



PC 306

Part 1



Zagazig University
Clinical Pharmacy Programme
Analytical Chemistry Department

Oxidation-Reduction Reactions

1. Definition

Lecture **1**

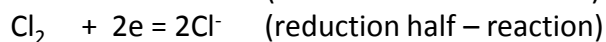
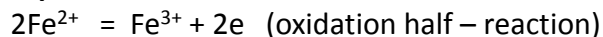
Old definition

Oxidation is the reaction of substance with oxygen

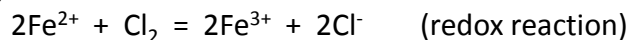
Reduction is the reaction in which hydrogen is involved

But there is many Oxidation reduction reactions which don't involve any Oxygen or hydrogen

For example:



Adding _____



From above equation we can define :

Oxidation reaction in which electrons are liberated

Reduction reaction in which electrons are consumed

Oxidizing agent is the substance which consume electrons and get reduced

Reducing agent is the substance which liberate electrons and get oxidized

N.B

- any oxidation reaction must be accompanied with reduction reaction.
- Electrons liberated in oxidation reaction must be the same consumed in reduction reaction

Reduction form – electrons = oxidized form

2. The oxidation number: ON#

ON# indicate the states of oxidation of atoms.

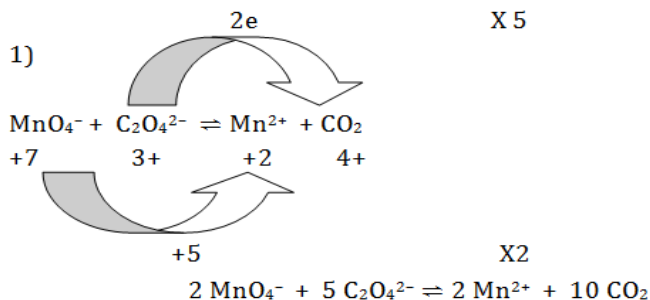
Rules of ON#.

1. Uncombined atom (e.g. Na), or atom in a molecule (e.g. H₂) = zero.
2. Simple, mono-atomic ion = charge O.N. of Zn²⁺ is 2+ and that of Cl⁻ is 1-.
3. Hydrogen = 1+ in all its compounds; except the metallic hydrides (e.g., NaH), in which hydrogen has an oxidation number of 1-.
4. Oxygen = 2-, except in peroxides (e.g., Na₂O₂), =1-
5. Complex ion, the algebraic sum = charge (Fe(CN)₆⁴⁻)
6. Neutral molecule, the algebraic sum =0 (NaCl,)
7. Sometimes O.N# is fractional. Sulphur in sodium tetrathionate, Na₂S₄O₆, is 2½ + ; and the oxidation number of carbon in butane , C₄H₁₀ is 2½ -.

3. Balancing redox equations

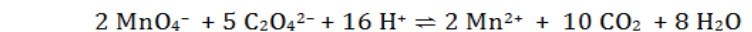
1 oxidation –number method.

Balance the equation, adding **water and hydrogen ion** as needed

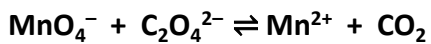


2) Balance the amount of O and H⁺

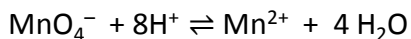
Final:



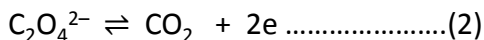
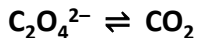
Another method, the ion – electron method, may also be used:



1. For oxidizing agent MnO_4^- half equation: adding **H⁺ & H₂O**

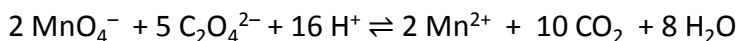


2. Second, treat the reducing agent ($\text{C}_2\text{O}_4^{2-}$):



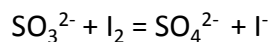
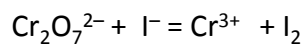
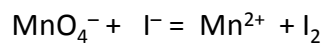
Finally, multiply equation (1) X2 , and equation (2) X5

So, final balanced equation representing the redox reaction:

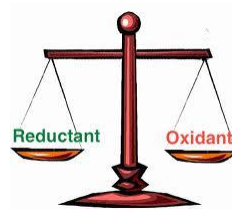
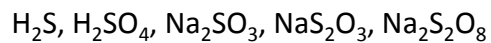


Quiz 1:

1. Balance the following equations:



2. Calculate the Oxidation number of S in the following compounds:



2. Electrode potentials: E

Lecture 2

- when a metal plate is dipped into a solution of its salt. There is an equilibrium potential difference between a metal and solution of its salt called electrode potential.



Two factors determine the electrode potential:

Electrolytic solution pressure, which is the tendency of an element to send its ions into solution (dissolved).

Ionic pressure, which is the tendency of the dissolved ions of the element to precipitate.

Nernst equation

The potential between a metal and its ions can be calculated from the equation formulated by **Nernst** as follows:

$$E_{25^\circ\text{C}} = E^\circ + \frac{0.0591}{n} \log [M^{n+}] \quad \text{for metal}$$

$$E_{25^\circ\text{C}} = E^\circ - \frac{0.0591}{n} \log [M^{n-}] \quad \text{for non metal}$$

if $[M^{n+}]$ and $[M^{n-}]$ are equal to **one molar** then its logarithm will be zero and

$$E = E^\circ \quad (\text{standard electrode potential})$$

The standard electrode potential, E^\ominus .

- Metals arranged in the order of their standard electrode (called *Electrochemical Series*)

Reaction at Interface	Half-cell Potential (E^\ominus)
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.706 V
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.763 V
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.744
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.409V
$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.401 V
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.230 V
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.126 V
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00 V
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	+0.223 V
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.268 V
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.340 V
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.799 V
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	+1.680 V

Easily reduced, Better Oxidizing Agent

Easily oxidized, Better Reducing Agent

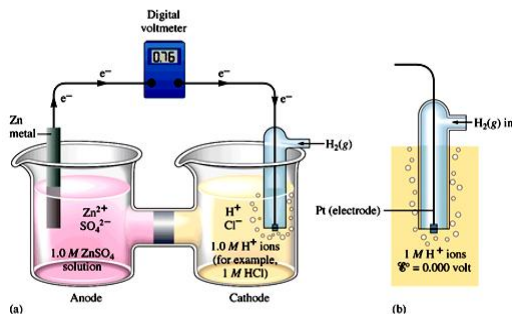
Electrochemical Series

- The greater the negative value of the potential the better reducing agent.

(Zn is reducing agent while Cu oxidizing agent)

- A metal with **more negative potential** will displace any other metal below it in the series from its salt solution. Thus iron will displace copper or mercury from their salt solutions.

It is only possible to measure the potential of one electrode relative to another electrode called the reference electrode



3. Reference electrodes

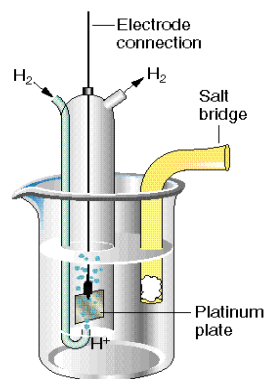
1. Standard Hydrogen Electrode

It's a primary reference electrode. Its potential is considered to be zero.

Redox half reaction $2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$

half cell: $\text{pt}/\text{H}_2, \text{H}^+(1\text{N}) \parallel$

$E^0 = \text{zero}$



The SHE is made of a small piece of platinum wire plating with a thin layer of platinum black and saturated with hydrogen gas by electrolysis.

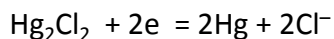
d-Limitation

1. It is difficult to be used and to keep H_2 - gas at one atmosphere during all determinations.
2. It needs periodical replating of Pt. Sheet with Pt. Black

2. Saturated calomel electrode (S.C.E.)

$\text{Hg} \mid \text{Hg}_2\text{Cl}_2 (\text{sat'd}), \text{KCl} (\text{sat'd}) \parallel$

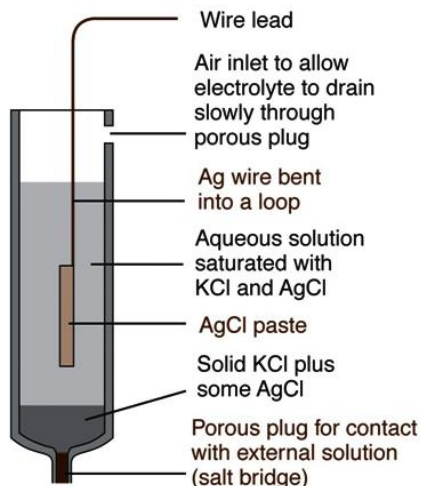
electrode reaction in calomel half-cell



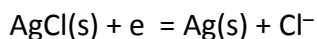
$$E^0 = +0.268\text{V}$$

$$E = E^0 - (0.05916/2) \log[\text{Cl}^-]^2 = 0.244\text{V}$$

Temperature dependent



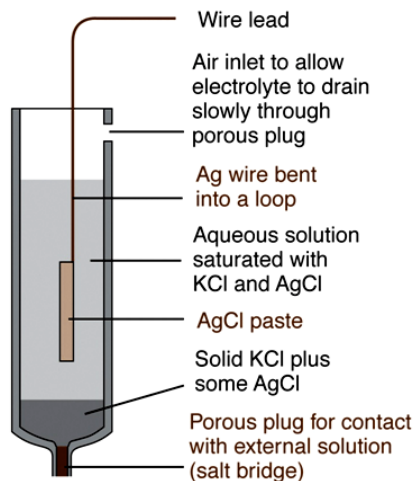
3. Silver-silver chloride electrode



$$E^\circ = +0.244\text{V}$$

$$E = E^\circ - (0.05916/1) \log [\text{Cl}^-]$$

$$E (\text{saturated KCl}) = + 0.199\text{V} (25^\circ\text{C})$$



4. Electrochemical Cell

1- Galvanic or voltaic cell

An electrochemical cell which produces current (or energy) when the electrodes are connected externally by a conducting wire

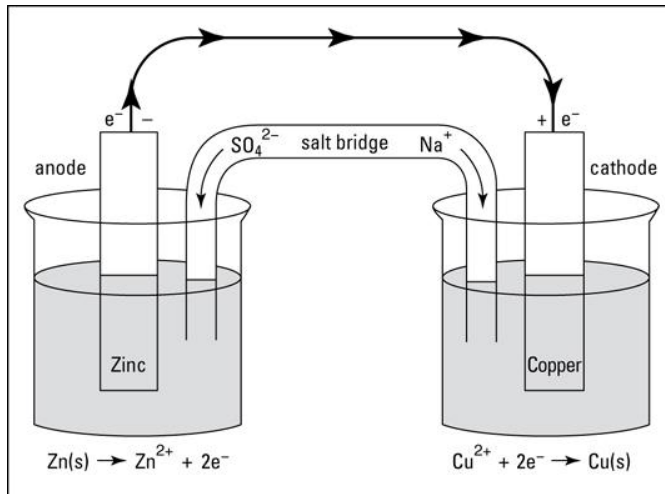
e.g. Daniell cell

For the galvanic cell shown in the following figure the copper electrode is the cathode. The cathode half reaction is



The zinc electrode is the anode. The anodic reaction is:

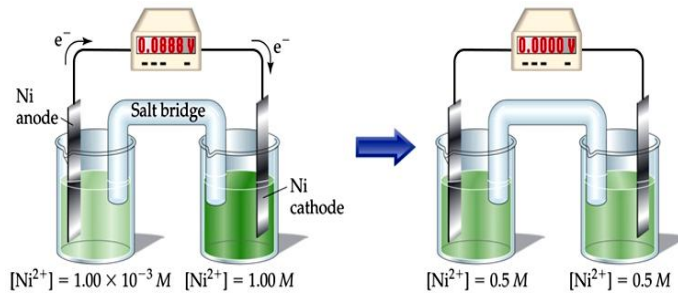




Schematic representation of cells:
 A cell such a Daniel cell can be represented as follows:
 $Zn / Zn^{2+} (C_1) || Cu^{2+} (C_2) / Cu$

2- Concentrated cell:

In these cells two electrodes of the same metal are dipped in solutions containing different concentration of the same ions.
 The e.m.f. of the cell = (the greater – the smaller one).

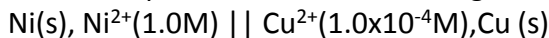


$$e.m.f. = \frac{0.059}{n} \log \frac{[M^{n+}]_1}{[M^{n+}]_2}$$

Quiz 2:

1. Calculate:

1. The cell potential for the following Galvanic cell at 25°C.



2. Find the potential of a $\text{Ag}^+(1.0 \times 10^{-7}\text{M}), \text{Ag(s)}$ electrode at 25°C.

3. A concentration cell is made up of two Ag/Ag^+ half cells. In the first half cell, $[\text{Ag}^+] = 0.010 \text{ M}$. In the second half cell, $[\text{Ag}^+] = 4.0 \times 10^{-4} \text{ M}$. What is the cell potential? Which half cell functions as the anode?

4. Calculate the standard free energy for the cell:



What will be the voltage if $[\text{Fe}^{2+}] = 0.50\text{M}$ and $[\text{Cr}^{3+}] = 0.30\text{M}$

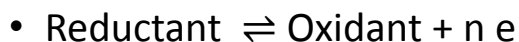
5. Calculate the e.m.f. for Daniel cell consists of Zn^0 , $\text{Zn}^{2+}(0.1\text{M}) \parallel \text{Cu}^{2+}(0.01), \text{Cu}^0$ ($E_{\text{Zn}^0/\text{Zn}^{2+}} = -0.76 \text{ V}$, $E_{\text{Cu}^0/\text{Cu}^{2+}} = 0.34 \text{ V}$)

6. The equivalent weight of potassium permanganate at different pH:

- strong acid medium
- slightly acidic or neutral medium
- strong alkaline medium

2. Draw the diagram represents the follow electrodes, mention the Nernst equation for electrode half reaction:

- silver/silver chloride
- calomel electrode
- NHE

5. Oxidation potential**Standard oxidation potentials:**

System	E°	System	E°
Co ³⁺ , Co ²⁺ /pt	+ 1.82	Fe ³⁺ , Fe ²⁺ /pt	+0.77
MnO ₄ ⁻ , Mn ²⁺ /pt	+1.52	H ₃ AsO ₄ , H ₃ AsO ₃ /pt	+ 0.57
Ce ⁴⁺ , Ce ³⁺ /pt	+ 1.45	I ₂ , I ⁻ /pt	+ 0.54
ClO ₃ ⁻ , Cl ⁻ /pt	+ 1.45	Fe(CN) ₆ ³⁻ , Fe(CN) ₆ ⁴⁻ /pt	+ 0.49
BrO ₃ ⁻ , Br ⁻ /pt	+ 1.42	Cu ²⁺ , Cu ⁺ /pt	+ 0.16
Cl ₂ , Cl ⁻ /pt	+ 1.36	Sn ⁴⁺ , Sn ²⁺ /pt	+ 0.14
Cr ₂ O ₇ ²⁻ , Cr ³⁺ /pt	+ 1.3	H ₂ , 2H ⁺ /pt	0.00
IO ₃ ⁻ , I ⁻ /pt	+ 11.2	Cr ³⁺ , Cr ²⁺ /pt	- 0.4
Br ₂ , 2Br ⁻ /pt	+ 1.07	S ⁰ , S ²⁻ /pt	- 0.55

- The most powerful oxidizing agents are those at the upper end of the table, i.e., of higher positive standard oxidation potential, and the most powerful reducing agents at the lower end. Thus permanganate ions oxidize S²⁻, Br⁻, I⁻, Fe²⁺ and Fe(CN)₆⁴⁻ ions; ferric ions can oxidize AsO₃³⁻ and I⁻ but not Cr₂O₇²⁻ or Cl⁻ ions.

Nernst equation for the oxidation potential:

$$E_{25^{\circ}\text{C}} = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Oxid}]}{[\text{red.}]}$$

if the concentration of the oxidant equals that of the reductant, the ratio [Oxid] / [Red.] will be equal to one and log [Oxid] / [Red.] = zero. In such a case $E_t = E^{\circ}$ and this is the **“standard oxidation potential”**

Factors affecting oxidation potential:

$\text{MnO}_4^- / \text{Mn}^{2+} / \text{pt}$	+1.52
$\text{Cl}_2, \text{Cl}^- / \text{pt}$	+ 1.36
$\text{Fe}^{3+}, \text{Fe}^{2+} / \text{pt}$	+0.77

1 – Common ion effect:

- Example : Titration of FeCl_2 with KMnO_4

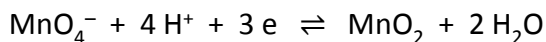
$$E_{\text{MnO}_4^- / \text{Mn}^{2+}} = E^\circ + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$

If $[\text{Mn}^{2+}]$ increases the oxidation potential (E), decreases i.e. the oxidation potential of the system will decrease in presence of excess manganous salt and, vice versa, it may increase if excess permanganate ion present.

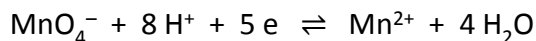
Manganous sulphate, in the form of **Zimmermann's reagent**, is added to the titrated solution; the fraction $[\text{MnO}_4^-] / [\text{Mn}^{2+}]$, and consequently E, is reduce and the permanganate is thus unable to oxidize chloride ions.

2 – Effect of increasing (H^+)

In the case of many redox systems (Oxygenated systems) the oxidation potential is increased by increasing acidity and decreases by decreasing it.



$$E_{\text{MnO}_4^- / \text{MnO}_2} = E^\circ + \frac{0.059}{3} \log \frac{[\text{MnO}_4^-][\text{H}^+]^4}{[\text{MnO}_2]}$$



$$E_{\text{MnO}_4^- / \text{Mn}^{2+}} = E^\circ + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$

Example 1: Titration of I⁻ with KMnO₄ in presence of Br⁻ and I⁻

MnO ₄ ⁻ , Mn ²⁺ /pt	+1.52
Cl ₂ , Cl ⁻ /pt	+ 1.36
Br ₂ , 2Br ⁻ /pt	+ 1.07
I ₂ , I ⁻ /pt	+ 0.54

- At pH= 5 bromides or chloride not affected.
- If the acidity is increased to pH= 3, E of permanganate is increased so that bromides are also oxidized into bromine; and on further increase of the [H⁺] chloride are also oxidized.

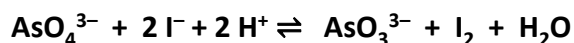
Example 2: Titration of AsO₄³⁻ / AsO₃³⁻ with I₂ solution



H ₃ AsO ₄ , H ₃ AsO ₃ /pt	+ 0.57
I ₂ , I ⁻ /pt	+ 0.54

□ E_{AsO₄³⁻ / AsO₃³⁻} system **increased** by increasing the [H⁺], so, iodides gets oxidized into free iodine.

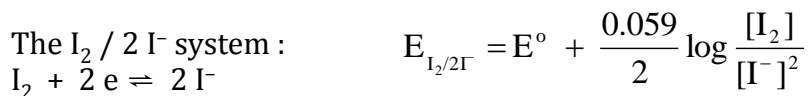
□And is **decreased** by reducing the [H⁺] and the arsenite is than oxidised with free iodine in an alkaline (**NaHCO₃**) medium, the reaction being reversed through changing the (H⁺).



$$E_{\text{AsO}_4^{3-} / \text{AsO}_3^{3-}} = E^\circ + \frac{0.059}{2} \log \frac{[\text{AsO}_4^{3-}][\text{H}^+]^2}{[\text{AsO}_3^{3-}]}$$

3- Effect of complexing agents: -

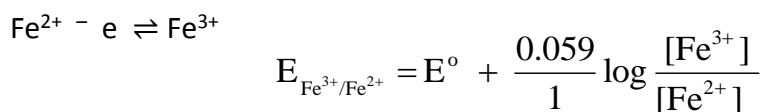
Example 1:



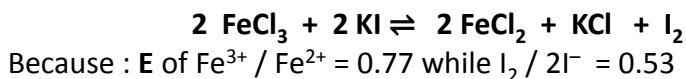
HgCl₂ form a complex with iodide, that is minimizing its concentration and, therefore increasing the oxidation potential of the $I_2 / 2 I^-$ system.

Example 2:

On the addition of fluorides or phosphates to a Fe^{3+} / Fe^{2+} system.



Ferric ions oxidise iodides thus:

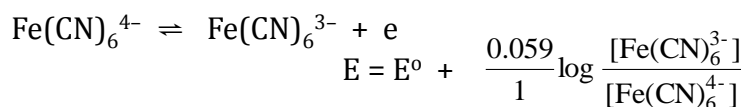


Phosphate or fluoride, if added, will lower the oxidation potential of Fe^{3+} / Fe^{2+} system (due to formation of **FeF_6^{3-}** or **$Fe(PO_4)_2^{3-}$** complexes with Fe^{3+}) so that it becomes unable to oxidise iodides anymore.

4 - Effect of precipitating agents:

Example:

Determination of zinc salt by Ferro cyanide



Addition of zinc salt will precipitate zinc ferrocyanide increasing the oxidation potential.

On titration with ferrocyanide, the zinc is precipitated leaving ferricyanide which **oxidises the diphenylbenzidine** violet indicator to blue violet, , when the end point is reached, any addition of ferrocyanide will greatly decrease the ratio $\text{Fe(CN)}_6^{3-} / \text{Fe(CN)}_6^{4-}$ the oxidation potential being consequently decreased and the blue violet colour of the **indicator disappears** due to its reduction.



Quiz 3:

1. Mark (v) for correct or (X) for false statements:

1. Zimmermann's reagent should be added when FeSO_4 is titrated with MnO_4^- .
2. The oxidation potential of Ferric/Ferrous system is decreased in presence of fluoride ion
3. Addition of zinc ion to ferricyanide / ferrocyanide system will decrease the oxidation potential of the system
4. The oxidation potential of oxygenated systems increases by increasing acidity

2. Write the equations represent the following:

1. Nernst equation for the oxidation potential.
2. Nernst equation for reduction of potassium permanganate in neutral or slightly acid medium
3. Nernst equation for arsenate/arsenite system
4. Nernst equation for $\text{Cr}_2\text{O}_7^{2-}$ half reaction in acid medium.

3. Circle the most correct answer:-

1. In iodometric determination of AsO_4^{3-} , the oxidation potential of $\text{AsO}_4^{3-}/\text{AsO}_3^{3-}$ system is decreased by

- a) The presence of Hg^{2+} c) The presence of phosphate
b) The presence of F^- d) The presence of bicarbonate

2. Zimmermann reagent is formed of

- a) MgSO_4 , H_3PO_4 and H_2SO_4 c) MgSO_4 , H_3BO_4 and H_2SO_4
b) MnSO_4 , H_3PO_4 and H_2SO_4 d) MnSO_4 , H_3PO_4 and HCl

3. The reduced form of KMnO_4 in neutral or slightly acidic medium is:

- a) Mn^{2+} c) MnO_4^{2-}
b) MnO_2 d) MnO_4^-

4. The oxidation potential of $\text{AsO}_4^{3-}/\text{AsO}_3^{3-}$ system is decreased by:

- a) The presence of Hg^{2+} C) The presence of F^-
b) Decrease the $[\text{H}^+]$ d) Decrease the pH

6. Titration curves

Lecture 4

Titration curves are graphs represent the relation between the potential change of the system being titrated (E) and the amount of titrant added.

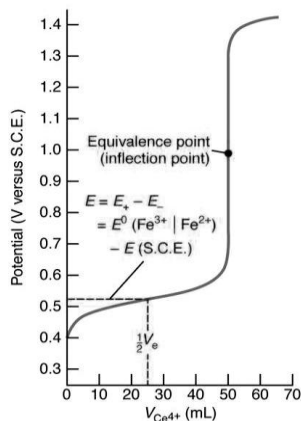
i.e E (Volt) # ml of titrant added

•Calculation of cell potential at equivalence point:

$$E_{e,p} = \frac{(n_1 E_1^0 + n_2 E_2^0)}{(n_1 + n_2)}$$

titration of ferrous ion with ceric ion

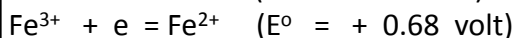
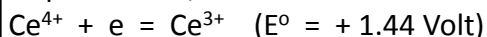
$$E_{e,p} = \frac{(E_1^0 + E_2^0)}{2}$$



Construction of titration curves:

Titration of ferrous iron with ceric:

Consider the titration of 100 ml. of 0.1 N solution of ferrous iron with 0.1 N solution of ceric. Assuming that both solutions are in 1 N sulphuric acid,



1. Initial potential. At the start, no cerium is present and the quantity of ferric ion present due to air oxidation is very small. The potential is equal to **zero**

2. Potential during titration: with the addition of titrant, three ions are Fe³⁺, Ce³⁺, and Fe²⁺; but the concentration of the fourth ion: Ce⁴⁺ will be very small.

1. On adding 10 ml. of titrant, equivalent amounts of ferric and cerous ions will be formed;

$$[\text{Ce}^{3+}] = [\text{Fe}^{3+}] = \frac{10 \times 0.1}{110} \quad [\text{Fe}^{2+}] = \frac{100 \times 0.1 - 10 \times 0.1}{110} = \frac{90 \times 0.1}{110}$$

$$E = E^{\circ} + \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad E = +0.68 + 0.059 \log \frac{\frac{10 \times 0.1}{110}}{\frac{90 \times 0.1}{110}} = 0.62 \text{ Volt.}$$

2. On adding 99.9 ml. of titrant, equivalent amounts of ferric and cerous ions will be formed

$$[\text{Ce}^{3+}] = [\text{Fe}^{3+}] = \frac{99.9 \times 0.1}{199.9} \quad [\text{Fe}^{2+}] = \frac{100 \times 0.1 - 99.9 \times 0.1}{199.9} = \frac{0.1 \times 0.1}{199.9}$$

$$E = +0.68 + 0.059 \log \frac{\frac{99.9 \times 0.1}{199.9}}{\frac{0.1 \times 0.1}{199.9}} = 0.857 \text{ Volt.}$$

3. Potential at equivalence point: The equivalence point is reached when 100 ml. of titrant are added

$$E_{e.p} = \frac{+1.44 + 0.68}{2} = 1.06 \text{ volt.}$$

4. Potential after equivalence point: on adding, for example, 100.1 ml titrant, the solution will contain an excess of Ce^{4+} ion in addition to equivalent amounts of Fe^{3+} and Ce^{3+} ions.

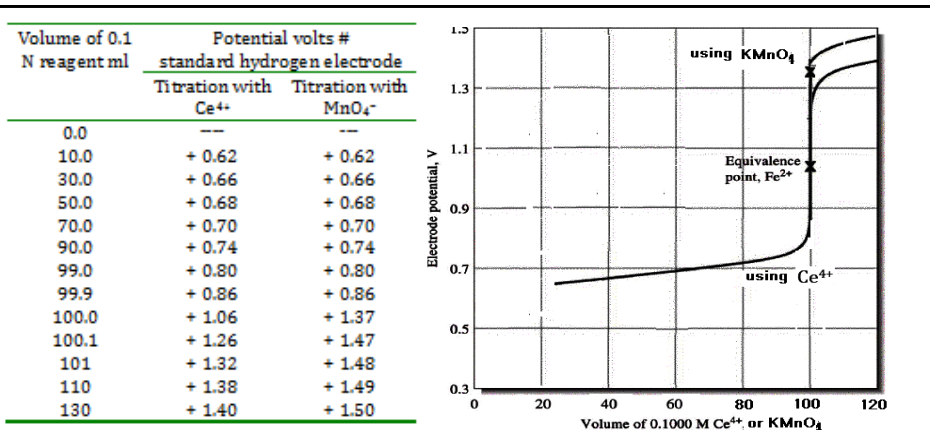
$$[\text{Ce}^{3+}] = [\text{Fe}^{3+}] = \frac{100 \times 0.1}{200.1}$$

$$[\text{Ce}^{4+}] = \frac{100.1 \times 0.1 - 100 \times 0.1}{200.1}$$

$$E_{\text{Ce}^{4+}, \text{Ce}^{3+}} = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$

$$E = +1.44 - 0.059 \log \frac{10 / 200.1}{0.01 / 200.1} = 1.25 \text{ volt}$$

Results shown in the next table plotted in the next figure were calculated similarly.



Characteristics of redox titration curves:

1. The shape of the titration curve depends upon the value of "n", (the number of electrons)
2. The titration curve is symmetrical, in case where the number of electrons lost by the reductant = number gained by the oxidant.

Calculate

Quiz 4:

1. Calculate the potential at the equivalent point when 10 ml of 0.1 N FeSO₄ are titrated with 0.1 N KMnO₄ ($E^{\circ}_{\text{Ferric/Ferrous}} = 0.76 \text{ V}$ and $E^{\circ}_{\text{permanganate/Manganese}} = 1.54 \text{ V}$)
2. Calculate the e.m.f. for Daniel cell consists of Zn⁰, Zn²⁺(0.1M) || Cu²⁺ (0.01), Cu⁰ ($E^{\circ}_{\text{Zn}^0/\text{Zn}^{2+}} = -0.76 \text{ V}$, $E^{\circ}_{\text{Cu}^0/\text{Cu}^{2+}} = 0.34 \text{ V}$)
3. Calculate the oxidation potential during titration of 100 ml 0.1 M ferrous sulphate with **0.2 M** Ceric sulphate after the addition of
 - a) 10 ml ceric sulphate
 - b) At the equivalent point
 - c) 0.1 ml excess after the equivalent point

7. Detection of end point

1. No indicator
2. External indicator: (spot test)
3. Internal redox indicator
4. Irreversible redox indicators

1. No indicator : – The standard acts as self indicator

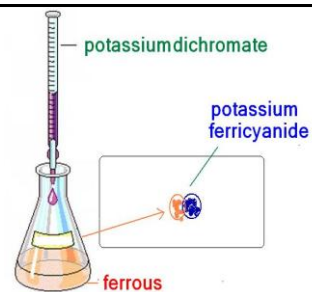
Example:

1. Permanganate as titrant in acid solution. (**change from pink colour of permanganate to colourless of Mn^{2+}**)
2. **Iodine** solution is used as standard without indicator (yellow colour) or with the use of an indicator – starch that gives an intense blue colour even with very small amounts of free iodine.

2. External indicator: (spot test)

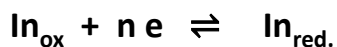
Example:

1. Titration of ferrous iron with potassium dichromate. Using potassium ferricyanide solution on a spot plate. (blue to colourless)
2. Titration of zinc ions with standard potassium ferrocyanide solution; using **uranyl acetate** as external indicator (brown to colourless)



3. Internal redox indicator:

Redox indicator is a compound which has different colours in the oxidised and reduced forms.



Applying Nernst equation: $E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{In}_{\text{ox}}]}{[\text{In}_{\text{red}}]}$

• ideal redox indicator when

$$\frac{[\text{In}_{\text{ox}}]}{[\text{In}_{\text{red}}]} = \frac{1}{10} \text{ or } \frac{10}{1}$$

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{1}{10} \text{ or } \frac{10}{1}$$

$$E = E^{\circ} \pm \frac{0.0591}{n}$$

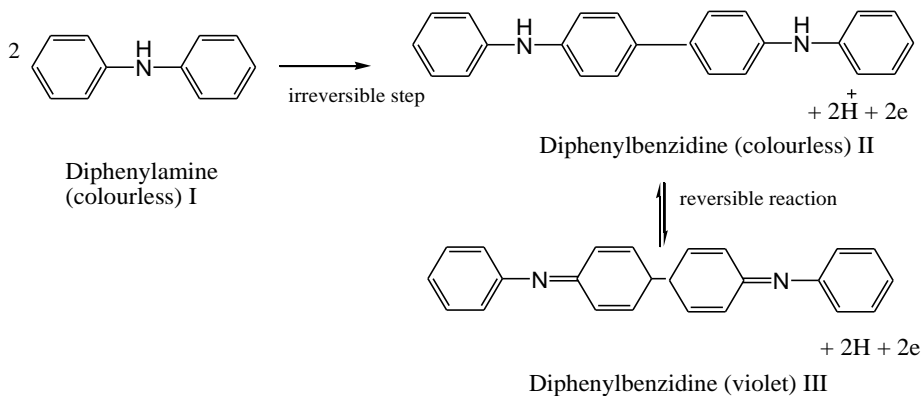
Desirable properties of redox indicators:

1. The colours of the indicator should be **very intense**,
2. The transition potential of the indicator should be **insensitive to change in pH**.
3. The indicator should be **soluble in water** or dilute acid solutions.
4. The oxidation potential of the redox indicator should be **intermediate between** that of the solution titrated and that of the titrant. $(E^{\circ}_1 - E^{\circ}_{\text{ind}})$ and $(E^{\circ}_{\text{ind}} - E^{\circ}_2)$ are not less than 0.15 mv

Examples

1. Diphenylamine and related compounds:

$$(E^{\circ}_{\text{ind}} = + 0.76 \text{ V and } n = 2)$$

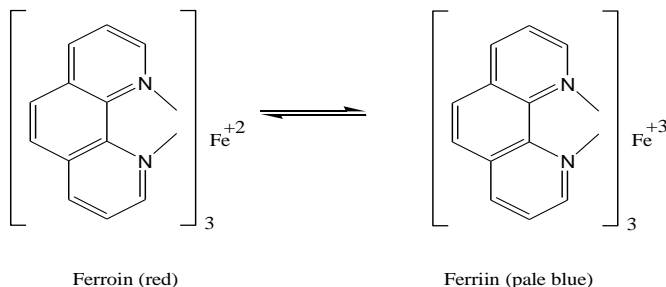


Diphenylamine is unsuitable indicator for the titration of ferrous iron with permanganate or dichromate due to the **overlapping** between oxidation potential of indicator ($E^{\circ}_{\text{ind}} = + 0.76 \text{ V}$) and that of ferric/ferrous system (0.77 V).

If, however, **ferric are complexed** by the addition of **phosphate ions**, it is then possible to lower the potential of ferric /ferrous system to the level which is sufficient to permit the indicator to function.

2. Orthophenanthroline and dipyrindine

Chalate of ferrous iron with 1, 10 orthophenanthroline (ferroin) is intensely red and is converted by oxidation into the pale blue ferric complex (ferriin):



It is an excellent indicator for Ce^{4+} . It has high E° which is affected by acidity.

4. Irreversible redox indicators:

Methyl red and methyl orange which are also neutralisation indicators, are examples of such irreversible redox indicators. In acid solutions they are red in colour but addition of strong oxidants would **destroy** the indicator and are thus decolorized irreversibility.

Quiz 5:

1. Enumerate the head title for:

General requirements for good internal redox indicators are:

- A) B) c) d)

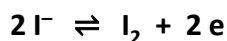
2. Draw the structure formula of the followings:

- i. Diphenylamine III
- ii. 1,10 Orthophenanthroline

Redox reaction involving iodine

Lecture **6**

Iodine/ iodide system, ($I_2/ 2I^- = + 0.535$), intermediate system



1. With strong oxidation system:
(indirect or iodometric methods

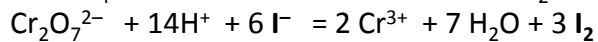
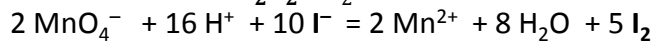
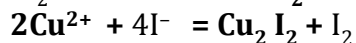
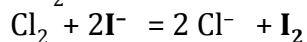
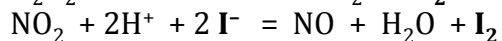
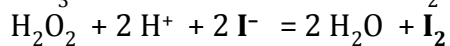
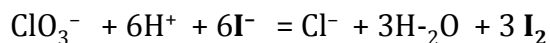
Analyte (**oxidizing sub.**) + excess of iodide = Iodine liberated and titrated by a standard solution of sodium thiosulphate)

2. With reducing system:
(Iodimetric method,

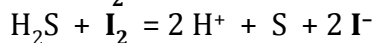
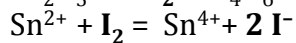
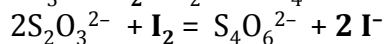
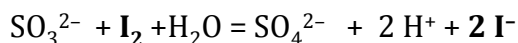
direct method, iodine solutions are used for titration of reducing agents (limited use)



1. iodometric methods



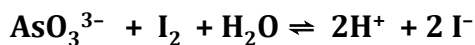
2. Iodimetric method



3. System intermediate E° near that of Iodine/ iodide system (as Fe³⁺ / Fe²⁺, AsO₄³⁻ / AsO₃²⁻)

a) AsO₄³⁻ / AsO₃²⁻ (E° = 0.57 v) (Oxygenated system)

- ❑ In presence of strong acid “E” of the AsO₄³⁻ / AsO₃²⁻ system increases and thus oxidize iodide with the liberation of iodine,
- ❑ but in slightly acid or neutral medium iodine oxidise arsenite quantitatively into arsenate;



It is to be noted that H⁺ is produced in the reaction; it has to be eliminated as soon as it is formed by including a mild alkali in the reaction. **Sodium bicarbonate** is suitable because if the pH of the reaction medium increases above pH 8, iodine reacts with OH⁻ ions forming hypoiodite and iodide.



If the oxidation potential of the system cannot be raised as above, we can lower the oxidation potential of the iodine / iodide system by increasing the concentration of the reduced form,

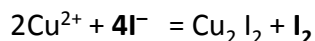
$$E_{\text{I}_2/\text{I}^-} = E^\circ + \frac{0.059}{2} \log \frac{[\text{I}_2]}{[\text{I}^-]^2}$$

b) Fe³⁺ / Fe²⁺ (E° =0.68)

If we want to oxidize iodide with ferric ion, where the difference between their oxidation potentials is not too large to allow for **complete and quantitative reaction**, it is advisable therefore, to increase the concentration of iodide by addition the excess iodide or to decrease the concentration of iodine by **extraction by an immiscible solvent such as chloroform or CCl₄**.

c) Cu²⁺ / Cu⁺ (E° =0.15)

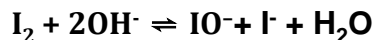
The Cu²⁺ / Cu⁺ system has an oxidation potential of 0.15 and would be expected to reduce the iodine into iodide. Instead, cupric ions liberate iodine from iodide. The reason for this is that Cu₂I₂ is insoluble. From the Nernst equation, it is expected that the oxidation potential of Cu²⁺ / Cu⁺ system is greatly increased to the extent that it can oxidise the iodide



In the presence of some ions which form stable complexes with cupric ions such as tartrates and citrates, iodine can oxidise cuprous compounds quantitatively to cupric ones.

• **Effect of increasing OH⁻ concentration: (IO⁻ / 2 I⁻ system)**

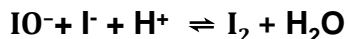
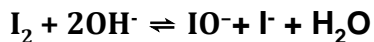
□ When the pH is higher than 8 iodine reacts with OH⁻ ions to form hypoiodite and iodide ions.



□ The hypoiodite is quite unstable and soon suffers self oxidation - reduction, thus;



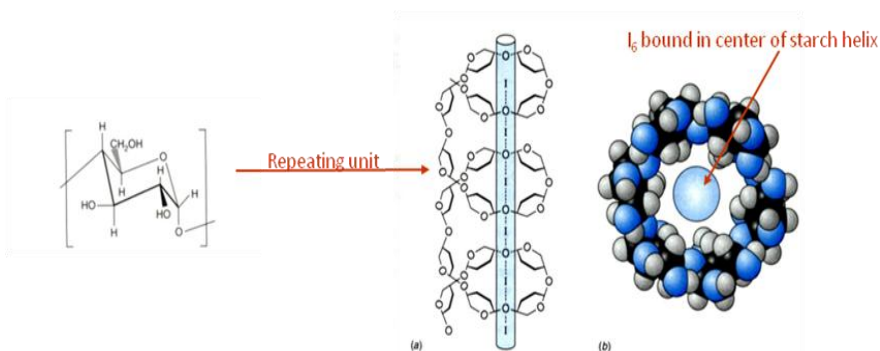
□ The hypoiodite has a high oxidation potential and by the use of iodine in alkaline medium many mild oxidations can be achieved, for example; Oxidation of aldehyde like glucose



Detection of end point:

1. Starch:

Starch gives a *deep blue* colour adsorbate with iodine which discharged when iodine is reduced to iodide ion. The colour change is reversible from blue to colorless.



Precaution must be considered:

1. The sensitivity of the colour decreases with increasing **temperature** of the solution.
2. In the titration of iodine, starch must not be added until **just before the end point**. (at high conc. some iodine may remain adsorbed on the surface of starch)
3. It cannot be used in **alcoholic** solution; or **strongly acid** medium.

2. Chloroform or carbon tetrachloride:

In alcoholic or strongly acidic solutions the end point is detected by the use of either chloroform or carbon tetrachloride. The solubility of iodine in chloroform is about **90** times as in water.

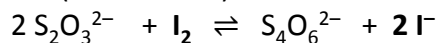
Iodine is **yellow** in aqueous medium and **violet** in organic layer

Source of error during titration involve iodine

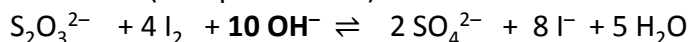
i) Instability of thiosulphate:

The reaction of thiosulphate ion with iodine:

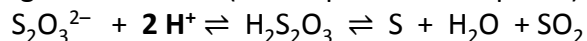
- In acid or neutral (Quantitative)



- Basic solutions (not quantitative)

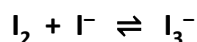


- In strong acid solutions (thiosulphate decomposes)



ii) Due to iodine liberated during iodometric titration:

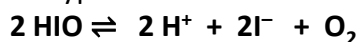
1. Care must be taken to prevent loss of iodine by vaporization (avoid **high temp.** and use glass Stoppard flask).
2. Iodine is sparingly soluble in water but dissolves readily in potassium iodide solutions because of formation of the complex I_3^- ion:



3. Iodine reacts with water, just as do other halogens, according to the equation,

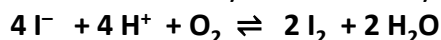


4. Light accelerates the hydrolysis of iodine by causing decomposition of hypo iodous acid:



5. Standard solutions of iodine should be preserved in the dark bottles or kept inside the desk to protect them from direct light.

6. Iodide ion in acid solution may be oxidized by air:



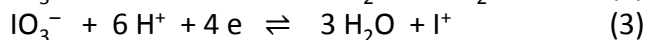
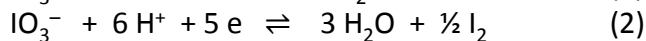
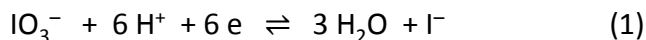
7. Certain metal ions such as cuprous can react and accelerate the reaction of oxidation (so must avoided in iodometric titration)

iii) Time of starch introducing:

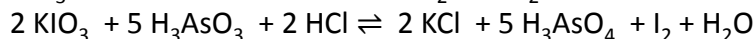
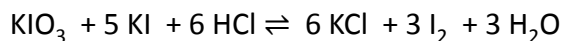
Starch must be added near the e.p where there is a lower concentration of I_2 (i.e the colour of the titrated solution is straw-yellow as the adsorbate formed between I_2 and starch is easily dis-charged, while if I_2 is present in high concentration, the adsorbate formed become irreversible during titration leading to high result

Iodates: – (IO_3^-)

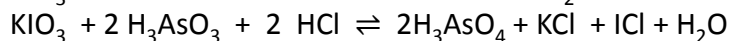
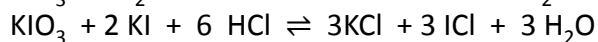
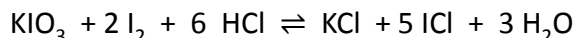
Another type of oxidising agents which is greatly connected with iodine is the iodate IO_3^- ion. For oxidation, it **requires hydrogen ions** like permanganate and the rest oxygenated compounds. But here, according to the concentration of the acid, the **iodate can be reduced to iodide or to iodine**. Still in the presence of more acid “Andrews” found that the iodine is further reduced to an ion carrying a positive charge iodonium ion , thus;



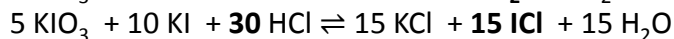
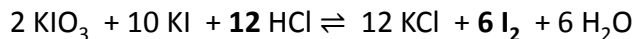
•In weak acid medium (0.1 – 2 HCl)



•In more concentrated hydrochloric acid solution (exceeding 4 N)



The effect of concentration of the acid and of the iodate may be shown by the following equations:



In the above reactions, I^+ ion is not stable except in the presence of high concentration of **chloride or cyanide** ions where it forms the fairly stable **iodine mono-chloride or iodine cyanide**.

The chloride ions are provided by the use of concentrated hydrochloric acid which provides hydrogen ions too. In case the cyanide ions are to be employed sodium or potassium cyanide must be added to the titration medium. The method has been worked out by **Lang**.

The use of iodate in the presence of a high concentration of hydrochloric acid is known as the **“Andrews Reaction”**.

In aqueous solution both iodine and iodine monochloride are **yellowish** brown colour, but in chloroform or carbon tetrachloride iodine is **purple** while iodine mono-chloride is **yellow**.

Quiz 6:

1. Formulated balance equations representing the following

1. Arsenious oxide with iodine in neutral medium.
2. Reaction of chlorate (ClO_3^-) with iodide.
3. Reaction of arsenite (AsO_3^{3-}) with iodine.
4. Reaction of potassium iodate (KIO_3) with iodide in high acidic medium ($> 4\text{N HCl}$).
5. Reaction of cupric ion with iodide.
6. Iodometric determination of chlorate ClO_3^-
7. Iodometric determination of thiosulphate
8. Andrew's determination of potassium iodide in strong acid medium ($> 4\text{N HCl}$)
9. Iodometric determination of potassium permanganate



10. Andrew's determination of arsenite in strong acid medium ($> 4\text{N HCl}$)
11. Oxidation of formaldehyde by hypoiodite in alkaline medium
12. $\dots\text{MnO}_4^- + \dots\text{H}^+ + \dots\text{I}^- =$
13. $\dots\text{Cr}_2\text{O}_7^{2-} + \dots\text{H}^+ + \dots\text{I}^- =$
14. $\dots\text{ClO}_3^- + \dots\text{H}^+ + \dots\text{I}^- =$
15. $\dots\text{H}_2\text{O}_2 + \dots\text{H}^+ + \dots\text{I}^- =$
16. $\text{NO}_2 + \dots\text{H}^+ + \dots\text{I}^- =$
17. $\dots\text{Cl}_2 + \dots\text{I}^- =$
18. $\dots\text{Cu}^{2+} + \dots\text{I}^- =$
19. $\text{SO}_3^{2-} + \text{I}_2 + \text{H}_2\text{O} =$
20. $\text{S}_2\text{O}_3^{2-} + \text{I}_2 =$
21. $\text{Sn}^{2+} + \text{I}_2 =$



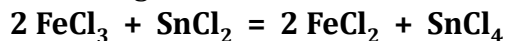
2. Ferric

I. Indirect :

Ferric must be reduced to the ferrous state first. Then the solution can be titrated as before.

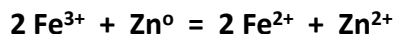
1. Reduction with stannous chloride:

The ferric salt + concentrated HCl (heated to 70° – 90°C) and concentrated stannous chloride solution is added, dropwise with stirring.



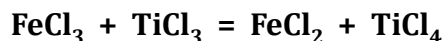
2. Reduction with Zinc and H₂SO₄:

Ferric salt solution + granulated zinc with acids + few drops of copper sulphate solution (accelerating agent); (test the presence of Fe³⁺ with thiocyanate.)



II. Direct:

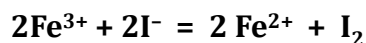
1. Titration with standard titanous solution



methylene blue or ammonium thiocyanate used as an indicator.

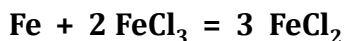
2. Iodometrically

Fe³⁺ + Known excess I⁻ using thiosulphate titrant and starch indicator in presence of cuprous iodide as a catalyst



3. Metallic iron

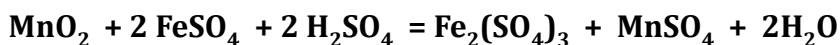
Fe⁰ dissolves in a neutral solution of ferric chloride with the formation of ferrous chloride.



If ferrous chloride formed is titrated with permanganate solution, one-third of the iron present is the sample.

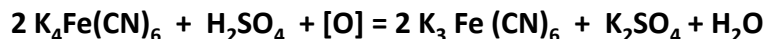
4. substances oxidise ferrous : MnO₂ (Mineral pyrolusite)

Boiling with a known excess of 0.1N ferrous sulphate solution acidified with 4 N sulphuric then titrate **back** the residual ferrous with 0.1 potassium permanganate.



5. Ferrocyanide

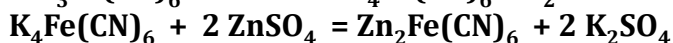
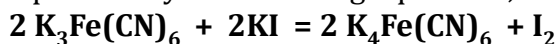
By oxidation of the ferrous iron complex to the ferric state, (ferricyanide) by titration with potassium permanganate.



6. Ferricyanide

i) Iodometrically

As expressed by the following equations;



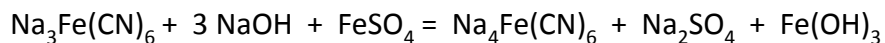
Zinc ions used to remove the ferrocyanide, iodine is then titrated with standard thiosulphate solution, using starch as an indicator

ii). Permanganometrically:

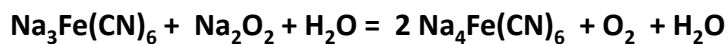
By first reducing the ferricyanide into ferrocyanide, and titrating the resultant ferrocyanide with standard permanganate solution.

The most commonly used reductants are:

1. The ferrous hydroxide method:



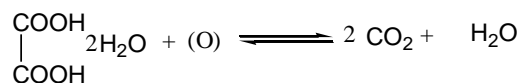
2. The sodium peroxide method;



□ Oxalate

1.Soluble oxalates

Oxalic acid and oxalates are of the strong reducing agents which can be titrated directly with standard permanganate or ceric solutions.



in a medium of sulphuric acid (1 – 1.5 N) and at a temperature of 55 – 60°C.

2. Cations that form insoluble oxalates

PbO content of litharge

PbO treated with known excess oxalic acid. The metal oxalate is **precipitated, filtered off and washed** free from soluble oxalate and either

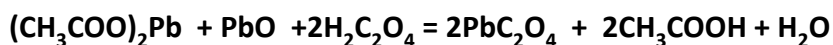
1. The precipitate is dissolved in dilute sulphuric acid and the oxalic acid set free is titrated **with standard permanganate or ceric solutions**. Or
2. The residual oxalic or oxalate in the filtrate and washing is back titrated by **standard permanganate or ceric solutions**.

Lead subacetate (contains lead oxide, lead acetate)

a) For total lead,

by precipitating all the lead as lead oxalate by adding a known excess of standard oxalic acid solution to sample. Filtered to remove the lead oxalate. The excess oxalic acid is determined by titrating with standard potassium permanganate solution.

b)The alkalinity of the subacetate solution is determined on a portion of the above filtrate, the determination depending upon the back titration of the excess acid (oxalic and acetic) with standard alkali, using phenolphthalein as indicator.



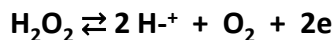
The back titration figure gives the amount of excess acid not required to neutralize the alkalinity of the sample. Although oxalic acid reacts with the lead acetate as well as the lead oxide it liberates an equivalent amount of acetic acid from the former and the determination of alkalinity is therefore not affected because phenolphthalein, which is sensitive to acetic and oxalic acids, is used as indicator.

☐ Peroxides

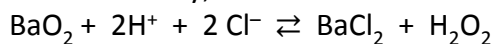
Peroxides can be determined as reducing agents, or as oxidising agents.

As reducing agents: (reaction with KMnO_4)

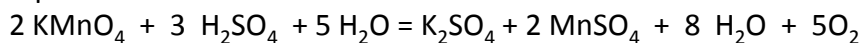
Hydrogen peroxide and alkaline peroxides in acid solution react according to the equation:



Any substance that will give hydrogen peroxide in acid solution reacts similarly;

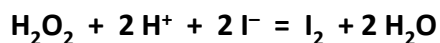


And the hydrogen peroxide is then oxidised as shown in the above equation.



As oxidising agents (Iodometrically)

H₂O₂ reacts with iodide in acid solution according to the following equation:

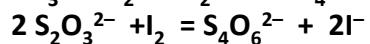
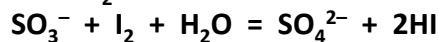
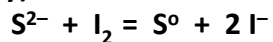


The iodine liberated is titrated with standard sodium thiosulphate solution, using starch as an indicator.

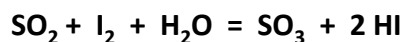
☐ Sulphur compounds

Determined according to the following equations

(Iodimetrically) :



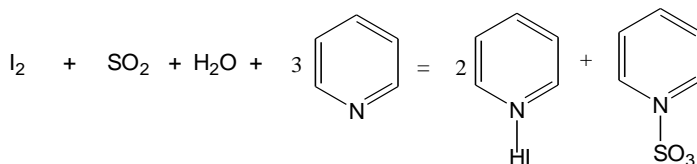
The necessity ? of the presence of water in the reaction between SO₂ and I₂ in the reaction:



has been used by **Karl Fischer for the determination of moisture in non aqueous media as organic solvent .**

Karl Fischer reagent

Small amounts of water in non-aqueous media are determined by titration with a reagent consisting of a solution of **iodine, sulphur dioxide, and pyridine** in absolute methanol.

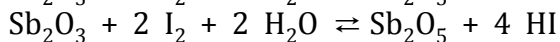
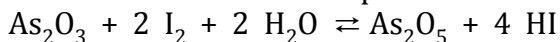


The products of the reaction colourless. Titration of a sample containing water is made with “**Karl Fischer reagent**” until the appearance of iodine colour.

□ Arsenic and antimony

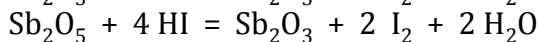
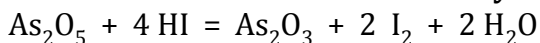
➤ Trivalent Arsenic and Antimony:

Trivalent arsenic and antimony are oxidised with iodine in neutral medium to be the pentavalent state



Sodium bicarbonate (but not NaOH) must be added why??? The titration carried out at pH 6.5

➤ Pentavalent arsenic or antimony:

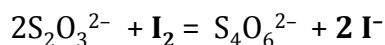


The reaction, being reversible, can be shifted to the right by addition of excess acid. In such strong acidic medium, starch cannot be used as indicator (use chloroform, why 1....., 2...?)

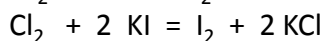
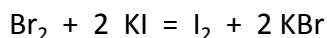
□ Free halogens

Iodine , Bromine or chlorine

Iodine Can be determined by direct titration with standard thiosulphate, iodate or arsenious solutions.

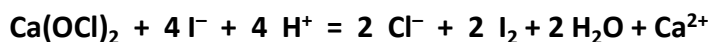


On the other hand, **Bromine or chlorine** has to be treated with an excess of potassium iodide and the iodine displaced is titrated.

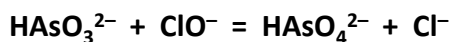


Bleaching powder

Contains about 30% of available chlorine. It consists of $\text{Ca}(\text{OCl})_2$ also some CaCl_2 , $\text{Ca}(\text{OH})_2$ and CaO . It is the hypochlorite which is responsible for bleaching action. **Potassium iodide** is added to the acidified suspension (with acetic acid), the liberated iodine titrated with thiosulphate.



hypochlorites could also be determined by direct titration with arsenite solution:



A drop of the titrated solution fails to give blue colour to starch/potassium iodide paper at the equivalence point.

Glucose & fructose

phenol

1. Give short notes of the following:

- Karl Fisher reagent (Uses and the represented equation)
- Redox determination of **pyrolusite**
- Determination of mixture of **Lead subacetate** (contains lead oxide, lead acetate)
- Redox determination of **Litharge**

2. Match each compound in group (A) with the appropriate statement in group (B)

(A)		(B)
<input type="checkbox"/>	Strong oxidizing agent	1 KI solution
<input type="checkbox"/>	Reduced to cationic iodine in strong acid medium	2 Sodium thiosulphate
<input type="checkbox"/>	Can be oxidized by I ₂ solution	3 Iodate solution (IO ₃ ⁻)
<input type="checkbox"/>	Decrease the oxidation potential of Fe ³⁺ / Fe ²⁺ system	4 Arsenite
<input type="checkbox"/>	The oxidant in Andrews reaction	5 Formaldehyde –acetic acid mixture
<input type="checkbox"/>	Can be used in determination of glycerol	6 Murexide
<input type="checkbox"/>	Used as carrier in Karl fisher reagent	7 Sodium fluoide
		8 Chloralhydrate
		9 Sodium nitroprusside
		10 Tartaric acid
		11 1,10 phenanthroline
		12 Xylenol orange
		13 Standard ferricyanide
		14 Standard K ₂ Cr ₂ O ₇ solution

3. Formulated balance equations representing the following

1. Hydrogen peroxide with potassium permanganate in acid medium.
2. Metallic iron with ferric chloride
3. Reaction of permanganate with ferrous in strong acid medium.
4. Reaction explain the determination of moisture in organic solvent
5. Reaction of ceric salts with oxalic acid ($C_2O_4^{2-}$)
6. Reaction of potassium permanganate with oxalate in acid medium.
7. Reaction of bromine with phenol
8. Iodometric determination of chlorate ClO_3^-
9. Determination of moisture in organic solvent by Karl Fischer reagent
10. Reaction of lead subacetate with oxalic acid

4. Circle the most correct answer:-

1. At the equivalent point the oxidation potential E of the system is related to the potential of

- | | |
|----------------------|----------------------|
| a) Titrant | c) Both a and b |
| b) Titrated solution | d) None of the above |

2. The ferric iron can be direct titrated against:

- | | |
|-------------|-------------|
| a) $KMnO_3$ | c) $TiCl_3$ |
| b) I_2 | d) $SnCl_2$ |

3. Karl Fischer reagent is consisting of

- | | |
|-----------------|------------------|
| a) $I_2 + SO_2$ | c) $IO^- + SO_2$ |
| b) $I^- + SO_2$ | d) $I^+ + SO_2$ |

4. In determination of H_2O_2 by permanganate it is oxidized to:

- a) $O_2 + OH^-$
- b) $O_2 + 2H^+$
- c) $2 H_2O + O_2$
- d) None of the above