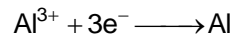


Class: 12
Subject: Chemistry
Topic: Electro Chemistry
No. of Questions: 26

1. Can we use direct current for experimental determination of resistance of a solution?
- Sol. No, it will cause electrolysis of solution. The concentration and resistance of solution will change with time.
2. Why is a salt bridge not necessary in lead storage cell?
- Sol. In lead storage cell, the oxidant (PbO_2), reductant (Pb) and their redox product (PbSO_4) are solids. Thus half cells need not to be in separate vessels; also they have common electrolyte solution of 40% of H_2SO_4 .
3. Colour of KI solution containing starch turns blue when Cl_2 water is added. Explain.
- Sol. Chlorine is placed below iodine in electrochemical series having higher E_{Red}^0 and thus undergoes reduction whereas I^- undergoes oxidation.
- $$2\text{I}^- \longrightarrow \text{I}_2 + 2\text{e}^-$$
- $$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$$
- $$\text{Cl}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Cl}^-$$
- The I_2 so formed gets absorbed in starch to give blue colour.
4. Why will Ag not react with dil. H_2SO_4 whereas zinc reacts?
- Sol. Ag is placed lower than hydrogen in electrochemical series having higher E_{red}^0 and thus reduction of Ag^+ occurs in place of H^+ whereas Zn being above hydrogen in the series will be oxidised to Zn^{2+} and H^+ will be reduced to H_2 .
- $$\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$$
- $$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$$
5. What is the role of ZnCl_2 in a dry cell?
- Sol. ZnCl_2 combines with NH_3 produced to form the complex salt $[\text{Zn}(\text{NH}_3)_2 \text{Cl}_2]$, otherwise the pressure developed due to NH_3 would crack the seal of the cell.
6. How much charge is required to reduce?
(a) 1 mole of Al^{3+} to Al and

(b) 1 mole of MnO_4^- to Mn^{2+} ?

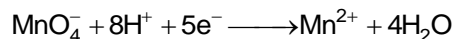
Sol. (a) Reduction reaction is:



Thus, 3 moles of e^- are needed to reduce 1 mole of Al^{3+} .

$$Q = 3 \times F \\ = 3 \times 96500 = 289500 \text{ coulomb}$$

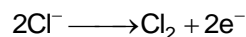
(b) The reduction reaction is :



$$Q = 5 \times F \\ = 5 \times 96500 = 482500 \text{ coulomb}$$

7. An electric current of 100 Amp is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at N.T.P.

Sol. The reaction taking place at anode is:-



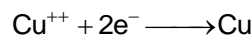
$$\text{Number of eq. of chloride} = \frac{W}{E} = \frac{I \times t}{F}$$

$$\text{Number of moles of chlorine} = \frac{I \times t}{F \times 2}$$

$$\text{Volume of } Cl_2 \text{ liberated at NTP} = \frac{22.4 \times I \times t}{2 \times F} \\ = \frac{22.4 \times 100 \times 5 \times 60 \times 60}{2 \times 96500} = 208.91 \text{ Lit.}$$

8. An ammeter and a copper voltameter are connected in series through which a constant current flows. The ammeter shows 0.52 amp. If 0.635 grams of copper is deposited in one hour, what is the percentage error of the ammeter?

Sol. The electrode is



$$\text{Deposited wt} = \frac{E \times I \times t}{F}$$

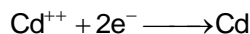
$$\text{or, } I = \frac{wt \times F}{E \times t} = \frac{0.635 \times 96500 \times 2}{63.5 \times 1 \times 60 \times 60} = 0.536$$

Difference in current = 0.536 - 0.52

$$\% \text{ error} = \frac{0.016 \times 100}{0.536} = 2.98\%$$

9. Cadmium amalgam is prepared by electrolysis of a solution of CdCl_2 using a mercury cathode. Find how long a current of 5 amp. should be passed in order to prepare 12% Cd – Hg amalgam on a cathode of 2 g mercury. [Atomic mass of Cd = 112.40].

Sol. 2 g Hg require Cd to prepare 12% amalgam = $\frac{12 \times 2}{88} = 0.273 \text{ g}$



Charge required to deposit 0.273 g of Cd = $\frac{2 \times 96500}{112.40} \times 0.273$ coulomb

Charge = amp. \times second

\therefore Second = $\frac{2 \times 96500 \times 0.273}{112.40 \times 5} = 93.75$

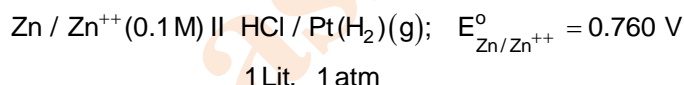
10. The equivalent conductivity of $\frac{N}{10}$ solution of acetic acid at 25°C is $14.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$. Calculate the degree of dissociation of CH_3COOH if $\Lambda_\infty \text{ CH}_3\text{COOH}$ is $390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$.

Sol. $\Lambda_\infty \text{ CH}_3\text{COOH} = 390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

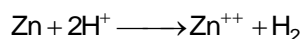
$\Lambda_{\text{CH}_3\text{COOH}} = 14.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

Degree of dissociation, $\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{14.3}{390.71}$
 $= 0.0366$ i.e. 3.66 % dissociation

11. Calculate the minimum amount of NaOH required to be added in R.H.S. to consume all the H^+ present in R.H.S. of the cell of emf +0.701 volt at 25°C before its use. Also report the emf of the cell after addition of NaOH.



Sol. Cell reaction is:-



Applying Nernst equation:

$$E_{\text{cell}} = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{++}]}{[\text{H}^+]^2}$$

$$0.701 = 0.760 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{++}]}{[\text{H}^+]^2}$$

$$\therefore \log \frac{[\text{Zn}^{++}]}{[\text{H}^+]^2} = \frac{0.0591 \times 2}{0.0591} = 2$$

$$\therefore \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = 10^2$$

$$\therefore [H^+]^2 = \frac{0.1}{10^2} = 10^{-3}$$

$$\therefore [H^+] = 0.0316 \text{ mol lit}^{-1}$$

Thus 0.0316 mol / lit of NaOH is required to neutralise H^+ ions.

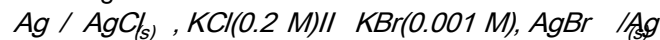
$$\begin{aligned} \text{Mass of NaOH} &= 0.0316 \times \text{Molecular mass of NaOH} \\ &= 0.0316 \times 40 = 1.264 \text{ g} \end{aligned}$$

After addition of NaOH, the solution becomes neutral i.e. the concentration of H^+ ions in cathodic solution becomes 10^{-7} .

Applying again Nernst equation

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[Zn^{++}]}{[H^+]^2} \\ &= 0.760 - \frac{0.0591}{2} \log \frac{0.1}{(10^{-7})^2} = 0.3759 \text{ volts} \end{aligned}$$

12. For the galvanic cell



Calculate the emf generated and assign correct polarity to each electrode for the spontaneous process after taking into account the cell reaction at 25°C .

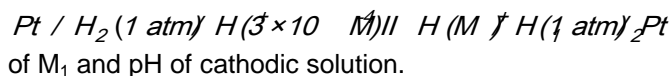
$$\text{Given } K_{\text{sp}} \text{ AgCl} = 2.8 \times 10^{-10}, K_{\text{sp}} \text{ AgBr} = 3.3 \times 10^{-13}$$

$$\text{Sol. } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{1} \log \frac{[Ag^+]_{\text{LHS}}}{[Ag^+]_{\text{RHS}}}$$

$$E_{\text{cell}} = \frac{-0.0591}{1} \log \frac{[Ag^+]_{\text{LHS}}}{[Ag^+]_{\text{RHS}}} \quad [E_{\text{cell}}^{\circ} = 0]$$

$$\begin{aligned} \text{or } E_{\text{cell}} &= 0.0591 \log \frac{[Ag^+]_{\text{RHS}}}{[Ag^+]_{\text{LHS}}} \\ &= 0.0591 \log \frac{K_{\text{sp}} \text{ AgBr} / [Br^-]}{K_{\text{sp}} \text{ AgCl} / [Cl^-]} \\ &= 0.0591 \log \frac{3.3 \times 10^{-13}}{0.001} \times \frac{0.2}{2.8 \times 10^{-10}} \\ &= -0.0371 \text{ Volts} \end{aligned}$$

13. The observed emf of the cell



is 0.154 V. Calculate the value

of M_1 and pH of cathodic solution.

$$\text{Sol. } E_{\text{cell}} = 0.0591 \log \frac{M_1}{3 \times 10^{-4}}$$

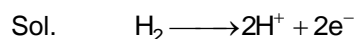
$$\text{or, } \log \frac{M_1}{3 \times 10^{-4}} = \frac{0.154}{0.0591} = 2.6058$$

$$\text{or, } \frac{M_1}{3 \times 10^{-4}} = 4.034 \times 10^2$$

$$\therefore M_1 = 4.034 \times 10^2 \times 3 \times 10^{-4} = 0.121 \text{ M}$$

$$\therefore \text{pH} = -\log[\text{H}^+] = -\log(0.121) = 0.917$$

14. In a fuel cell H_2 and O_2 react to produce electricity. In the process H_2 gas is oxidised at the anode and O_2 is reduced at the cathode. If 67.2 Lit. of H_2 at NTP reacts in 15 minutes, what is the average current produced? If the entire current is used for electro – deposition of Cu from Cu^{++} , how many gram of Cu are deposited.



$$67.2 \text{ Lit of } \text{H}_2 \text{ correspond} = \left(\frac{2 \times 96500}{22.4} \times 67.2 \right) \text{ coulomb.}$$

$$\text{Time} = 15 \times 60 \text{ second}$$

$$\text{Average current} = \frac{2 \times 96500 \times 67.2}{22.4 \times 15 \times 60} = 643.3 \text{ amp}$$

$$\text{Mass of copper deposited by} \left(\frac{2 \times 96500}{22.4} \times 67.2 \right) \text{ coulomb}$$

$$= \frac{63.5 \times 2 \times 96500 \times 67.2}{2 \times 96500 \times 22.4} = 190.5 \text{ g}$$

15. Neglecting the liquid – liquid junction potential, calculate the emf of the following cell at 25°C $\text{H}_2(1 \text{ atm}) / 0.5 \text{ M HCOOH} \parallel 1 \text{ M CH}_3\text{COOH} / \text{H}_2(1 \text{ atm})$. K_a for HCOOH and CH_3COOH are 1.77×10^{-4} and 1.8×10^{-5} respectively.

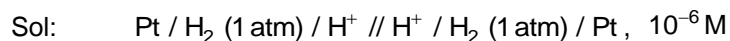
Sol. $[\text{H}^+] \text{ in HCOOH} = \sqrt{K_a \times c} = \sqrt{1.77 \times 10^{-4} \times 0.5} = 0.9407 \times 10^{-2} \text{ M}$

$$[\text{H}^+] \text{ in CH}_3\text{COOH} = \sqrt{K_a \times c} = \sqrt{1.8 \times 10^{-5} \times 1} = 4.2426 \times 10^{-3} \text{ M}$$

$$E_{\text{cell}} = 0.0591 \log \frac{[\text{H}^+]_{\text{RHS}}}{[\text{H}^+]_{\text{LHS}}}$$

$$= 0.0591 \log \frac{4.2426 \times 10^{-3}}{0.9407 \times 10^{-2}} = -0.0204 \text{ Volt}$$

16. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 Volt at 25°C . Calculate the concentration of hydrogen ions at the positive electrode.



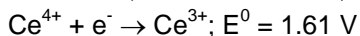
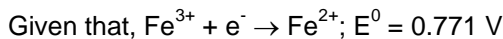
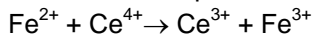
$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \frac{[10^{-6}]^2}{[\text{H}^+]^2} = \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{[10^{-6}]^2}$$

$$\text{or, } 0.118 = (0.0591) \times \log \frac{[\text{H}^+]}{[10^{-6}]}$$

$$\text{or, } \log \frac{[\text{H}^+]}{[10^{-6}]} = \frac{0.118}{0.0591} = 2$$

$$\therefore [\text{H}^+] = 10^{-4} \text{ M}$$

17. Calculate the equilibrium constant for the reaction:



Sol: The equilibrium reaction is $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Ce}^{3+} + \text{Fe}^{3+}$

Since the reaction is at equilibrium, $E_{\text{cell}} = 0$

$$E_{\text{cell}}^0 = \frac{0.0591}{1} \log K$$

$$E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 = 0.0591 \log K$$

$$-0.771 + 1.61 = 0.0591 \log K$$

$$\log K = \frac{0.839}{0.0591} = 14.1963$$

$$\therefore K = 1.57 \times 10^{14}$$

18. Iron is corroded by atmospheric oxygen under acidic condition to product $\text{Fe}^{2+}(\text{aq})$ ions initially.

The standard reduction potential



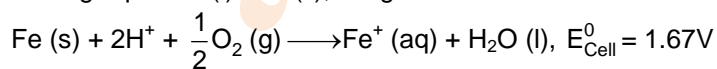
$$E^0 = -1.23 \text{ V}$$

Find whether the formation of $\text{Fe}^{2+}(\text{aq})$ is thermodynamically favorable or not.

Sol: The reactions are



Adding equation (i) and (ii), we get



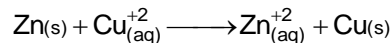
$$\therefore \Delta G^0 = -nFE^0_{\text{Cell}}$$

$$\therefore E^0_{\text{Cell}} = \text{positive} = 1.67 \text{ V}$$

$$\therefore \Delta G^0 \text{ is negative.}$$

So, the reaction is thermodynamically favourable or spontaneous.

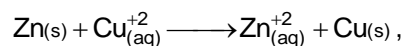
19. The emf of the cell reaction,



Calculate the entropy change. Given that enthalpy of the reaction is $-216.7 \text{ KJ mol}^{-1}$

And $E_{\text{Zn}^{+2}/\text{Zn}}^0 = -0.76\text{V}$ and $E_{\text{Cu}^{+2}/\text{Cu}}^0 = +0.34\text{V}$.

Sol: For the cell reaction



$$\therefore E_{\text{cell}}^0 = E_{\text{Zn}_{(s)}/\text{Zn}_{(aq)}^{+2}}^0 + E_{\text{Cu}_{(aq)}^{+2}/\text{Cu}_{(s)}}^0$$

$$= 0.76 + 0.34$$

$$= 1.1\text{V}$$

$$\Delta G^0 = -nF E_{\text{cell}}^0$$

$$= -2 \times 96500 \times 1.1 = -212.3 \text{ KJ}$$

$$\therefore \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{-216.7 - (-212.3)}{298} = -14.76 \text{ J K}^{-1} \text{ mol}^{-1}.$$

20. For how long a current of three amperes has to be passed through a solution of AgNO_3 to coat a metal surface of 80cm^2 area with 0.005mm thick layers? Density of silver is 10.5 g/cc and atomic weight of Ag is 108 gm/mol .

Sol: Assuming that the coating has to be done on only side of the surface, volume of Ag required for

$$\text{coating} = \frac{80 \times 0.005}{10} = 0.04\text{cc}$$

$$\text{Mass of silver} = 10.5 \times 0.04 = 0.42\text{gm}$$

$$\text{Moles of silver} = \frac{0.42}{108} = 0.00389$$

$$\text{Moles of electrons} = 0.00389 \text{ (since } \text{Ag}^+ + \text{e}^- \rightarrow \text{Ag})$$

$$\text{Charge passed} = 0.00389 \times 96500 = 375.385 \text{ coulombs}$$

$$\therefore \text{Time} = \frac{375.385}{3} = 125.1212 \text{ sec.}$$

21. Given the standard electrode potentials,

$$\frac{\text{K}^+}{\text{K}} = -2.93\text{V}, \frac{\text{Ag}^+}{\text{Ag}} = 0.80\text{V},$$

$$\frac{\text{Hg}^{2+}}{\text{Hg}} = 0.79\text{V}$$

$$\frac{\text{Mg}^{2+}}{\text{Mg}} = -2.37\text{V}, \frac{\text{Cr}^{3+}}{\text{Cr}} = -0.74\text{V}$$

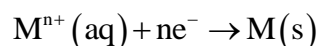
Arrange these metals in their increasing order of reducing power.

Sol: The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of $\frac{K^+}{K} < \frac{Mg^{2+}}{Mg} < \frac{Cr^{3+}}{Cr} < \frac{Hg^{2+}}{Hg} < \frac{Ag^+}{Ag}$.

Hence, the reducing power of the given metals increases in the following order:
 $Ag < Hg < Cr < Mg < K$

22. How can you increase the reduction potential of an electrode?

For the reaction



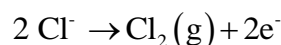
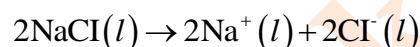
Sol: Nernst equation is:

$$E_{M^{n+}/M}^0 = E_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

$E_{M^{n+}/M}$ can be increased by

- A. Increase in concentration of M^{n+} ions in solution
- B. By increasing the temperature.

23. How many grams of chlorine can be produced by the electrolysis of NaCl with a current of 1.02 A for 15 min?



2 mole 1mol

$$Q = nf$$

$$Q = 2\text{mol} \times 96500 \text{ C/mol} = 1.93 \times 10^5 \text{ C}$$

$$\text{Quantity of electricity used} = IT$$

$$= 1.02 \text{ A} \times (15 \times 60) \text{ sec}$$

$$= 900 \text{ C}$$

Molar mass of $Cl_2 = 2 \times 35.5 = 71 \text{ gmol}^{-1} \times 10^{-5} \text{ C}$ of charge produce

Chlorine = 71 g

$1.93 \times 10^5 \text{ C}$ of charge produce chlorine = 71 gm

$$900 \text{ C of charge produces chlorine } \frac{71 \times 900}{1.93 \times 10^5} = 0.331 \text{ gm}$$

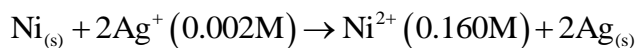
24. Why an electrochemical cell stops working after sometime?

Sol: The reduction potential of an electrode depends upon the concentration of solution with which it is in contact.

As the cell works, the concentration of reactants decrease. Then according to Le chatelier's principle it will shift the equilibrium in backward direction. On the other hand if the concentration is more on the reactant side then it will shift the equilibrium in forward direction. When cell works concentration in anodic compartment increases and in the cathodic compartment decrease and hence E^0 cathode will decrease. Now EMF of cell is $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$

A decrease in E^0_{cathode} and a corresponding increase in E^0_{anode} will mean that EMF of the cell will decrease and will ultimately become zero i.e., cell stops working after sometime.

25. Calculate the emf of the cell in which the following reaction takes place:



Given that $E^0_{(\text{Cell})} = 1.05 \text{ V}$

Sol: Applying Nernst equation we have:

$$\begin{aligned} E_{(\text{cell})} &= E^0_{(\text{cell})} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} \\ &= 1.05 - \frac{0.0591}{2} \log \frac{(0.160)}{(0.002)^2} \\ &= 1.05 - 0.02955 \log \frac{0.16}{0.000004} \\ &= 1.05 - 0.02955 \log 4 \times 10^4 \\ &= 1.05 - 0.02955 (\log 10000 + \log 4) \\ &= 1.05 - 0.02955 (4 + 0.6021) \\ &= 0.914 \text{ V} \end{aligned}$$

26. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm^{-1} . Calculate its molar conductivity.

Sol: Given,

$$K = 0.0248 \text{ S cm}^{-1}$$

$$C = 0.20 \text{ M}$$

$$\therefore \text{Molar conductivity, } \Lambda = \frac{K \times 1000}{c}$$

$$= \frac{0.0248 \times 1000}{0.2}$$

$$= 124 \text{ Scm}^2 \text{ mol}^{-1}$$

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