Oxidation reduction

Dr.S.Alexandar,M.Pharm,Ph.D,
Associate Professor
Vinayaka Missions College of Pharmacy,
Yercaud main road,
Kondappanaickanpatty,
Salem, Tamilnadu,
Pin:636008

Oxidation

Loss of electrons

(*Gain of oxygen*)

Reduction

Gain of electrons

(*Loss of oxygen*)

"LEO the lion goes GER."

Losing Electrons is Oxidation

Gaining Electrons is Reduction

Oxidation of Food: What a Waste!

- Fruits and Vegetables oxidised when left in open air
  - Solution: Seal in plastic wrap
  - More radical: Add lemon juice to the cut fruit

Oxidation of... People!

- Oxidation of nutrients causes increased activity of cells, leading to aging skin
  - Solution: Beauty products?

What is a redox reaction?

- Redox – reduction + oxidation
- Both processes occur simultaneously
- Hence, one species is oxidised, another is reduced
- So, what is oxidation, and what is reduction?
- 3 different versions of the definition:

Redox

Oxidation	Reduction
gain in oxygen	loss of oxygen
loss of hydrogen	gain in hydrogen
loss of electrons	gain of electrons

Oxidation and Reduction

- In terms of Oxygen:
  - Oxidation: Gain of oxygen in a species
    - E.g. Mg is oxidized to MgO
  - Reduction: Loss of oxygen in a species
    - E.g. H_2O is reduced to H_2
  - Note: It's the gain or loss of O, not O^{2-}

Oxidation and Reduction

- In terms of Hydrogen:
  - Oxidation: Loss of hydrogen in a species
    - E.g. H_2O is oxidised to O_2
  - Reduction: Gain of hydrogen in a species
    - E.g. O_2 is reduced to H_2O_2
  - Note: It's the gain or loss of H, not H^+

Oxidation and Reduction

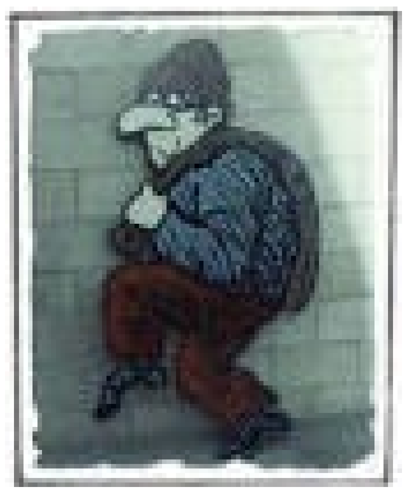
- In terms of Electrons (OIL RIG: Oxidation Is Loss, Reduction Is Gain):
  - Oxidation: Loss of electrons in a species
    - E.g. Mg is oxidized to MgO (Mg from 12 electrons to 10 electrons in Mg^{2+})
  - Reduction: Gain of electrons in a species
    - E.g. O_2 is reduced to H_2O_2(O from 8 electrons to 9 electrons per O in O_2^{2-})

Oxidising and Reducing agent

- An oxidising agent is a chemical species that causes the other reactant in a redox reaction to be oxidised, and it is always reduced in the process.
- A reducing agent is a chemical species that causes the other reactant in a redox reaction to be reduced, and it is always oxidised in the process.

The substance that donates electrons in a redox reaction is the REDUCING AGENT

The substance that takes electrons in a redox reaction is the OXIDIZING AGENT



Oxidation is…

- –the loss of electrons
- –an increase in oxidation state
- –the addition of oxygen
- –the loss of hydrogen

$$2\ Mg + O_2 \rightarrow 2\ MgO$$

notice the magnesium is losing electrons

Reduction is…

- –the gain of electrons
- –a decrease in oxidation state
- –the loss of oxygen
- –the addition of hydrogen

$$MgO + H_2 \rightarrow Mg + H_2O$$

notice the Mg^{2+} in MgO is gaining electrons

Development of oxidation and reduction reaction concept

1. Reaction of reduction oxidation based on releasing (lossing) and gaining of oxygen

a. *Oxidation reaction*

Oxidation reaction is a reaction of gaining (capturing) of oxygen by a substance

Example :

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{g)}$$

$$P_{4(s)} + 5O_{2(g)} \longrightarrow 2P_2O_{5(s)}$$

b. **Reduction reaction**

Reduction reaction is a reaction of releasing (lossing) of oxygen from a oxide compound

Example:

$$CuO_{(s)} + H_{2(g)} \longrightarrow Cu_{(s)} + H_2O_{(g)}$$

$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

2. Reduction oxidation reaction based on electron transfer

a. Oxidation reaction

Oxidation reaction is a reaction of **electron releasing (lossing)** from a substance.

Example:

$$Na \longrightarrow Na^{+} + e^{-}$$

$$Mg \longrightarrow Mg^{2+} + 2e^{-}$$

$$Cu \longrightarrow Cu^{2+} + 2e^{-}$$

b. Reduction reaction

Reduction reaction is a reaction of **electron gaining** by a substance.

Example:

$$Cl_2 + 2e^{-} \longrightarrow 2Cl^{-}$$

$$S + 2e^{-} \longrightarrow S^{2-}$$

Oxidizing Agent (Oxidant) and Reducing Agent (Reductant)

The reactants that involve in a redox reaction can be differentiated into two kinds, that is oxidizing agent (oxidant) and reducing agent (reductant)

Oxidizing agent (oxidant)

Oxidizing agent is:

- a reactant that **oxidizes** other reactant
- a reactant that can **gain electron**
- a reactant that in a reaction undergoes **reduction**
- a reactant that in a reaction undergoes **decreasing** in **oxidation number**

Examples:

Halogen, F_2, Cl_2, Br_2, I_2

Oxygen, O_2

$$Cl_{2(g))} \quad + \quad 2\,e^{-} \longrightarrow Cl^{-}_{(aq}$$

$0 \qquad\qquad\qquad\qquad (-1) \times 2$

(o. n. of Cl decreases 0 to -1)

(reduction)

Cl_2 is **oxidizing agent** (**oxidant**),
because in that reaction Cl_2 undergoes **reduction** or **decreasing** in **oxidation number**, from 0 to -1

•Reducing agent (reductant)

Reducing agent is:

- ❖ a substance (reactant) that **reduces** other substances (reactants)
- ❖ a substance (reactant) that can **loss electron**
- ❖ a substance (reactant) that in the reaction undergoes **oxidation**
- ❖ a substance (reactant) that undergoes **increasing** in **oxidation number**

Example:

Hydrogen, H_2

Ion halides; F^-, Cl^-, Br^-, I^-

metals

$$H_{2(g)} \longrightarrow 2\,H^+_{(aq)} + 2\,e^-$$

$$\underbrace{0 \qquad\qquad\qquad (+1) \times 2}_{\text{(oxidation)}}$$

o. n. of H increases from 0 to +1

H_2 is **reducing agent** (**reductant**),
because in that reaction H_2 undergoes **oxidation** or **increasing** in **oxidation number,** from 0 to +1

Reagents used in redox titration

Oxidizing agents

1) Potassium permanganate $KMnO_4$: Permanganometry

2) Ceric sulfate / Ceric ammonium sulfate $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 4H_2O$: Cerimetry

3) Potassium dichromate $K_2Cr_2O_7$: Dichrometry

4) Iodine I_2 : Iodimetry, Iodometry

5) Potassium iodate KIO_3 : Iodatimetry

6) Potassium bromate $KBrO_3$: Bromatimetry

Some common oxidizing agents

- Oxygen!
  - Oxidized coal in electric power
  - Gas in automobiles
  - Wood in campfires
  - Food we eat
- Antiseptics
  - Hydrogen Peroxide
  - Benzoyl peroxide
- Disinfectants
  - Chlorine

Reagents used in redox titration

Reducing agents

1) ammonium iron(II) sulfate hexahydrate (Mohr's salt) $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$

2) iron(II) ethylene diamine sulfate (Oesper's salt) $FeC_2H_4(NH_3)_2(SO_4)_2 \cdot 4H_2O$

3) Sodium thiosulfate pentahydrate $Na_2S_2O_3 \cdot 5H_2O$

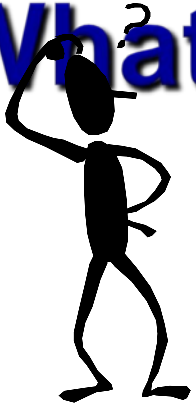
4) Arsenic trioxide: arsenious oxide As_2O_3

5) Sodium oxalate and oxalic acid dihydarte $Na_2(COO)_2$, $(COOH)_2 \cdot 2H_2O$

Some common reducing agents

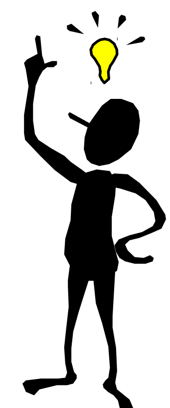
- Metals
- Antioxidants
  - Ascorbic acid is used to prevent the browning of fruits by inhibiting air oxidation
  - Many antioxidants are believed to retard various oxidation reactions that are potentially damaging to vital components of living cells

What's the point ?



REDOX reactions are important in …

- Purifying metals (e.g. Al, Na, Li)
- Producing gases (e.g. Cl_2, O_2, H_2)
- Electroplating metals
- Electrical production (batteries, fuel cells)
- Protecting metals from corrosion
- Balancing complex chemical equations
- Sensors and machines (e.g. pH meter)



Assigning Oxidation Numbers

- An oxidation number is a positive or negative number assigned to an atom to indicate its degree of oxidation or reduction.

As a general rule, *a bonded atom's oxidation # is* ***the charge that it would have if the electrons in the bond were assigned to the atom of the more electronegative element.***

TABLE 19-1 Rules for Assigning Oxidation Numbers

Rule	Example
1. The oxidation number of any uncombined element is 0.	The oxidation number of Na(*s*) is 0.
2. The oxidation number of a monatomic ion equals the charge on the ion.	The oxidation number of Cl^- is –1.
3. The more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.	The oxidation number of O in NO is –2.
4. The oxidation number of fluorine in a compound is always –1.	The oxidation number of F in LiF is –1.
5. Oxygen has an oxidation number of –2 unless it is combined with F, when it is +2, or it is in a peroxide, such as H_2O_2, when it is –1.	The oxidation number of O in NO_2 is –2.
6. The oxidation state of hydrogen in most of its compounds is +1 unless it is combined with a metal, in which case it is –1.	The oxidation number of H in LiH is –1.
7. In compounds, Group 1 and 2 elements and aluminum have oxidation numbers of +1, +2, and +3, respectively.	The oxidation number of Ca in $CaCO_3$ is +2.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.	The oxidation number of C in $CaCO_3$ is +4.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals the charge of the ion.	The oxidation number of P in $H_2PO_4^-$ is +5.

The sum of the oxidation numbers of all the atoms in a compound is zero.

- CuO

  Oxygen is -2

  The oxidation number of copper must be calculated

  X + -2 = 0

  X = +2

- Na_2SO_4
  - Na is +1 because it is a group 1 metal
  - O is -2
  - The oxidation number of Sulfur must be calculated

  2(+1) + X + 4(-2) = 0

  (2) + X + (-8) =0

  X = +6

The sum of the oxidation numbers of all the atoms in a polyatomic ion is the charge of the ion.

- NO_3^-

  Oxygen is 2-

  The oxidation number of nitrogen must be calculated

  X + 3(-2) = -1

  X = 5+

- PO_4^{3-}

  Oxygen is 2-

  The oxidation number of phosphorous must be calculated

  X + 4(-2) = -3

  X + (-8) = -3

  X = +5

20.5 Balancing Redox Equations

There are two methods used to balance redox reactions

1) the oxidation number change method

2) the half reaction method

- Using the oxidation-number change method
- $Fe_2O_{3(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$ (unbalanced)
- **Step 1** – assign oxidation #s to all the atoms in the equation.
- **Step 2** – ID atoms oxidized and reduced.

$$\overset{+3\ \ -2}{Fe_2O_3(s)} + \overset{+2\,-2}{CO(g)} \longrightarrow \overset{0}{Fe(s)} + \overset{+4\,-2}{CO_2(g)}$$

- **Step 3** – Use one bracketing line to connect the atoms that undergo oxidation & another to connect reduced.

+2 (oxidation)

$$\overset{+3\ \ -2}{Fe_2O_3(s)} + \overset{+2\,-2}{CO(g)} \longrightarrow \overset{0}{Fe(s)} + \overset{+4\,-2}{CO_2(g)}$$

−3 (reduction)

- **Step 4** – Make the total increase in oxidation # equal to the total decrease in oxidation # by using appropriate coefficients.

$3 \times (+2) = +6$

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

$2 \times (-3) = -6$

Electrochemical Cells

There are two kinds of electro chemical cells, galvanic or electrolytic.

In galvanic cells, the chemical reaction occurs spontaneously to produce electrical energy.

In a electrolytic cell, electrical energy is used to force the non spontaneous chemical reaction.

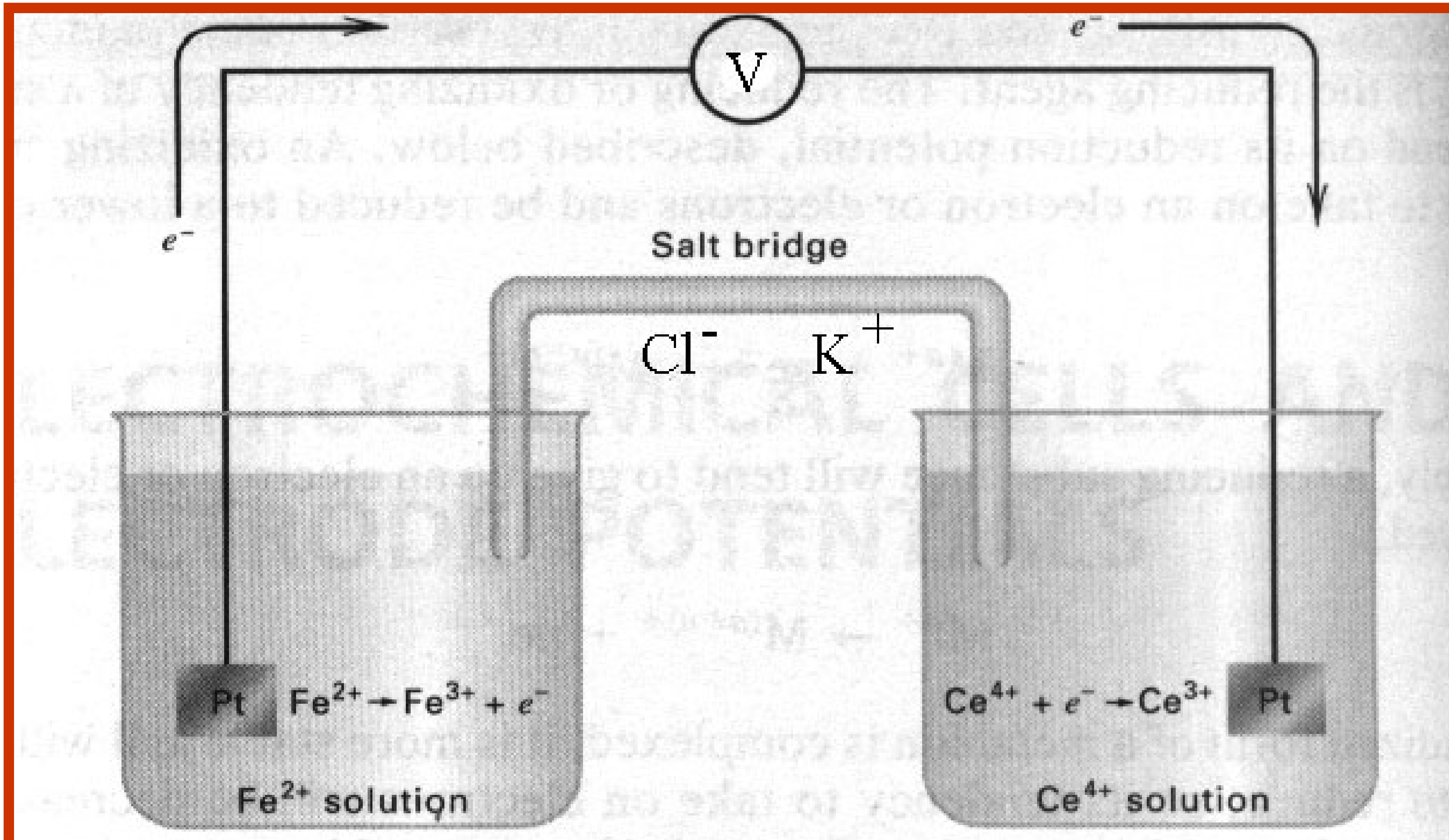
If a solution containing Fe^{2+} is mixed with another solution containing Ce^{4+}, there will be a redox reaction situation due to their tendency of transfer electrons. If we consider that these two solution are kept in separate beaker and connected by salt bridge and a platinum wire that will become a galvanic cell. If we connect a voltmeter between two electrode, the potential difference of two electrode can be directly measured.

The Fe^{2+} is being oxidised at the platinum wire (the anode):

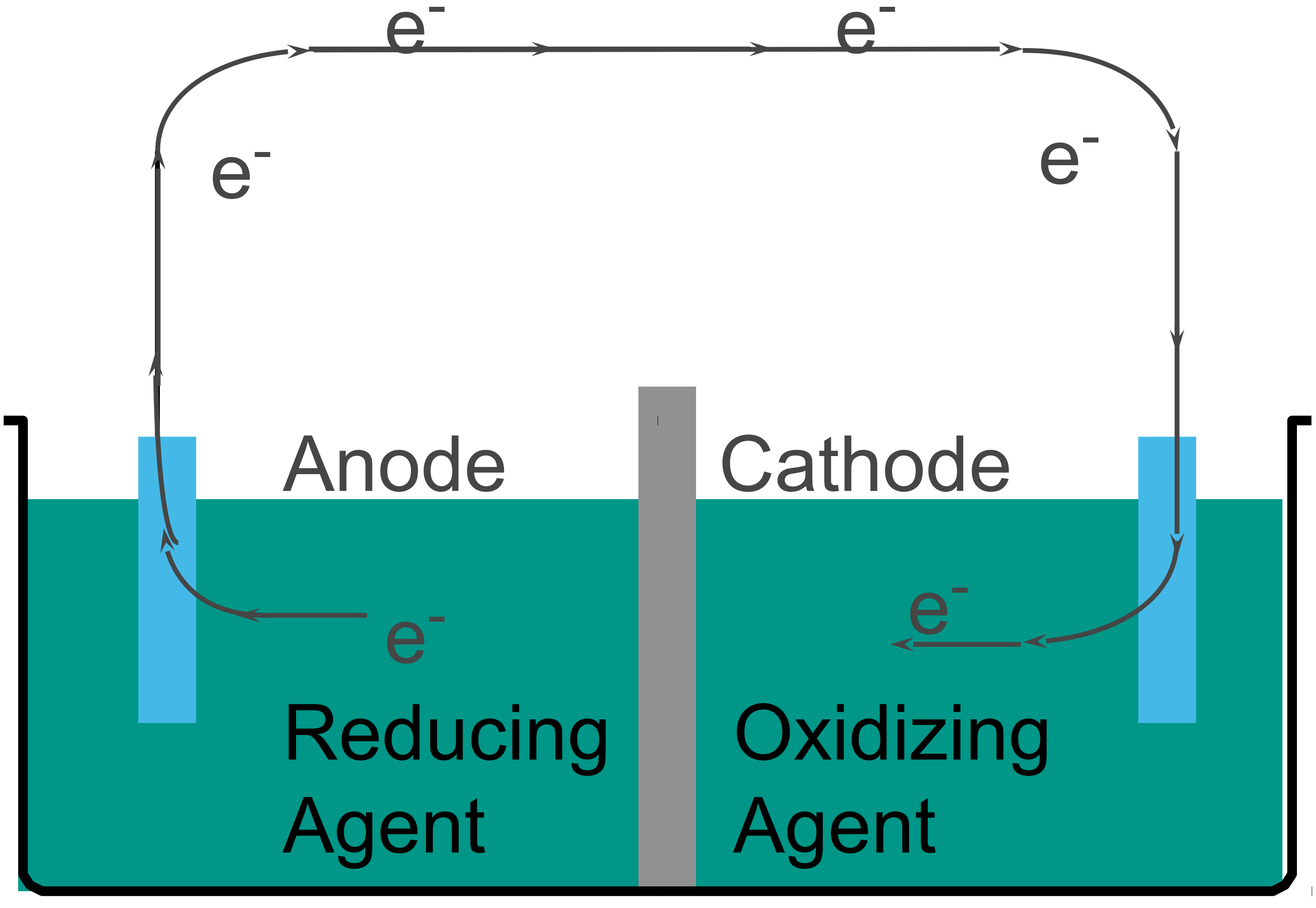
$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

The electron thus produced will flow through the wire to the other beaker where the Ce^{4+} is reduced (at the cathode).

$$Ce^{4+} + e^{-} \rightarrow Ce^{3+}$$



Galvanic Cell

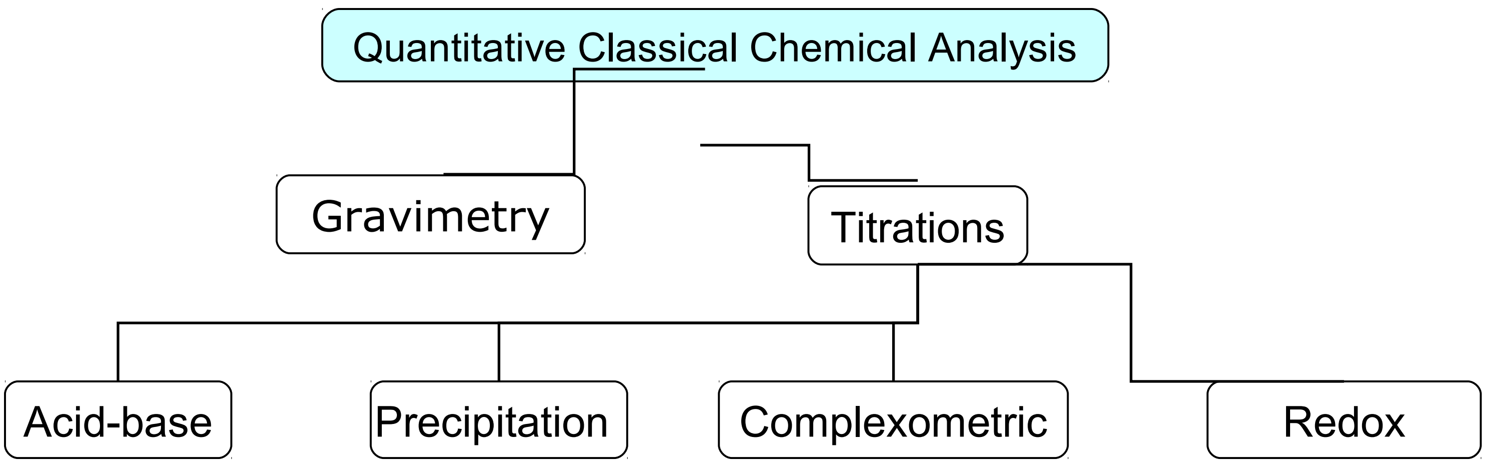


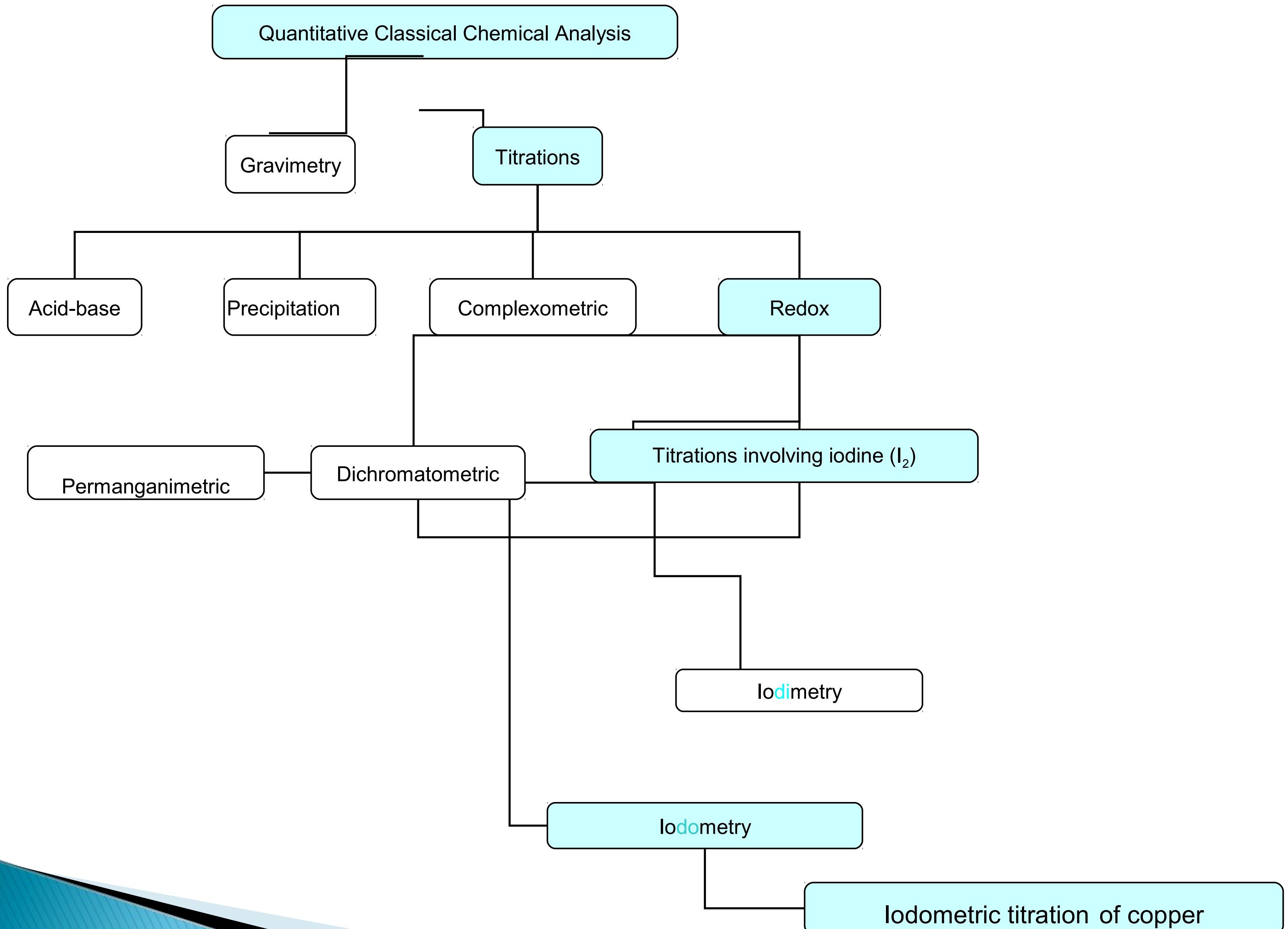
e-
e-
e-
e-
Anode
Cathode
e-
e-
Reducing Agent
Oxidizing Agent

Cell Potential

- Oxidizing agent pulls the electron.
- Reducing agent pushes the electron.
- The push or pull ("driving force") is called the cell potential E_{cell}
- Also called the electromotive force (emf)
- Unit is the volt(V)
- = 1 joule of work/coulomb of charge
- Measured with a voltmeter

Introduction to iodometric and iodimetric titrations





Quantitative Classical Chemical Analysis
Gravimetry
Titrations
Acid-base
Precipitation
Complexometric
Redox
Permanganimetric
Dichromatometric
Titrations involving iodine (I_2)
Iodimetry
Iodometry
Iodometric titration of copper

	Titration example	Analyte	Titrant	Indicator
Acid-base	Quantification of acetic acid in avinegar	Acetic acid (CH_3COOH)	NaOH (sodium hydroxide)	Phenolphthalein
Complexometric	Water Hardness (Calcium and magnesium)	Calcium and magnesium (Ca^{2+}, Mg^{2+})	EDTA	Eriochrome black T Murexide
Precipitation	Quantification of chloride (Cl^-) in water	Chlordie	$AgNO_3$ (silver nitrate)	Mohr, Volhard, Fajans
Redox	Quantification of hydrogen peroxide (H_2O_2)	Hydrogen peroxide (H_2O_2)	$KMnO_4$ (potassium permanganate)	No indicator

Titrations:

- Direct Titrations
- Indirect Titrations
- Back Titrations
- Iodometry

Titrations	Example		Type of reaction
Acid-base	Quantification of acetic acid in vinegar		□ Direct Titration □ Indirect Titration □ Back Titration
Complexo metric	Water Hardness (Calcium and magnesium)		□ Direct Titration □ Indirect Titration □ Back Titration
Precipitation	Quantification of Cl in Water	Mohr Method	□ Direct Titration □ Indirect Titration □ Back Titration
		Fajans Method	□ Direct Titration □ Indirect Titration □ Back Titration
		Volhard Method	□ Direct Titration □ Indirect Titration □ Back Titration
Redox	Quantification of hydrogen peroxide (H_2O_2)		□ Direct Titration □ Indirect Titration □ Back Titration

There are a lot of **redox titrations** classified according to the **titrant** used.

1) Permanganimetric: Titrant $KMnO_4$

2) Dichromatometric: Titrant $K_2Cr_2O_7$

3) Titrations involving **iodine (I_2)**

- **Iodimetry**
- **Iodometry**

Titrations that create or consume I_2 are widely used in **quantitative analysis**.

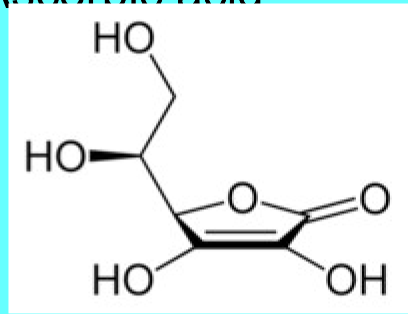
When a reducing analyte is titrated with iodine (the titrant), the method is called iodimetry.

Example: Quantification of Ascorbic Acid (Vitamin C)

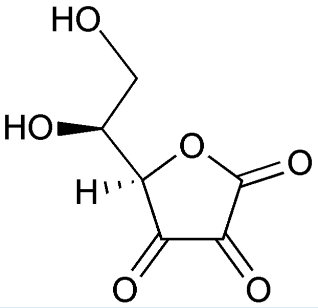
$C_6H_8O_6 + I_2 \rightarrow C_çH_6O_6 + 2I^- + 2H^+$

Iodine rapidly oxidizes ascorbic acid, $C_6H_8O_6$, to produce dehydroascorbic acid, $C_6H_6O_6$.

Ascorbic acid



Dehydroascorbic acid



Pictures taken from: http://en.wikipedia.org

Iodometry is the titration of iodine (I_2) produced when an oxidizing analyte is added to excess I^-(iodide).

Then the iodine (I_2) is usually titrated with standard **thiosulfate** solution.

Iodometry: Not a direct titration because there are 2 reactions:

analyte + I^- → I_2
unknown

I_2 + titrant (standard thiosulfate) → product
Known

Iodimetric titrations:

a) A reducing analyte

b) One reaction

c) Standard solution: Iodine (I_2)

Iodometric titrations:

a) An oxidizing analyte

b) Two reactions

c) Standard solution: Sodium thisoufate

Analytical applications:

Iodimetric titrations:

Species analyzed (reducing analytes)

SO_2 , H_2S, Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+}

Cysteine, glutathione, mercaptoethanol

Glucose (and other reducing sugars)

Iodometric titrations:

Species analyzed (oxidizing analytes)

HOCl ,Br_2, IO_3^- , IO_4^- , O_2, H_2O_2, O_3

NO_2^- , Cu^{2+}

MnO_4^-, MnO_2

	Direct Iodimetric method	Indirect Iodometric method
Titrating agent	Iodine for determination of reducing agents	I^- is added to oxidizing agents,the librated I_2 is titr. with $Na_2S_2O_3$
Indicator (Starch)	Added at the beginning of titr.	Added near the end of titr (when the brown color of I_2 becomes pale)
Type of reaction	One step reaction	Two step reactions
Standard solution	Standard solution: Iodine (I_2)	Standard solution: Sodium thisoufate
E.P.	permanent blue color	disappearance of blue color

Iodine as oxidant