# Oxidation

Loss of electrons

(*Gain of oxygen*)

# Reduction

Gain of electrons

(*Loss of oxygen*)

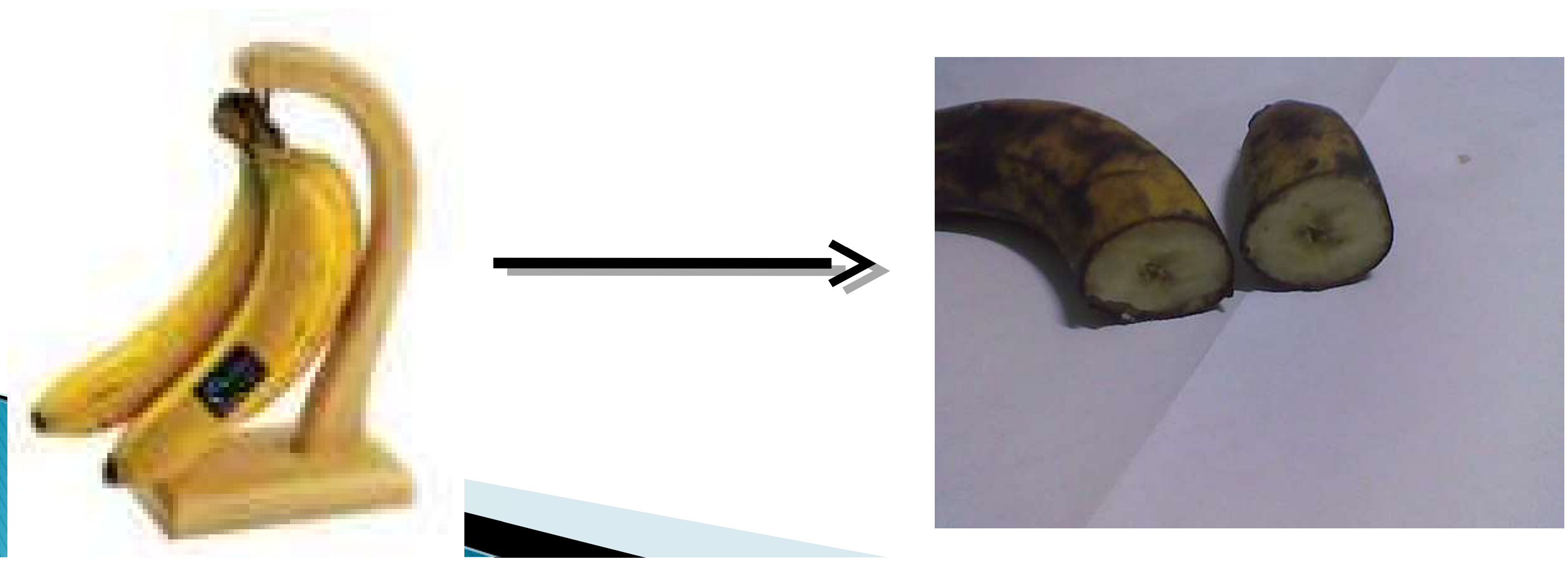
"**LEO** the lion goes **GER**."

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:

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

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

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

### b. **Reduction reaction**

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

Example:

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

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

## 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, $O_2$

$Cl_{2(g))}$ + $2e^-$ ⟶ $Cl^-_{(aq}$

0          (-1) x 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

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

0 ⟶ (+1) x 2

(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 $Na_2S_2O_3 \cdot 5H_2O$

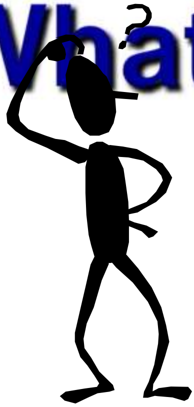
4) Arsenic trioxide: arsenious oxide $As_2O_3$

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

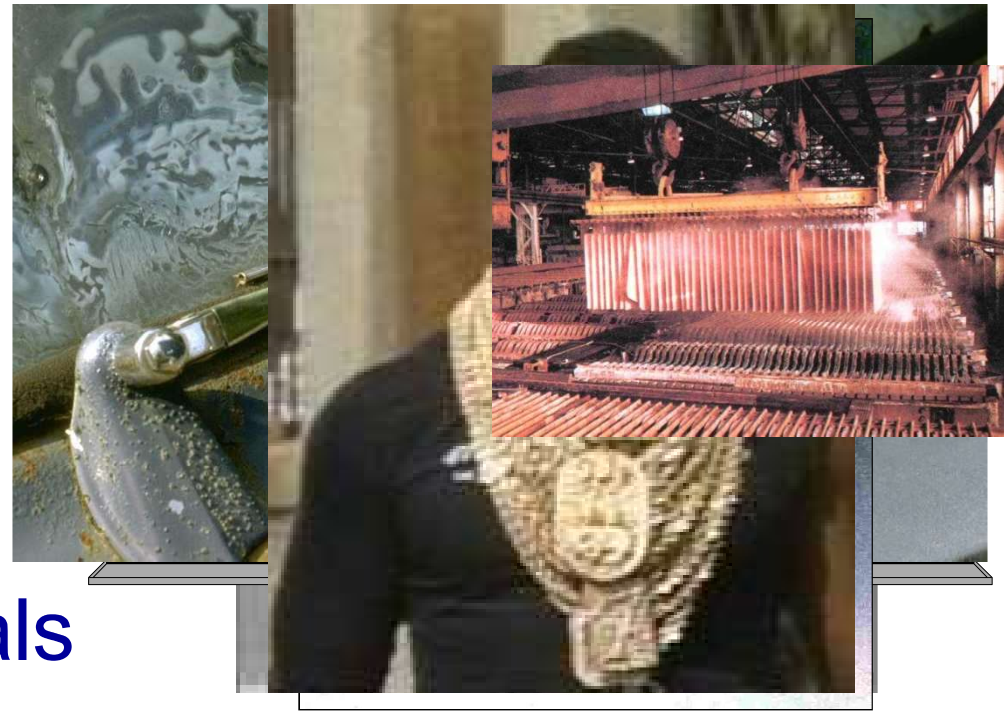
# Some common reducing agents

- 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.

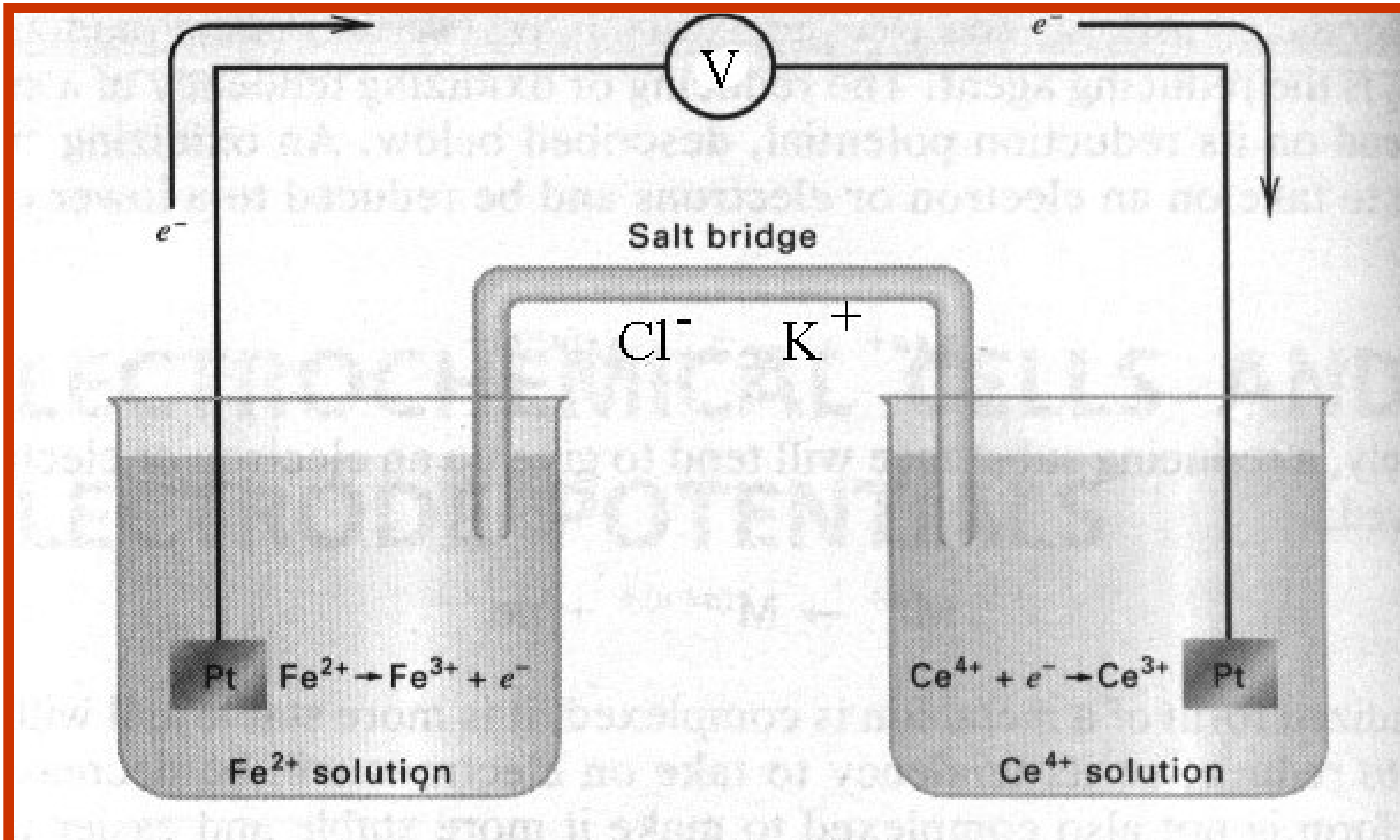
If a solution containing $Fe^{2+}$ is mixed with another solution containing $Ce^{4+}$, there will be a redox reaction situation due to their tendency of transfer electrons. If we consider that these two solution are kept in separate beaker and connected by salt bridge and a platinum wire that will become 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):

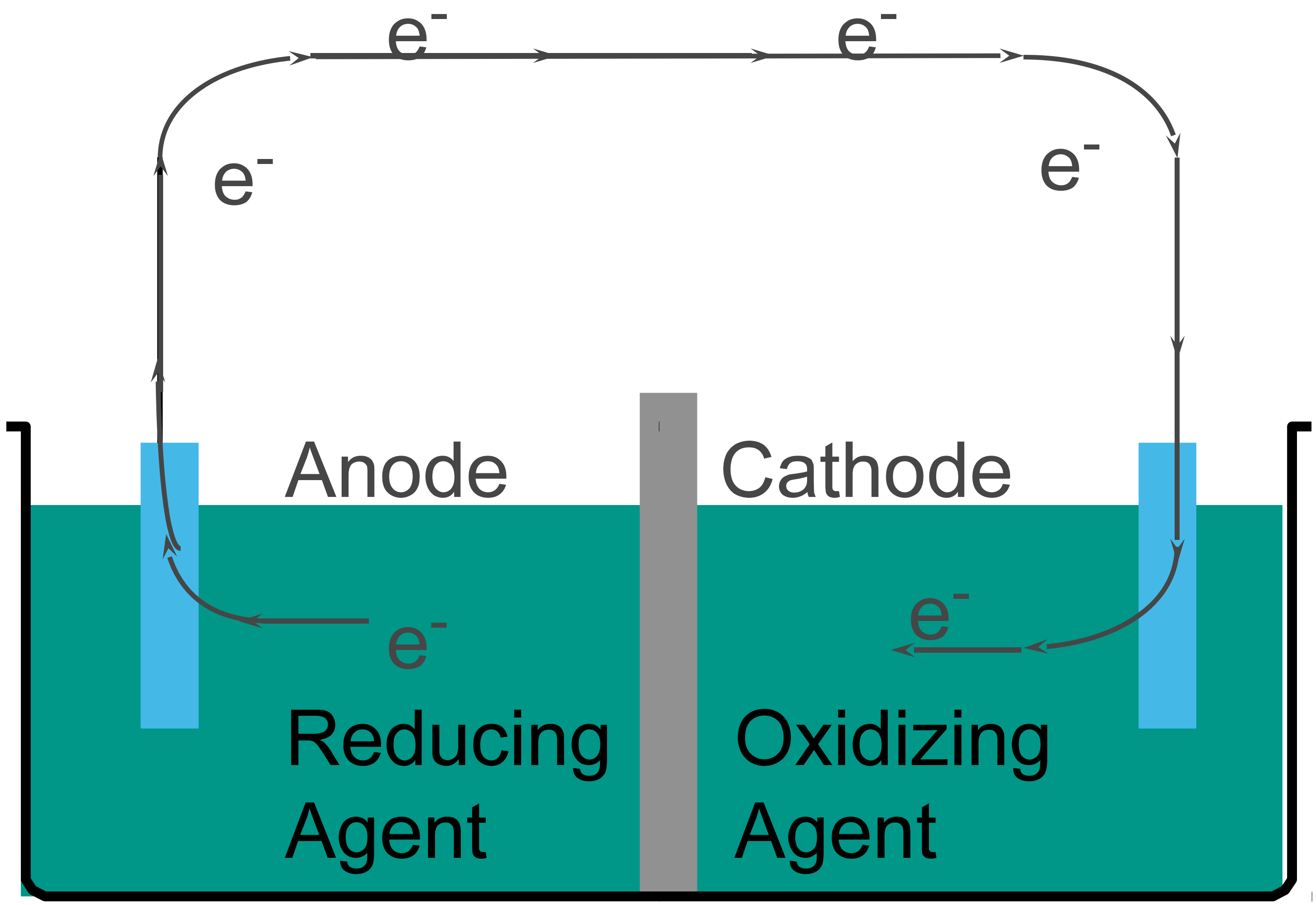
$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

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

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



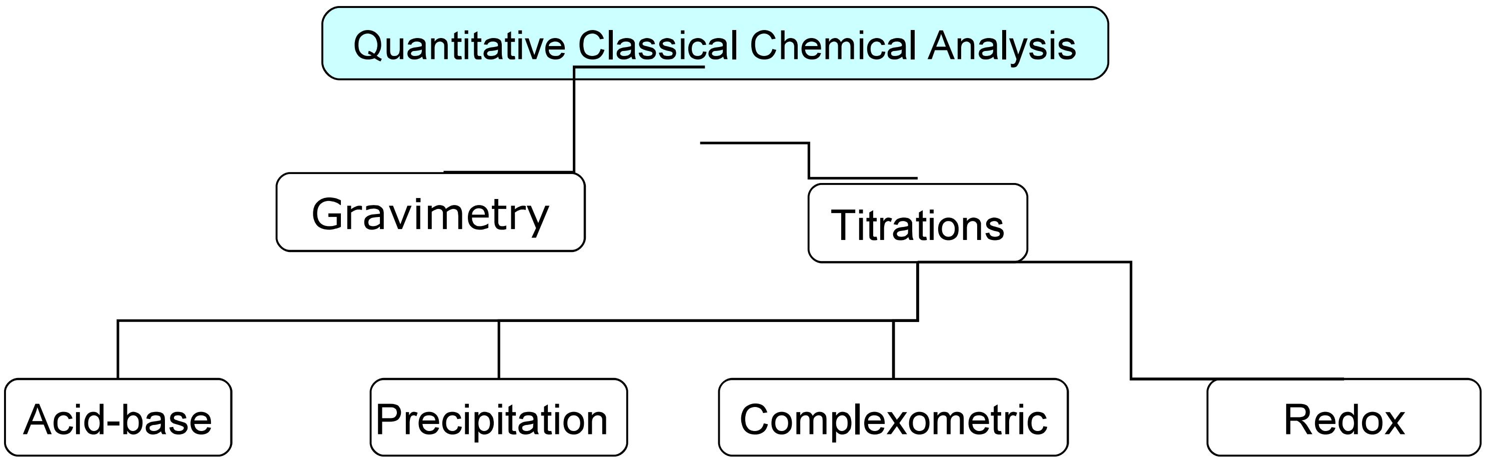
Galvanic Cell

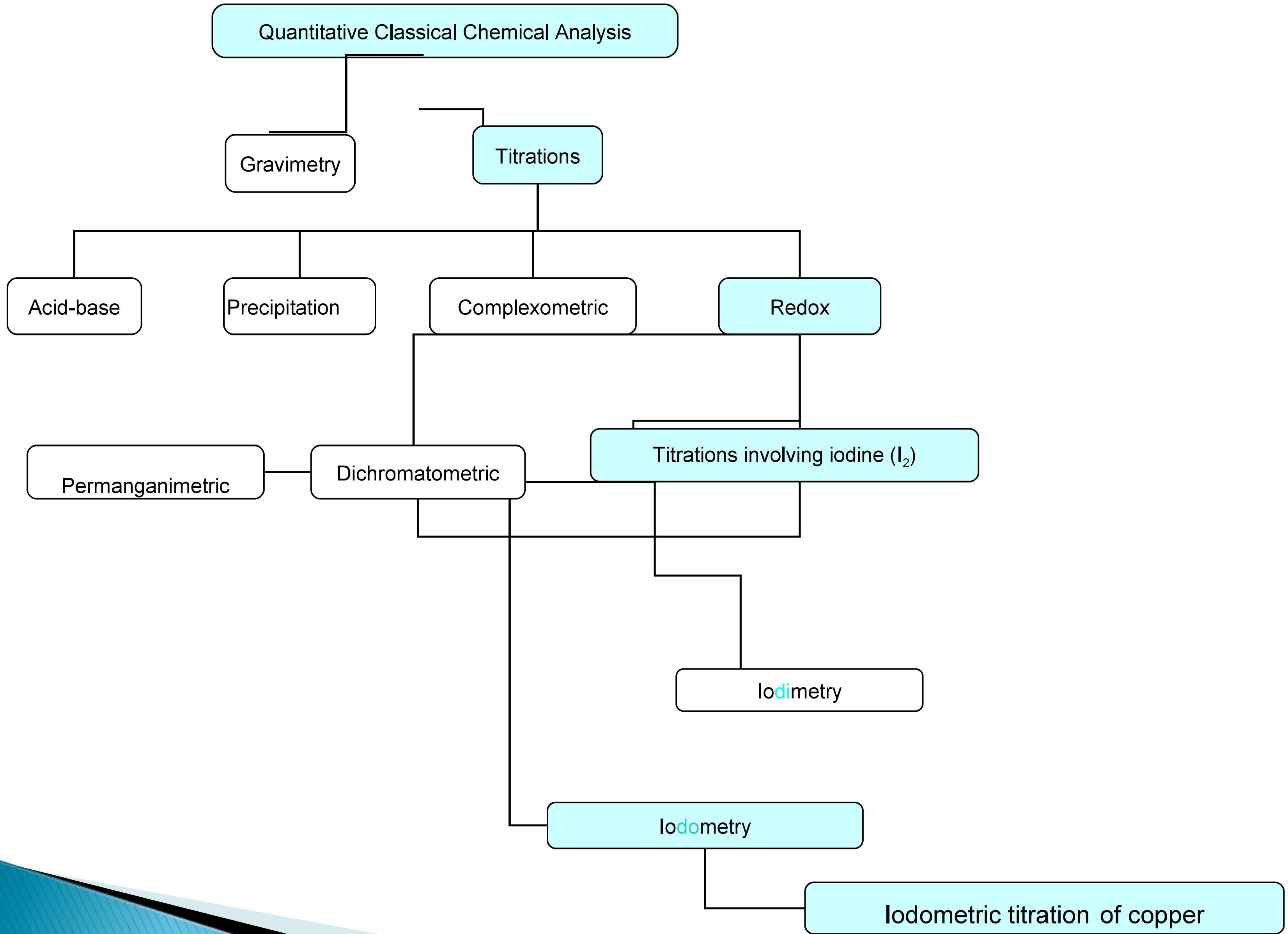

e-
e-
e-
e-
Anode
Cathode
e-
e-
Reducing Agent
Oxidizing Agent

# 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<br>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**.

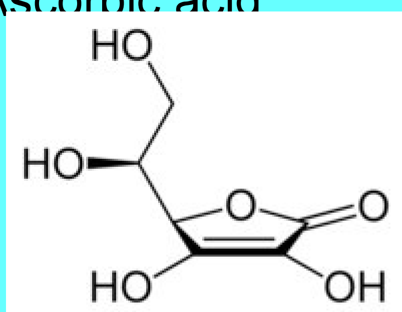
**When a reducing analyte is titrated with iodine (the titrant), the method is called iodimetry.**

**Example: Quantification of Ascorbic Acid (Vitamin C)**

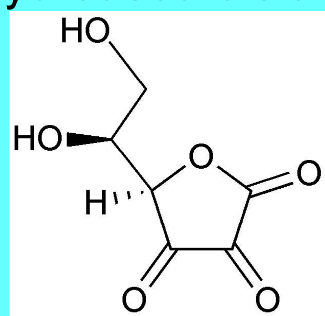
$C_6H_8O_6 + I_2 \rightarrow C_{ç}H_6O_6 + 2I^- + 2H^+$

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<br>Iodimetric method | Indirect<br>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