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Internal Assessment Test 1 – January 2022

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(Chief Course Instructor)

Answer 1 (a) When a metal is placed in its own ionic solution, the potential which develops at the interface between metal and its own ionicsolution is known as single electrode potential.

Derivation of Nernst equation for single electrode potential:

Consider an electrode assembly undergoing a reversible reaction.

 M^{n+} + ne⁻ $\leftarrow \longrightarrow M$

For above reaction the equilibrium constant is $Kc = \frac{[M]}{[M^{n+1}]}.$

The equilibrium constant (Kc) is related to change in free energy by Vant Hoff equation as follows

 $\Delta G = \Delta G^{\circ} + RT \ln Kc$ (1)

According to thermodynamics, for any reversible system the decrease in free energy (- ∆*G*)represents maximum amount of work that can be obtained from a chemical reaction.

 $-\Delta G$ = W_{max} -----------------------------(2)

 W_{max} = n x F x E ---------------------------(3)

 $n =$ moles of electrons, $F =$ Cmol⁻¹, $E = JC^{-1}$ Equating equations (2) & (3)

 $-\Delta G = n \times F \times E$ or

$$
\Delta G = \text{- n} \times F \times E
$$

Under standard conditions, when concentrations of all species is unity, standard free energy change is given by equation

 ΔG° = - n × F × E[°]

Where ΔG^0 = Change in free energy under standard conditions, E° is a constant called standard electrode potential.

Therefore by substituting values of ∆*G* , ∆*G* ° and Kc in equation (1), we get

 $-nFE = -nFE^{\circ} + RT \ln \frac{[M]}{[M^{n+1}]}$ $-nFE = -nF E[°] + RT ln [M] - RT ln [Mⁿ⁺]$ Dividing whole equation by –nF $-nFE$ -nF E° RT $\ln [M]$ RT $\ln [M^{n+}]$ ------ = ------- + ----------- – --------------- $-nF$ –nF –nF –nF RT $\ln [M]$ RT $\ln [M^{n+}]$ $E = E^{\circ}$ -- ----------- + -------------- nF nF Under standard condition $[M] = 1$, RT $E = E^{\circ} + \cdots = \ln [M^{n+}]$ nF

Converting natural log to base 10, we get

 2.303RT $E = E^{\circ}$ + ------------ log $[M^{n+}]$ nF

Substituting the values for R $(8.314 \text{ JK}^{-1} \text{mol}^{-1})$, F $(96500 \text{ Cmol}^{-1})$ and T (298K)

Answer 1(b)

According to Nernst equation $E = E^{\circ} + 2.203$ RT log [Mnⁿ⁺]

$$
E = 0.34 + \frac{2.303 \times 8.314 \times 313}{2 \times 96500}
$$
log [Cu²⁺]
\nE = 0.34 + 2.303 × 8.314 × 313 log [0.025]
\n2×96500
\nE = 0.290 V

Answer 2(a)

The electrodes whose potentials is known and constant and they are used to determine the potential of another unknown electrode are known as reference electrodes.

Construction and working of calomel electrodes:

It is a metal-insoluble salt electrode, where metal in contact with its insoluble salt and the solution containsthe anion of the salt. Mercury is placed at the bottom of the glass tube above which a paste of mercury and mercurous chloride are present. It is filled on the top with the saturated solution of KCl. A platinum wire sealed into a glass tube is dipped into mercury and used toprovide the external electrical contact. Depending on the nature of the other electrode it can either acts as anode or cathode.

Electrode representation: $Hg_{(s)}/Hg_2Cl_2$ (paste); Cl⁻

Working:

If the electrode behaves as anode, the electrode reaction is:

 $2Hg_{(1)} \rightarrow Hg_2^{+2} + 2e^{-}$

 Hg_2^{+2} +2Cl \rightarrow Hg₂Cl_{2(s)}

 $2Hg_{(1)} + 2Cl \rightarrow Hg_2Cl_{2(s)} + 2e^{-}$

If the electrode behaves as cathode, the electrode reaction is:

 Hg_2^{+2} +2e⁻ \rightarrow 2Hg (1) $Hg_2Cl_{2(s)} \rightarrow Hg_2^{+2}+2Cl^{-}$

 $Hg_2Cl_{2(s)} + 2e \rightarrow 2Hg_{(1)} + 2Cl^-$

 The electrode potential of calomel electrode depends on concentration of chloride ions. For saturated KCl E=0.2422V (called Saturated calomel

electrode)

Uses: It is used as a secondary reference electrode in the measurement of single electrode potential. It is the most commonly used reference electrode in all potentiometric determination

Answer 2 (b)

Solution: Given Ecell = ?? $[Ag^+] = 0.25$ M $[Cu^{2+}] = 0.5 M$ $E^{o}{}_{Cu}{}^{2+}{}_{/Cu} = 0.34V = E^{o}{}_{Anode}$; $E^{o}{}_{Ag}{}^{+}{}_{/Ag} = 0.80V = E^{o}{}_{Cathode}$ **T = 308 K Cell representation: Cu(s)/Cu 2+ (0.5 M)//Ag + (0.25)/Ag**

At cathode: 2Ag 2Ag ⁺ + 2e Cell Reaction: At anode: $Cu \rightarrow Cu^{2+} + 2e^{-}$ **Net cell Reaction: ⁺ Cu 2+ + 2 Ag Ecell = E o cell + 2.303RT log [Species at cathode] nF [Species at anode]** $E_{\text{cell}} = (E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}) + \frac{2.303X8.314X308}{2}$ log $\underline{[Ag^+]^2}$ **2X96500 [Cu 2+]** $E_{cell} = (0.80 - 0.34) + 2.303X8.314X308$ $log [0.25]^2$ **2X96500 [0.5]**

 $E_{cell} = 0.432 V$

Answer 3(a) Definition: Ion selective electrodes selectively respond to a specific ion in a mixture and

potential developedis a function of concentration of that ion in the solution. Eg. Glass electrode.

Glass Electrode:

Construction: The glass electrode consist of glass tube, the bottom of the glass tube is glass bulb covered with glass membrane made up of special glass of low melting point and high electrical conductivity (SiO_2 , Na₂O, Al₂O₃ etc., and it allows only H^+ ions). Glass bulb consists of 0.1 N HCl (Assume concentration is C_2) and Ag/AgCl electrode, which serves as internal reference electrode .

Working: The glass electrode is dipped into any solution containing H⁺ ions then glass electrode develops potential called as glass electrode potential. It is represented as **EG.**

Then, E^G = Eb+ E Ag/AgCl + E assy …………….. (1) Where, E_b = Boundary potential, $E_{Ag/AgCl}$ = Potential due to Ag/AgCl and E _{assy}= asymmetric potential

Boundary potential (Eb); It is a potential developed across the glass membrane when concentration of the solution inside and outside the glass membrane are different. Mathematically it is represented as, $E_b = E_1 - E_2$

Where, \mathbf{E}_1 = Potential due to H^+ present inside the bulb (Unknown solution)

 \mathbf{E}_2 = Potential due to H⁺ present in outside solution (Unknown solution) According to Nernst equation

Glass selects only H⁺ ions ignoring other ions. Hence $C_1 = H^+$ $E_b = K + 0.0591 \log[H^+]$, Where, $\log[H^+] = -pH$ Hence Eb= **K -** 0.0591pH ---------------------(2) **Substituting eqn (2) in (1)** $E_G = K - 0.0591pH + E_{Ag/AgCl} + E_{assy}$ $E_G = E^{\circ}_G - 0.0591pH$ Where, $E^{\circ}{}_{G} = \mathbf{K} + E_{Ag/AgCl} + E_{\text{assy}}$

n

Answer 3(b) Definition: Battery is a device consisting of two or more Galvanic (Voltaic) cells connected in series that can generate power and can act as a portable source of electrical energy.

Secondary batteries: In secondary batteries, the net cell reaction is completely reversible and hence these are rechargeable.

For example: Lead storage battery, $Ni - Cd$ battery etc.

Reserve batteries: One of the key components i.e. electrolyte, in reserve batteries is incorporated into the battery when required. When one of the key components is separated from remainder, chemical reaction between cell components (self discharge) is prevented and battery can be stored for a long period of time. For example: Mg-AgCl, Mg-CuCl, Zinc – Silver oxide reserve batteries, etc.

Answer 4(a) This is a rechargeable battery in which Li ions move from the negative electrode to the positive electrode during discharge and back when charging. (Anode and cathode are layered structure and they are able to insert lithium ion into their layer structure reversibly).

Construction

Anode: The negative electrode of a conventional lithium ion cell is made up of graphite C (Lithiated intercalated material, $Li_xC₆$)

Cathode: It is made up of lithiated transition metal intercalated compound i.e. metal oxide $(M = Mn, Co)$. **Electrolyte:** Lithium salt (LiPF₆) in an org solvent or mixture of orgaic carbonates such as ethylene carbonate or diethyl carbonate containing complex of Li-ions.

Working:

In the electrochemical reaction in a Li-ion battery both electrodes allow lithium ions to move in and out of

their interiors. When a lithium ion cell is discharging, the positive Li ions moves from the negative electrode and enters the cathode, and when the cell is charging reverse occur.

Discharge

At anode: Li_xC_6 \longrightarrow 6C + xLi^+ + xe^-

Charge

Discharge

At cathode: $Li_{1-x}CoO_2 + xLi^{+} + xe^{-}$ LiCoO₂

Overall cell reaction : $xLiC_6 + Li\,CoO_2 \rightarrow LiCoO_2 + 6C$

Charge

Electrochemical process is uptake of Li-ions at the anode during charge and their release during discharge.

The voltage of LIB is about **3.5-3.7** V.

Applications:

1. Mobile phones, smartphone, Laptops and tablets, digital cameras camcorders and torches.

2. They are used for energy storage for many electric vehicles.

3. Li-ion batteries are used in telecommunications applications.

Answer 4 (b)

Solution: Given Ecell = ?? $[Ni^{2+}] = 0.04$ M $[Zn^{2+}] = 0.4$ M E^{o} _{Zn}²⁺/_{Zn} = -0.76V = E^{o} _{Anode} ; E **o Ni 2+ /Ni = -0.25V = E o Cathode T = 308 K Cell representation: Zn(s)/Zn 2+ (0.4 M)//Ni 2+ (0.04)/Ni**

Cell Reaction: At anode:
$$
Zn \longrightarrow Zn^{2+} + 2e^{-}
$$

\nAt cathode: $Ni^{2+} + 2e^{-} \longrightarrow Ni$
\nNet cell Reaction: $Zn + Ni^{2+} \longrightarrow Zn^{2+} + Ni$
\n $E_{cell} = E^{o}_{cell} + \frac{2.303RT \log [\text{species at cathode}]}{nF} \text{ [Species at anode]}$
\n $E_{cell} = (E^{o}_{cathode} - E^{o}_{anode}) + \frac{2.303X8.314X298 \log [Ni^{2+}]}{2X96500} \text{ [Zn}^{2+}]\n$
\n $E_{cell} = (-0.25) - (-0.76) + 2.303X8.314X298 \log [0.04]$
\n $2X96500 \text{ [0.4]}$

$$
\mathsf{E}_{\text{cell}} = 0.4804 \text{ V}
$$

Answer 5(a) Conductometry: Theory: Ohm's law states that the current i (amperes) flowing in a conductor is directly proportional to the applied electromotive force, E (volts), and inversely proportional to the resistance R (ohms) of the conductor. The reciprocal of the resistance is called the conductance. The resistance of a homogeneous material of uniform cross section with an area of a sq. cm. and length *l* cm is given by

$$
R = \frac{\rho \times 1}{a}; \quad k = C \text{ } [\mathbf{l}/a]
$$

where ρ is the specific resistance. The reciprocal of the specific resistance is termed the specific conductance, к. It is the conductance of a cube of material 1 cm in length and 1cm in cross section. **Specific conductance:** Specific conductance of a solution is defined as the conductance of a solution present between two parallel electrodes which have 1 cm^2 area of cross section and which have kept 1 cm apart. Instrumentation

Conductometer consists of two platinum electrodes and a conductance measuring device. The two electrodes have unit area of cross section and are placed unit distance apart. The assembly responds rapidly to the changes in the concentration of the analyte under. A simple arrangement of conductometric titration is depicted in figure. The solution to be titrated is taken in the beaker.

Applications

Used to check water pollution in lakes as well as rivers. **Conductometric titrations of acids and base:** Pipette out 50ml of sample (Acid mixture) into a beaker. Immerse the conductivity cell into it. Connect the conductivity cell to a conductivity meter and measure the conductance by adding NaOH from the burette by increment of 1 ml. Plot a graph of conductance against volume of NaOH. Determine the neutralization point from the graph as shown below**.**

Answer 5(b) Advantages of Li-ion battery as an electrochemical energy system for electric vehicles:

Li-ion based Electric vehicles (EVs) had clear advantages over the competing steam- and gasoline-powered vehicles, such as absence of the loud noise. Compared to other batteries, Li-ion batteries used in EVs considering several characteristics and advantages which are based on the factors listed below:

Specific energy demonstrates how much energy a battery can hold per unit weight. Li-ion batteries which superior than other existing batteries.

Specific power is the ability to deliver high current and for Li ion batteries.

Safety: is naturally one of the most important aspects when choosing a battery for the EV.

Low maintenance: One major lithium ion battery they require low maintenance to ensure their performance. **Performance** reflects the condition of the battery when driving the EV in extreme temperature conditions.

Answer 6 (a) Theory: Colorimetry is an analytical technique used for the determination of concentration of compounds in a solution. It is used for solutions which are themselves cooured or which give a colour when mixed with a suitable reagent. A measure of the variation of the color of a solution with change in concentration of the solute forms the basis of colorimetry. Colorimetric estimation is based on the Beer-Lambert's law.

Beer-Lambet's Law: When a monochromatic radiation of intensity I is passed through a solution of a sample, a portion of light is absorbed (Ia), a portion is reflected (Ir) and the remainder is transmitted (It), then, $I_0 = I_a + Ir + It$

For glass cell, Ir is negligible, hence,

 $Io = Ia + It$

Lambert's Law: It states that when a monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the light.

Beer's Law: It states that when a monochromatic light passes through a solution, the rate of decrease in intensity with concentration of the light absorbing species is proportional to the intensity of the light.

$$
\log \frac{I_o}{I_t} = \epsilon ct \qquad \text{Or} \qquad A = \epsilon ct
$$

where ϵ called *molar absorptivity* or *molar absorption coefficient*, is a constant for a given substance at a given wavelength. If c is expressed in mol. dm^{-3} and t in centimeters, \in has the unit $dm^{3}mol^{-1}cm^{-1}$. This **equation is referred to as Beer-Lambert's law.** If the path length of the cell is kept constant, then, absorbance A is proportional to the concentration c.

Instrumentation: The instrument used to measure the absorbance of a solution is called photoelectric colorimeter.

It consist of

- (i) Tungsten lamp as the light source.
- (ii) A filter which provides the desired wavelength range wherein the solution gives the maximum absorbance.
- (iii) A sample cell
- (iv) A photocell detector

Fig: Schematic layout of colorimeter

Light from a tungsten lamp is allowed to fall on the solution taken in the sample call after passing through the filter. First a blank solution is taken in the sample cell and placed in the path of the light beam. Its absorbance is adjusted to zero on the meter. Next the analyte solution is placed in the path of the light beam and the quantity of light absorbed is measured as its absorbance.

Application: Colorimetry is versatile method of determining the concentration of metals and nonmetals present in small quantities in ores, soil, samples and alloys. **Colorimetric estimation of Cu in CuSO4.** Draw out 2, 4, 6, 8, and 10 ml cm³ of the Copper sulphate solution into 50cm^3 volumetric flask. Add 5cm^3 of ammonia solution to each of them and dilute upto the mark with distilled water and mix well. Prepare a blank solution by diluting 5cm³ of ammonia solution in 50cm³ volumetric flasks. For test solution add 5ml of NH₃ and make up to the mark. Measure the absorbance of each of these against blank solution at 620 nm. Plot a graph of absorbance (OD) against volume of copper sulphate solution and determine the volume of copper sulphate solution in the test sample as shown in the figure and find the amount of copper present in it.

Answer 6(b) Determination of pH using glass electrode:

To determine the pH of given solution, glass electrode is dipped in a solution whose pH is to be determined. It is combined with a saturated calomel electrode (ref electrode) through a salt bridge.The cell assembly is represented as

Hg / Hg₂Cl₂ / Cl⁻ // solution of unknown pH / glass / 0.1N HCl / AgCl / Ag

EMF of the So formed cell is determined by using electronic voltmeter.

 $E_{cell} = E_{Cathode} - E_{anode}$ (Conventionally glass electrode is cathode)

 $E_{cell} = E_G - E_{cal}$

WKT, E^G = Eº^G **-** 0.0591pH $E_{cell} = E^{o}$ - 0.0591pH - E_{cal}

 E^{o} _G - E_{cal} - E_{cell} pH = -------------------------- 0.0591

 $pH = K - E_{cell}/0.0591$

where, K is known as glass electrode assembly constant.

 E^o_G value or K is evaluated by dipping the glass electrode in a solution of known pH and measuring emf of the cell formed when coupled with a calomel electrode. Next the same assembly is dipped into test solution and the pH of test solution can be determined.

Answer 7. (a) Potentiometry is the determination of concentration of a solution by measuring the e.m.f.

Theory : When a metal M is immersed in a solution containing its own ions M^{n+} , the electrode potential is given by Nernst equation.

> J 1 Ŀ $E = E^{0} + \frac{0.0591}{n} log^{n} M^{n+1}$

Thus, the concentration can be calculated, provided E° of the electrode is known.

Potentiometric titration involves the measurement of the potential of an electrode as a function of the volume of the titrant. If an electrode of the metal reversible with respect to the corresponding ions is placed in the solution, the potential will vary throughout the titration. Initially the change in potential will be small. At the equivalence point, there will be a steep rise in the potential. The equivalence point can be determined by plotting the change in potential against volume of titrant added.

Instrumentation: A potentiometer consists of a reference electrode, an indicator electrode and a device for measuring the potential.

Application: The potentiometric titrations find applications in redox and precipitation reactions.

Application: Analysis of pollutants in water, Drug Analysis, Food quality analysis. **Potentiometric estimation of FAS using standard K2Cr2O⁷ solution**: Pipette out 25ml of FAS into a beaker. Add 1 t.t dil H2SO4, immerse calomel electrode + platinum electrode into it. Connect the assembly to a potentiometer and measure the potential by adding $K_2Cr_2O_7$ in the increments of 0.5ml.

Plot graph $\Delta E/\Delta V$ against volume of $K_2Cr_2O_7$, and determine the equivalence point. From the normality and volume $K_2Cr_2O_7$, solutions calculate the normality and the weight of FAS in the given solution.

Answer 7(b)

Recycling of used Li-ion batteries can be achieved by the methods listed belw:

Pyrometallurgy, or smelting, treats the input as if it were an ore, exposing it to a high temperature (over 1100 ^oC) to volatilize, combust, or melt and reduce all of the components of the cell. Not economical to recover lithium.

Hydrometallurgy, or leaching,: Cells are shredded, to remove the copper and aluminum foil current collectors.

The remaining material is dissolved in strong acid to break up the crystal structure of the cathode material. For cathode materials such as LMO, little amount of lithium can be extracted.

Direct recycling: It has also been called direct cathode recycling and cathode-to-cathode recycling.

Direct recycling separates the different components of the black mass (active material powder from shredding of cells) by physical processes, like gravity separation, which recover separated materials without causing chemical changes, enabling recovery of cathode material that is reusable with minimal treatment. By recovering cathode material, several costly processing steps can be avoided.

