DON BOSC0 CATHOLIC HIGH SCHOOL AND PREPARATORY CHEMISTRY SHORT NOTE FOR GRADE 12

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 $NH_4^{+¿¿}$ 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 $ClO^{-¿¿}$, +3 in $ClO_2^{-¿¿}$, +5 in $BrO_3^{-¿¿}$, and +7 in Cl_2O_7 and $IO_4^{-¿¿}$, 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. Na_2O_2) and –½ in super oxides (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: $KClO_3$ (s) → KCl (s) + O_2 (g)

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, $KClO_3$ is both the oxidizing and reducing agent, i.e. the oxidized and the reduced substance is the $ClO_3^{-¿¿}$ 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 Reduction occurs is called the Cathode.

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 $K_2Cr_2O_4$
   (b) Cr in $Cr_2O_7^{-2}$
   (c) Cl in $HClO_4$
   (d) O in F_2O
   (e) I in IF_7

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

   (a) $MnO_4^{-1} + SO_3^{-2} \rightarrow SO_4^{-2} + Mn^{+2}$

   (b) $CuO + NH_3 \rightarrow cu + N_2 + H_2O$

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

Method 2: **Ion – Electron**

Check point 2.

1. Balance the equation for the reaction between per manganate ion (MnO_4^{-1}) and sulfite ion (SO_3^{2-1}) to give manganese (IV) oxide (MnO_2) and sulfate ion (SO_4^{2-1}) 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_2O when the reaction: $NO_2^{-1} + Cr_2O_7^{-2} \rightarrow Cr^{+3} + NO_3^{-1}$ 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 Na^+ and Cl^-.

Oxidation at the anode: $Cl^{-¿¿}(l) \rightarrow 1/2\ Cl_2(g) + e^{-¿¿}$

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

Cell reaction: $NaCl(l) \rightarrow Na(s) + ½\ Cl_2(g)$

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 H^+ and OH^- ions in pure water. H_2O is not a conductor of electricity!! The oxidation and reduction of water (*acidified*) proceeds as follows.

Oxidation: $2H_2O(l) \rightarrow O_2(g) + 4H^{+¿¿}(aq) + 4e^{-¿¿}$ $E^0 = -1.23$ V

Reduction: $2H_2O(l) + 2e^{-¿¿} \rightarrow H_2(g) + 2OH^{-¿¿}(aq)$; $E^0 = -0.83$ V

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

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 $CuCl_2$, the substances competing for reduction (at the cathode) are Cu^{2+} and H_2O while the substances competing for oxidation (at the anode) are Cl^- and H_2O. At the cathode, Cu^{2+} is reduced in preference to H_2O because the reduction potential of Cu^{2+} is more positive (+ 0.34 V) than that of H_2O (–0.83 V). On the other hand, H_2O is oxidized at the anode in preference to Cl^- because the oxidation potential of H_2O is more positive (–1.23 V) than that of Cl^- (–1.36 V).

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

Oxidation at the anode: $2H_2O(l) \rightarrow O_2(g) + 4H^{+¿¿}(aq)$; $E^0 = -1.23$ V

Cell reaction: $2CuCl_2 + 2H_2O \rightarrow 2Cu + O_2 + 4HCl$, $E^0_{cell} = -0.89$ V.

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

1. **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), Cl^- is oxidized first because it is more concentrated. On the other hand, even though Na^+ is concentrated, H_2O is reduced at the cathode because the reduction potential of Na^+ is very large negative (–2.71 V) as compared to that of H_2O (–0.83 V). This shows that electrode potential has more effect than concentration.

Oxidation at the anode: $Cl^{-¿¿}(l) \rightarrow 1/2\, Cl_2(g) + e^{-¿¿}$

Redaction at the cathode: $2H^{+¿¿} + e^{-¿¿} \rightarrow H_2(g)$

Cell reaction: $2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$

A. 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 $CuSO_4$ solution using graphite (inert) electrodes

This solution is blue because of Cu^{2+} ions in water. At the cathode, Cu^{2+} ion is reduced in preference to H_2O because E^0 of Cu^{2+} is more positive than that of H_2O. At the anode, H_2O is oxidized in preference to SO_4^{2-} because the oxidation potential of H_2O (–1.23 V) is more positive than that of SO_4^{2-} (–2.0 V).

Reeducation at the cathode: $2Cu^{+2} + 4e^{-¿¿} \rightarrow 2Cu$

Oxidation at the anode: $2H_2O(l) \rightarrow O_2(g) + 4H^{+¿¿}(aq)$

Cell reaction: $2CuSO_4 + 2H_2O \rightarrow 2Cu + O_2 + 2H_2SO_4$

Electrolysis of $CuSO_4$ solution using inert electrodes results in decrease of pH of the electrolyte and it is one industrial method of preparing H_2SO_4 in a pure state. The solution turns colorless since Cu^{2+} ions are discharged.

*Electrolysis of $CuSO_4$ solution using copper (**active**) electrodes*

The cathode reaction is the same as above, i.e. Cu^{2+} ion is reduced to Cu metal. At the anode, three substances compete for oxidation, namely H_2O, SO_4^{2-} and the copper *electrode* itself! If we compare the oxidation potentials of the three substances (–1.23 V, –2.0 V & –0.34 V, respectively), E^0 of Cu is more positive than the rest. Hence, Cu (the anode) is oxidized into Cu^{2+}.

Reduction (cathode): $Cu^{+2}(aq) + 2e^{-¿¿} \rightarrow Cu(s)$

Oxidation (anode): $Cu(electrode) \rightarrow Cu^{+2}(aq) + 2e^{-¿¿}$

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

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_2 per mole	1.0 mol Na	-----
Dilute H_2SO_4, NaCl, NaOH or H_2O	Pt or graphite	0.50 mol (volume) O_2 per mole of the electrolyte	1.0 mol (volume) H_2 per mole	Each is the same as electrolysis of H_2O
Conc. NaCl (Brine)	graphite	0.50 mol Cl_2 per mole	0.50 mol H_2 per mole	Pure form of NaOH is the residual product
$CuSO_4$ solution (blue)	graphite	0.50 mol O_2	1.0 mol Cu per mol	pH decreases, pure H_2SO_4 is the residual product, solution turns colorless
$CuSO_4$ solution (blue)	Copper	Copper anode "dissolves" into Cu^{2+}	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^+, K^+, Li^+, Mg^{2+}, Ca^{2+}, Al^{3+}, F^-, NO_3^-, SO_4^{2-}.

Check point 3.

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

   (a) Fe (l) (b) NaCl (s) (c) CH_3CH_2OH (aq)

   (d) S (l) (e) Cu (s) (f) $CaCl_2$ (l)

   (g) C (diamond) (h) Na (g) (i) $Cu(NO_3)_2$ (aq)

2. A coulometer contains a mixture of dilute $CaCl_2$ and $Zn(NO_3)_2$ aqueous solutions. If this mixture is electrolyzed using inert electrodes:

   (a) What are the first products at the anode and the cathode?

(b) 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, $m \alpha Q$

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 1.602×10^{-19} Coulombs. Thus, a mole of electrons carry a total of 6.02×10^{23} electrons $\times 1.602 \times 10^{-19}$ C /electron = 96,485 C / mol ≈ 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 = 1.0 mol electrons = 1.0 equivalent of a substance = 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 $m_1 \alpha E_1$, $m_2 \alpha E_2$, $m_3 \alpha E_3$, 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.

$$\mathbf{2H_2O\ (l)\ \rightarrow\ O_2\ (g) + 4\ H^+ + 4e^-.}$$

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)

$$\mathbf{2H_2O\ (l\ ) + 2e^- \rightarrow H_2\ (g) + 2\ OH^-.}$$

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

Check point 4.

1. Three coulometers, containing concentrated aqueous solutions of $ZnCl_2$, $AgNO_3$ and Al $(NO_3)_3$, 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. $K_2Cr_2O_7$ is reduced into Cr^{3+} by an electrolytic process in acidic medium. What is the equivalent mass of $K_2Cr_2O_7$? What mass of H_2O 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:

1. Electroplating
2. Electro refining
3. Extraction of active metals, and

4. 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 CrO_3 in dilute H_2SO_4 solution.

$$CrO_3\,(aq) + 6\,H^+\,(aq) + 6\,e^- \rightarrow Cr\,(s) + 3\,H_2O$$

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 slaps that serves as the anode in electrolytic cells. Aqueous $CuSO_4$ 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 O_2, H_2, Cl_2, etc. Some industrial compounds such as NaOH, H_2SO_4, HCl are obtained by the electrolysis of brine, $CuSO_4$ and $CuCl_2$ 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 25^0 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 $CuSO_4$ solution and the other half – cell made of a strip of Zn metal immersed in

1.0 M $ZnSO_4$ 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:

Anode (–): $Zn\ (electrode) \rightarrow Zn^{2+}\ (aq) + 2e^-$ $\quad E^0 = +0.76\ V$

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

Cathode (+): $Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$ $\quad E^0 = +0.34\ V$

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_4NO_3 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

***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 // Cathode electrolyte / *Cathode

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

$$Zn / Zn^{2+}\ (1.0\ M)\ //\ Cu^{2+}\ (1.0\ M) / Cu$$

Standard reduction potentials, E^0

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^0_{red}. The cell potential is the sum of the standard oxidation potential (E^0_{Ox}) and the standard reduction potential (E^0_{red}).

$$\mathbf{E^0_{Cell} = E^0_{(Oxidation)} + E^0_{(Reduction)}}$$

Note: The more positive $E^0_{Reduction}$ means the greater the tendency for the substance to be reduced.

For example, $F_2 + 2e^- \rightarrow 2\ F^-$, $E^0_{Reduction} = +2.87$ V. This means F_2 readily accepts electrons (is readily reduced). Therefore, F_2 is a stronger oxidizing agent.

On the other hand, $Li^+ + e^- \rightarrow Li$; $E^0_{Reduction} = -3.05$ V, which means Li^+ 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: **$Zn^{2+} < Cu^{2+} < Ag^+$ (– 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, $\mathbf{E^0_{Cell}}$, and the total charge (in coulombs) that passes through the cell. $\mathbf{w = Q \times E^0_{Cell}}$, (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, Δ G. Therefore, at

Standard state: $\boldsymbol{w_{maximum} = -nFE^0_{Cell} = \Delta G^0}$

Non – standard condition: $\boldsymbol{\Delta G = -nFE_{cell}}$

The useful work obtained from the standard Daniel cell is – 2 x 1.10 V x 96500 C = –212.3 kJ.

The standard free – energy change ΔG^0, is related to the equilibrium constant K, as follows.

$$\mathbf{\Delta G^0 = -nFE^0_{cell} = -RT \ln K = -2.303\ RT \log K.}$$

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

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

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

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

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.

$Zn\ (s) + Cu^{2+}\ (1.0\ M) \rightarrow Cu\ (s) + Zn^{2+}\ (1.0\ M);\quad E^0_{cell} = 1.10\ V$

$[Cu^{2+}]$, M	$[Zn^{2+}]$, M	E^0_{cell}, 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^{2+} (reactant) is greater than that of Zn^{2+} (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, $\mathbf{\Delta G = \Delta G^0 + RT\ lnQ}$:

Where Q is the reaction **quotient = [Product]** ^{x} **/ [Reactant]** ^{y}(x and y are coefficients in the equation). Furthermore, we know that $\mathbf{\Delta G = -nFE_{cell}}$ and $\mathbf{\Delta G^0 = -\ n\ F}\ E^\circ_{cell}$.

Therefore,

$$\mathbf{-\ nF}E^\circ_{cell} \mathbf{= -\ n\ F\ E^0_{cell} + RT\ lnQ}$$

or

$$\mathbf{E_{cell}} = E^\circ_{cell} - \frac{2.303RT}{nF}\log Q$$

Substituting the values of the variables produces: $E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log Q$. This is the ***Nernst equation*.**

As the cell operates, Q increases steadily which in turn decreases E_{cell}. At standard condition, $E_{cell} = E^0_{cell}$. At equilibrium, $E_{cell} = 0$ and $Q = K_{equilibrium}$. The working *Nernst equation* for the

Daniel cell is;

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

Check point 5.

1. Which of the following express reduction potentials?

(a) E^0 ***(***NO_3^{-}¿/NO_2¿

(b) E^0 ($SO_4^{-2}/S_2O_8^{-2}$)

(c) E^0 (Hg_2^{+2}/Hg^{+2} ¿

(d) E^0 ($CO_2/C_2O_4^{-2}$)

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 (A^{3+} / A) or E^0 (B^{2+} / B)?
3. A galvanic cell is denoted by: Mg (s) / Mg^{2+} (0.01 M) // Al^{3+} (0.01 M) / Al (s). Calculate E_{cell} and Δ G.

4.6 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.

Examples

The Dry Cell Battery

The voltage produced by a dry cell is about 1.5 V. The LeClanchè cells are widely used because of their low cost, but they have several disadvantages. If the current is drawn from the battery very rapidly, the gaseous products cannot be consumed immediately. As a result, the cell resistance increases and the voltage drop.

Cathode electrode: graphite

Anode electrode: zinc metal

Electrolytes: NH_4Cl & $ZnCl_2$ in H_2O

Cell reaction

Anode reaction: Zn (s) → Zn^{2+} (aq) + 2e $^-$, E^0 = 0.74 V

Cathode reaction: $2NH_4^+$ (aq) + $2MnO_2$ (s) + 2e $^-$ → Mn_2O_3 + $2NH_3$ + H_2O, E^0 = 0.76 V

Alkaline Battery

Alkaline batteries are more expensive than LeClanchè batteries. Alkaline cells use the oxidation of zinc and reduction of MnO_2 to generate a current, but NaOH or KOH is used in the cell instead of the acidic salt NH_4Cl.

Anode: zinc electrode

Cathode: graphite electrode

Electrolyte: NaOH or KOH

Anode reaction: Zn (s) + 2 OH^- → ZnO + H_2O + 2e^-

Cathode reaction: $2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$

The cell produces 1.35 V. These cells are widely used, but their disposal is an environmental problem, and there are ongoing efforts to phase them out. Mercury and its compounds are poisonous.

Mercury cell

Mercury cells are alkaline cells that are typically used in calculators, cameras, watches and other devices.

Anode electrode: zinc metal

Cathode: Mercury (II) oxide (HgO)

Electrolyte: NaOH or KOH

The cell produces 1.35 V.

Cell reaction

$$\textit{Anode} \quad : \quad Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$$

$$\textit{Cathode} \quad : \quad HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(s) + 2OH^-(aq)$$

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.

Examples

Nickel-Cadmium Battery

The nickel cadmium battery is rechargeable and especially is used in battery-operated tools and portable computers. The cadmium metal serves as the anode, and the NiO_2(s), which is reduced to $Ni(OH)_2$(s), serves as the cathode.

Anode electrode: cadmium metal(Cd)

Cathode electrode: NiO_2

Electrolyte: NaOH or KOH

Cell reaction:

$$\textit{Anode} : Cd(s) + 2OH^-(aq) \rightleftharpoons Cd(OH)_2(s) + 2e^-$$

$$\textit{Cathode} : NiO_2(s) + 2H_2O(l) + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$$

$$\textit{Overall reaction} : NiO_2(s) + Cd(s) + 2H_2O(l) \rightleftharpoons Ni(OH)_2(s) + Cd(OH)_2(s)$$

The Lead Storage Battery

The lead storage battery commonly used in automobiles consists of six identical cells joined together in series. This is an example of a secondary rechargeable cell. The reactions within the cell can be reversed.

Anode electrode: Lead

Cathode electrode: lead(IV)oxide (PbO_2)

Electrolyte: aqueous solution sulphuric acid

Cell reaction:

$$\textit{Anode} : Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e^-$$

$$\textit{Cathode} : PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$$

$$\textit{Overall reaction} : Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightleftharpoons 2PbSO_4(s) + 2H_2O(l)$$

Under normal operating conditions, each cell produces 2 V. Therefore a total of 12 V is supplied by the six cells. Lead storage battery is used to power the ignition circuit of automobile and other electrical systems. The lead storage battery can deliver large amounts of current in short time, such as the time it takes to start up the engine.

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: Fe (s) → Fe^{2+} + 2e⁻, E^0 = 0.44 V

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

Cathode: O_2 (g) + 4 H^+ + 4e$^-$ → 2 H_2O, E^0 = 1.23 V

Rusting: 2 Fe + O_2 + 4H^+ (aq) → 2 Fe^{2+} (aq) + 2H_2O; E^0_{cell} = 1.67 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.