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# **GRADE – 12 CHEMISTRY**

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**HANDOUT FOR SECOND SEMESTER LESSONS**



**OROMIA EDUCATION  
BUREAU**

**In Collaboration with  
*EXCEL ACADEMY***

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# UNIT 4: ELECTROCHEMISTRY

## 4.1. Introduction

Electrochemistry is the study of the inter conversion of electrical energy into chemical energy (using electrolytic cells) and chemical energy into electrical energy (using voltaic or galvanic cells). All electrochemical reactions involve the transfer of electrons in atoms, molecules or ions, and are therefore oxidation – reduction (Redox) reactions.

**Oxidation:** involves increase in oxidation number. This happens because of loss of electron(s).

**Reduction:** involves decrease in oxidation number. This is due to gain of electron(s).

**Oxidation number:** the oxidation number of a bonded atom is the charge it would have if all the electrons in each bond were given to the more electronegative atom of the pair. The one from which the electrons are taken (the less electronegative atom) assumes a positive charge while the one which takes all the bonding electrons (the more electronegative atom) assumes a negative charge. The oxidation number of an element is zero.

The following general guideline helps to assign oxidation numbers to atoms in most of the common compounds.

1	All alkali metals (Group IA) take +1 oxidation state in their compounds
2	All alkaline earth metals (Group IIA) assume +2 oxidation state in their compounds
3	All Group VIIA elements (halogens) take (–1) oxidation state in compounds they form with metals and $\text{NH}_4^+$ ion. Atoms of this group (except fluorine) may take positive oxidation states ranging from 1 up to 7 depending on the atom to which they are bonded. A halogen bonded to oxygen atom always takes positive oxidation state, e.g. +1 in $\text{ClO}^-$ , +3 in $\text{ClO}_2^-$ , +5 in $\text{BrO}_3^-$ , and +7 in $\text{Cl}_2\text{O}_7$ and $\text{IO}_4^-$ , etc. Fluorine always takes –1 oxidation state in all its compounds.
4	Oxygen takes –2 oxidation state in normal oxides, –1 in per oxides (e.g. $\text{Na}_2\text{O}_2$ ) and $-\frac{1}{2}$ in super oxides ( $\text{KO}_2$ ).

A substance that gains (accepts) electron(s) is said to be *reduced*. The reduced substance causes the donor to be oxidized. Therefore, a reduced substance is the *oxidizing agent*. Similarly, a species that loses (donates) electron(s) is said to be *oxidized*. This substance makes the electron acceptor to be reduced. Therefore, the oxidized substance is the *reducing agent*. **Example:**

Label (a) the oxidation number of each substance; (b) the oxidizing and reducing agents and (c) the number of electrons transferred by each species in the decomposition reaction given by:



Atom	Reactant	Product	process	Electrons transferred
K	+1	+1	none	none
Cl	+5	–1	reduced	6
O	–2	0	oxidized	2 per atom

In the above Redox reaction,  $\text{KClO}_3$  is both the oxidizing and reducing agent, i.e. the oxidized and the reduced substance is the  $\text{ClO}_3^-$  ion.

Note that oxidation and reduction processes occur simultaneously. Each process usually takes place on metal surfaces called electrodes. The one at which **O**xidation occurs is called the **A**node while the electrode at which **R**eduction occurs is called the **C**athode.

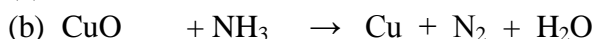
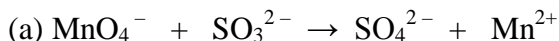
Electrical conduction occurs either by movement of electrons or ions. The former, which occurs because of movement of electrons, is called metallic conduction. Here, electrons carry the electric charge and this is a property of metallic elements. Conduction due to movement of ions is called electrolytic conduction. This movement of ions occurs through a solution or a pure (molten) liquid. Substances whose aqueous solutions or molten states conduct electricity are called electrolytes.

### Check point 1.

1. Assign oxidation number to:

(a) Cr in  $\text{K}_2\text{Cr}_2\text{O}_4$       (b) Cr in  $\text{Cr}_2\text{O}_7^{2-}$       (c) Cl in  $\text{HClO}_4$       (d) O in  $\text{F}_2\text{O}$       (e) I in  $\text{IF}_7$

2. Label the oxidizing and reducing agents. Also, count the number of electrons lost or gained in each case.



3. Which type of reactions (neutralization, decomposition, double replacement, synthesis, combustion, etc.) are always Redox and which types are always non-Redox?

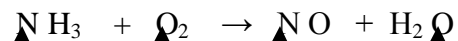
## 4.2. Balancing Oxidation – Reduction Reactions

Since matter can neither be created nor destroyed in a chemical reaction, the total mass, atoms of each type and the net charge in the reactant side must be equal to that of the product side. In other words, mass, atoms and charge are conserved because of the law of the conservation of matter and energy. This is the basis for the need to balance all chemical reactions.

### Method 1: Oxidation number – change

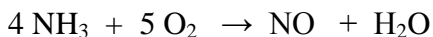
This is particularly applied for non-aqueous Redox reactions. It starts by assigning oxidation number to each atom in the reactant and product sides, and focusing only on those atoms that show change in oxidation numbers. Then, determine the number of electrons lost and gained by each atom undergoing oxidation and reduction, respectively. Finally, balance the number of electrons lost in oxidation with that of gained in reduction by assigning proper coefficients to the substances oxidized and reduced. The atoms that do not show change in oxidation number can be balanced easily by inspection (counting the atoms). **Example:**

Apply oxidation number – change method to balance:  $\text{NH}_3 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow \text{NO} (\text{g}) + \text{H}_2\text{O} (\text{l})$

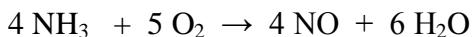


5 electrons lost      2 electrons gained per oxygen atom (a total of 4 electrons)

Therefore, the balancing coefficients in the reactant side are 4 and 5, respectively.



The coefficients in the product side are obtained simply by counting the atoms, which gives 4 & 6, respectively.



### Method 2: The Ion – Electron (Half – reaction) method

This method is particularly applicable for Redox reaction that occur in aqueous solution and when the net ionic equation is given (without spectator ions). For simplicity, let us assume that the reaction proceeds in acidic medium. One can change this result into a reaction in basic medium by simply adding  $\text{OH}^-$  ions equal in number to that of  $\text{H}^+$  ions to both sides of the equation. In this method, the whole reaction equation is split into two half-reactions: one oxidation half-reaction

and another reduction half - reaction. Then each half reaction is separately balanced by applying the following four steps, in the given order.

Material balance → Oxygen balance → Hydrogen balance → Charge balance!

Material balance: Balance all elements except oxygen and hydrogen by inspection (counting atoms)

Oxygen balance: This is balanced by *adding* enough number of H<sub>2</sub>O to the deficient side of the equation

Hydrogen balance: This is balanced by *adding* sufficient number of H<sup>+</sup> ions to the deficient side

Charge balance: The charge is balanced by *adding* sufficient number of electrons, e<sup>-</sup>, to the more positive side of the half – equation.

Finally, balance the number of electrons lost in the oxidation half – equation with the number of electrons gained in the reduction half – equation. The number used for balancing electrons is also a multiplier (coefficient) of the substances in the respective half – equations. Example:

Apply the ion – electron method to balance:  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{S} \rightarrow \text{Cr}^{3+} + \text{S}$

Item	Oxidation half – reaction	Reduction half – reaction
	$\text{H}_2\text{S} \rightarrow \text{S}$	$\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$
Material	balanced	$\text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+}$
Oxygen	balanced	$\text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$
Hydrogen	$\text{H}_2\text{S} \rightarrow \text{S} + 2 \text{H}^+$	$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$
Charge	$\text{H}_2\text{S} \rightarrow \text{S} + 2 \text{H}^+ + 2 \text{e}^-$	$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$

The oxidation half – equation must be multiplied by 3 to balance the number of electrons lost in the oxidation half – equation with that of the electrons gained in the reduction half – equation.

Oxidation:  $3 \text{H}_2\text{S} \rightarrow 3 \text{S} + 6 \text{H}^+ + 6 \text{e}^-$

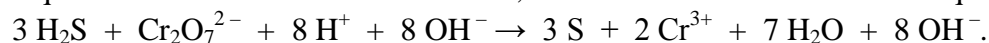
Reduction:  $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$

Adding the two half – equations and cancelling common terms gives the final balanced equation.

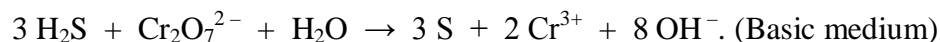


Oxygen count =	7	7
Hydrogen count =	14	14
Net charge =	+ 6	+ 6

To convert this equation to a reaction in basic medium, add 8 OH<sup>-</sup> to both sides of the equation.



Simplifying gives:



Oxygen count =	8	8
Hydrogen balance =	8	8
Net charge =	-2	-2

### Check point 2.

1. Balance the equation for the reaction between per manganate ion (MnO<sub>4</sub><sup>-</sup>) and sulfite ion (SO<sub>3</sub><sup>2-</sup>) to give manganese (IV) oxide (MnO<sub>2</sub>) and sulfate ion (SO<sub>4</sub><sup>2-</sup>) in acidic solution.
2. Copper metal reacts with concentrated nitric acid to produce copper nitrate, nitrogen (IV) oxide gas and water. Apply oxidation number – change method to balance the equation of this reaction.
3. What is the coefficient of H<sub>2</sub>O when the reaction:  $\text{NO}_2^- + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} + \text{NO}_3^-$  is balanced to the simplest whole number ratio in acidic medium?

### 4.3. Electrolysis of Molten and Aqueous Electrolytes

Electrolysis is a process in which electrical energy is used to cause a non –spontaneous oxidation – reduction to occur. This takes place in an electrolytic cell. The apparatus consists of a battery or some other source of direct electrical current connected to two separate electrodes, which are immersed in the electrolyte. An electrode can be *inert*, passing electrons into and out of the electrolyte without itself undergoing a change or *active*, undergoing oxidation during the electrolysis process. Graphite (carbon) and platinum are typical inert electrodes whereas metals like zinc, magnesium, and copper may behave active depending on the nature of the electrolyte used.

During electrolysis, the anions migrate towards the electrode connected to the positive terminal of the electric source or battery. This electrode is called the *anode* and oxidation half – reaction occurs at this electrode. Here, anions lose electrons (supply electrons to the anode) and become discharged as atoms or molecules. Since negatively charged substances (anions) migrate towards the anode, it is the positive electrode.

The cations migrate towards the electrode connected to the negative terminal of the electric source. This electrode is called the *cathode*. Cations accept electrons from this electrode and become discharged as an element. Therefore, reduction half –reaction occurs at the cathode and it is the negative electrode. Electrons move from anode to cathode through an external conducting wire.

Let us see what happens during electrolysis of molten NaCl using graphite or platinum electrodes. (Refer to Fig. 4.3, page 168 of Grade 12 student text book.) Ions present are  $\text{Na}^+$  and  $\text{Cl}^-$ .

Oxidation at the anode:  $\text{Cl}^- (\text{l}) \rightarrow \frac{1}{2} \text{Cl}_2 (\text{g}) + \text{e}^-$

Reduction at the cathode:  $\text{Na}^+ (\text{l}) + \text{e}^- \rightarrow \text{Na} (\text{s})$

Cell reaction:  $\text{NaCl} (\text{l}) \rightarrow \text{Na} (\text{s}) + \frac{1}{2} \text{Cl}_2 (\text{g})$

In aqueous solutions, the substances that compete for discharge at each electrode are the cation and anion of the electrolyte plus the solvent, water. Note that there are no  $\text{H}^+$  and  $\text{OH}^-$  ions in pure water.  $\text{H}_2\text{O}$  is not a conductor of electricity!! The oxidation and reduction of water (*acidified*) proceeds as follows.

Oxidation:  $2 \text{H}_2\text{O} (\text{l}) \rightarrow \text{O}_2 (\text{g}) + 4 \text{H}^+ (\text{aq}) + 4 \text{e}^-$ ;  $E^0 = -1.23 \text{ V}$

Reduction:  $2 \text{H}_2\text{O} (\text{l}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2 \text{OH}^- (\text{aq})$ ;  $E^0 = -0.83 \text{ V}$

The ease of discharge of substances from an aqueous solution at each electrode is governed by three factors.

**A. Electrode potential,  $E^0$**  (Refer to Table 4.2, page 192 in the student text book)

This is the potential associated with the oxidation or reduction of the substance, denoted by  $E^0$ . The more *positive* this potential, the more preferred is the substance to be discharged. For example, in an aqueous solution of  $\text{CuCl}_2$ , the substances competing for reduction (at the cathode) are  $\text{Cu}^{2+}$  and  $\text{H}_2\text{O}$  while the substances competing for oxidation (at the anode) are  $\text{Cl}^-$  and  $\text{H}_2\text{O}$ . At the cathode,  $\text{Cu}^{2+}$  is reduced in preference to  $\text{H}_2\text{O}$  because the reduction potential of  $\text{Cu}^{2+}$  is more positive (+ 0.34 V) than that of  $\text{H}_2\text{O}$  (–0.83 V). On the other hand,  $\text{H}_2\text{O}$  is oxidized at the anode in preference to  $\text{Cl}^-$  because the oxidation potential of  $\text{H}_2\text{O}$  is more positive (–1.23 V) than that of  $\text{Cl}^-$  (–1.36 V).

Reduction at the cathode:  $2 \text{Cu}^{2+} + 4 \text{e}^- \rightarrow 2 \text{Cu}$ ,  $E^0 = +0.34 \text{ V}$

Oxidation at the anode:  $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$ ,  $E^0 = -1.23 \text{ V}$

Cell reaction:  $2\text{CuCl}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Cu} + \text{O}_2 + 4\text{HCl}$ ,  $E^0_{\text{cell}} = -0.89\text{ V}$ .

The negative potential of the cell denotes that the process (electrolysis) is non – spontaneous. Note that  $E^0$  is an *intensive* property!

### B. Concentration of the electrolyte

For substances of *comparable* electrode potentials  $E^0$ , the more concentrated species discharges first at the respective electrode. During the electrolysis of concentrated NaCl solution (also called brine),  $\text{Cl}^-$  is oxidized first because it is more concentrated. On the other hand, even though  $\text{Na}^+$  is concentrated,  $\text{H}_2\text{O}$  is reduced at the cathode because the reduction potential of  $\text{Na}^+$  is very large negative ( $-2.71\text{ V}$ ) as compared to that of  $\text{H}_2\text{O}$  ( $-0.83\text{ V}$ ). This shows that electrode potential has more effect than concentration.

Oxidation at the anode:  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

Reduction at the cathode:  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$

Cell reaction:  $2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2\text{NaOH}$

### C. Nature of electrode used

Active electrodes such as zinc, magnesium, copper, silver, etc. may interfere in the electrolysis process and affect the type of product collected at the electrodes. **Example:**

*Electrolysis of  $\text{CuSO}_4$  solution using graphite (inert) electrodes*

This solution is blue because of  $\text{Cu}^{2+}$  ions in water. At the cathode,  $\text{Cu}^{2+}$  ion is reduced in preference to  $\text{H}_2\text{O}$  because  $E^0$  of  $\text{Cu}^{2+}$  is more positive than that of  $\text{H}_2\text{O}$ . At the anode,  $\text{H}_2\text{O}$  is oxidized in preference to  $\text{SO}_4^{2-}$  because the oxidation potential of  $\text{H}_2\text{O}$  ( $-1.23\text{ V}$ ) is more positive than that of  $\text{SO}_4^{2-}$  ( $-2.0\text{ V}$ ).

Cathode:  $2\text{Cu}^{2+} + 4\text{e}^- \rightarrow 2\text{Cu}$

Anode:  $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

Cell reaction:  $2\text{CuSO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Cu} + \text{O}_2 + 2\text{H}_2\text{SO}_4$

Electrolysis of  $\text{CuSO}_4$  solution using inert electrodes results in decrease of pH of the electrolyte and it is one industrial method of preparing  $\text{H}_2\text{SO}_4$  in a pure state. The solution turns colorless since  $\text{Cu}^{2+}$  ions are discharged.

*Electrolysis of  $\text{CuSO}_4$  solution using copper (active) electrodes*

The cathode reaction is the same as above, i.e.  $\text{Cu}^{2+}$  ion is reduced to Cu metal. At the anode, three substances compete for oxidation, namely  $\text{H}_2\text{O}$ ,  $\text{SO}_4^{2-}$  and the copper *electrode* itself! If we compare the oxidation potentials of the three substances ( $-1.23\text{ V}$ ,  $-2.0\text{ V}$  &  $-0.34\text{ V}$ , respectively),  $E^0$  of Cu is more positive than the rest. Hence, Cu (the anode) is oxidized into  $\text{Cu}^{2+}$ .

Cathode (–):  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$

Anode (+):  $\text{Cu}(\text{electrode}) \rightarrow \text{Cu}^{2+} + 2\text{e}^-$

Cell reaction:  $\text{Cu}^{2+}(\text{aq}) + \text{Cu} \rightarrow \text{Cu} + \text{Cu}^{2+}(\text{aq})$

In this process, the only detectable reaction taking place is the oxidation of the anode followed by its reduction into copper metal. In other words, the anode is deposited (plated – out) on the cathode leaving no change in the nature of the electrolyte. This result demonstrates that the **type** of product during electrolysis is affected by the electrode used.

## Summary of the results of electrolysis

Electrolyte	Electrodes	At the anode	At the cathode	Remark
Molten NaCl	graphite	0.50 mol Cl <sub>2</sub> per mole	1.0 mol Na	-----
Dilute H <sub>2</sub> SO <sub>4</sub> , NaCl, NaOH or H <sub>2</sub> O	Pt or graphite	0.50 mol (volume) O <sub>2</sub> per mole of the electrolyte	1.0 mol (volume) H <sub>2</sub> per mole	Each is the same as electrolysis of H <sub>2</sub> O
Conc. NaCl (Brine)	graphite	0.50 mol Cl <sub>2</sub> per mole	0.50 mol H <sub>2</sub> per mole	Pure form of NaOH is the residual product
CuSO <sub>4</sub> solution (blue)	graphite	0.50 mol O <sub>2</sub>	1.0 mol Cu per mol	pH decreases, pure H <sub>2</sub> SO <sub>4</sub> is the residual product, solution turns colorless
CuSO <sub>4</sub> solution (blue)	Copper	Copper anode "dissolves" into Cu <sup>2+</sup>	Copper metal is deposited (plated on the cathode)	No change in color, pH and concentration of the electrolyte

Note: Common Substances that do not discharge from aqueous solutions using inert electrodes (even when concentrated) include Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>.

### Check point 3.

1. Which of the following substances may conduct electric current? Which of these are electrolytes?

- |                 |              |   |
|-----------------|--------------|---|
| (a) Fe (I)      | (b) NaCl (s) | (c) CH <sub>3</sub> CH <sub>2</sub> OH (aq) |
| (d) S (I)       | (e) Cu (s)   | (f) CaCl <sub>2</sub> (I)                   |
| (g) C (diamond) | (h) Na (g)   | (i) Cu (NO <sub>3</sub> ) <sub>2</sub> (aq) |

2. A coulometer contains a mixture of dilute CaCl<sub>2</sub> and Zn (NO<sub>3</sub>)<sub>2</sub> aqueous solutions. If this mixture is electrolyzed using inert electrodes:

- What are the first products at the anode and the cathode?
- What are the first products at the respective electrodes had the electrolytes been concentrated?

## 4.4. Quantitative Aspects of Electrolysis

The relationship between amount of substance discharged at an electrode and quantity of electricity consumed during electrolysis was first established by Michael Faraday. It is known as Faraday's law of electrolysis.

*First Law:* states that the mass or number of moles of a substance oxidized or reduced at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte,  $m \propto Q$

The quantity of electricity passed through an electrolytic cell is normally measured in coulombs. The charge passed through an electrolytic cell is the product of the current and the time for which it is supplied,  **$Q = I \times t$** .

An electron carries a charge of  $1.602 \times 10^{-19}$  Coulombs. Thus, a mole of electrons carry a total of

$6.02 \times 10^{23}$  electrons  $\times 1.602 \times 10^{-19}$  C /electron = 96,485 C / mol  $\approx$  96,500 C / mol. The quantity of electrical charge equivalent to one mole of electrons is called the *Faraday* (F). 1.0 F of electricity discharges 1.0 equivalent of any substance.

1.0 F  $\leftrightarrow$  1.0 mol electrons  $\leftrightarrow$  1.0 equivalent of a substance  $\leftrightarrow$  molar mass /electrons transferred = E.

The amount of product in an electrolysis reaction is calculated from the stoichiometry of the half – reaction and the current and time for which the current flows. That is,

$m / M = (I \times t) / Z F = n$  where m is the mass discharged, M is the molar mass and Z is the charge on the ion or number of moles of electrons transferred during the process.

*Second Law:* This is not a new idea but a re – definition of Faraday’s first law. It states that “For the same quantity of electricity consumed by different electrolytes (coulometers arranged in series), the masses of the different substances deposited (discharged) at the respective electrodes ( $m_1, m_2, m_3$ , etc.) will be directly proportional to their equivalent masses ( $E_1, E_2, E_3$ , etc.)”.

Since  $m_1 \propto E_1, m_2 \propto E_2, m_3 \propto E_3$ , etc. it follows that  $m_1 / E_1 = m_2 / E_2 = m_3 / E_3$ , etc. For example, if 32.0 g of oxygen gas is liberated at the anode during electrolysis, then 4.0 g of hydrogen will be collected at the cathode during the electrolysis of (acidified) water. Each mass represents 4.0 equivalent of the substance.

$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$ . This means that the transfer of 4.0 mol electrons from anode to cathode liberates 1.0 mol or 32.0 g of  $O_2$  gas. Since the number of moles of electrons transferred (Z) by the reaction is 4.0, the equivalent mass of oxygen gas is 8.0 g. (32.0 g  $O_2$  = 4.0 equivalents)

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ . This means that the transfer of 2.0 mol electrons from anode to cathode liberates 1.0 mol or 2.0 g of  $H_2$  gas. Since the number of moles of electrons transferred by the reaction is 2.0, the equivalent mass of hydrogen gas is 1.0 g. (2.0 g  $H_2$  = 2.0 equivalents)

Transfer of 1.0 mol electrons or Using 1.0 F or 96500 C of electrical charge liberates / deposits	1.0 g $H_2$ , 8.0 g of $O_2$ , 9.0 g of Al, 23.0 g of Na, 32.0 g of Cu, 108.0 g of Ag, etc.	Each is equal to 1.0 equivalent or each value represents equivalent mass of the respective element
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### Example:

1. What mass of copper metal and oxygen gas would be produced if a current of 3.20 A passed for 1.0 hour through an aqueous solution of  $CuSO_4$ ?

*Solution:* Cathode reaction:  $Cu^{2+} + 2e^- \rightarrow Cu$ ;  $Z = 2.0$

Anode reaction:  $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$   $Z = 4.0$

Applying Faraday’s first law as:  $m / M = (I \times t) / Z F$  for each reaction,

Copper:  $m / 64 \text{ g} = (3.20 \text{ A} \times 3600 \text{ s}) / (2 \times 96500 \text{ C})$ ; thus  $m = 3.82 \text{ g} = 0.1194$  equivalent

Oxygen:  $m / 32 \text{ g} = (3.20 \text{ A} \times 3600 \text{ s}) / (4 \times 96500 \text{ C})$ ; thus  $m = 0.955 \text{ g} = 0.1194$  equivalent

2. Find the time it takes to deposit all cadmium from 500 cc of 0.40 M  $Cd(NO_3)_2$  using 2.0 A?

*Solution:* Amount of cadmium = 0.40 mol /L  $\times$  0.50 L = 0.20 mol

Using the formula in the form:  $n = (I \times t) / Z F$ , we arrive at:  $0.20 \text{ mol} = (2.0 \text{ A} \times t) / 2 \times 96500 \text{ C}$

Thus, the time of electrolysis,  $t = 19300 \text{ s} = 5.36$  hours.



3. What current is required to plate out 0.030 mol of gold from  $\text{AuCl}_3$  solution in 3.0 hours?

$$I = n Z F / t, \text{ therefore, } I = (0.03 \text{ mol} \times 3 \times 96500 \text{ C/mol}) / 10800 \text{ s} = \mathbf{1.34 \text{ A}}$$

**Check point 4.**

1. Three coulometers, containing concentrated aqueous solutions of  $\text{ZnCl}_2$ ,  $\text{AgNO}_3$  and  $\text{Al}(\text{NO}_3)_3$ , were arranged in series. If 1.50 mol of electrons transferred from anode to cathode during the electrolysis process, what are the masses of the different substances discharged at the cathode and anode of each coulometer?

2. What mass of aluminum is deposited by electrolysis in 30 minutes by a current of 40 A?

3.  $\text{K}_2\text{Cr}_2\text{O}_7$  is reduced into  $\text{Cr}^{3+}$  by an electrolytic process in acidic medium. What is the equivalent mass of  $\text{K}_2\text{Cr}_2\text{O}_7$ ? What mass of  $\text{H}_2\text{O}$  will be produced if 3.0 mol electrons transferred from anode to cathode above?

## 4.5. Industrial Application of Electrolysis

Electrolysis has the following industrial applications.

Electroplating

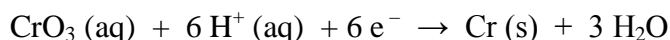
Electro refining

Extraction of active metals, and

Production of non – metals and industrial chemicals

*Electroplating* is a process in which a metal is electrolytically deposited or “plated – out” on the surface of another metal. It is often done to protect the base metal from corrosion or to give it a richer appearance. The electrolyte contains the plating metal in the form of dissolved ions. The anode is often made of the plating metal, while the cathode is usually the metal being plated.

One of the most familiar examples of electroplating is “*chrome plating*” in which a thin layer of chromium is deposited on another metal. The electrolyte is prepared by dissolving  $\text{CrO}_3$  in dilute  $\text{H}_2\text{SO}_4$  solution.



Chromium deposits on the cathode as a hard protective film.

*Electro refining* (purification of metals) is another application of electrolysis. For example, impure copper from the chemical reduction of copper ore is cast into large slabs that serve as the anode in electrolytic cells. Aqueous  $\text{CuSO}_4$  is the electrolyte, and thin sheets of ultra pure copper function as the cathode. This produces up to 99.95 % pure copper at the cathode.

*Extraction of active metals:* The compounds of very active metals (Na, K, Mg, Ca, Ba, etc) are difficult to decompose chemically, so electrolytic reduction is the only method for obtaining such metals. Molten metal chlorides are usually used as electrolytes because they generally have lower melting points.

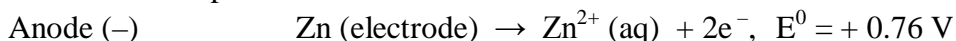
Electrolysis is also used in the manufacture of non – metals, such as  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{Cl}_2$ , etc. Some industrial compounds such as  $\text{NaOH}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  are obtained by the electrolysis of brine,  $\text{CuSO}_4$  and  $\text{CuCl}_2$  solutions, respectively.

## 4.6. Voltaic or Galvanic Cells

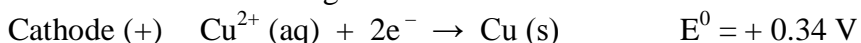
Voltaic or galvanic cells are electrochemical cells in which spontaneous oxidation – reduction reaction produces electrical energy. In other words, these are devices that convert chemical energy into electrical energy. A cell in which all reactants and products are in their thermodynamic standard states (1.0 M of dissolved species and 1.0 atm. partial pressure for gases at  $25^\circ \text{C}$ ) is called a *standard cell*.

Consider a standard cell made of two half – cells: one in which a strip of Cu metal is immersed in 1.0 M CuSO<sub>4</sub> solution and the other half – cell made of a strip of Zn metal immersed in 1.0 M ZnSO<sub>4</sub> solution. (Refer to Fig. 4.7, page 187 of Grade 12 student text book) This cell is called the *Daniel cell*, invented in 1836.

The reaction that takes place in a closed circuit is:



These electrons travel through the external wire to the copper electrode, where they are accepted by copper ions from the surrounding solution.

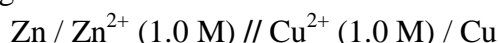


The copper metal deposits on the copper electrode. As a result, the mass of zinc electrode decreases while that of copper cathode increases. The solutions in the two half – cells are connected by a salt bridge in order to complete the circuit. A *salt bridge* is an inverted U – tube filled with an electrolyte such as KCl or NH<sub>4</sub>NO<sub>3</sub> paste. Because ions move into and out of the salt bridge, the electrolytes (solutions) remain electrically neutral. The initial voltage of the Daniel cell is 1.10 V (0.76 V + 0.34 V).

*Cell notation*: represents a galvanic cell without drawing the apparatus and diagram associated with it. It is a short hand representation of a galvanic cell in the following order. (The more negative electrode acts as anode)

*Anode* / Anode electrolyte & its concentration // Cathode electrolyte & its concentration / *Cathode*

The standard Daniel cell is denoted by the following cell notation. Here, the double lines represent the salt bridge.



*Standard reduction potentials, E<sup>0</sup>*

A cell potential is the difference between two electrode potentials, one associated with the cathode and the other associated with the anode. Standard electrode potentials are tabulated for reduction reaction (by convention) and are denoted as E<sup>0</sup><sub>red</sub>. The cell potential is the sum of the standard oxidation potential (E<sup>0</sup><sub>ox</sub>) and the standard reduction potential (E<sup>0</sup><sub>red</sub>).

$$E^0_{\text{Cell}} = E^0_{\text{Oxidation}} + E^0_{\text{Reduction}}$$

Note: The more positive E<sup>0</sup><sub>Reduction</sub> means the greater the tendency for the substance to be reduced. For example, F<sub>2</sub> + 2e<sup>-</sup> → 2 F<sup>-</sup>, E<sup>0</sup><sub>Reduction</sub> = + 2.87 V. This means F<sub>2</sub> readily accepts electrons (is readily reduced). Therefore, F<sub>2</sub> is a stronger oxidizing agent.

On the other hand, Li<sup>+</sup> + e<sup>-</sup> → Li; E<sup>0</sup><sub>Reduction</sub> = -3.05 V, which means Li<sup>+</sup> ion is difficult to reduce. Conversely, Li metal is a stronger reducing agent. We can arrange substances in order of increasing strength as oxidizing agents and as reducing agents as follows.

Oxidizing agent: Zn<sup>2+</sup> < Cu<sup>2+</sup> < Ag<sup>+</sup> (- 0.76V, +0.34V, +0.80V)      Reducing agent: Zn > Cu > Ag

When electrons move through metallic wire, they encounter resistance from localized particles in their paths. The driving force that allows the electrons to overcome this resistance and move around the circuit is called *electro motive force (e m f)*. This force comes from the oxidation – reduction reaction (in galvanic cells) that pushes electrons from the higher potential anode to the lower potential cathode through the external circuit. Energy that overcomes resistance appears as heat or light emitted by a glowing filament (bulb).

*Electrical work* is the product of the *emf* of the cell, E<sup>0</sup><sub>Cell</sub>, and the total charge (in coulombs) that passes through the cell.  $w = Q \times E^0_{\text{Cell}}$ , (Joule = Coulomb x Volt)

1.0 mol electrons = 96500 C = 1.0 F; 2.0 mol electrons = 2 x 96500 C = 2.0 F, etc. Therefore, the total charge Q in coulombs = n F, where n is the number of moles of electrons involved. The measured emf or cell voltage is the maximum voltage that the cell can generate and this in turn gives the maximum (useful) work. In thermodynamics, useful work is called Gibb's free energy,  $\Delta G$ . Therefore, at standard state

$$w_{\text{maximum}} = -n F E_{\text{cell}}^0 = \Delta G^0 \quad \text{At non – standard condition, } \Delta G = -n F E_{\text{cell}}$$

The useful work obtained from the standard Daniel cell is  $-2 \times 1.10 \text{ V} \times 96500 \text{ C} = -212.3 \text{ kJ}$ .

The standard free – energy change  $\Delta G^0$ , is related to the equilibrium constant K, as follows.

$$\Delta G^0 = -n F E_{\text{cell}}^0 = -RT \ln K = -2.303 RT \log K.$$

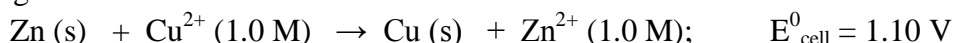
From this, the equation for the standard cell voltage is:  $E_{\text{cell}}^0 = 2.303 RT \log K / n F$ . When the variables are replaced by their respective values, we get:

$$E_{\text{cell}}^0 = (2.303 \times 8.314 \text{ J/mol K} \times 298 \text{ K}) / (n \times 96500 \text{ C}) = (0.0592 \text{ V} \log K) / n.$$

The equilibrium constant at the initial stage in the Daniel cell is:

$$\log K = (1.10 \text{ V} \times 2.0) / 0.0592 \text{ V} = 37 \text{ and } K = 10^{37}!$$

Electrode potential (emf) depends on concentration and temperature. A change in concentration results in change of cell voltage. The effect of change in concentration is given in the following table for the Daniel cell.



[Cu <sup>2+</sup> ], M	[Zn <sup>2+</sup> ], M	E <sub>cell</sub> <sup>0</sup> , V
1.0	0.001	1.219
1.0	0.01	1.160
0.1	0.1	1.10
0.01	1.0	1.042
0.001	10	0.983

The cell voltage increases when concentration of Cu<sup>2+</sup> (reactant) is greater than that of Zn<sup>2+</sup> (product). When a voltaic cell operates, the concentration of the reactant decreases while that of the product increases. As time passes, the voltage drops steadily. Eventually it becomes zero, and we say the cell is “dead”. At this point, the Redox reaction taking place within the cell is at equilibrium and there is no driving force to produce a voltage.

Quantitatively, we use the *Nernst equation* to determine the effect of concentration upon cell potential. To find this equation, we work through the free – energy changes as follows.

In thermodynamics,  $\Delta G = \Delta G^0 + RT \ln Q$ , where Q is the reaction quotient = [Product]<sup>x</sup> / [Reactant]<sup>y</sup> (x and y are coefficients in the equation). Furthermore, we know that  $\Delta G = -n F E_{\text{cell}}$  and  $\Delta G^0 = -n F E_{\text{cell}}^0$ . Therefore,  $-n F E_{\text{cell}} = -n F E_{\text{cell}}^0 + RT \ln Q$ , or  $E_{\text{cell}} = E_{\text{cell}}^0 - (2.303 RT \log Q) / n F$ . Substituting the values of the variables produces:

$$E_{\text{cell}} = E_{\text{cell}}^0 - (0.0592 \log Q) / n. \text{ This is the } Nernst \text{ equation.}$$

As the cell operates, Q increases steadily which in turn decreases E<sub>cell</sub>. At standard condition, E<sub>cell</sub> = E<sub>cell</sub><sup>0</sup>. At equilibrium, E<sub>cell</sub> = 0 and Q = K<sub>equilibrium</sub>. The working *Nernst equation* for the Daniel cell is;

$$E_{\text{cell}} = 1.10 \text{ V} - 0.0296 \log ([\text{Zn}^{2+}] / [\text{Cu}^{2+}]).$$

### Check point 5.

1. Which of the following express reduction potentials?

(a)  $E^0(\text{NO}_3^- / \text{NO}_2)$  (b)  $E^0(\text{SO}_4^{2-} / \text{S}_2\text{O}_8^{2-})$  (c)  $E^0(\text{Hg}_2^{2+} / \text{Hg}^{2+})$  (d)  $E^0(\text{CO}_2 / \text{C}_2\text{O}_4^{2-})$

2. When a piece of metal A is placed in a solution that contains ions of A and B, metal B plates A. Which metal is more reactive, A or B? Which value is more positive:  $E^0(\text{A}^{3+} / \text{A})$  or  $E^0(\text{B}^{2+} / \text{B})$ ?

3. A galvanic cell is denoted by:  $\text{Mg (s)} / \text{Mg}^{2+} (0.01 \text{ M}) // \text{Al}^{3+} (0.01 \text{ M}) / \text{Al (s)}$ . Calculate  $E_{\text{cell}}$  and  $\Delta G$ .

### 4.7. Batteries

A battery is a series of combined galvanic cells that can be used as a source of direct current at constant voltage. The principal advantages offered by batteries are convenience and portability, rather than efficiency and economy. Based on their recharge ability, we can classify batteries as primary and secondary.

*Primary batteries* use Redox reactions that cannot be returned to their original state by recharging (use and throw – type). Examples include dry cell, alkaline battery, and mercury cell.

*Secondary batteries* are often called storage or recharge able batteries. The reaction in these batteries can be reversed. Examples include nickel – cadmium (NiCad) and lead storage batteries.

Battery	Anode / Reaction	Cathode / Reaction	Electrolyte	Remark
Le Clanche (Dry cell)	$\text{Zn (s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^-$ , $E^0 = 0.74 \text{ V}$	$2\text{NH}_4^+ (\text{aq}) + 2\text{MnO}_2 (\text{s}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{NH}_3 + \text{H}_2\text{O}$ , $E^0 = 0.76 \text{ V}$	$\text{NH}_4\text{Cl}$ & $\text{ZnCl}_2$ in $\text{H}_2\text{O}$	$E^0_{\text{cell}} = 1.50 \text{ V}$ , <b>graphite</b> cathode
Alkaline battery	$\text{Zn (s)} + 2 \text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$	$2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$ ( <b>graphite</b> electrode)	$\text{NaOH}$ or $\text{KOH}$	50 % longer current than dry cell
Mercury cell	$\text{Zn (s)} + 2 \text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$	$\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg (l)} + 2 \text{OH}^-$	$\text{NaOH}$ or $\text{KOH}$	$E^0 = 1.35 \text{ V}$ , Used in calculators, camera; environmental hazard
NiCad battery	$\text{Cd (s)} + 2 \text{OH}^- \rightleftharpoons \text{Cd(OH)}_2 + 2\text{e}^-$	$\text{NiO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Ni(OH)}_2 + 2\text{OH}^-$	$\text{NaOH}$ or $\text{KOH}$	In lap tops & battery – operated tools
Storage battery	$\text{Pb (s)} + \text{SO}_4^{2-} (\text{aq}) \rightleftharpoons \text{PbSO}_4 + 2\text{e}^-$	$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightleftharpoons \text{PbSO}_4 + 2\text{H}_2\text{O}$	$\text{H}_2\text{SO}_4$	Six identical cells with a total of 12 V

### Corrosion of Metals

*Corrosion* is a deterioration of a metal by Redox process, which converts the metal to unwanted compound. The simplest way to prevent corrosion is to ensure that the surface of a metal is not exposed to air and water. The most familiar example of corrosion is *rusting* of iron. This electrochemical reaction can be represented as follows.

Anode:  $\text{Fe (s)} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ ,  $E^0 = 0.44 \text{ V}$

These electrons reduce atmospheric oxygen to water at the cathode which is another surface the same metal

Cathode:  $\text{O}_2 (\text{g}) + 4 \text{H}^+ + 4\text{e}^- \rightarrow 2 \text{H}_2\text{O}$ ,  $E^0 = 1.23 \text{ V}$

Rusting:  $2 \text{Fe} + \text{O}_2 + 4\text{H}^+ (\text{aq}) \rightarrow 2 \text{Fe}^{2+} (\text{aq}) + 2\text{H}_2\text{O}$ ;  $E^0_{\text{cell}} = 1.67 \text{ V}$

Corrosion is prevented by painting or coating a metal with zinc, tin or chromium. Tin protects iron only as long as the coated layer is not scratched or damaged. Once it is scratched and exposed to air, tin actually promotes the corrosion of iron because iron is easily oxidized than tin. Here, the iron becomes the anode and tin the cathode in the electro chemical corrosion

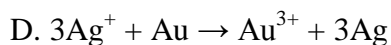
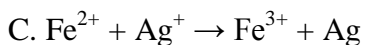
Galvanized iron is produced by coating iron with zinc. The zinc metal protects the iron against corrosion even after the zinc coat is scratched. In this case, the iron serves as the cathode in the electro chemical corrosion because zinc is oxidized more readily than iron. Protecting a metal by making it the cathode in an electro chemical cell is known as *cathodic* protection. The metal that is oxidized while protecting the cathode is called *sacrificial anode*. In galvanized iron, zinc is the sacrificial anode.

## REVIEW EXERCISE ON UNIT 4

### Part 1. Choose the correct answer

1. A galvanic cell ceases to function after a certain time because
  - A. Potentials of both electrodes become zero
  - B. Solutions of the two half –cells become neutral
  - C. The electrodes are completely used up.
  - D. Potentials of both electrodes become equal.
2. Zinc rod is placed in 100 cc of 1.0 M  $\text{CuSO}_4$  solution so that the concentration of  $\text{Cu}^{2+}$  changes to 0.70 M. The concentration of  $\text{SO}_4^{2-}$  at this stage will be
  - A. 0.30 M
  - B. 1.0 M
  - C. 0.70 M
  - D. 1.80 M
  - E. 0.10 M
3. If potentials of  $\text{Ni}^{2+} / \text{Ni}$  and  $\text{Au}^{3+} / \text{Au}$  are  $-0.25 \text{ V}$  and  $1.50 \text{ V}$ , respectively, then the *emf* of the cell:  $\text{Ni} / \text{Ni}^{2+} (10^{-2} \text{ M}) // \text{Au}^{3+} (0.10 \text{ M}) / \text{Au}$ , at  $25^\circ \text{C}$  will be
  - A. 1.73 V
  - B. 1.868 V
  - C. 1.789 V
  - D. 1.76 V
  - E. 1.77 V
4. The standard reduction potentials for four metals ions  $\text{W}^{2+}$ ,  $\text{X}^{2+}$ ,  $\text{Y}^{2+}$  and  $\text{Z}^{2+}$  are  $-1.24 \text{ V}$ ,  $-1.46 \text{ V}$ ,  $-0.36 \text{ V}$  and  $0.15 \text{ V}$ , respectively. This indicates that
  - A. Y displaces Z from its solution
  - B. Z displaces W from its solution
  - C. Y is more reactive than X
  - D. X displaces W from its solution
  - E. Z is a stronger reducing agent than W
5. The amount of electricity required for the electrolytic reduction of 0.40 mol of  $\text{K}_2\text{Cr}_2\text{O}_7$  to  $\text{Cr}^{3+}$  ion in acidic solution is
  - A. 0.6 F
  - B. 2.4 F
  - C. 6.0 F
  - D. 12.4 F
  - E. 1.2 F
6. Which of the following is a stronger reducing agent?
  - A.  $\text{Fe}^{2+}$
  - B.  $\text{F}_2$
  - C.  $\text{Zn}^{2+}$
  - D.  $\text{Fe}^{3+}$
  - E.  $\text{Br}^-$ .
7. Which of the following statements is *incorrect*?
  - A. Electrons flow from a point of high potential to that of low potential.
  - B. If cell equation is multiplied by two, the corresponding potential is doubled.
  - C. Voltage of a galvanic cell is algebraic difference of the two electrode potentials
  - D. Faraday's laws apply both to galvanic and electrolytic cells.
8. More quantity of electricity will be consumed to produce 1.0 mol of
  - A. Al
  - B. Pb
  - C.  $\text{Cl}_2$
  - D. Ag
  - E.  $\text{O}_2$
9. A certain quantity of current passed through three electrolytic cells connected in series, which contain solutions of  $\text{AgNO}_3$ ,  $\text{Hg}(\text{NO}_3)_2$  and  $\text{HgNO}_3$ . If the electrolysis process deposited 0.216 g of Ag, what are the masses of Hg deposited at the mercuric ( $\text{Hg}^{2+}$ ) and mercurous ( $\text{Hg}^+$ ) cells, respectively?
  - A. 0.4012 g & 0.8024 g
  - B. 0.4012 g & 0.2006 g
  - C. 0.1003 g & 0.2006 g
  - D. 0.2006 g & 0.4012 g

10. Two electrolytic cells that contain 0.10 M Iron (II) sulfate and 0.10 M Iron (III) chloride are subjected to electrolysis. The ratio of iron deposited in the two cells for the same quantity of electricity, respectively, is  
 A. 1: 1      B. 2: 3      C. 1: 3      D. 3: 2      E. 2: 1
11. For the oxidation of ammonia  $4 \text{NH}_3(\text{g}) + 3 \text{O}_2(\text{g}) \longrightarrow 2 \text{N}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$ ,  $\Delta G^\circ = -1356.0$  kJ. If this reaction is run in a galvanic cell, what will be its standard potential  $E^\circ$ ? A. 4.68 V      B. 3.51 V      C. 1.17 V      D. 14.04 V      E. 7.02 V
12. 12.0A current passed through consecutive electrolytes that contain dischargeable  $\text{X}^{2+}$  and  $\text{Y}^{3+}$  ions, for 9650 seconds. The amount of substance that can be obtained at one of the cathodes is  
 A. 1.20 mol X      B. 0.60 mol Y      C. 0.40 mol X      D. 0.40 mol Y
13. A current of 3.0 A passed through a solution of  $\text{AuCl}_4^-$  ions using gold electrodes and it deposited 1.234 g of gold. The time of electrolysis is  
 A. 302 s      B. 806 s      C. 1208 s      D. 1812 s      E. 604 s
14. The standard voltage  $E^\circ$ , for the cell  $\text{Pb} / \text{Pb}^{2+} // \text{Sn}^{2+} / \text{Sn}$ , is  $-0.01 \text{ V}$ . If it is to exhibit  $E_{\text{Cell}} = 0$ , then the value of  $[\text{Sn}^{2+}] / [\text{Pb}^{2+}]$  should be  
 A. 3.16      B. 31.60      C. 2.19      D. 1.48      E. 0.46
15. Addition of powdered lead & iron to 1.0 M solution both in  $\text{Pb}^{2+}$  and  $\text{Fe}^{2+}$  would result in (Reduction potentials of Fe and Pb are  $-0.44 \text{ V}$  and  $-0.13 \text{ V}$ , respectively)  
 A. Increase in concentration of both  $\text{Pb}^{2+}$  and  $\text{Fe}^{2+}$   
 B. Decrease in  $[\text{Pb}^{2+}]$  and  $[\text{Fe}^{2+}]$       C. Increase in  $[\text{Pb}^{2+}]$  but decrease in  $[\text{Fe}^{2+}]$   
 D. Decrease in  $[\text{Pb}^{2+}]$  but increase in  $[\text{Fe}^{2+}]$   
 E. Decrease in amount of Pb but increase in amount of Fe
16. The number of moles of electrons that must be **added** when balancing the reaction  $\text{NO}_3^- + \text{H}_2\text{O} \longrightarrow \text{NH}_3 + \text{OH}^-$ , is  
 A. 8 to the reactant side      B. 6 to the product side      C. 4 to the reactant side  
 D. 5 to the reactant side      E. charge is already balanced
17. Number of electrons removed from the cathode to deposit 0.27 g aluminum is  
 A. 0.01 mol      B.  $6.023 \times 10^{23}$       C.  $1.81 \times 10^{22}$       D. 0.03 mol      E.  $1.81 \times 10^{21}$
18. If 4825.0 coulombs of electricity were required to deposit 7.50 g of a certain metal, then the equivalent mass of the metal is  
 A. 27      B. 15      C. 643      D. 300      E. 150
19. Which of the following produces higher voltage by a Redox reaction?  
 A. Alkaline battery      B. Le Clanche cell      C. rusting of iron      D. Mercury cell
20. During the electrolysis of acidified water,  $2.4092 \times 10^{24}$  electrons passed from anode to cathode. The total volume of gases produced (measured at STP) will be  
 A. 67.20 L      B. 44.80 L      C. 33.60 L      D. 89.60 L
21. Consider the following standard data (unbalanced)  
 $\text{Ag}^+_{(\text{aq})} + \text{Cd}_{(\text{s})} \rightarrow \text{Cd}^{2+}_{(\text{aq})} + \text{Ag}; E^\circ = 1.20 \text{ V}$        $\text{Ag}^+_{(\text{aq})} + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}; E^\circ = 0.80 \text{ V}$   
 $\text{Nb}_{(\text{s})} + \text{Cd}^{2+}_{(\text{aq})} \rightarrow \text{Nb}^{3+}_{(\text{aq})} + \text{Cd}_{(\text{s})}; E^\circ = 0.70 \text{ V}$   
 What is the reduction potential,  $E^\circ$  for  $\text{Nb}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{Nb}_{(\text{s})}$ ?  
 A.  $-1.50 \text{ V}$       B.  $-0.30 \text{ V}$       C.  $-0.40 \text{ V}$       D.  $-1.10 \text{ V}$
22. One coulometer containing  $\text{AgNO}_3$  and another containing  $\text{MCl}_4$  (metal chloride) were arranged in series and electrolyzed for 30 seconds. If 5.40 g of Ag (atomic mass = 108 g) and 1.325 g of the unknown metal M were deposited at the respective cathodes, what is the atomic mass of metal M?  
 A. 106.0 g      B. 54.0 g      C. 212.0 g      D. 159.0 g
23. Which of the following is a spontaneous reaction? (Refer to standard reduction potentials)  
 A.  $2\text{Au} + 3\text{Ni}^{2+} \rightarrow 2\text{Au}^{3+} + 3\text{Ni}$       B.  $2\text{Ag} + \text{I}_2 \rightarrow 2\text{AgI}$



24. The amount of electrolytic product during electrolysis is not affected by

- A. oxidation number      B. current      C. time      D. Electrode used

25. What is the oxidizing agent in the reaction:  $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{FeCl}_2 + \text{HCl} \rightarrow \text{CrCl}_3 + \text{FeCl}_3$ ?

- A. Chromium      B. Chloride      C. Iron      D. Di chromate ion

### Part 2. Answer each question as indicated

26. The equilibrium constant for the reaction:  $\text{MnO}_4^- + \text{Fe}^{2+} \rightleftharpoons \text{Mn}^{2+} + \text{Fe}^{3+}$ , in acidic medium is  $10^{63}$  at  $25^\circ\text{C}$ . If  $E^0(\text{Fe}^{3+}/\text{Fe}^{2+})$  is 0.771 V, calculate  $E^0(\text{MnO}_4^-/\text{Mn}^{2+})$ .

27. Give reason (explanation) for each of the following observations (facts).

- A. Manganese can serve as sacrificial anode but not nickel to protect iron from corrosion.
- B. The electrolyte in a discharged car battery freezes at a higher temperature than in a fully charged battery.
- C. A dry cell battery (Le' Clanche cell) cannot be stored indefinitely.
- D. The blue  $\text{CuSO}_4$  solution fades and turns to colorless during electrolysis.

28. Which of the following aqueous solutions exhibit (s)  $\text{pH} > 7.0$ ,  $\text{pH} < 7.0$  and  $\text{pH} = 7.0$  after electrolysis?

- A. dilute  $\text{NiCl}_2$       B.  $\text{AgNO}_3$       C. dilute  $\text{KCl}$   
 D. conc.  $\text{NiCl}_2$       E. conc.  $\text{KCl}$       F.  $\text{NaOH}$

29. A *fuel cell* is a galvanic cell that consists of hydrogen – oxygen fuel and  $\text{NaOH}$  as an electrolyte. To which class is this cell classified: primary or secondary battery? In what way does this cell differ from the others?

30. Aluminum has more negative reduction potential than iron. This “suggests” that aluminum is readily oxidized (rusts) than iron. Practically, we see that aluminum does not corrode but iron does. Suggest a reason for this observation.

## UNIT 5: ELEMENTS IN NATURE & INDUSTRY

### 5.1. Some Elements in Nature and Recycling

There are more than 103 elements known at present. 92 elements occur in nature. A solid material that occurs naturally in the earth's crust is called *mineral*. A mineral from which an element can be extracted easily and economically is called *ore*. (Refer to Table 5.2, page 224 for main types of minerals)

The most abundant element in the earth's crust is oxygen (45.5 %) followed by silicon (27.2 %). Aluminum (8.3 %) and iron (6.2 %) are the first and second most abundant metals. In the atmosphere, nitrogen takes the highest percentage (78%) followed by oxygen (21%). Hydrogen is the most abundant gas in the universe.

The elements carbon, nitrogen and phosphorus are known for their recycling in nature. Here are the key processes taking place during this cycle.

Cycle	Enters into the living world	Returns back to its origin
Carbon cycle	<ul style="list-style-type: none"><li>. Photosynthesis by plants use atmospheric <math>\text{CO}_2</math></li><li>. Animals (including humans) eat plants and other animals that have eaten plants.</li></ul>	<ul style="list-style-type: none"><li>. Respiration by both animals and plants releases <math>\text{CO}_2</math></li><li>. Decomposition of organic matter</li><li>. Combustion of fossil fuels</li></ul>
Nitrogen cycle	<ul style="list-style-type: none"><li>. Nitrogen fixation: Lightening converts <math>\text{N}_2</math> to <math>\text{NO}_2</math>; bacteria in the nodules of leguminous plants convert <math>\text{N}_2</math> to <math>\text{NO}_3^-</math>, Haber process converts <math>\text{N}_2</math> to <math>\text{NH}_3</math></li><li>. Animals eat plants and convert plant proteins into animal proteins</li></ul>	<ul style="list-style-type: none"><li>. Excretion by animals (as urea and uric acid)</li><li>. Decomposition of dead animals and plants by bacteria releases ammonia</li><li>. De nitrification (by anaerobic bacteria) converts <math>\text{NH}_3</math> and <math>\text{NH}_4^+</math> salts back to atmospheric <math>\text{N}_2</math></li></ul>
Phosphorus cycle (slow process)	<ul style="list-style-type: none"><li>. Phosphate rocks release phosphate salts by rain fall, weathering, etc. and roots of plants absorb the soluble phosphates</li><li>. Animals eat plants &amp; other animals that eat plants</li></ul>	<ul style="list-style-type: none"><li>. Decomposition of dead animals &amp; plants return phosphorus into soil and water</li></ul>

### 5.2. Some Elements in Industry

**Metallurgy** is the science and technology of extracting metals from their natural sources **and** preparing them for practical use. The principal steps carried out include concentrating the ore (beneficiation), pre – treatment, extracting the metal and refining (purifying) the crude metal.

#### 1. Concentrating the ore

This is done to increase the fraction of metal – bearing ore by eliminating most of the accompanying rock and soil called *gangue*. The step may involve:

- Gravity separation (for high density substances such as gold)
- Magnetic separation for ferromagnetic minerals such as  $\text{Fe}_3\text{O}_4$  (magnetite) using strong electromagnets



- (iii) Froth floatation which involves adding ore – bearing material into a mixture of water, oil and a detergent. The ore floats in a form of froth or foam while the gangue settles down. This is particularly used for sulfide ores.
- (iv) Amalgamation: involves forming an amalgam with mercury. Gold and silver are concentrated by this method.
- (v) Leaching: a **chemical** process used to dissolve only the target substance, leaving the impurities un– dissolved

## **2. Pre treatment**

This step converts an ore to a form that is easy to reduce. The conversion is mainly to an oxide for chemical reduction and to a chloride for electrolytic reduction. Sulfide ores are converted to oxides (by roasting) for chemical reduction; magnesium ion from sea water is precipitated as a hydroxide (Dow process) and then to chloride for electrolysis, etc.

## **3. Extracting the metal**

Very reactive metals (Groups IA and IIA, and aluminum) are extracted by electrolytic reduction of the chloride (oxide for aluminum). Other metals are reduced chemically by using appropriate reducing agents, such as a more reactive metal, hydrogen, carbon and carbon monoxide.

## **4. Refining of metals**

This step is used for impure metals that are obtained by chemical reduction *only*. The process may involve distillation (for low melting metals), electrolysis or zone – refining.

### ***Check point 6.***

1. How many elements are (a) gases (b) non – metals (c) metalloids?
2. If you enter a car whose doors and windows stayed closed in a very sunny day, the inside of the car is warmer than the outside environment. Explain this incidence parallel to global warming.
3. More phosphate fertilizers must be produced industrially as compared to nitrate fertilizers. Explain why.
4. Aluminum, an active metal, is extracted from its oxide by electrolysis but not from its chloride. Why?
5. Assume that argentite ( $\text{Ag}_2\text{S}$ ) deposit is reported in one area of Ethiopia. As a chemistry student, narrate all the steps and methods applied to extract silver in a pure form.
6. What is the difference between roasting and calcination of an ore?

### Extraction, Properties and Uses of Some Metals

Metal	Ore	Metallurgy	Properties & Uses
Sodium	NaCl (Halite)	Electrolysis of a molten mixture of 40 % NaCl and 60 % CaCl <sub>2</sub> in a Down cell. working temperature decreases from 800 to 600 <sup>0</sup> C because of CaCl <sub>2</sub>	. A soft, very reactive metal which must be kept under paraffin; used to make Na / Pb alloy needed to produce tetra ethyl lead (TEL) (anti – knock additive); coolant for nuclear reactors in liquid state
Tin	SnO <sub>2</sub> (cassiterite)	Chemical reduction by coke at high temperature: $\text{SnO}_2 (\text{s}) + 2\text{C} (\text{s}) \rightarrow \text{Sn} (\text{l}) + 2\text{CO} (\text{g})$	. Reacts with steam producing SnO <sub>2</sub> & H <sub>2</sub> . Reacts with dilute and conc. acids and halogens . Used for electroplating of iron, to make tin plate, and alloys (bronze, solder, etc)
Lead	PbS (galena)	Concentrating the ore by <i>froth floatation</i> , then roasting to an oxide followed by reduction using carbon	. Forms protective oxide film hence inert towards H <sub>2</sub> O . Dissolves in dilute HCl and HNO <sub>3</sub> but not in H <sub>2</sub> SO <sub>4</sub> . Reacts with alkalis to form plumbates e.g. Na <sub>2</sub> Pb(OH) <sub>6</sub> , hence lead is amphoteric . Used to make lead storage battery, paints and pigments
Zinc	ZnS (Zinc blende)	The ore is concentrated by froth floatation and then roasted to ZnO, finally reduced to zinc by CO (g)	. Dissolves in dilute HCl as well as in NaOH solution, hence it is amphoteric . Used for galvanizing iron, to make brass, as an electrode in batteries, for making white pigment in ZnO form
Chromium	FeCr <sub>2</sub> O <sub>4</sub> (Chromite)	Reduction in an electric furnace $\text{FeCr}_2\text{O}_4 + 4\text{C} \rightarrow \text{Fe} + 2\text{Cr} + 4\text{CO}$ , or Converting the ore into Cr <sub>2</sub> O <sub>3</sub> then reduction by aluminum $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3$	. Active metal but forms protective oxide in air, in conc. HNO <sub>3</sub> & other oxidizing agents . Dissolves in HCl and dilute H <sub>2</sub> SO <sub>4</sub> to form blue Cr <sup>2+</sup> ion . Used to make alloy with nickel (nichrome) and iron (ferrochrome), for electroplating, an oxidizing agent as Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> & CrO <sub>3</sub>
Silicon (metalloid)	SiO <sub>2</sub> (Silica or quartz)	Heating silica with coke at about 3000 <sup>0</sup> C in an electric furnace, purified by reducing its chloride with magnesium and zone refining	. Silica is resistant to attack by all acids except HF. It forms SiF <sub>4</sub> with HF, a chemical process used in the <i>etching of glass</i> . Used to construct transistors & micro processors . Quartz is used to control the frequency of radio & TV transmission . Silicon polymers are used in making lubricants, lipstick, car polish, etc.

### Industrial Chemicals of Some Nonmetals

Chemical	Industrial Preparation	Properties	Uses
NH <sub>3</sub> (Ammonia)	<i>Haber process</i> (Nitrogen fixation) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}); \Delta H = -92 \text{ kJ}$ using iron catalyst at 380 – 450 °C and 200 atm. (high pressure)	Colorless gas with pungent odor, liquid at –33 °C, has high heat of vaporization	To make fertilizers, HNO <sub>3</sub> , explosives (TNT and nitro glycerin)
H <sub>2</sub> SO <sub>4</sub> (Sulfuric acid)	<i>Contact process</i> ⇌ (i) $\text{S}(\text{s}) + \text{O}_2 \rightarrow \text{SO}_2(\text{g})$ (ii) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ at 400 °C using V <sub>2</sub> O <sub>5</sub> catalyst (contact on the catalyst) (iii) $\text{SO}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{H}_2\text{S}_2\text{O}_7$ (oleum), this can be diluted to required concentration	m. p. = 10.5 °C; b. p. = 338 °C $\Delta H_{\text{sol.}} = -880 \text{ kJ/mol}$ , Oxidizing agent when concentrated or hot, good dehydrating agent for gases, an electrolyte	For the production of fertilizers, detergents, plastics & paints (most important industrial chemical)
HNO <sub>3</sub> (Nitric acid)	<i>Ostwald process</i> : Combustion of NH <sub>3</sub> using Pt catalyst at 850 °C & 5.0 atm $4\text{NH}_3 + 5\text{O}_2 \rightleftharpoons 4\text{NO} + 6\text{H}_2\text{O}$ $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \rightleftharpoons + \text{H}_2\text{O} \rightarrow \text{HNO}_3$	Colorless liquid, but turns brown on exposure to sunlight, strong oxidizing agent	To synthesize NH <sub>4</sub> NO <sub>3</sub> , To make plastics, drugs and explosives

Di ammonium hydrogen phosphate (DAP)

(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> is a white crystalline, soluble fertilizer. It is prepared from ammonia and phosphoric acid as follows.

$$2\text{NH}_3(\text{g}) + 2\text{H}_3\text{PO}_4(\text{l}) \rightarrow (\text{NH}_4)_2\text{HPO}_4(\text{s}) + \text{NH}_4\text{H}_2\text{PO}_4(\text{recycled})$$

$$\text{NH}_4\text{H}_2\text{PO}_4(\text{s}) + \text{NH}_3(\text{g}) \rightarrow (\text{NH}_4)_2\text{HPO}_4(\text{s})$$

In addition to a fertilizer, DAP can be used as fire retardant, a yeast nutrient in wine making and brewing beer.

# REVIEW EXERCISE ON UNIT 5

## Part 1. Choose the correct answer

1. Heating pyrites in air to remove sulfur is known as  
A. Bessemerization    B. Calcinations    C. Roasting    D. Reduction
2. Which method is used for concentrating a bauxite ore?  
A. Magnetic separation    B. Froth floatation    C. Leaching    D. Levigation
3. The salt, which is least likely to be found in mineral form, is  
A. Nitrate    B. sulfide    C. carbonate    D. phosphate
4. Iron ore that resembles gold and hence called "fool's gold" is  
A. Iron pyrite    B. Magnesite    C. Argentite    D. Hematite
5. An ore is concentrated by froth floatation because the ore particles are  
A. lighter    B. insoluble in all solvents    C. charged    D. hydrophobic
6. Zone refining is used for  
A. concentrating an ore    B. purification of a metal  
C. preliminary treatment    D. purification of an ore
7. An explanation which is not common to both Contact and Ostwald processes is  
A. There is Redox reaction    B. smaller oxides are changed to higher oxides  
C. metal catalyst is used    D. gaseous reactant is oxidized to gaseous product
8. Which metal differs from the others in methods employed to extract it from its ore?  
A. Ca    B. Al    C. Na    D. Pb
9. Which process involves carbon sinking?  
A. Photosynthesis    B. Decay of animals    C. Respiration    D. Combustion of fuels
10. **Properties:** Can be found free in nature // Liberates  $H_2$  from alkalis // Does not form amalgam // Which of the above properties does not belong to any one of the following metals?  
A. Cu    B. Mg    C. Al    D. Fe

## Part 2. Answer each question as indicated

11. What is the most abundant transition metal in the earth's crust?
12. Give the chemical formula of each mineral.  
(a) Cinnabar    (b) Galena    (c) Bauxite    (d) Dolomite    (e) Gypsum    (f) Lime stone
13. Classify each of the following minerals as a carbonate, oxide, sulfide, sulfate or halide.  
(a) Corundum    (b) Cryolite    (c) Epsomite    (d) Pyrite    (e) Magnesite
14. If  $Al_2O_3$  ore contains  $Fe_2O_3$  &  $PbS$  impurities, what method is applicable to concentrate the ore?
15. What physical property is responsible for concentrating an ore by froth floatation method?
16. Hydrogen is preferred than the cheaper carbon for the reduction of  $WO_3$  to W. Why can't carbon be used?
17. If you have containers made of lead, zinc, silica, tin, aluminum and chromium, which of these containers can be used to store nitric acid? Explain your answer.
18. Which gases can be dried using sulfuric acid?  $NH_3$  /  $SO_3$  /  $CO_2$  /  $N_2H_4$  /  $CO$

## Part 3. Fill in the blanks.

19. Copper metal dissolves in concentrated nitric acid to form a solution of \_\_\_\_ color and a gas with \_\_\_\_ color.
20. Gold is frequently recovered from its ore by forming water soluble complex with \_\_\_\_\_.

# UNIT 6: POLYMERS

## 6.1. Introduction

*Polymers* are macro molecules made from smaller and *repeating* units called monomers, i.e. monomers are the building blocks of polymers. A polymer might be made from identical or different types of monomers. *Homo* polymers are made from only one type of monomer; e.g. ethylene  $\rightarrow$  poly ethylene. *Co* polymers are prepared by the combination of more than one kind of monomer units, e.g. Formaldehyde + phenol  $\rightarrow$  Bakelite. The method of synthesis of polymers is called polymerization.

Copolymers are classified as random or regular, based on the way the monomers are arranged along the polymer chain, e.g. Regular:  $\sim A - B - A - B - A - B \sim$

Random:  $\sim A - B - B - A - B - A - A - A - B \sim$

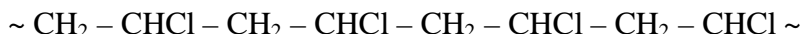
Based on their sources, polymers are classified as *synthetic* or *natural*. The later (natural polymers) are those that exist naturally and their number does not change. These include polysaccharides, nucleic acids, proteins and natural rubber. Synthetic polymers are man – made (or plastics), whose number increases from time to time. Some of these are nylon, poly (vinyl chloride), polyester (Dacron), Teflon, Bakelite, polyethylene, etc. Polymers are generally prepared by either *addition* or *condensation* polymerization.

Addition polymerization: requires monomer molecules with carbon – carbon double bond (s), which undergo addition reaction in forming a polymer. It is also known as chain – growth polymerization. The molecular formula of an addition polymer is n times that of the monomer and upon polymerization, the double bond of the active site is converted into a single bond.

Condensation polymerization involves the combination of monomer molecules with the elimination of simple molecules like water, hydrogen chloride, ammonia, etc. The reaction is also known as step – growth polymerization. Each monomer for this type of polymerization must have two or more functional groups. (*Refer to pages 263 – 268 of your text book for graphic structures of monomers and their polymers.*)

### Check point 7

1. The following structure represents a segment of poly (vinyl chloride) or PVC.



(a) Draw and name the monomer unit

(b) Classify this polymer as addition, condensation, homo, copolymer, synthetic, etc.

(c) How many monomer units must combine to form a PVC molecule of mass  $1.25 \times 10^5$  g?

2. Ethylene glycol,  $\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH}$  and butandioic acid,  $\text{HOOC} - \text{CH}_2\text{CH}_2 - \text{COOH}$  react with each other to form a polymer.

(a) Classify this polymerization as addition or condensation.

(b) If two monomers from each type (alcohol and acid) combine to form a segment of the polymer, how many carbon atoms appear in this segment? How many smaller units are eliminated during this process? How many new bonds appear in the new segment?

(c) Draw the graphic structure of the segment formed in (b).

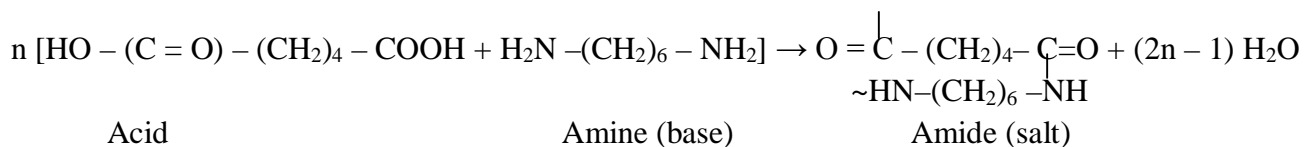
## 6.2. Synthetic Polymers

### A. Synthetic Addition Polymers

Polymer	Monomer	Properties and Uses
Polyethylene ~CH <sub>2</sub> – CH <sub>2</sub> – CH <sub>2</sub> – CH <sub>2</sub> ~	Ethylene H <sub>2</sub> C = CH <sub>2</sub> (ethene)	. Light weight (simplest polymer), cheaper, the low density polyethylene (LDPE) is more transparent, branched, waxy & flexible; the high density (HDPE) is more opaque, rigid . Used for making squeeze bottles, plastic wrappings, garment bags, trash bags, electrical insulation, milk jugs ...
Polypropylene ~CH <sub>2</sub> – CH (CH <sub>3</sub> ) – CH <sub>2</sub> – CH (CH <sub>3</sub> ) ~	Propylene CH <sub>2</sub> = CHCH <sub>3</sub>	. Stronger than polyethylene . Used for making food containers, ropes, fishing nets, carpets, and bottles
Poly (vinyl chloride) ~CH <sub>2</sub> – CHCl – CH <sub>2</sub> – CHCl~	Vinyl chloride CH <sub>2</sub> = CHCl (Chloroethene)	. 3 <sup>rd</sup> widely produced plastic after polyethylene & polypropylene . used for making pipes, leather – like materials, shoes, rain coats, aprons, floor tile & phonograph recorders
Poly(methyl methacrylate) ~[CH <sub>2</sub> – C(CH <sub>3</sub> )] <sub>n</sub> ~ H <sub>3</sub> CO- C = O	Methyl methacrylate H <sub>2</sub> C = C(CH <sub>3</sub> ) H <sub>3</sub> CO- C = O	. PMMA is sold under the trade name Lucite or Plexi glass . Light weight, glass – like polymer . It is a substitute of glass for air plane windows, street lights
Poly (tetra fluoro ethylene) ~ CF <sub>2</sub> – CF <sub>2</sub> – CF <sub>2</sub> – CF <sub>2</sub> ~	Tetra fluoro ethylene F <sub>2</sub> C = CF <sub>2</sub>	. PTFE is also known as Teflon . Has good resistance to chemical attack, workable in –73 up to 260 °C, has very low coefficient of friction, slippery to touch . Used for coating cooking utensils and making insulators
Polystyrene ~ CH – CH <sub>2</sub> – CH – CH <sub>2</sub> ~ C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub>	Styrene C <sub>6</sub> H <sub>5</sub> –CH=CH <sub>2</sub>	. One of the most widely used polymers, impact absorbent . For making packing materials, CD and DVD cases, toys, flower pots & architectural models

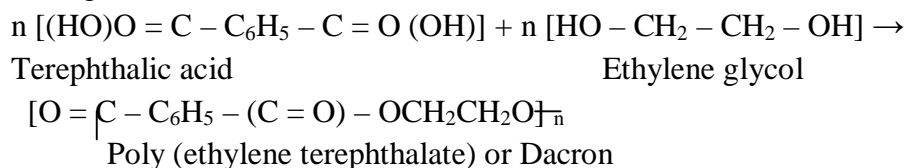
### B. Synthetic Condensation polymers

Nylons are polyamides, which contain the  $\text{O} = \text{C} - \text{NH} -$  (amide) bond. They can be produced by the condensation reaction of di acids (or the more reactive di acid chlorides) and di amines. One of the most common poly amide is Nylon – 66. It is a co – polymer of 1, 6 – di amino hexane (or hexa methylene di amine) and 1, 6 – hexane dioic acid (common name adipic acid). The polymerization involves an acid – base reaction, which forms “salt” and water!



Both monomers contain six carbon – skeleton, hence the name Nylon – 66. Nylon is used to make parachutes, ropes, clothes, stockings, hair combs, etc.

Another example of a condensation polymer is the polyester poly (ethylene tere phthalate) or *Dacron*. It is a co – polymer formed when, equal amounts (concentrations) of 1, 4 – benzene di carboxylic acid (commonly called terephthalic acid) and 1, 2 – ethane diol (or ethylene glycol) undergo condensation.



Dacron is a strong and impact resistance polymer. It has high transparency and is mainly used for synthetic fibers. Mixing it with various amounts of cotton gives fabrics that are durable easily dyed & crease – resistant. It is also used for making bottles and packing materials.

The first semi – synthetic polymer produced was Bakelite in 1909. Nowadays, Bakelite is synthesized by the condensation of phenol and formaldehyde. The *ortho* and *para* positions of large number of phenols join by a – CH<sub>2</sub> – bridge after eliminating water. Bakelite has been used for making rotary dial telephones, whistles, billiard balls, dominos, purses, chess, checkers and porcelains, etc.

Based on their response to heat, synthetic polymers can be classified into *thermoplastics* and *thermosetting* plastics. Thermosetting plastics cannot be reheated to soften, shape and mold. Once set, they assume a permanent shape. The molecules are cross – linked in three dimensions exhibiting very strong bonds. Such plastics cannot be reshaped and recycled. Bakelite is a typical example.

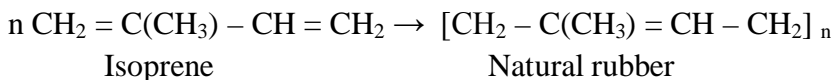
Thermoplastics can be re – heated and therefore re – shaped in various ways due to (linear) long – chain polymeric units that are not inter connected. The bond between the molecules is Vander Waals and this force becomes weaker when heated. All the polymers discussed above, except Bakelite, are thermoplastics.

### ***Check point 8.***

1. One advantage of synthetic polymers is their durability. However, durability has its own disadvantage. What is it?
2. Give an example of an addition polymer that is a co – polymer.
3. Kevlar is used in bulletproof vests. It is a co – polymer of 1, 4 – diamine benzene and 1, 4 – benzene di carboxylic acid. Show graphically a segment of Kevlar.
4. If the di amine used to synthesize Kevlar is replaced by 1, 3 – diamine benzene, we get fire – resistant clothing, named Nomex. Draw a segment structure of Nomex.
5. Direct disposal (littering or dumping) and incineration (burning) of plastic wastes is a common practice. Explain how both methods are harmful to health and the environment.

### 6.3. Natural Polymers

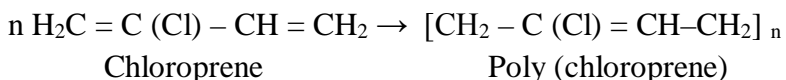
Natural Rubber is an addition polymer obtained from rubber tree. The monomer of natural rubber is isoprene (or 2 – methyl – 1, 3 – butadiene).



Rubber is an example of elastomeric – type polymer, in which the polymer can return to its original shape after being stretched. Natural rubber is a soft and sticky solid. Its properties are improved by introducing cross – linkages between its polymer chains. This can be achieved by heating natural rubber with sulfur. This process is known as *vulcanization* of rubber. Di sulfide cross – links are established between polymer chains. Vulcanized rubber is hard and non – sticky. It has higher elasticity, higher tensile strength and is insoluble in solvents.

Synthetic rubber is produced either by the polymerization of conjugated dienes in the presence of a catalyst or by co – polymerization of conjugated dienes with other olefins.

Neoprene: This is a synthetic polymer of 2 – chloro – 1, 3 – butadiene, obtained by addition polymerization.



Neoprene is a linear thermoplastic polymer. Because of its resistance to chemicals, it is used for making hoses for chemicals, petrol, and oils.

Styrene – Butadiene Rubber: It is an addition co – polymer of styrene and 1, 3 – butadiene. This rubber, after vulcanization, is superior to natural rubber with regard to mechanical strength. Its primary use is in the manufacture of tires.

Butyl rubber is a polymer of 2 – methyl propene, commonly called iso butylene, with 1 to 2 % of 2 – methyl butadiene (i.e. isoprene). Butyl rubber holds air better than natural rubber and thus is used for inner tubes.

### **Poly saccharides (Natural Polymers)**

These are polymers of monosaccharide units made of carbohydrates. Carbohydrates are poly hydroxyl aldehydes or poly hydroxyl ketones, or compounds that yield such substances upon hydrolysis. For example, glucose is a poly hydroxyl aldehyde & fructose is a poly hydroxyl ketone.

Carbohydrates contain carbon, hydrogen and oxygen only. They are classified on the basis of acid catalyzed hydrolysis products (if any) as monosaccharide, disaccharide and polysaccharide.

Monosaccharide groups are also called simple sugars and cannot be hydrolyzed into simpler (smaller) units. Three up to seven carbon skeleton compounds of this class are known in nature. A three – carbon monosaccharide is called a *triose*. Four, five and six – carbon skeletons are known as *tetrose*, *pentose* and *hexose*, respectively.

Monosaccharide groups are classified as *aldoses* or *ketoses* based on the main functional group present. A three – carbon skeleton is either an aldo triose or a keto triose. In this context, glucose is an aldo hexose while fructose is a keto hexose. The functional group appears at C – 1 in aldohexoses and at C – 2 in ketohexoses.

The simplest aldose and ketose are glyceraldehyde and di hydroxyl acetone. Their IUPAC names are 2, 3 – di hydroxyl propanal and 1, 3 – di hydroxyl propanone, respectively. There is no carbohydrate with less than three carbon atoms.



The most common monosaccharides are glucose, galactose, fructose and ribose. Glucose and galactose are aldohexoses while ribose is an aldopentose. The only difference between the structures of glucose and galactose is in the configuration of – OH group at C – 4. Glucose is the most abundant monosaccharide in nature. It is called blood sugar because blood contains dissolved glucose (70 – 100 mg / 100 m L blood). Fructose is the sweetest of all naturally occurring substances, found in many fruits and in honey.

Monosaccharide	Formula	Class	IUPAC name	Remark
Glycer aldehyde	$C_3H_6O_3$	<i>Aldo</i> triose	2, 3 – di hydroxyl propanal	Simplest aldose, reducing sugar
Di hydroxyl acetone	$C_3H_6O_3$	<i>Keto</i> triose	1, 3 –di hydroxyl propanone	Simplest ketose, non – reducing
Ribose	$C_5H_{10}O_5$	<i>Aldo</i> pentose	2, 3, 4, 5- tetra hydroxyl pentanal	Sugar component of RNA & ATP
Glucose	$C_6H_{12}O_6$	<i>Aldo</i> hexose	2, 3, 4, 5, 6 – penta hydroxyl hexanal	Most abundant mono saccharide, blood sugar
Galactose	$C_6H_{12}O_6$	<i>Aldo</i> hexose	2, 3, 4, 5, 6 – penta hydroxyl hexanal	Synthesized from glucose in the mammary glands
Fructose	$C_6H_{12}O_6$	<i>Keto</i> hexose	1, 3, 4, 5, 6 – penta hydroxyl hexanone	Sweetest naturally occurring substance

Monosaccharides containing five or more carbon atoms in solution exhibit an open –chain (Fischer projection), and two cyclic structures in equilibrium with each other. The cyclic forms of monosaccharides result from the ability of their carbonyl group to react *intra* molecularly with a hydroxyl group. The result is a cyclic hemi – *acetal* or cyclic hemi – *ketal*.

If a six member ring is formed, it is called *pyranose*. This ring is formed when the – OH group at C – 5 reacts with the carbonyl carbon at C – 1. The C – 1 carbon in the cyclic structure is called anomeric. It is bonded to (H) and (OH) in addition to (O) and C – 2 of the ring structure. If the – OH on the anomeric carbon points down; it is called  $\alpha$  (alpha) and if it points upward it is called  $\beta$  (beta). Therefore, the cyclic structure of glucose is either  $\alpha$  – gluco pyranose (- OH pointing down) or  $\beta$  – gluco pyranose (- OH pointing upward). (*Refer to pages 290 & 291 in your text book*)

Galactose, like glucose, forms a six member ring (galacto pyranose) but both fructose and ribose form a five – membered ring structure called *furanose*. Therefore, fructose exists as  $\alpha$  – fructo furanose and  $\beta$  – fructo furanose at equilibrium in solution.

A disaccharide is a dimer made up of two monosaccharide molecules. They are joined by glycoside linkage between anomeric carbon of one monosaccharide and the – OH group of the other. The most glycoside linkage is between the C – 4 hydroxyl group of one monosaccharide and  $\alpha$  – or  $\beta$  – positions of the anomeric carbon. Such linkage is called  $\alpha$  – 1, 4 – or  $\beta$  – 1, 4 – glycoside linkage, depending on the configuration at the anomeric carbon atom.

Disaccharide	Monomers	Linkage	Broken by	Remark
Maltose	$\alpha$ – glucose + glucose	$\alpha$ – 1, 4 – glycoside	<i>Maltase</i>	Malt sugar, from hydrolysis of starch
Cellulose	$\beta$ – glucose + glucose	$\beta$ – 1, 4 – glycoside	<i>Cellobiase</i>	Humans cannot digest it
Lactose	$\beta$ – galactose + glucose	$\beta$ – 1, 4 – galactoside	<i>Lactase</i>	Milk sugar
Sucrose	$\alpha$ – glucose + $\beta$ – fructose	$\alpha$ , $\beta$ –1,2– glycoside	<i>Surcease</i>	Table sugar

### Polysaccharides

The three important polysaccharides, all made of glucose units, are cellulose, starch and glycogen.

Cellulose is the most abundant polysaccharide, made from  $\beta$  – glucose. It is the structural component of cell wall in plants. Cellulose is a linear polymer in which the glucose units are linked by  $\beta$  – 1, 4 – glycoside linkage. Cellulose is not digested by humans because of lack of the enzyme *cellulase* that hydrolyzes  $\beta$  – 1, 4 – glycoside bonds into free glucose units. Cotton is composed of pure cellulose.

Starch is a polymer of  $\alpha$  – glucose and is the energy – reserve in plants. If excess glucose enters a plant cell, it is converted to starch and stored for later use. It has two principal polysaccharides: amylose & amylopectin.

Amylose is a *straight – chain* glucose polymer and accounts for 20 – 25 % of starch. The glucose units in amylose are connected by 1, 4 – glycoside bonds.

Amylopectin is a highly *branched* glucose polymer accounting to 75 – 80 % of starch. Glucose units are connected by  $\alpha$  – 1, 4 – and branched  $\alpha$  – 1, 6 – glycoside linkages. A branch occurs at every 25 to 30 glucose units.

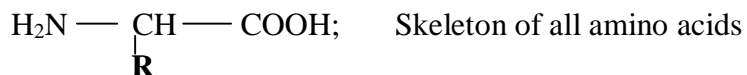
Glycogen is a polymer of  $\alpha$  – glucose, which is energy storage in humans and animals. It is called animal starch. Like amylopectin, glucose units are joined by  $\alpha$  – 1, 4 – and  $\alpha$  – 1, 6 – glycoside bonds. However, glycogen is about three times more branched than amylopectin. When blood glucose level decreases in humans, some stored glycogen is hydrolyzed back to glucose.

### Check point 9

1. What is the hydrocarbon skeleton common (basic) in all synthetic and natural rubbers?
2. In making candy, sucrose (table sugar) is boiled in water with drops of lemon juice added.
  - (a) Which one is sweeter: candy or table sugar? Why?
  - (b) Why is lemon juice required in this process?
3. Some people do not like milk. If they consume dairy products or drink milk, they will experience diarrhea or vomiting. This is called lactose intolerance. Why does this problem occur?
4. Describe the structural differences and similarities between each of the following pairs.
  - (a) Glycogen and amylopectin
  - (b) Glucose and galactose
  - (c) Amylose and cellulose
5. When potato (starch) is cooked in water to a higher temperature, the inner portion of the potato becomes hollow. Explain this effect in relation to the polymer structure and its solubility.

## 6.4. Proteins

Proteins contain carbon, hydrogen, hydrogen, oxygen and nitrogen. Some contain sulfur as well. Proteins are made by the condensation polymerization of the 20 naturally occurring amino acids. An amino acid is a compound that contains amine ( $-NH_2$ ) and carboxylic ( $-COOH$ ) groups attached to a tetrahedral carbon. All amino acids found in nature assume  $\alpha$  – structure.



Amino acids differ from one another only in the  $-R$  group, which is called a side chain. The individual property of an amino acid is determined by the side chain ( $R$ ).

Classification:

*Non –polar* amino acids: Glycine (Gly), Alanine (Ala), Valine (Val), Leucine (Leu), Isoleucine (Ile), Methionine (Met), Phenyl alanine (Phe), Proline (Pro).

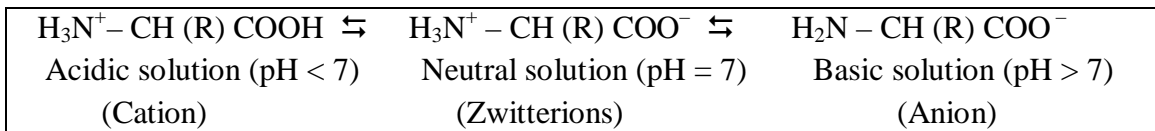
*Polar neutral* amino acids: Serine (Ser), Cysteine (Cys), Asparagine (Agn), Glutamine (Gln), Tyrosine (Tyr), Tryptophan (Trp), Threonine (Thr)

*Acidic* amino acids: contain additional  $-COOH$  group; Aspartic (Asp) and Glutamic (Glu)

*Basic* amino acids: contain additional  $-NH_2$  group; Histidine (His), Lysine (Lys), Arginine (Arg)

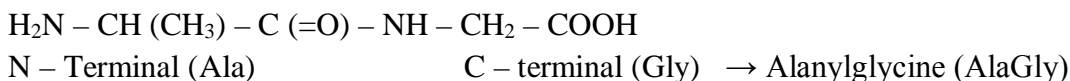
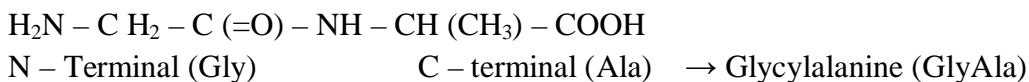
Physical properties: High melting points, colorless, and crystalline (resemble ionic compounds)

In aqueous solution, the  $-COOH$  and  $-NH_2$  groups react with each other to form a dipolar ion or internal salt. The dipolar ion of an amino acid is called zwitterions.



When two amino acids react with each other, the carboxyl group of one amino acid condenses with the amino group of the other, forming a peptide bond ( $-NH - C = O$ ). A compound containing two amino acids joined by a peptide bond is called a di peptide; three amino acids joined by two peptide bonds form a tri peptide, etc.

A polypeptide is a sequence of amino acids, containing up to 50 amino acid units joined by peptide bonds. Proteins are polypeptides that contain more than 50 amino acid units. By convention, the sequence of amino acids in a peptide is written with the N – terminal amino acid at the left and the C – terminal amino acid at the right, e.g.



Glycylalanine is totally a different compound from alanylglycine even though both contain the same amino acids. (Refer to Table 6.2, page 305 of your text book for functions of proteins.

### Check point 10

1. Classify each amino acid as non polar, acidic, basic or polar neutral based on the side – chain R.

- (a)  $R = -CH_2SH$                       (b)  $R = -(CH_2)_4 - NH_2$                       (c)  $R = -CH_2CH_2 - S - CH_3$   
 (d)  $R = -CH_2CH_2COOH$                       (e)  $R = -CH_2OH$

2. Consider the following polypeptide segment: *Alanylglycylserylphenylalanylseryllucine*

This polypeptide is made of \_\_\_\_ amino acids and contains \_\_\_\_ peptide bonds. Therefore, it is a \_\_\_\_ (tri, tetra, etc) peptide. The second peptide linkage is formed by the \_\_\_\_ (C or N) terminal of \_\_\_\_ and the \_\_\_\_ terminal of \_\_\_\_.

3. What is the net charge on alanine ( $R = -CH_3$ ) at (a)  $pH = 3.0$  (b) ( $pH = 7.0$ )?
4. Which part of an amino acid shows acidic property in water solution at  $pH = 7.0$ ?
5. When human hair burns, it has unpleasant smell similar to that of burning tire. What is the cause?
6. Which class of polymers: addition or condensation, are usually non – biodegradable? Why?

# REVIEW EXERCISE ON UNIT 6

## Part 1. Choose the correct answer

1. Identify the naturally occurring polymer among the following  
A. Sucrose    B. Nylon    C. Dacron    D. Cellulose
2. Which of the following is more abundant among organic molecules?  
A. Starch    B. Cellulose    C. Glucose    D. Proteins    E. Oxygen
3. Dacron is an example of  
A. Synthetic rubber    B. Thermosetting polymer    C. Fiber    D. Polyamide
4. Ribose is an example of  
A. RNA    B. Keto triose    C. Aldotetrose    D. Aldopentose
5. The enzyme that converts starch into maltose is called  
A. Zymase    B. Maltase    C. Invertase    D. Amylase    E. Pepsin
6. Which of the following is non –biodegradable?  
A. Cotton    B. Polyethylene    C. Wood    D. Polysaccharide
7. Which of the following is used to make non –stick cook wares?  
A. PVC    B. Polystyrene    C. PTFE    D. PMMA
8. From the given class of compounds, stronger inter molecular forces are present in  
A. Elastomers    B. Thermoplastics    C. Addition polymers    D. Thermosetting polymers
9. A sucrose molecule on hydrolysis yields  
A. Glucose only    B. Invert sugar    C. Polysaccharide    D. Glucose and galactose
10. Which among the following is a step –growth polymer?  
A. PTFE    B. Polyester    C. Polyethylene    D. Rubber
11. Which of the following proteins transports oxygen in the blood stream?  
A. Myoglobin    B. Insulin    C. Hemoglobin    D. Albumin
12. An example for human structural protein is  
A. Insulin    B. Actin    C. Cellulose    D. Keratin
13. The functional group in cyclic glucose or fructose is  
A. Ether    B. Aldehyde    C. Ketone    D. Anomeric
14. Which one of the following polymer – monomer pairs is wrongly matched?  
A. Teflon – propylene    B. Perspex – methyl methacrylate  
C. PVC – chloro ethene    D. Cellulose –  $\beta$  – glucose
15. How many tri peptides can be formed that contain all the three amino acids glycine, alanine and valine in their structures?  
A. 3    B. 6    C. 9    D. 27

## Part 2. Answer each question as indicated

16. Is there a natural polymer made by addition polymerization? If yes, what is this polymer?
17. Write the molecular **formula** of (a) Glucopyranose    (b) a keto tetrose    (c) GlyAla.
18. A simple method of differentiating woolen fiber (synthetic) from cotton fiber (natural) is burning a piece of each fiber. Perform this task and write the results.
19. Which one has nutritional value for humans: cellobiose, lactose or both? Why?
20. All amino acids have very high melting points. What factor is responsible for this property?

