to O_2 and causes O_2 to be reduced

Oxidizing Agent: accepts electrons from Mg and causes Mg to be oxidized

Thermodynamics of Redox Reactions

Unlike precipitation reactions, acid–base reactions, and complexation reactions, we rarely express the equilibrium position of a redox reaction using an equilibrium constant. Because a redox reaction involves a transfer of electrons from a reducing agent to an oxidizing agent, it is convenient to consider the reaction's thermodynamics in terms of the electron.

For a reaction in which one mole of a reactant undergoes oxidation or reduction, the net transfer of charge, Q, in coulombs is

$$Q = nF \hspace{6cm} (6.4.56)$$

where n is the moles of electrons per mole of reactant, and F is Faraday's constant (96,485 C/mol). The free energy, ΔG, to move this charge, Q, over a change in **potential**, E, is

$$\Delta G = EQ \hspace{6cm} (6.4.57)$$

The change in free energy (in kJ/mole) for a redox reaction, therefore, is

$$\Delta G = -nFE \hspace{6cm} (6.4.58)$$

The electrical potential is a measure of the relative energy of an electron on a molecule/atom.
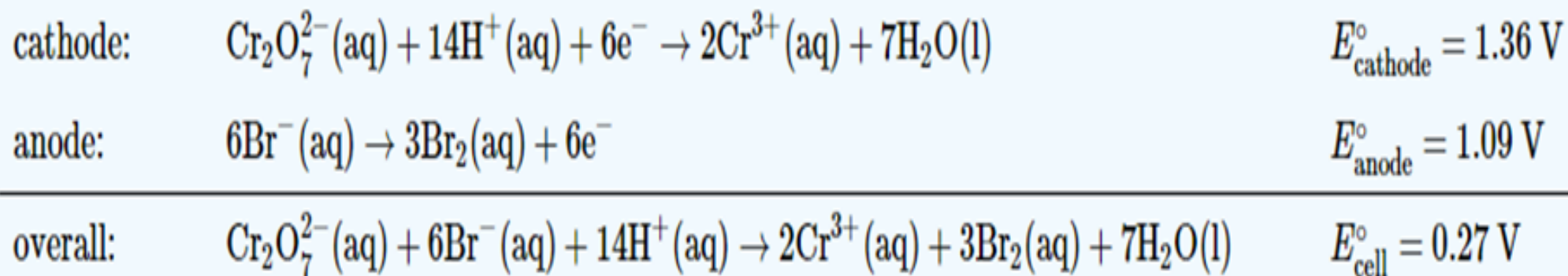
- When $\Delta G^0 < 0$, energy is released and reactions proceed without added energy. When $\Delta G^0 > 0$, energy is required to make a reaction proceed. It is possible for NO_2 - to oxidize H_2O to O_2, but this would require additional energy. Reduction potential values can be used to calculate ΔG^0 according to the Nernst Equation:

$$\Delta G = -nF\Delta E^o$$

- **n = number of e- transferred**
- **F = Faraday constant (23 kcal V^{-1} mol^{-1})**
- **ΔE^0 = E^0 (oxidizing agent) - E^0 (reducing agent)= E^o (reduction) – E^o (oxidation)**
- **ΔE^0 and ΔG^0 have opposite signs, so when $\Delta E^0 > 0$, then ΔG^0 will be negative**
- Since a redox reaction is spontaneous, the amount of energy released must be greater than the amount of energy absorbed. Thus, all redox reactions are exothermic in nature.

- A spontaneous redox reaction is characterized by a negative value of $\Delta G°$, which corresponds to a positive value of $E°_{cell}$.

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Equilibrium Constant and Free Energy Change for an Electrochemical Cell

- Two important parameters that can be determined from a cell potential are the **equilibrium constant** for the cell reaction and the **free energy** change for the cell reaction.

- 1- Determining the Equilibrium Constant from E^o_{cell}

- 2- Determining the Standard State Free Energy Change from E^o_{cell}

- 3- Determining the Non-Standard Free Energy Change

- To calculate the **equilibrium constant** for an electrochemical cell we need to know:

- **the standard state potential for a cell**

- **the half-reactions involved**

- **The Nernst equation is used in calculating the equilibrium constant.**

cathode:	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	$E^\circ_{cathode} = 1.36\ V$
anode:	$6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-$	$E^\circ_{anode} = 1.09\ V$
overall:	$Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)$	$E^\circ_{cell} = 0.27\ V$

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We can now calculate ΔG° using Equation 20.5.7. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\Delta G^\circ = -(n)(F)(E^\circ_{cell})$$
$$= -(6\ mole)[96,485\ J/(V \cdot mol)(0.27\ V)]$$
$$= -15.6 \times 10^4\ J$$
$$= -156\ kJ/mol\ Cr_2O_7^{2-}$$

- The free energy change of any reaction is given by the following

$$\Delta G = \Delta G^0 + RT \ln \frac{[products]}{[reactants]}$$

$$-nF\Delta E = -nF\Delta E^\circ + RT \ln \frac{[products]}{[reactants]}$$

$$\Delta E = \Delta E^\circ - \frac{RT}{nF} \ln \frac{[products]}{[reactants]}$$

When Ecell = + the reaction proceeds spontaneously to the right. As the reaction proceeds the E+cell becomes smaller and smaller until eventually it reaches zero. An Ecell= 0 means that there is no net reaction occurring and that the cell has reached equilibrium. When Ecell = 0 The Q term in the Nernst equal equals to **K (Q = K)**

$E = E^O — \log K$ Where K = equilibrium constant

and

$E^\circ = \dfrac{0.0592}{n} \log K$

- The Nernst equation allows the reduction potential to be calculated at any temperature and concentration of reactants and products; **the standard reaction potential must be measured at 298K and with each solution at 1M.**

- **The Nernst equation is:**

- $E^0{}_{cell} = \dfrac{RT}{nF} \ln Q$

- E: is the reduction potential for the specified non-standard state

- E_0 : is the standard reduction potential

- R: and F are the gas and Faraday constants, respectively

- N: is the number of electrons transferred in the reaction

- If T is held constant at 298K, the Nernst equation can be condensed using the values for the constants R and F:

-
  At equilibrium **Q = K**. Substituting in K for Q, and the values for R, T, and F, we get:

- $E^0{}_{cell} = \dfrac{0.0257}{n} \ln Q = E^0{}_{cell} = \dfrac{0.0592}{n} \log K$

- $\Delta G = \Delta G^0 + RT \ln Q$

- $- nF\ E_{cell} = - nF\ E^0{}_{cell} + RT \ln Q$

- It can be further simplified if the reaction has reached equilibrium, as in that case Q is the equilibrium constant K:

- This equation allows the equilibrium constant to be calculated just from the standard reduction potential and the number of electrons transferred in the reaction

- $\ln K = \dfrac{nE_0}{0.0257}$

- $\log K = \dfrac{nE_0}{0.0592}$

Standard Potentials

A redox reaction's **standard potential**, E^o, provides an alternative way of expressing its equilibrium constant and, therefore, its equilibrium position. Because a reaction at equilibrium has a ΔG of zero, the potential, E, also must be zero at equilibrium. Substituting these values into equation 6.4.61 and rearranging provides a relationship between E^o and K.

$$E^o = \frac{0.05916}{n} \log K \qquad\qquad (6.4.62)$$

Note

A standard potential is the potential when all species are in their standard states. You may recall that we define standard state conditions as: all gases have partial pressures of 1 atm, all solutes have concentrations of 1 mol/L, and all solids and liquids are pure.

We generally do not tabulate standard potentials for redox reactions. Instead, we calculate E^o using the standard potentials for the corresponding oxidation half-reaction and reduction half-reaction. By convention, standard potentials are provided for reduction half-reactions. The standard potential for a redox reaction, E^o, is

$$E^\circ = E^\circ_{red} - E^\circ_{ox} \qquad\qquad (6.4.63)$$

where E^o_{red} and E^o_{ox} are the standard reduction potentials for the reduction half-reaction and the oxidation half-reaction.

$$E_{\text{Box/Bred}} = E_{\text{Aox/Ared}}$$

   This is an important observation because we can use either half-reaction to monitor the titration's progress.

Before the equivalence point the titration mixture consists of appreciable quantities of the titrand's oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we use the Nernst equation for the titrand's half-reaction

$$E_{\text{rxn}} = E^o_{\text{Aox}/\text{Ared}} - \frac{RT}{nF} \ln \frac{[A_{\text{red}}]}{[A_{\text{ox}}]}$$

**Note** : Although the Nernst equation is written in terms of the half-reaction's standard state potential, a matrix-dependent **formal potential** often is used in its place. See Appendix 13 for the standard state potentials and formal potentials for selected half-reactions.

After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E_{\text{rxn}} = E^o_{\text{Box}/\text{Bred}} - \frac{RT}{nF} \ln \frac{[B_{\text{red}}]}{[B_{\text{ox}}]}$$

Because we cannot measure the potential for a single half-reaction, we arbitrarily assign a standard reduction potential of zero to a reference half-reaction and report all other reduction potentials relative to this reference. The reference half-reaction is

$$2H_3O^+(aq) + 2e- \rightleftharpoons 2H_2O\ (l) + H_2(g) \qquad\qquad (6.4.64)$$
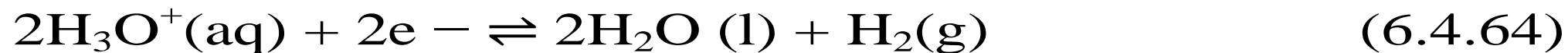
Appendix 13 contains a list of selected standard reduction potentials. The more positive the standard reduction potential, the more favorable the reduction reaction under standard state conditions. Thus, under standard state conditions the reduction of Cu^{2+} to Cu ($E° = +0.3419$ V) is more favorable than the reduction of Zn^{2+} to Zn ($E° = -0.7618$ V).

Example 6.5

Calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential when $[Ag^+] = 0.020$ M and $[Cd^{2+}] = 0.050$ M, for the following reaction at 25°C.

$$Cd\ (s) + 2Ag^+(aq) \rightleftharpoons 2Ag\ (s) + Cd^{2+}(aq) \qquad\qquad (6.4.65)$$

Solution

(a) In this reaction Cd is undergoing oxidation and Ag^+ is undergoing reduction. The standard cell potential, therefore, is

$$E° = E°_{Ag+/Ag} - E°_{Cd^{2+}/Cd} = 0.7996-(-0.4030) = 1.2026 \text{ V} \qquad (6.4.66)$$

(b) To calculate the equilibrium constant we substitute appropriate values into equation 6.4.62.

$$E° = 1.2026 \text{ V} = \frac{0.05916 \text{ V}}{2} \log K \qquad (6.4.67)$$

Solving for K gives the equilibrium constant as

$$\text{Log K} = 40.6558 \qquad (6.4.68)$$

$$K = 4.527 \times 10^{40} \qquad (6.4.69)$$

(c) To calculate the potential when $[Ag^+]$ is 0.020 M and $[Cd^{2+}]$ is 0.050 M, we use the appropriate relationship for the reaction quotient, Q, in equation 6.4.61.
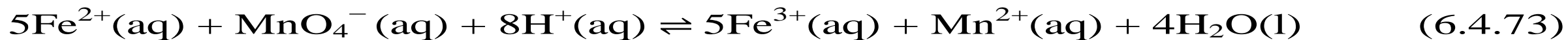
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$$E = E° - \frac{0.05916 \text{ V}}{n} \log \frac{[Cd^{2+}]}{[Ag^+]^2} \qquad (6.4.70)$$

$$E = 1.2606 \text{ V} - \frac{0.05916 \text{ V}}{2} \log \frac{(0.050)}{(0.020)^2} \qquad (6.4.71)$$

$$E = 1.14V \qquad\qquad (6.4.72)$$

Practice Exercise 6.4

For the following reaction at 25°C

$$5Fe^{2+}(aq) + MnO_4^- (aq) + 8H^+(aq) \rightleftharpoons 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l) \qquad (6.4.73)$$

calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential under these conditions: $[Fe^{2+}] = 0.50$ M, $[Fe^{3+}] = 0.10$ M, $[MnO_4^-] = 0.025$ M, $[Mn^{2+}] = 0.015$ M, and a pH of 7.00. See Appendix 13 for standard state reduction potentials.

The two half-reactions are the oxidation of Fe^{2+} and the reduction of MnO_4^-.

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$$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e-$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$

From <u>Appendix 13</u>, the standard state reduction potentials for these half-reactions are

$$E°_{Fe3+/Fe2+} = 0.771 \text{ V} \quad E°_{MnO4-/Mn2+} = 1.51 \text{ V}$$

(a) The standard state potential for the reaction is

$$E° = E°_{MnO4^- / Mn^{2+}} - E°_{Fe^{3+} / Fe^{2+}} = 1.51V - 0.771V = 0.74V$$

(b) To calculate the equilibrium constant we substitute appropriate values into <u>equation 6.4.62</u>.

$$E° = 0.74 \text{ V} = \frac{0.05916}{5} \log K$$

Solving for K gives its value as

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$$\text{Log } K = 62.5 \qquad K = 3.2 \times 10^{62}$$

(c) To calculate the potential under these non-standard state conditions, we make appropriate substitutions into the Nernst equation.

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$$

$$E = 0.74 - \frac{0.05916}{5} \log \frac{(0.015)(0.10)^5}{(0.025)(0.50)^5(1 \times 10^{-7})^8}$$

$$E = 0.74 - \frac{0.05916}{5} \log \frac{(0.015)(0.10)^5}{(0.025)(0.50)^5(1 \times 10^{-7})^8} = 0.12 \text{ V}$$

○

Note

When writing precipitation, acid–base, and metal–ligand complexation reaction, we represent acidity as H_3O^+. Redox reactions are more commonly written using H^+ instead of H_3O^+. For the reaction in Practice Exercise 6.4, we could replace H^+ with H_3O^+ and increase the stoichiometric coefficient for H_2O from 4 to 12, e.g.,

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H_3O^+(aq) \rightleftharpoons 5Fe^{3+}(aq) + Mn^{2+}(aq) + 12H_2O(l) \qquad (6.4.74)$$
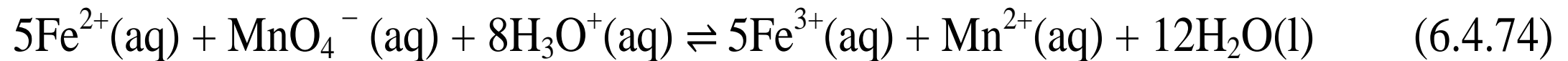
- **Example:**
    - **Calculate the equilibrium constant for the redox reaction at 25 ^0C ,**

$$\text{Sr(s) + Mg}^{+2}\text{ (aq)} \rightleftarrows \text{Mg(s) + Sr}^{+2}$$

- **that occurs in the Galvanic cell.**

$E^O{}_{Mg+2/Mg}$ **= -2.37 V and** $E^O{}_{Sr+2/Sr}$ **= -2.89 V**

Hint: As per the electrochemical series of the elements, the metals that are placed below in the series are reduced by accepting electrons in the presence of the elements that are placed higher in the electrochemical series. We shall calculate the value of $E^0{}_{cell}$ from the potential of cathode and anode given and use the formula given to find the equilibrium constant.

Formula Used: $E^0{}_{cell} = E^0{}_{reduction} - E^0{}_{oxidation}$

- **Complete Step By Step Solution**
- **Given that,**
- **Sr(s) + Mg²⁺ (aq) ⇌ Mg(s) + Sr²⁺ (aq) ,**
- as per this reaction, strontium is oxidized in the presence of magnesium to form strontium dispositive ions in the solution and the magnesium metal are discharged at the cathode. The equilibrium constant for the above reaction is as follows:
- $Kc = \dfrac{[Sr^{+2}][Mg]}{[Sr][Mg^{+2}]}$
- Now, this equilibrium constant is related to the cell potential by the Nernst Equation which is as follows:

$$\bullet\ E^0{}_{cell} = \frac{0.059}{n}\log K$$

- where, E^0_{cell} is the cell potential and n is the number of electrons transferred in the process. Since strontium gives up two electrons in the process to get oxidized hence **n = 2.**

- $E^0_{cell} = E^0_{reduction} - E^0_{oxidation}$

- As strontium is getting oxidized and magnesium is getting reduced, so the E^0_{cell} is,

- $E^0cell = E^0_{reduction} - E^0_{oxidation}$

- $E^0_{cell} = -2.37 - (-2.89) = 0.52$ V

- Now, $\Delta G^0 = -RT \ln K_{eq}$

- Or, $-\Delta nFE^0 = -RT \ln K_{eq}$

- Therefore, $\ln K_{eq} = \dfrac{-nF\Delta E^0}{RT} = \dfrac{2\times96500\times0.52}{8.314\times298} = 40.507$

- Therefore, $\ln K_{eq} = 40.507$,
- Or $K_{eq} = 3.908\times10^{17}$

Calculating the Titration Curve

Let's calculate the titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$. The reaction in this case is

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Ce^{3+}(aq) + Fe^{3+}(aq) \qquad\qquad 9.1$$

Note

In 1 M $HClO_4$, the formal potential for the reduction of Fe^{3+} to Fe^{2+} is +0.767 V, and the formal potential for the reduction of Ce^{4+} to Ce^{3+} is +1.70 V.

Because the equilibrium constant for reaction 9.1 is very large—it is approximately 6×10^{15}—we may assume that the analyte and titrant react completely.

Note

Step 1: Calculate the volume of titrant needed to reach the equivalence point.

The first task is to calculate the volume of Ce^{4+} needed to reach the titration's equivalence point. From the reaction's stoichiometry we know that

moles Fe^{2+} = moles Ce^{4+}

$M_{Fe} \times V_{Fe}$ = $M_{Ce} \times V_{Ce}$

Solving for the volume of Ce^{4+} gives the equivalence point volume as

$$V_{eq} = V_{Ce} = \frac{M_{Fe}V_{Fe}}{M_{Ce}} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{(0.100 \text{ M})} = 50.0 \text{ mL}$$

Note

Step 2: Calculate the potential before the equivalence point by determining the concentrations of the titrand's oxidized and reduced forms, and using the Nernst equation for the titrand's reduction half-reaction.

Before the equivalence point, the concentration of unreacted Fe^{2+} and the concentration of Fe^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Fe^{3+}/Fe^{2+} half-reaction.

$$E = E^o_{Fe^{3+}/Fe^{2+}} - \frac{RT}{nF}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = +0.767V - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

9.2

For example, the concentrations of Fe^{2+} and Fe^{3+} after adding 10.0 mL of titrant are

$$[Fe^{2+}] = \frac{\text{initial moles } Fe^{2+} - \text{moles } Ce^{4+} \text{ added}}{\text{total volume}} = \frac{M_{Fe}V_{Fe} - M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 6.67 \times 10^{-2} \text{ M}$$

$$[Fe^{3+}] = \frac{\text{moles } Ce^{4+} \text{ added}}{\text{total volume}} = \frac{M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 1.67 \times 10^{-2} \text{ M}$$

Substituting these concentrations into equation 9.2 gives a potential of

$$E = +0.767 \text{ V} - 0.05916 \log \frac{6.67 \times 10^{-2} \text{ M}}{1.67 \times 10^{-2} \text{ M}} = +0.731 \text{ V}$$

Note

   Step 3: Calculate the potential after the equivalence point by determining the concentrations of the titrant's oxidized and reduced forms, and using the Nernst equation for the titrant's reduction half-reaction.

   After the equivalence point, the concentration of Ce^{3+} and the concentration of excess Ce^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Ce^{4+}/Ce^{3+} half-reaction.

$$E = E^o_{Ce^{4+}/Ce^{3+}} - \frac{RT}{nF} \log \frac{[Ce^{3+}]}{[Ce^{4+}]} = +1.70\ V - 0.05916 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

For example, after adding 60.0 mL of titrant, the concentrations of Ce^{3+} and Ce^{4+} are

$$[Ce^{3+}] = \frac{\text{initial moles } Fe^{2+}}{\text{total volume}} = \frac{M_{Fe}V_{Fe}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(0.100\ M)(50.0\ mL)}{50.0\ mL + 60.0\ mL} = 4.55 \times 10^{-3}\ M$$

$$[Ce^{4+}] = \frac{\text{moles } Ce^{4+} \text{ added} - \text{initial moles } Fe^{2+}}{\text{total volume}} = \frac{M_{Ce}V_{Ce} - M_{Fe}V_{Fe}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(0.100\ M)(60.0\ mL) - (0.100\ M)(50.0\ mL)}{50.0\ mL + 60.0\ mL} = 9.09 \times 10^{-3}\ M$$

Substituting these concentrations into equation 9.3 gives a potential of

$$E = +1.70 \text{ V} - 0.05916 \log \frac{4.55 \times 10^{-2} \text{ M}}{9.09 \times 10^{-3} \text{ M}} = +1.66 \text{ V}$$

Note

Step 4: Calculate the potential at the equivalence point.

At the titration's equivalence point, the potential, E_{eq}, in equation 9.2 and equation 9.3 are identical. Adding the equations together to gives

$$2E_{eq} = E^{o}_{Fe^{3+}/Fe^{2+}} + E^{o}_{Ce^{4+}/Ce^{3+}} - 0.05916 \log \frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}$$

Because $[Fe^{2+}] = [Ce^{4+}]$ and $[Ce^{3+}] = [Fe^{3+}]$ at the equivalence point, the log term has a value of zero and the equivalence point's potential is

$$E = E^{o}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{nF} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} = +0.767\text{V} - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \qquad (9.16)$$

$$E = E^{o}_{Ce^{4+}/Ce^{3+}} - \frac{RT}{nF} \log \frac{[Ce^{3+}]}{[Ce^{4+}]} = +1.70 \text{ V} - 0.05916 \log \frac{[Ce^{3+}]}{[Ce^{4+}]} \qquad (9.17)$$

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + E^o_{Ce^{4+}/Ce^{3+}}}{2} = \frac{0.767 \text{ V} + 1.70 \text{ V}}{2} = 1.23 \text{ V}$$

Additional results for this titration curve are shown in Table 9.15 and Figure 1.

Table 9.15 Data for the Titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}

Volume of Ce^{4+} (mL)	E (V)	Volume Ce^{4+} (mL)	E (V)
10.0	0.731	60.0	1.66
20.0	0.757	70.0	1.68
30.0	0.777	80.0	1.69
40.0	0.803	90.0	1.69
50.0	1.23	100.0	1.70
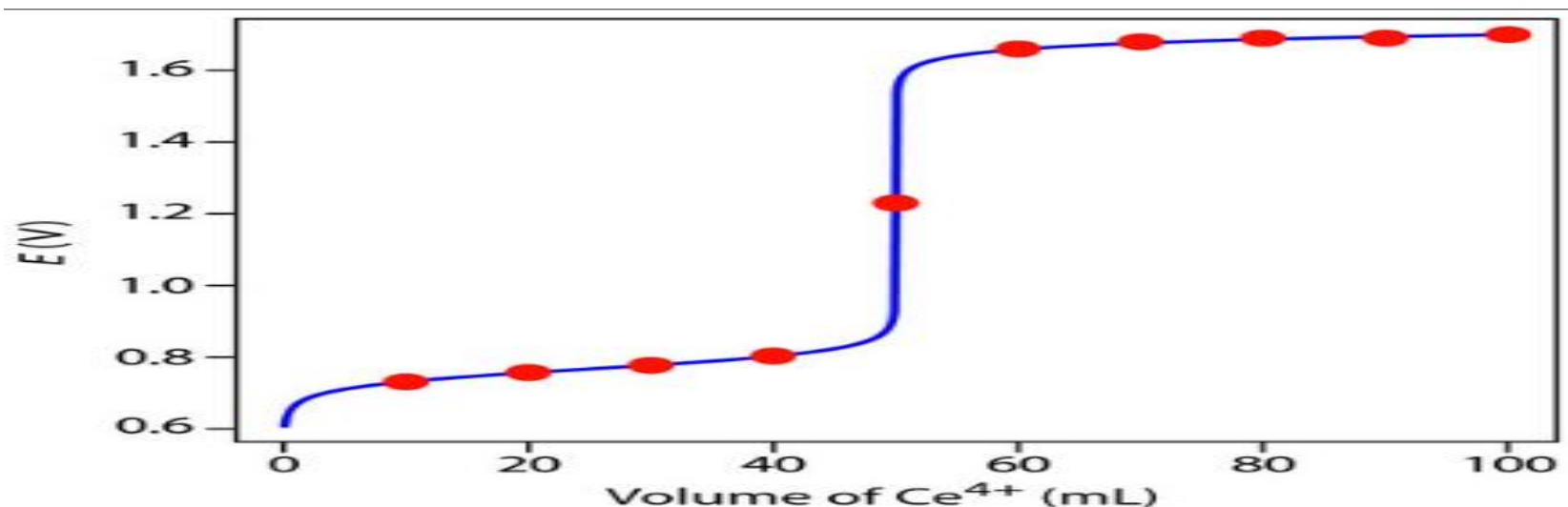
Figure 1 Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The red points correspond to the data in Table 9.15. The blue line shows the complete titration curve.

Practice Exercise 1

Calculate the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+} (aq) + Tl^{3+} (aq) \longrightarrow Sn^{4+} (aq) + Tl^{+} (aq)$$
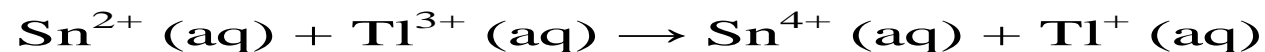
Sketching a Redox Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a

Concept of the Instrumental Chemical Analysis

Instrumental analysis is a field of analytical chemistry that investigates analytes using scientific instruments.

Classification of Instrumental Analytical Methods:-

1- **Qualitative** instrumental analysis is that measured property indicates presence of analyte in matrix

2- **Quantitative** instrumental analysis is that magnitude of measured property is

proportional to concentration of analyte in matrix

Species of interest: All constituents including **analyte** and **Matrix**-analyte (concomitants)

Often need pretreatment - **chemical extraction, distillation, separation, precipitation**

- **Classical:**
- **Qualitative -** identification by **color, indicators, boiling points, odors**
- **Quantitative - mass or volume (e.g. gravimetric, volumetric)**

- **Instrumental:**
- **Qualitative - chromatography**, **electrophoresis** and identification by measuring physical property (e.g. **spectroscopy, electrode potential**)
- **Quantitative -** measuring property and determining relationship to concentration (e.g. **spectrophotometry, mass spectrometry**) **Often, same instrumental method used for qualitative and quantitative analysis.**

- **Instrumental techniques**
- **1- Spectroscopic methods** - measuring the interaction between the analyte and electromagnetic radiation (or the production of radiation by an analyte).
- **2- Electroanalytic methods** - measure an electrical property (i.e., potential, current, resistance, amperes, etc.) chemically related to the amount of analyte.

- **Features of instrumental analysis methods compared to classical**

- 1- **More sensitive:** they can detect very small amounts of a substance in a small amount of sample that can be up to the **ppm**

- **2- More selective and quality**

- **3- great speed and accuracy** (they reliably identify elements and compounds)

- **4- Most of the methods are non-destructive**, that is used in cases that do not require destroying the sample

| Light Source | Collimator | Prism or Grating | Wavelength Selector | Sample Solution | Detector |
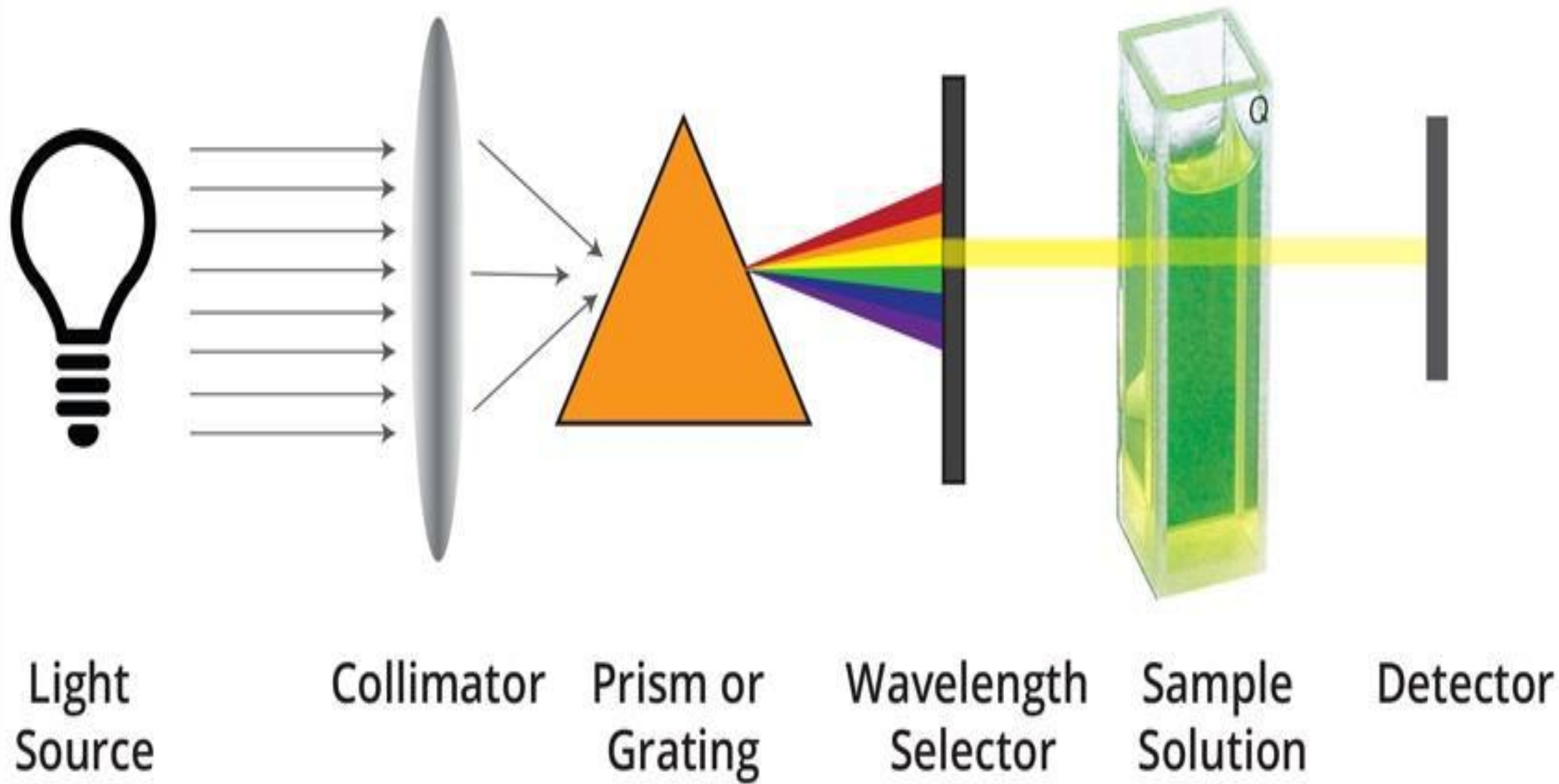
Spectroscopy

- **Spectroscopy** is a branch of science which studies the **interaction** of **electromagnetic radiation with matter** where the interaction of radiation with chemical species is measured to obtain characteristics quality and quantity of the species.

❖ Spectroscopic techniques can be divided in to two

➢ Atomic spectroscopy (**atomic absorption and atomic emission spectroscopy**)

➢ Molecular spectroscopy **(Uv-Vis, IR, NMR, MS)**

Electromagnetic radiation is a form of energy that is transmitted through space at enormous velocities. **Electromagnetic radiation, or light**, is described by the properties of both **waves and particles nature.**

A "particle" of light is called a photon.

- We can use different terms to describe light:

- **Color**

- **Wavelength**

- **Frequency**

- Light is composed of **electromagnetic waves** that travel through some medium.

- The properties of the medium determine how light travels through it.

- In a vacuum, light waves travel at a speed of **3.00×10^8 m/s OR 186,000 miles/s.**

- The speed of light in a vacuum is a constant that is tremendously important in nature and science—it is given the symbol, **c**

HIGH ENERGY   LOW ENERGY

γ rays   x rays   uv vis   ir   microwaves   radiowaves

10^{-3} 10^{-1} 10 10^3 10^5 10^7 10^9 10^{11}

Wavelength (nm)

Wavelength, nm	100	200	400	700	1000	2000	4000	7000	10,000	20,000	40,000
Spectral region	VAC	UV	Visible		Near IR		IR				Far IR

(a) Materials for cells, windows, lenses, and prisms

Lithium fluoride

Fused silica or quartz

Corex glass

Silicate glass

NaCl

KBr

TlBr or TlI

ZnSe

(b) Wavelength selectors

Fluorite prism

Fused silica or quartz prism

Glass prism

Continuum

NaCl prism

KBr prism

3000 lines/mm   Gratings   50 lines/mm

Interference wedge

Interference filters

Discontinuous

Glass filters

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The Electromagnetic Spectrum
Chart by LASP/University of Colorado, Boulder

|			
10^{-6} nm		Gamma-Rays	
10^{-5} nm			
10^{-4} nm			
10^{-3} nm			
10^{-2} nm			
10^{-1} nm	1 Å	X-Rays	Violet
1 nm			Indigo
10 nm			Blue
100 nm	UVIS EUV - 55.8-118nm UVIS FUV - 110-190nm	Ultraviolet	
10^3 nm	1 µm	Visible Light	Visible Light: ~400 nm – ~700 nm · Green
10 µm		Near Infrared	Yellow
100 µm		Far Infrared	Orange
1000 µm	1 mm		Red
10 mm	1 cm	Microwave	
10 cm			
100 cm	1 m	UHF	
10 m		VHF	
100 m		HF	
1000 m	1 km	MF	
10 km		LF	Radio
100 km			
1 Mm		Audio	
10 Mm			
100 Mm			

nm=nanometer, Å=angstrom, µm=micrometer, mm=millimeter,
cm=centimeter, m=meter, km=kilometer, Mm=Megameter

- An electromagnetic wave is characterized by several fundamental properties, including its **frequency, velocity, amplitude, phase angle, polarization, and direction of propagation.**

- Because light behaves like a **wave**, we can describe it in one of two ways—by its **wavelength or by its frequency.**

➢**Wavelength,¯λ":** the linear distance between successive maxima or minima of a wave. Mostly measured in nm = 10^{-9} m

➢The units of wavelength are the micrometer (1 μm = 10^{-6} m), usually called

➢micron. The unit widely used in spectroscopy is the angstrom (1A = 10^{-10}m).

➢ **Frequncȳ: (v)** the umber of oscillations of the field that occurs per second.

➢**Frequency (v) :** how many times the wave goes up and down in a period of time. n has units of inverse time (**1/s = Hz** [hertz]).
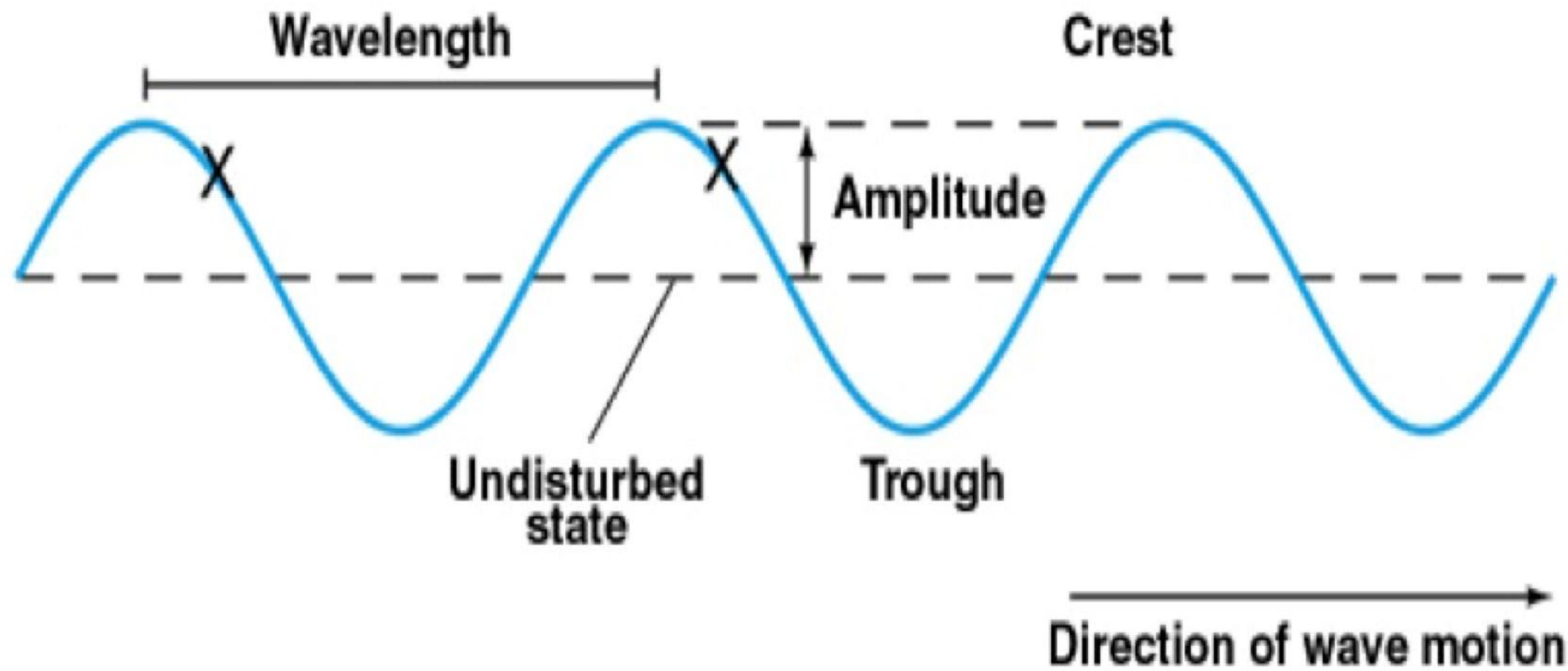
Electromagnetic Radiation

- Speed of light can be expressed as $C = v\lambda$

- where "λ" is the **wavelength;**

- v is the **frequency**, and c the **speed of light** in a medium.

- **c** = speed of light (3.00×10^8 m/s)

- λ = wavelength (m)

- v = frequency (s^{-1})

- The **type of light** (ultraviolet, visible, infrared, x-ray, etc.) is **defined** by either its **frequency or wavelength:**

- The higher the frequency, the higher the energy of radiation a photon of high frequency (short wavelength) has higher energy content than one of lower frequency (longer wavelength).
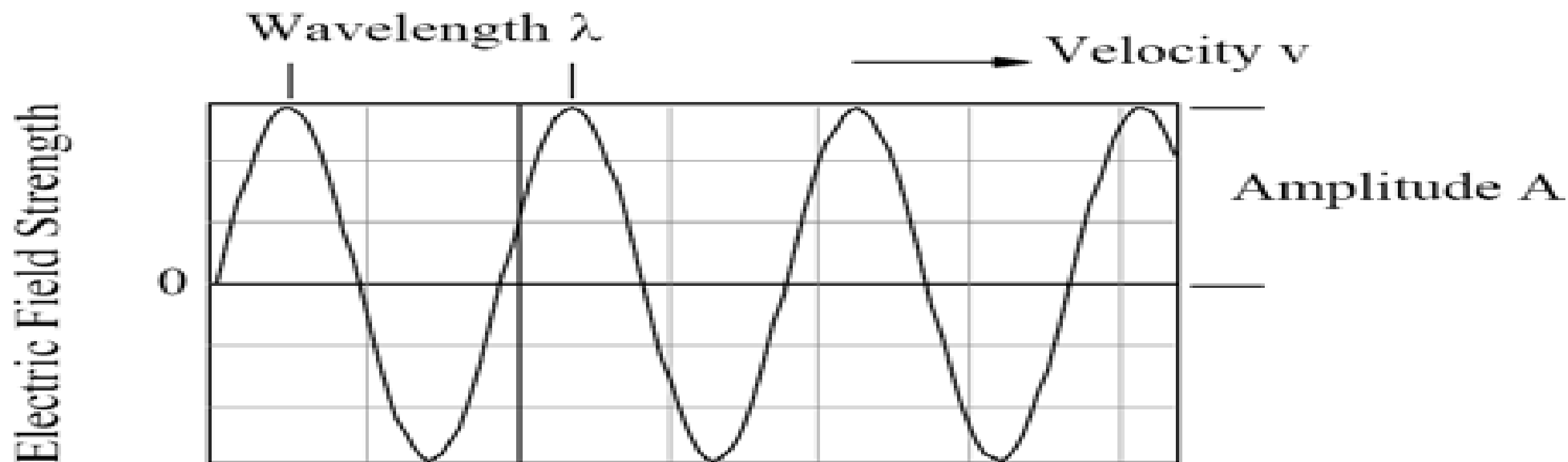
- wavenumber, $\bar{\tilde{v}}$" another unit used to describe the wave properties of
- electromagnetic radiation which is the reciprocal of wavelength $\bar{\tilde{v}} = 1/\lambda$

➢ **Particle Nature of light.** When matter **absorbs** electromagnetic radiation it undergoes a change in energy. The **interaction between matter and electromagnetic radiation** is easiest to understand if we assume that radiation consists of a beam of energetic particles called **photons.** When a **photon** is **absorbed** by a sample it is **destroyed** and its **energy acquired** by the sample. The energy of a photon, in **joules**, is related to its **frequency, wavelength, and wavenumber.**

➢ **The energy of light can be determined either from its wavelength or frequency:**

➢ $E = \dfrac{hc}{\lambda}$ **OR** $E = hv$

➢ **Planck's constant: h = 6.626 x 10^{-34} J s**

- The electromagnetic spectrum is composed of a large range of wavelengths and frequencies (energies). It varies from the **highly energetic gamma rays** to the **very low energy radio-waves**. The entire range of radiation is commonly referred to as the **electromagnetic spectrum**.

- **Example . The energy difference between the 3p and the 3s orbitals in a sodium atom is 2.107 eV. Calculate the λ (in nm) that would be absorbed in exciting the 3s electron to the 3p state (l eV = 1.60 X 10^{-19} J).**

➢**Solution: $\lambda = \dfrac{hc}{E}$ = $\dfrac{6.626 \text{ x } 10^{-34} \text{ J.s x } 3\text{x}10^{8} \, m/s}{2.107 \text{ eV x } 1.60 \text{ X } 10^{-19} \text{ J/ev}}$ = 590 nm**

➢**electron volt, unit of energy commonly used in atomic and nuclear physics, equal to the energy gained by an electron (a charged particle carrying unit electronic charge) when the electrical potential at the electron increases by one volt. The electron volt equals 1.602 × 10^{-19} joule.**

- **Example: Violet light from a mercury lamp has a wavelength of 436 nm:**
- **Calculate energy of light**

$$E = \frac{hc}{\lambda}$$

$$= \frac{(6.626 \times 10^{-34} \, J \, s)(3.00 \times 108 \, m \, s^{-9})}{436 \times 10^{-9} \, m} = \textbf{4.56 x 10}^{-19} \textbf{ J}$$

➢Atoms and molecules **absorb and emit** light in the ultraviolet **(UV),** visible **(vis),** infrared **(IR),** and microwave **(μwave)** regions of the electromagnetic spectrum.

➢**Absorption or emission** of light in the **UV** and **vis** regions involves movement of electrons in the atom or molecule.

➢One reason **UV light** is so damaging is that the light has enough energy to break chemical bonds—biological and chemical systems

•**E** (λ = 300 nm) = 399 kJ mol

•**Average bond energy** = 380 kJ mol^{-1}

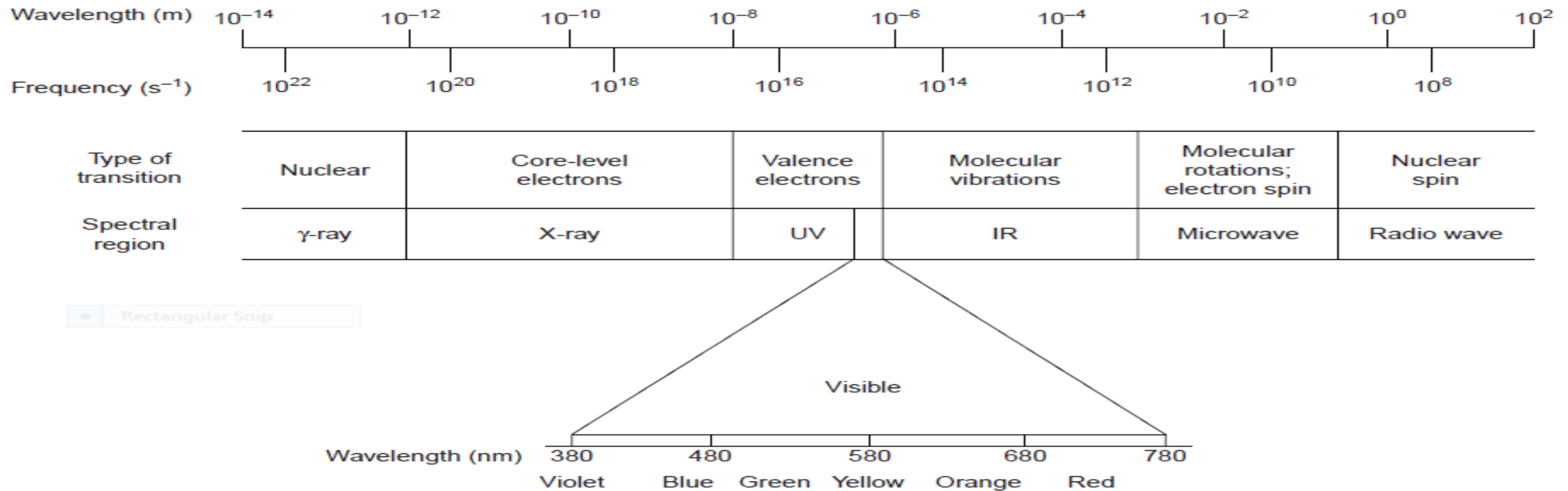# Electromagnetic radiation and its interactions with matter

- The interactions of radiation and matter are the subject of spectroscopic studies. The most interesting types of interactions in spectroscopy are **absorption and emission** of radiation by molecular or atomic species of interest which involve transitions between different energy levels of the chemical species.

- Electromagnetic radiation can interact with matter in a number of ways.

- If the interaction results in the transfer of energy from a beam of radiant energy to the matter, it is called "**absorption**" The reverse process in which a portion of the internal energy of matter converted into radiant energy is called "**emission**"..

- **Absorption:** When radiation passes through a transparent layer of a solid, liquid, or gas, certain frequencies may be selectively removed by the process of absorption. Here, electromagnetic energy is transferred to the atoms or molecules constituting the sample; as a result, these particles are promoted from a **lower energy state** to **higher-energy states**, or **excited states**. Note that at room temperature, most substances are in their **lowest energy or ground state.**

- In **emission** process, species in an excited state can emit photons of characteristic energies by returning to lower energy states or ground states. Part of the radiation which passes into matter, instead of being absorbed, may be **scattered or reflected** or may be re-emitted at the same wavelength or a different wavelength upon emerging from the sample. Radiation, which is neither absorbed nor scattered, may undergo changes in **orientation or polarization** as it passes through the sample.

- **Emission:** when an atom or molecule in an excited state returns to a lower energy state, the excess energy often is released as a photon, a process we call emission.

- **Eg - Ee =ΔE= h ν Absorption**   **Ee - Eg = h ν emission**
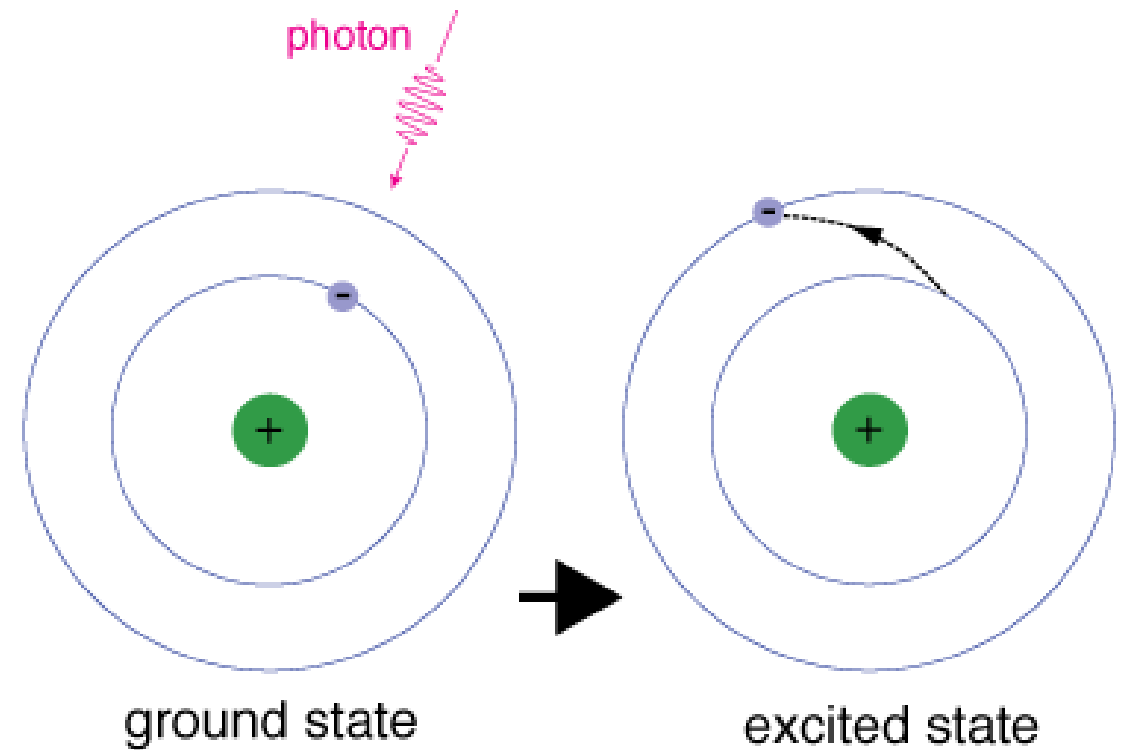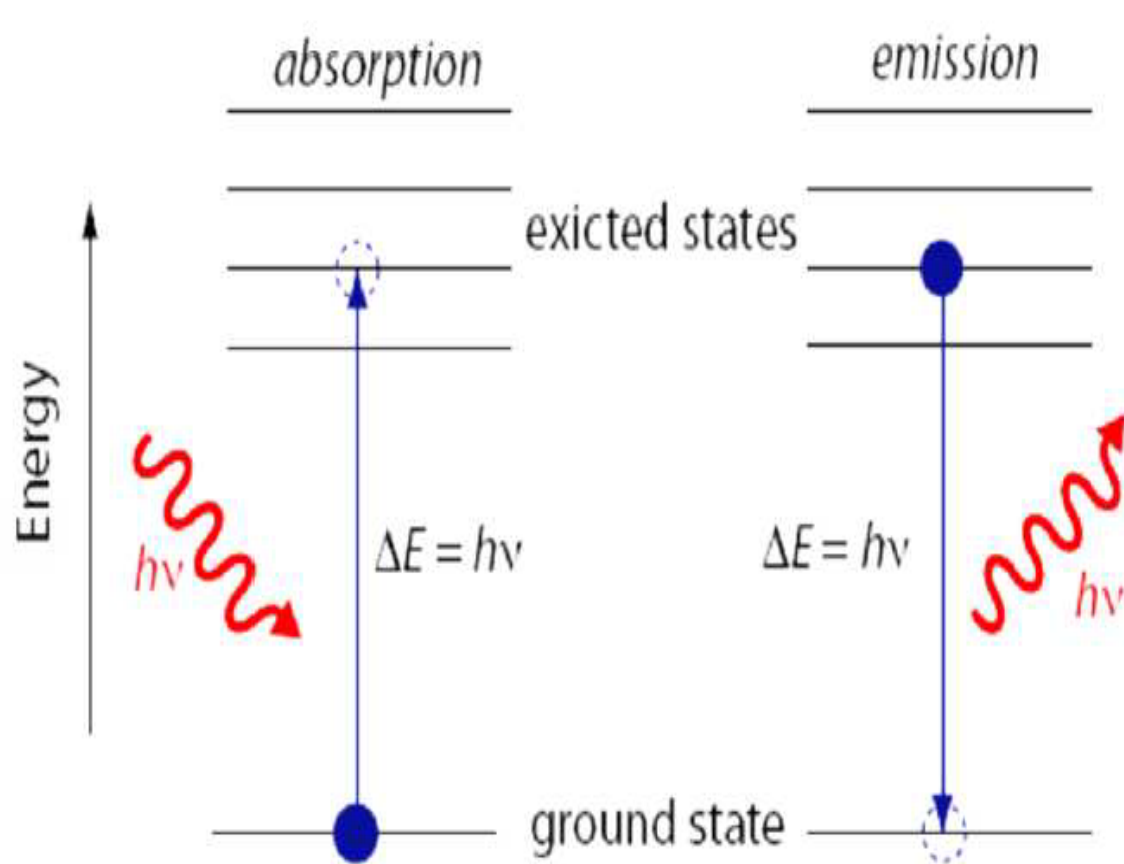
- **The frequency and wavelength** of electromagnetic radiation vary over many orders of **magnitude**. For convenience, we divide electromagnetic radiation into different regions. The electromagnetic spectrum-based on the type of **atomic or molecular transition** that gives rise to the absorption or emission of photons. The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

Wavelength (m) 10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2}

Frequency (s^{-1}) 10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8}

Type of transition	Nuclear	Core-level electrons	Valence electrons	Molecular vibrations	Molecular rotations; electron spin	Nuclear spin
Spectral region	γ-ray	X-ray	UV	IR	Microwave	Radio wave

Visible

Wavelength (nm) 380 480 580 680 780

Violet Blue Green Yellow Orange Red

➢ X-ray photons excite **inner-shell electrons**

➢ ultra-violet and visible-light photons **excite outer-shell (valence) electrons**

➢ infrared photons are less energetic, and induce **bond vibrations**

➢ Microwaves are less energetic still, and induce **molecular rotation**.

Microwave region in electromagnetic spectrum

- **Wave number = 1-100 cm^{-1}**
- **Wavelength = 1 cm – 100 μm**
- **Frequency = 3 x10^{10} – 3 x 10^{12} Hz**
- **Energy = 10 -10^{3} Joules/mole**

Infrared region in electromagnetic spectrum

- **Wave number = 14,286-12,800 cm-1**

- **Wavelength = 700– 1000 nm**

- **Frequency = 3×10^{13} Hz**

- **Energy = 1.7 eV – 1.24 meV (1.07×10^{-23})**

$1 J = 6.242 \times 10^{18}$ ev

visibil region in electromagnetic spectrum

- **Wave number = 14,286-12,800 cm^{-1}**

- **Wavelength = 400– 700 nm**

- **Frequency = 430 THz – 750 THz**

- **Energy = 3.3 eV – 1.7 eV**

Ultraviolte region in electromagnetic spectrum

- **Wave number = 25,000 – 50,000 cm-1**
- **Wavelength = 100– 400 nm**
- **Frequency = 750 THz – 30 PHz**
- **Energy = 124 eV – 3.3 eV**

ANALYTICAL CHEMISTRY

LECTURE-13

BY

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- **REFERENCES**

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