

Chapter 11: Electrochemistry

Review Questions

1. If $E_{\text{Cu}^{2+}}^{\circ}$ had been chosen as a standard reference electrode and assigned a potential of 0.00 V, what would be the reduction potential of the hydrogen electrode relative to it?

Solution

The difference between the reduction potentials for hydrogen and copper is a constant, that is, it is independent of the choice of the reference potential. In other words, the reduction half-cell potential for copper is to be 0.34 units higher for copper than for hydrogen, regardless of the chosen point of reference. If E° for copper is taken to be 0 V, then it must be 0.34 V for hydrogen.

2. What is a concentration cell? Why is $E_{\text{Cu}^{2+}}^{\circ}$ for such a cell equal to zero?

Solution

A concentration cell consists of two almost identical half-cells, which are composed of same substances, but have different concentrations of the solute species.

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln \frac{[\text{ion}]_{\text{dilute}}}{[\text{ion}]_{\text{conc.}}}$$

where $E_{\text{cell}}^{\circ} = 0$ because the standard cell potential is the reduction potential of the substance being reduced less than the reduction potential of the substance being oxidized, and the two are equal to each other because both are of the same substance.

3. Why must electrolysis reactions must occur at the electrodes in order for electrolytic conduction to continue?

Solution

The flow of electrons in the external circuit must be accompanied by the electrolysis reaction. Otherwise the electrodes would accumulate charge, and the system would cease to function.

4. Using the same current, which will require the greater length of time, depositing 0.10 mol Cu from a Cu^{2+} solution or depositing 0.10 mol of Cr from a Cr^{3+} solution? Explain.

Solution

The deposition of 0.10 mol of Cr from a Cr^{3+} solution will take longer than the deposition of 0.10 mol Cu from Cu^{2+} solution because Cr^{3+} requires 1.5 times as many electrons for deposition than Cu^{2+} . This is due to the difference in charges on the two ions.

5. Molar conductance of an acetic acid solution increases drastically with dilution. Explain.

Solution

As the concentration of acetic acid is reduced, it is ionized to a greater extent. Thus, increase in the conductance with decrease in the concentration is due to the increase in the number of ions in the solution.

6. Electrolytic conductivity decreases with dilution. Explain.

Solution

Conductivity of a solution is the conductance of ions present in a unit volume of the solution. After dilution, the number of ions per unit volume decreases, hence, the conductivity decreases.

7. An electric current is passed through two electrolytic cells connected in series (so the same amount of current passes through each of them). One cell contains Cu^{2+} and the other contains Fe^{2+} . In which cell the greater mass of the metal will be deposited? Explain your answer.

Solution

Copper has larger atomic mass than iron; therefore, copper will deposit greater mass of metal. Both metals are in the same +2 state.

8. Explain the following:

(a) The emf of a lead storage battery is dependent on the concentration of sulphuric acid.

(b) In primary alkaline cells, the electrolyte KOH is invariant.

Solution

(a) In lead storage battery, 20% sulphuric acid is used as an electrolyte with lead forming the anode and lead oxide forming the cathode.

The overall cell reaction is $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$

The potential of the lead storage cell at any given temperature will depend on the concentration of sulphuric acid solution. As sulphuric acid is consumed, water is produced that reduces the concentration of sulphuric acid as electrolyte and cell potential decreases.

(b) In primary alkaline cells, alkalis like KOH or NaOH are used as electrolyte. For example, in mercuric oxide–zinc cell, mercuric oxide (with 5–10% graphite) is cathode and amalgamated zinc powder is anode. A 40% potassium hydroxide solution saturated with zinc oxide is the electrolyte, the electrode reactions are

At the anode: $\text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2e^-$

At the cathode: $\text{HgO} + \text{H}_2\text{O} + 2e^- \rightarrow \text{Hg} + 2\text{OH}^-$

Overall cell reaction: $\text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$

The net cell reaction indicates that electrolyte KOH is non-variant and a minimal amount of it is required for the cell reaction.

9. How is hydrogen held as a reactant in a nickel–metal hydride battery? Write the chemical formula for a typical alloy used in this battery. What is the electrolyte?

Solution

The hydrogen is held in a metal alloy, Mg_2Ni , which has the ability to absorb and hold substantial amounts of hydrogen. The electrolyte used here is KOH.

10. Give two reasons why lithium is an attractive anode material for use in a battery? What are the problems associated with using lithium for this purpose?

Solution

Lithium has the most negative reduction potential of any metal, so it is very easy to oxidize making it an excellent material for an anode, and it is also a very lightweight metal. The major problem with lithium in a cell is that it reacts vigorously with water. Also, lithium batteries often have a large negative ΔH .

11. What advantages do fuel cells offer over conventional means for obtaining electrical power by the combustion of fuels?

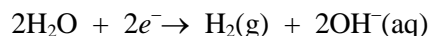
Solution

The electrode materials in a typical lithium ion cell are graphite and cobalt oxide. When the cell is charged, Li^+ ions leave LiCoO_2 and travel through the electrolyte to the graphite. When the cell discharges, the Li^+ ions move back through the electrolyte to the cobalt oxide, while electrons move through the external circuit to keep the charge in balance.

12. Describe the electrolysis of aqueous sodium chloride. How do the products of the electrolysis compare for stirred and unstirred reactions? Write the chemical equations for the reactions that occur at the electrodes.

Solution

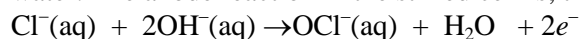
It is one of the various methods as diagramed in Fig.11.1 of the text. The physical apparatus influences the products that are obtained. Cathode reaction is same in stirred and unstirred cells



Unstirred anode reaction is $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2e^-$

The net reaction is $2\text{NaCl}(\text{aq}) + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH}(\text{aq}) + \text{Cl}_2(\text{g}) + \text{H}_2(\text{g})$

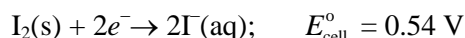
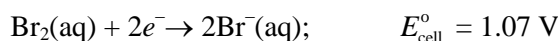
In an unstirred cell, the $\text{Cl}_2(\text{g})$ that is produced reacts with the $\text{OH}^-(\text{aq})$ forming $\text{Cl}^-(\text{aq})$, $\text{OCl}^-(\text{aq})$, and water. The anode reaction in the stirred cell is, therefore,



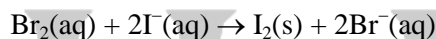
The net reaction in a stirred cell is $\text{NaCl}(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{NaOCl}(\text{aq}) + \text{H}_2(\text{g})$

13. What will be the spontaneous reaction among Br_2 , I_2 , Br^- , and I^- ?

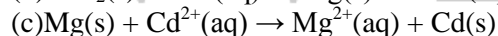
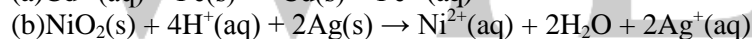
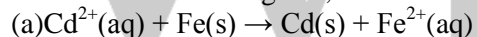
Solution



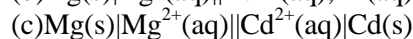
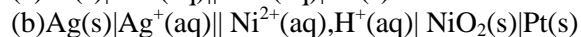
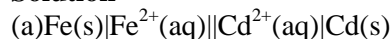
Since the first of these reactions has the larger reduction half-cell potential, it occurs as a reduction, and the second is reversed to become an oxidation:



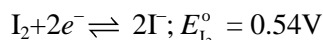
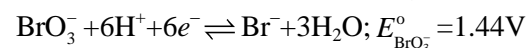
14. Write the cell notation for the following galvanic cells. For half-reactions in which all the reactants are in solution or are gases, assume the use of inert platinum electrodes.



Solution

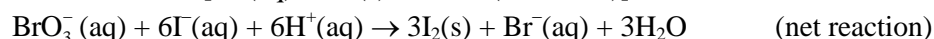
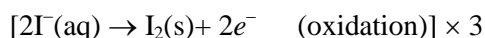
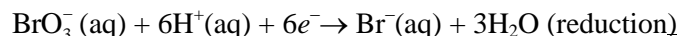


15. From the half-reactions below, determine the cell reaction and standard cell potential.



Solution

The half-cell with the more positive E_{cell}° will appear as a reduction, and the other half-reaction is reversed, to appear as an oxidation:

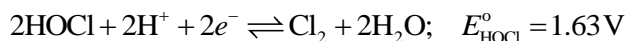
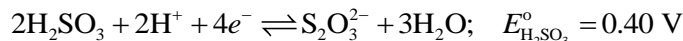


$$E_{\text{cell}}^{\circ} = E_{\text{substance reduced}}^{\circ} - E_{\text{substance oxidized}}^{\circ}$$

or

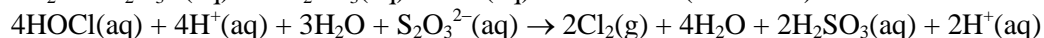
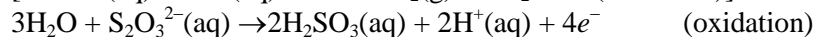
$$E_{\text{cell}}^{\circ} = E_{\text{reduction}}^{\circ} - E_{\text{oxidation}}^{\circ} = 1.44 \text{ V} - (0.54 \text{ V}) = 0.90 \text{ V}$$

16. What will be the spontaneous reaction among H_2SO_3 , $\text{S}_2\text{O}_3^{2-}$, HOCl , and Cl_2 ? The half-reactions involved are

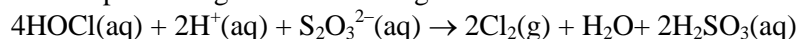


Solution

The half-reaction having more positive standard reduction potential is the one that occurs as a reduction, and the other one is written as an oxidation:



this simplifies to give the following net reaction:



17. Explain why:

(a) Nickel spatula cannot be used to stir copper sulphate solution.

(b) Blue color of copper sulphate fades when electrolyzed using platinum electrode.

Solution

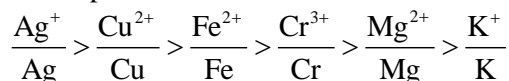
(a) Nickel spatula cannot be used to stir copper sulphate solution because $E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25 \text{ V}$ and $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34 \text{ V}$, which means nickel will reduce copper when stirred in copper sulphate solution.

(b) Platinum electrodes do not take part in the electrode reaction because they are inert. At cathode, Cu^{2+} ions will be reduced in comparison with H_2O as the E° reduction value for Cu is more than H_2O . At cathode, the half-cell reaction is $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$. As a result, Cu is deposited at cathode and the blue color of the solution fades due to the reduction of Cu^{2+} ions to Cu.

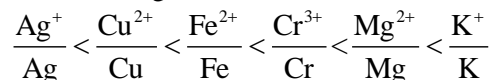
18. Given that the standard electrode potentials: $\text{K}^+/\text{K} = -2.93 \text{ V}$, $\text{Ag}^+/\text{Ag} = 0.80 \text{ V}$, $\text{Cu}^{2+}/\text{Cu} = 0.34 \text{ V}$, $\text{Mg}^{2+}/\text{Mg} = -2.37 \text{ V}$, $\text{Cr}^{3+}/\text{Cr} = -0.74 \text{ V}$, $\text{Fe}^{2+}/\text{Fe} = -0.44 \text{ V}$. Arrange these metals in the increasing order of their reducing power.

Solution

With the help of electrochemical series, we can predict the relative reducing strengths of substances. The decreasing order of standard electrode potentials is



and therefore the reducing power in increasing order is



That is, potassium has the least tendency to get reduced or is the strongest reducing agent and silver has highest tendency to get reduced or is the weakest reducing agent amongst all the six.

19. What do the positive and negative signs of reduction potentials tell us?

Solution

A positive reduction potential indicates that the substance is more easily reduced than the hydrogen ion and is a stronger oxidizing agent. Conversely, a negative reduction potential indicates that the substance comprising the half-cell is less easily reduced than the hydrogen ion and is stronger reducing agent.

20. Why do electrochemical cells stop working after sometime?

Solution

In an electrochemical cell, the emf of the cell is positive. This implies that the electrode potential of cathode is greater than the electrode potential of anode as

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

According to Nernst equation, electrode potential of an electrode varies directly with the concentration of ions of that species in the solution. As the cell reaction progresses, the concentration of metal ions in reduction half-cell decreases and increases in oxidation half-cell. As a result, the electrode potential of anode gradually increases and that of cathode decreases. At a point both become equal and the emf of the cell becomes zero. This is when the cell stops working.

21. In a concentration cell, give reasons for the following:

- The cell potential doubles when concentration ratio is changed from 0.0001 to 0.01.
- No electricity flows when the metal ion concentration at the two electrodes is the same.

Solution

(a) The emf for the concentration cell with concentration ratio 0.0001 is given by Nernst equation as

$$E_1 = -\frac{2.303}{nF} RT \log \frac{C_2}{C_1}$$

as $E_{\text{cell}}^{\circ} = 0$ for a concentration cell.

Given that $C_2/C_1 = 0.001$, therefore

$$E_1 = -\frac{2.303}{nF} RT \log 0.0001 = -(-4) \times \left(-2.303 \frac{RT}{nF} \right)$$

When $C_2/C_1 = 0.01$

$$E_2 = -\frac{2.303}{nF} RT \log 0.01 = (-2) \times \left(-2.303 \frac{RT}{nF} \right)$$

The ratio of E_1/E_2 is

$$\frac{E_1}{E_2} = \frac{-(2.303/nF)RT \times (-4)}{-(2.303/nF)RT \times (-2)} = 2$$

Thus, the cell potential is doubled when concentration ratio is changed from 0.0001 to 0.01.

(b) When the metal ion concentration at the two electrodes is same, $C_1 = C_2$.

The emf of the cell is given by

$$E_{\text{cell}} = E^{\circ} - \frac{2.303}{nF} RT \log \frac{C_2}{C_1} = -\frac{2.303}{nF} RT \log 1 = 0$$

As $E^{\circ} = 0$ for concentration cell and $C_1 = C_2$, therefore, $E_{\text{cell}} = 0$. Since the emf of the cell is zero, no electricity flows in the cell.

22. What is the effect of dilution on

- specific conductivity.
- equivalent conductance of weak electrolytes.
- equivalent conductance of strong electrolytes.

Solution

(a) The specific conductivity of an electrolyte decreases with increasing dilution because of the decrease in the number of ions per unit volume.

(b) Equivalent conductance of weak electrolyte increases with increase in dilution because increased dissociation of electrolyte takes place at low concentrations, thus increasing number of ions per unit volume.

(c) The equivalent conductance of a strong electrolyte does not vary much with dilution.

23. Predict the products of electrolysis in each of the following:

- (a) An aqueous solution of AgNO_3 with silver electrodes.
(b) An aqueous solution of AgNO_3 with platinum electrodes.
(c) A dilute solution of H_2SO_4 with platinum electrodes.
(d) An aqueous solution of CuCl_2 with platinum electrodes.

Solution

(a) At the cathode: $\text{Ag}^+ + e^- \rightarrow \text{Ag}$

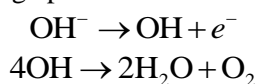
The Ag^+ ions have lower discharge potential than H^+ ions.

At the anode: $\text{Ag} \rightarrow \text{Ag} + e^-$

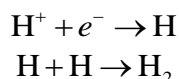
(b) At the cathode: $\text{Ag} + e^- \rightarrow \text{Ag}$

The Ag^+ ions have lower discharge potential than H^+ .

At the anode: OH^- ions have lower discharge potential than NO_3^-

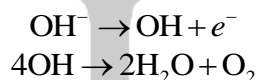


(c) At the cathode:



that is, H_2 gas is evolved at cathode.

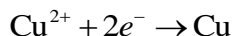
At the anode:



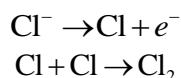
that is, oxygen gas is evolved.

(d) At the cathode:

Cu^{2+} ions have lower discharge potential so it will be reduced.



At the anode:



that is, chlorine gas is evolved at the anode.

24. What happens to the pH of the solution near the cathode and anode during the electrolysis of K_2SO_4 ? What function does K_2SO_4 serve in the electrolysis of a K_2SO_4 solution?

Solution

It is reduction that occurs at the cathode and near it, the pH increases due to the formation of OH^- (aq). At the anode, where the oxidation of water occurs, the pH decreases due to the production of H^+ (aq).

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

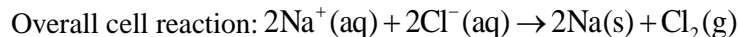
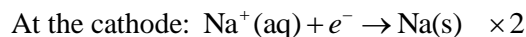
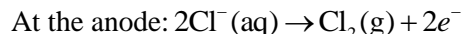
Oxidation at the anode: $2\text{H}_2\text{O} \rightarrow 4\text{H}^+(\text{aq}) + 4e^- + \text{O}_2(\text{g})$

The overall change in pH is 0 since the amount of H^+ formed and the amount of OH^- formed are equal. K_2SO_4 serves as charge carriers to balance the charge that occurs upon electrolysis of the K_2SO_4 solution.

25. Why NaCl must be melted before it is electrolyzed to give Na and Cl_2 ? Write the anode, cathode, and the overall cell reactions for the electrolysis of molten NaCl.

Solution

In solid NaCl, the ions are held in place and cannot move about. In molten NaCl, the crystal lattice of the solid has been destroyed; the ions are free to move, and consequently conduct current by migrating either to the anode or to the cathode.



26.(a) Why does the dry cell become dead after sometime even if it has not been used?

(b) What is the role of ZnCl_2 in a dry cell?

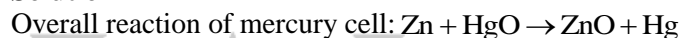
Solution

(a) A dry cell consists of a zinc anode, which is draped as a container. A graphite rod serves as a cathode and is surrounded by MnO_2 and moist electrolyte paste of NH_4Cl and ZnCl_2 . NH_4Cl corrodes the zinc container acting as anode even when the cell is not in use. Hence, dry cell becomes dead after sometimes even if it has not been used.

(b) Zn^{2+} and Cl^- ions combine with NH_3 formed during the reaction to form a complex salt $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$.

27. Why a mercury cell gives a constant voltage throughout its life?

Solution



Since there are no ions involved in the reaction, so the emf of the cell does not change. That is why, a mercury cell gives a constant voltage throughout its life.

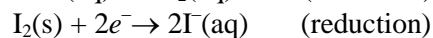
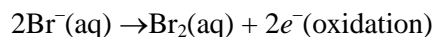
Numerical Problems

1. Calculate ΔG° for the following reaction:



Solution

First, separate the overall reaction into its two half-reactions:



$$E_{\text{cell}}^\circ = E_{\text{reduction}}^\circ - E_{\text{oxidation}}^\circ = 0.54 \text{ V} - (1.07 \text{ V}) = -0.53 \text{ V}$$

$$\text{The value of } n \text{ is } 2: \Delta G^\circ = -nF E_{\text{cell}}^\circ = -(2)(96500 \text{ C})(-0.53 \text{ J C}^{-1}) = 1.0 \times 10^5 \text{ J} = 1.0 \times 10^2 \text{ kJ}$$

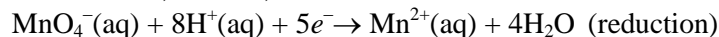
2. Calculate ΔG° for the reaction $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{HCHO}_2 \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{CO}_2$

for which $E_{\text{cell}}^\circ = 1.69 \text{ V}$

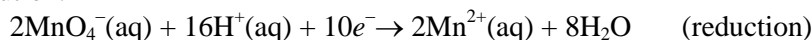
Solution

Using the equation $\Delta G^\circ = -nF E_{\text{cell}}^\circ$, we have $\Delta G^\circ = -n(96500 \text{ C/mole}^-)(1.69 \text{ V})$ for which we need n .

Upon writing the two half-reactions, that are,



we see that we need to multiply the reduction half-reaction by 2 and the oxidation reaction by 5 in order to balance the equation:



The net reaction has $n = 10$. So, $\Delta G^\circ = -(10 \text{ mol } e^-)(96500 \text{ C/mol } e^-)(1.69 \text{ V}) = -1.63 \times 10^3 \text{ kJ}$.

3. The system $2\text{AgI} + \text{Sn} \rightleftharpoons \text{Sn}^{2+} + 2\text{Ag} + 2\text{I}^-$ has a calculated E_{cell}° of -0.015 V . What is the value of K_c for this system?

Solution

Sn is oxidized by two electrons and Ag is reduced by two electrons:

$$E_{\text{cell}}^{\circ} = \frac{0.0592}{n} \log K_c$$

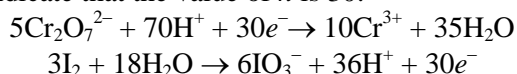
$$0.015 = \left(\frac{0.0592}{2} \right) \times \log K_c$$

Solving, we get $\log K_c = -0.51 \Rightarrow K_c = \text{antilog}(-0.51) = 0.31$.

4. The E_{cell}° is 0.135 V for reaction $3\text{I}_2(\text{s}) + 5\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 34\text{H}^+ \rightarrow 6\text{IO}_3^-(\text{aq}) + 10\text{Cr}^{3+}(\text{aq}) + 17\text{H}_2\text{O}$. What is E_{cell} if $[\text{Cr}_2\text{O}_7^{2-}] = 0.010 \text{ M}$, $[\text{H}^+] = 0.10 \text{ M}$, $[\text{IO}_3^-] = 0.00010 \text{ M}$, and $[\text{Cr}^{3+}] = 0.0010 \text{ M}$?

Solution

The following half-reactions indicate that the value of n is 30:

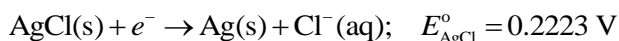


$$E_{\text{cell}} = 0.135 \text{ V} - \frac{0.0592 \text{ V}}{30} \log \frac{[\text{IO}_3^-]^6 [\text{Cr}^{3+}]^{10}}{[\text{H}^+]^{34} [\text{Cr}_2\text{O}_7^{2-}]^5}$$

$$= 0.135 \text{ V} - \frac{0.0592 \text{ V}}{30} \log \frac{[0.00010]^6 [0.0010]^{10}}{[0.10]^{34} [0.010]^5}$$

$$= 0.135 \text{ V} - \frac{0.0592 \text{ V}}{30} \log 1.0 \times 10^{-10} = 0.155 \text{ V}$$

5. A silver wire coated with AgCl is sensitive to the presence of chloride ion because of the half-cell reaction



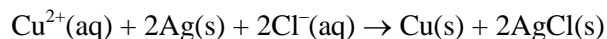
A student, wishing to measure the chloride ion concentration in a number of water samples, constructed a galvanic cell using the AgCl electrode as one half-cell and a copper wire dipping into 1.00 M CuSO_4 solution as the other half-cell. In one analysis, the potential of the cell was measured to be 0.0895 V with the copper half-cell serving as the cathode. What was the chloride ion concentration in the water? (Take $E_{\text{Cu}^{2+}}^{\circ} = +0.3419 \text{ V}$.)

Solution

Since the copper half-cell is the cathode, where reduction takes place, the silver half-cell is therefore the anode, where oxidation of silver occurs. The standard cell potential is

$$E_{\text{cell}}^{\circ} = E_{\text{reduction}}^{\circ} - E_{\text{oxidation}}^{\circ} = 0.3419 \text{ V} - 0.2223 \text{ V} = 0.1196 \text{ V}.$$

The overall cell reaction is



and the Nernst equation becomes

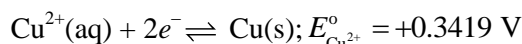
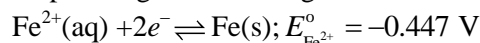
$$E_{\text{cell}} = 0.1196 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{1}{[\text{Cu}^{2+}][\text{Cl}^-]^2}$$

If we use the values given in the exercise, we arrive at

$$0.0895 \text{ V} = 0.1196 \text{ V} - 0.0296 \text{ V} \times \log\left(\frac{1}{[\text{Cl}^-]^2}\right)$$

this rearranges to give $\log\left(\frac{1}{[\text{Cl}^-]^2}\right) = 1.017 \Rightarrow [\text{Cl}^-] = 0.310 \text{ M}$

6. At 25°C, a galvanic cell was set up having the following half-reactions:



The copper half-cell contained 100 mL of 1.00 M CuSO₄. The iron half-cell contained 50.0 mL of 0.100 M FeSO₄. To the iron half-cell was added 50.0 mL of 0.500 M NaOH solution. The mixture was stirred and the cell potential was measured to be 1.175 V. Calculate the value of K_{sp} for Fe(OH)₂.

Solution

In the iron half-cell, we are initially given

$$0.0500 \text{ L} \times 0.100 \text{ mol L}^{-1} = 5.00 \times 10^{-3} \text{ mol Fe}^{2+}(\text{aq})$$

The precipitation of Fe(OH)₂(s) consumes some of the added hydroxide ion, as well as some of the iron ion: $\text{Fe}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_2(\text{s})$. The number of moles of OH⁻ that have been added to the iron half-cell is

$$0.500 \text{ mol L}^{-1} \times 0.0500 \text{ L} = 2.50 \times 10^{-2} \text{ mol OH}^-$$

The stoichiometry of the precipitation reaction requires that the following number of moles of OH⁻ be consumed on the precipitation of 5.00×10^{-3} mol of Fe(OH)₂(s):

$$5.00 \times 10^{-3} \text{ mol Fe}(\text{OH})_2 \times \left(2 \frac{\text{mol OH}^-}{\text{mol Fe}(\text{OH})_2}\right) = 1.00 \times 10^{-2} \text{ mol OH}^-$$

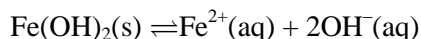
The number of moles of OH⁻ that are unprecipitated in the iron half-cell is

$$2.50 \times 10^{-2} \text{ mol} - 1.00 \times 10^{-2} \text{ mol} = 1.50 \times 10^{-2} \text{ mol OH}^-$$

Since the resulting volume is 50.0 mL + 50.0 mL, the concentration of hydroxide ion in the iron half-cell becomes, upon precipitation of the Fe(OH)₂:

$$[\text{OH}^-] = \frac{1.50 \times 10^{-2} \text{ mol}}{0.100 \text{ L}} = 0.150 \text{ M}$$

We have assumed that the iron hydroxide that forms in the above precipitation reaction is completely insoluble. This is not accurate, though, because some small amount does dissolve in water according to the following equilibrium:



This means that the true [OH⁻] is slightly higher than 0.150 M as calculated above. Thus, we must set up the usual equilibrium table, in order to analyze the extent to which Fe(OH)₂(s) dissolves in 0.150 M OH⁻ solution:

	[Fe ²⁺]	[OH ⁻]
I	–	0.150
C	+x	+2x
E	+x	0.150+2x

The quantity x in the above table is the molar solubility of Fe(OH)₂ in the solution that is formed in the iron half-cell.

$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^-]^2 = (x)(0.150 + 2x)^2$$

The standard cell potential is

$$E_{\text{cell}}^{\circ} = E_{\text{reduction}}^{\circ} - E_{\text{oxidation}}^{\circ} = 0.3419 \text{ V} - (-0.447 \text{ V}) = 0.7889 \text{ V}$$

The Nernst equation is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]}$$

$$1.175 = 0.7889 - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{2(96500 \text{ C mol}^{-1})} \ln \frac{[\text{Fe}^{2+}]}{[1.00]}$$

$$1.175 = 0.7889 - 0.01284 \ln[\text{Fe}^{2+}]$$

Solving, we get $\ln[\text{Fe}^{2+}] = -30.07 \Rightarrow [\text{Fe}^{2+}] = 8.72 \times 10^{-14} \text{ M}$

This is the concentration of Fe^{2+} in the saturated solution, and it is the value to be used for x in the above expression for K_{sp} .

$$K_{\text{sp}} = (x)(0.150 + 2x)^2 = (8.72 \times 10^{-14})[0.150 + (2)(8.72 \times 10^{-14})]^2 = 1.96 \times 10^{-15}$$

7. Suppose a galvanic cell was constructed at 25°C using a Cu/Cu^{2+} half-cell (in which the molar concentration of Cu^{2+} was 1.00 M) and a hydrogen electrode having a partial pressure of H_2 equal to 1 atm. The hydrogen electrode dipped into a solution of unknown hydrogen ion concentration, and the two half-cells were connected by a salt bridge. The precise value of $E_{\text{Cu}^{2+}}^{\circ} = +0.3419 \text{ V}$.

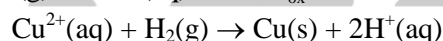
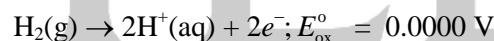
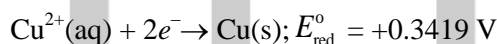
(a) Derive an equation for the pH of the solution with unknown hydrogen ion concentration, expressed in terms of E_{cell} and E_{cell}° .

(b) If the pH of the solution were 5.15, what would be the observed potential of the cell?

(c) If the potential of the cell were 0.645 V, what would be the pH of the solution?

Solution

The half-cell reactions and the overall cell reaction are



(a) The standard cell potential is

$$E_{\text{cell}}^{\circ} = E_{\text{reduction}}^{\circ} - E_{\text{oxidation}}^{\circ} = 0.3419 \text{ V} - 0 \text{ V} = +0.3419 \text{ V}$$

The Nernst equation for this system is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{2} \log \frac{[\text{H}^{+}]^2}{[\text{Cu}^{2+}]}$$

which becomes, under the circumstances defined in the problem

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{2} \log [\text{H}^{+}]^2$$

Rearranging the last equation gives

$$\frac{2 \times (E_{\text{cell}} - E_{\text{cell}}^{\circ})}{0.0592 \text{ V}} = -\log [\text{H}^{+}]^2$$

which becomes the desired relationship

$$\frac{(E_{\text{cell}} - E_{\text{cell}}^{\circ})}{0.0592} = -\log [\text{H}^{+}] = \text{pH}$$

(b) The equation derived in part (a) is conveniently rearranged to give

$$E_{\text{cell}} = (0.0592 \text{ V})(\text{pH}) + E_{\text{cell}}^{\circ} = (0.0592 \text{ V})(5.15) + 0.3419 \text{ V} = 0.647 \text{ V}$$

(c) The equation that was derived in part (A) may be used directly

$$\text{pH} = \frac{(E_{\text{cell}} - E_{\text{cell}}^{\circ})}{0.0592 \text{ V}} = \frac{(0.645 \text{ V} - 0.3419 \text{ V})}{0.0592 \text{ V}} = 5.12$$

8. How many grams of Cl_2 are produced when molten NaCl undergoes electrolysis at a current of 4.25 A for 35.0 min?

Solution

The reaction is $2\text{Cl}^-(\text{l}) \rightarrow \text{Cl}_2(\text{g}) + 2e^-$. The number of Coulombs is

$$4.25 \text{ A} \times 35.0 \text{ min} \times 60 \text{ s min}^{-1} = 8.92 \times 10^3 \text{ C}$$

The number of grams of Cl_2 that will be produced is

$$\text{g Cl}_2 = (8.92 \times 10^3 \text{ C}) \left(\frac{1 \text{ mol } e^-}{96500 \text{ C}} \right) \left(\frac{1 \text{ mol Cl}_2}{2 \text{ mol } e^-} \right) \left(\frac{70.91 \text{ g Cl}_2}{1 \text{ mol Cl}_2} \right) = 3.28 \text{ g Cl}_2$$

9. How many hours would it take to produce 75.0 g of metallic chromium by the electrolytic reduction of Cr^{3+} with a current of 2.25 A?

Solution

The reaction is $\text{Cr}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Cr}(\text{s})$. The number of Coulombs that will be required is

$$\text{Coulombs} = (75.0 \text{ g Cr}) \left(\frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} \right) \left(\frac{3 \text{ mol } e^-}{1 \text{ mol Cr}} \right) \left(\frac{96500 \text{ C}}{1 \text{ mol } e^-} \right) = 4.18 \times 10^5 \text{ C}$$

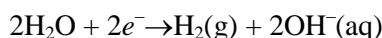
The time that will be required is

$$t = (4.18 \times 10^5 \text{ C}) \left(\frac{1 \text{ s}}{2.25 \text{ C}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) = 51.5 \text{ h}$$

10. An unstirred solution of 2.00 M NaCl was electrolyzed for a period of 25.0 min and then titrated with 0.250 M HCl . The titration required 15.5 mL of the acid. What was the average current in amperes during the electrolysis?

Solution

The electrolysis of NaCl solution results in the reduction of water, together with the formation of hydroxide ion:



The number of seconds is $25.0 \text{ min} \times 60 \text{ s/1 min} = 1.50 \times 10^3 \text{ s}$

The number of moles of OH^- is

$$\text{mol OH}^- = (15.5 \text{ mL H}^+) \left(\frac{0.250 \text{ mol H}^+}{1000 \text{ mL H}^+} \right) \left(\frac{1 \text{ mol OH}^-}{1 \text{ mol H}^+} \right) = 3.87 \times 10^{-3} \text{ mol OH}^-$$

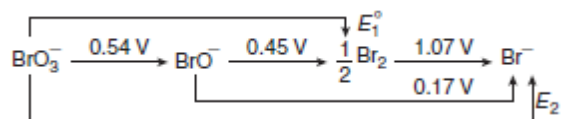
The number of Coulombs that will form these OH^- is

$$\text{Coulombs} = (3.87 \times 10^{-3} \text{ mol OH}^-) \left(\frac{2 \text{ mol } e^-}{2 \text{ mol OH}^-} \right) \left(\frac{96500 \text{ C}}{1 \text{ mol } e^-} \right) = 3.74 \times 10^2 \text{ C}$$

The average current in amperes is

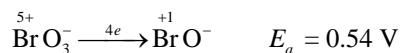
$$\text{Current} = \frac{3.74 \times 10^2 \text{ C}}{1.50 \times 10^3 \text{ s}} = 0.250 \text{ A}$$

11. From the standard potentials shown in the following diagram, calculate potentials E_1° and E_2° .

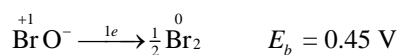


Solution

Given that

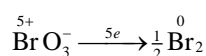


$$\Delta G_a = -nFE_a = -4F \times 0.54$$



$$\Delta G_b = -nFE_b = -1F \times 0.45$$

Overall reaction



$$\Delta G_1 = -nFE_1 = -5FE_1$$

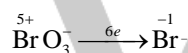
$$\Delta G_1 = (\Delta G_a + \Delta G_b)$$

$$-5F \frac{1}{2} E_1 = -(4F \times 0.54 + 1F \times 0.45)$$

Solving we get,

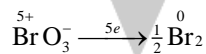
$$E_1 = 0.52 \text{ V}$$

For the reaction

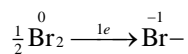


$$\Delta G_2 = -nFE_2 = -6FE_2$$

The reaction can be considered to take place through following steps:



$$\Delta G_c = -nFE_1 = -5F \times 0.52$$



$$\Delta G_d = -nFE_b = -1FE_c = -1F \times 1.07$$

$$\Delta G_2 = (\Delta G_c + \Delta G_d)$$

$$-6FE_2 = -(5F \times 0.52 + 1F \times 1.07)$$

Solving we get,

$$E_2 = 0.61 \text{ V}$$

12. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline if the current efficiency for the process is 50%. If the potential drop across the cell is 3 V, how much energy will be consumed?

Solution

Suppose we have 115800 C, 347.40 kJ.

So, 123 g of nitrobenzene requires 6×96500 C if efficiency is 100%.

12.3 g requires $6 \times (96500/123) \times 12.3 = 57900$ C.

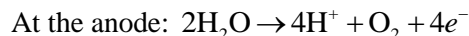
The charge required (if efficiency is 50%) = 2×57900 C = 115800 C

$$E = V \times F = 3 \times 96500 = 28900 \text{ J}$$

13. An acidic solution of CuSO_4 containing 0.4 g of Cu^{2+} is electrolyzed until all the Cu is deposited. The electrolysis is continued for seven more minutes with the volume kept at 100 mL and current 1.2 A. Calculate the volume of gases evolved at STP during entire electrolysis.

Solution

The reactions involved are



Therefore, gram equiv. of O_2 = gram equiv. of $\text{Cu} = \frac{0.4 \times 2}{63.6} = 0.001258$ g equiv.

Once all the Cu is deposited, the electrolysis is continued for seven more minutes with the following reactions taking place:



Therefore, gram equiv. of H_2 = gram equiv. of $\text{O}_2 = \frac{It}{96500} = \frac{1.2 \times 7 \times 60}{96500} = 0.00522$ g equiv.

At STP, volume of O_2 and H_2 are calculated using the above equations as:

$$V_{\text{O}_2} = \frac{22.4 \times (0.00522 + 0.01258)}{4} = 0.09968 \text{ L} = 99.68 \text{ mL}$$

$$V_{\text{H}_2} = \frac{22.4 \times (0.00522)}{2} = 0.05846 \text{ L} = 58.46 \text{ mL}$$

Hence, total volume of gases = 99.68 + 58.46 = 158.14 mL.

14. Calculate ΔG° and ΔS° (at 298 K) for the fuel cell reaction.



Solution

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -4 \times 96500 \times 1.23 = -474780 \text{ J}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \Rightarrow -474780 = -285800 - 278\Delta S^\circ$$

$$-474780 + 285800 = -278\Delta S^\circ \Rightarrow \Delta S^\circ = 634.16 \text{ JK}^{-1}$$

15. The standard reduction potential of Cu^{2+}/Cu is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple in a saturated solution of cupric hydroxide. $K_{\text{sp}}(\text{Cu}(\text{OH})_2) = 1 \times 10^{-19} \text{ M}^3$.

Solution

Given that pH = 14, so pOH = 0. Therefore, $[\text{OH}^-] = 1 \text{ M}$.

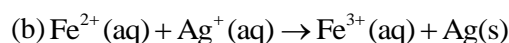
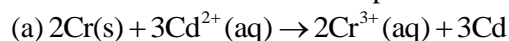
Now, the solubility product is $K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2 \Rightarrow [\text{Cu}^{2+}] = 10^{-19} \text{ M}$.

Also given that for the reaction $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34 \text{ V}$.

Applying Nernst equation, we get

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}]} = 0.34 - \frac{0.0591}{2} \log \frac{1}{10^{-19}} \\ &= 0.34 - 0.56 = -0.22 \text{ V} \end{aligned}$$

16. Calculate the standard cell potentials of galvanic cells in which the following reactions take place:



Calculate the ΔG° and equilibrium constant of the reactions.

Solution

(a) Consider the individual electrode reactions:

At the anode: $(\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-) \times 2$; $E_{\text{Cr}^{3+}/\text{Cr}}^\circ = -0.74 \text{ V}$

At cathode: $(\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}) \times 3$; $E_{\text{Cd}^{2+}/\text{Cd}}^\circ = -0.40 \text{ V}$

The E_{cell}° is given by

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.40 - (-0.74) = 0.34 \text{ V}$$

The Gibbs' energy is given by

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -6 \times 96500 \times 0.34 = -196860 \text{ J mol}^{-1}$$

Also $-\Delta G^\circ = 2.303RT \log K$. Substituting values, we get

$$196860 = 2.303 \times 8.314 \times 298 \times \log K \Rightarrow \log K = 34.5014$$

$$K = \text{antilog}(34.5014) = 3.192 \times 10^{34}$$

(b) Consider the individual electrode reactions:

At anode: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$; $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = 0.77 \text{ V}$

At cathode: $\text{Ag}^+ + e^- \rightarrow \text{Ag}$; $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.80 \text{ V}$

The E_{cell}° is given by

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.80 - 0.77 = 0.03 \text{ V}$$

The Gibbs' energy is given by

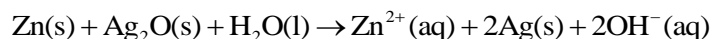
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -1 \times 96500 \times 0.03 = -2895 \text{ J mol}^{-1}$$

Also $-\Delta G^\circ = 2.303RT \log K$. Substituting values, we get

$$2895 = 2.303 \times 8.314 \times 298 \times \log K \Rightarrow \log K = 0.5074$$

$$K = \text{antilog}(0.5074) = 3.22$$

17. In the silver button cells, which are widely used in watches and other devices, the following reaction takes place:



Determine ΔG° and E° for the reaction.

Solution

Here Zn is oxidized to Zn^{2+} (anode) and Ag_2O is reduced first to Ag^+ and then to Ag.

The E_{cell}° is given by

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.344 - (-0.76) = 1.104 \text{ V}$$

and ΔG° is calculated as

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -1 \times 96500 \times 1.104 = -2.13 \times 10^5 \text{ J mol}^{-1}$$

18. For the cell reaction, $\text{Sn(s)} + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + \text{Pb(s)}$; $E_{\text{Sn}^{2+}/\text{Sn}}^\circ = -0.136 \text{ V}$, $E_{\text{Pb}^{2+}/\text{Pb}}^\circ = -0.126 \text{ V}$.

Calculate the ratio of concentration of Pb^{2+} to Sn^{2+} ion at which the cell reaction will be reversed?

Solution

The cell reaction is $\text{Sn} + \text{Pb}^{2+} \rightarrow \text{Sn}^{2+} + \text{Pb}$

Using Nernst equation $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]}$

Since $E_{\text{cell}}^{\circ} = -0.126 - (-0.136) = 0.01 \text{ V}$, we get

$$E_{\text{cell}} = 0.01 - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]}$$

At equilibrium $E_{\text{cell}} = 0$, so

$$0.01 = \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} \Rightarrow \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = \frac{0.01 \times 2}{0.0591} = 0.3384$$

$$\frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = \text{antilog}(0.3384) = 2.179$$

Thus, so long as $[\text{Sn}^{2+}]/[\text{Pb}^{2+}] > 2.179$, the cell reaction as given will take place. When $[\text{Sn}^{2+}]/[\text{Pb}^{2+}] < 2.179$, E_{cell} will become negative and the reaction will be reversed.

19. The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are as follows:

Concentration (M)	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa (\text{S m}^{-1})$	1.237	11.85	23.15	55.53	106.74

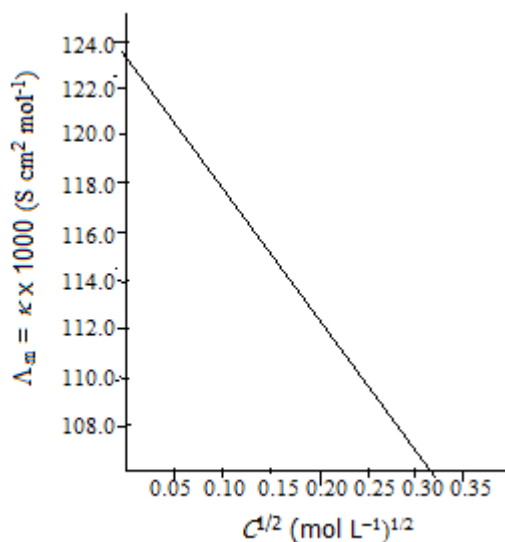
Calculate Λ_m for all concentrations and draw a plot between Λ_m and $C^{1/2}$. Find the value of Λ_m° .

Solution

From the given data, we have

Concentration (C) (M)	$\kappa (\text{S cm}^{-1})$	$\Lambda_m = \frac{\kappa \times 1000}{C} (\text{mol}^{-1})$	$(C)^{1/2} (\text{M}^{1/2})$
10^{-3}	1.237×10^{-4}	123.7	0.0316
10^{-2}	11.85×10^{-4}	118.5	0.100
2×10^{-2}	23.15×10^{-4}	115.8	0.141
5×10^{-2}	55.53×10^{-4}	111.1	0.224
10^{-1}	106.74×10^{-4}	106.7	0.316

The graph between Λ_m and $C^{1/2}$ is shown as follows:



The value of Λ_m^0 obtained from the graph = $124 \text{ S cm}^2 \text{ mol}^{-1}$

20. Three electrolytic cells A, B, C containing solutions of ZnSO_4 , AgNO_3 , and CuSO_4 , respectively, are connected in series. A steady current of 1.5 A was passed through them until 1.45 g of silver was deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Solution

The reaction is: $\text{Ag}^+ + e^- \rightarrow \text{Ag}$

108 g of Ag is deposited by 1 F (96500 C). $\frac{96500 \times 1.45}{108} = 1295.6 \text{ C}$

1.45 g of Ag is deposited by

From the expression of charge and current

$$Q = I \times t \Rightarrow t = \frac{Q}{I} = \frac{1295.6}{1.5} = 863.7 \text{ s}$$

The reaction of copper is: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$

2 F ($2 \times 96500 \text{ C}$) of electricity deposits 63.5 g of Cu.

1295.6 C of electricity deposits = $\frac{63.5 \times 1295.6}{2 \times 96500} = 0.426 \text{ g of Cu}$

The reaction for Zn is: $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$

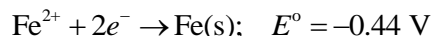
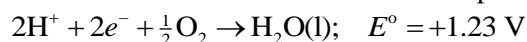
2 F ($2 \times 96500 \text{ C}$) of electricity deposits 65.3 g of Zn.

1295.6 C of electricity deposits $\frac{65.3 \times 1295.6}{2 \times 96500} = 0.438 \text{ g of Zn}$

Additional Objective Questions

Single Correct Choice Type

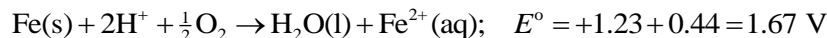
1. The rusting of iron takes place as follows. Calculate ΔG° for the net process.



- (A) -322 kJ mol^{-1} (B) -161 kJ mol^{-1} (C) -152 kJ mol^{-1} (D) -76 kJ mol^{-1}

Solution

(A) The expression is $\Delta G^\circ = -nFE^\circ$. Reversing the second equation and adding to the first equation, we get the net reaction as



Therefore, $\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.67 = 322310 \text{ J mol}^{-1} = 322.31 \text{ kJ mol}^{-1}$

2. Specific conductance of 0.01 M KCl solution is $xS \text{ cm}^{-1}$. When conductivity cell is filled with 0.01 M KCl the conductance observed is yS . When the same cell is filled with 0.01 M H_2SO_4 , the observed conductance is $zS \text{ cm}^{-1}$. Hence specific conductance of 0.01 M H_2SO_4 is

- (A) xz (B) z/xy (C) xz/y (D) xy/z

Solution

(C)

$$\text{Cell constant} = \frac{\text{Specific conductance of KCl}}{\text{Conductance of KCl}} = \frac{xS}{yS}$$

For 0.01 M H_2SO_4 ,

$$\text{Specific conductance} = \text{Cell constant} \times \text{Conductance} = xz/y$$

3. When a sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are

Cathode	Anode
(A) Pure zinc	Pure copper
(B) Impure sample	Pure copper
(C) Impure zinc	Impure sample
(D) Pure copper	Impure sample

Solution

(D) Impure copper is made anode and cathode is a sheet of pure copper. As the current is passed, the positive Cu^{2+} ions are attracted to the negative cathode where they take up the electrons and deposit themselves as neutral copper atoms.

4. A current of 0.193 A is passed through 100 mL of 0.2 M NaCl for an hour. Calculate the pOH of the solution after electrolysis if current efficiency is 90%. Assume no volume change.

- (A) 11.9 (B) 12.82 (C) 12.0 (D) 11.5

Solution

(B) Given that $i = 0.193 \text{ A}$, $t = 1 \text{ h} = 60 \times 60 \text{ s}$. Hence,

$$Q = it = 0.193 \times 3600 = 694.8 \text{ C} = 7.2 \times 10^{-3} \text{ F}$$

$$[\text{OH}^-] = \frac{7.2 \times 10^{-3}}{0.1} = 7.2 \times 10^{-2} \text{ M}$$

Therefore, $\text{pOH} = 2 - \log 7.2$; $\text{pH} = 14 - \text{pOH} = 12 + \log 7.2 = 12.82$

5. Find the equilibrium constant for the reaction, $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V, respectively, for $\text{Fe}^{3+} | \text{Fe}^{2+}$ and $\text{I}_3^- | \text{I}^-$ couples.

- (A) 5.2×10^8 (B) 6.26×10^7 (C) 3.8×10^7 (D) 4.3×10^7

Solution

(B) For the given reaction, $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{2} \log K$

At equilibrium, $E_{\text{cell}} = 0$. Therefore, $E_{\text{cell}}^{\circ} = \frac{0.059}{2} \log K$

$$0.23 = \frac{0.059}{2} \log K \Rightarrow K = 6.26 \times 10^7$$

6. One coulomb of charge passes through solution of AgNO_3 and CuSO_4 connected in series and the concentration of the two solutions being in the ratio 1:2. The ratio of weight of Ag and Cu deposited on Pt electrode is

- (A) 107.9:63.54 (B) 54:31.77 (C) 107.9:31.77 (D) 54:63.54

Solution

(C) Faraday's second law $\frac{W}{E} = \text{constant}$

$$\text{So, } \frac{W_{\text{Ag}}}{E_{\text{Ag}}} = \frac{W_{\text{Cu}}}{E_{\text{Cu}}} \left(\text{Ag}^+ + e^- \rightarrow \text{Ag}, E_{\text{Ag}} = \frac{M}{1} \right)$$

$$\text{Therefore } \frac{W_{\text{Ag}}}{E_{\text{Ag}}} = \frac{W_{\text{Cu}}}{E_{\text{Cu}}} = \frac{107.9}{63.54/2} = \frac{107.9}{31.77} \quad \left(\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}, E_{\text{Cu}} = \frac{M}{2} \right)$$

7. When a lead storage battery is discharged

- (A) SO_2 is evolved. (B) lead sulphate is consumed.
(C) lead is formed. (D) H_2SO_4 is consumed.

Solution



So, H_2SO_4 is consumed during discharging of lead storage battery.

8. Which of the following statements is true for the electrochemical Daniell cell?

- (A) Electrons flow from copper electrode to zinc electrode.
(B) Current flows from zinc electrode to copper electrode.
(C) Cations move toward copper electrode.
(D) Cations move toward zinc electrode.

Solution

(C) Cu^{2+} ions gain electrons and are deposited on copper.

9. The density of Cu is 8.94 g cm^{-3} . The quantity of electricity needed to plate an area of $10 \text{ cm} \times 10 \text{ cm}$ to a thickness of 10^{-2} using CuSO_4 solution would be

- (A) 13586 C (B) 27172 C (C) 40758 C (D) 20348 C

Solution

(B) The reaction is $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$

$$\text{Now, } \text{Volume} = \frac{\text{Mass}}{\text{Density}} = \text{Area} \times \text{Thickness deposited} = 100 \times 10^{-2} \text{ cm}^3$$

$$\text{Mass of } \text{Cu}^{2+} \text{ ion deposited on plate} = 1 \times 8.94 \text{ g}$$

$$\text{Now, Mass} = \frac{EIt}{96500} = \frac{Eq}{96500}$$

$$8.94 = \frac{63.5 \times Q}{2 \times 96500} \Rightarrow Q = 27172 \text{ C}$$

10. The specific conductance of a N/10KCl solution at 18°C is $1.12 \times 10^{-2} \text{ S cm}^{-1}$. The resistance of the solution contained in the cell is found to be 65 Ω. Calculate the cell constant.

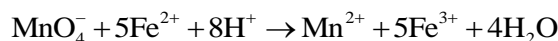
- (A) 0.912 cm^{-1} (B) 0.512 cm^{-1} (C) 0.728 cm^{-1} (D) 0.632 cm^{-1}

Solution

(A) Given that $\kappa = 1.12 \times 10^{-2} \text{ S cm}^{-1}$ for N/10 KCl solution

$$\text{We know that } \kappa = \frac{1}{R} \times \frac{l}{A} \Rightarrow 1.12 \times 10^{-2} = \frac{1}{65} \times \frac{l}{A} \Rightarrow \frac{l}{A} = 0.725 \text{ cm}^{-1}$$

11. The standard emf of the cell in which the reaction



occurs is 0.59 V at 25°C. The equilibrium constant for the given reaction is approximately.

- (A) 50 (B) 10 (C) 10^{50} (D) 10^5

Solution

(C) For the given cell reaction

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -RT \ln K_{\text{eq}}$$

$$-5 \times 96500 \times 0.59 = 2.303 \times 8.314 \times 298 \log K_{\text{eq}}$$

Solving, we get $K_{\text{eq}} = 7.8 \times 10^{49} \approx 10^{50}$.

12. The specific conductance of a saturated AgCl solution is found to be $1.86 \times 10^{-6} \text{ S cm}^{-1}$ and that for water is $6.0 \times 10^{-8} \text{ S cm}^{-1}$. The solubility of AgCl is ($\Lambda_{\text{eq}}^\circ = 137.2 \text{ S equivalent}^{-1} \text{ cm}^2$)

- (A) $1.7 \times 10^{-3} \text{ mol L}^{-1}$ (B) $1.3 \times 10^{-5} \text{ mol L}^{-1}$
(C) $1.3 \times 10^{-4} \text{ mol L}^{-1}$ (D) $1.3 \times 10^{-6} \text{ mol L}^{-1}$

Solution

(B) Specific conductance (κ)_{AgCl} = $\kappa_{\text{solution}} - \kappa_{\text{water}} = 1.86 \times 10^{-6} - 6 \times 10^{-8} = 180 \times 10^{-8}$}

Therefore, solubility is found as

$$S_{\text{AgCl}} = \kappa_{\text{AgCl}} \times \frac{1000}{\Lambda_{\text{eq}}^\circ} = 180 \times 10^{-8} \times \frac{1000}{137.2} = 1.3 \times 10^{-5} \text{ mol L}^{-1}$$

13. In the electrolytic cell, flow of electrons is from

- (A) cathode to anode through internal supply. (B) cathode to anode through external supply.
(C) anode to cathode through internal supply. (D) cathode to anode in solution.

Solution

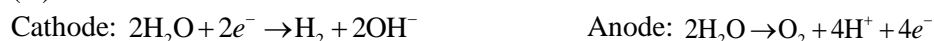
(B) Concept based.

14. A dilute aqueous solution of Na_2SO_4 is electrolyzed using platinum electrodes. The products at the cathode and anode are, respectively,

- (A) H_2, O_2 (B) O_2, H_2 (C) O_2, Na (D) O_2, SO_2

Solution

(A) The reactions at the cathode and anode are



15. Faraday's laws of electrolysis are related to the

(A) atomic number of cation.

(B) atomic number of anion.

(C) equivalent weight of the electrolyte.

(D) speed of the cation.

Solution

(C) Faraday's second law states that "The number of faradays passed is equal to the number of gram equivalents of electrolytes discharged".

16. The useful work done during the reaction $\text{Ag(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{AgCl(s)}$ would be

(A) 110 kJ mol⁻¹

(B) 220 kJ mol⁻¹

(C) 55 kJ mol⁻¹

(D) 100 kJ mol⁻¹

Given $E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$, $E^\circ_{\text{AgCl}/\text{Ag}/\text{Cl}^-} = 0.220 \text{ V}$, $p_{\text{Cl}_2} = 1 \text{ atm}$, and $T = 298 \text{ K}$.

Solution

(A) For the cell reaction $\text{Ag(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{AgCl(s)}$ $E^\circ = -1.14 \text{ V}$

or
$$E = E^\circ - \frac{0.0592}{1} \log p_{\text{Cl}_2}^{1/2}$$

Under standard conditions $p_{\text{Cl}_2} = 1$, therefore $\log p_{\text{Cl}_2}^{1/2} = 0$.

Useful work = $-W_{\text{max}} = -nFE = (-1) \times (-1.14) \times 96500 \times 10^{-3} \text{ kJ} = 110 \text{ kJ mol}^{-1}$.

17. The compound exhibiting maximum value of equivalent conductance in a fused state is

(A) SrCl₂

(B) CaCl₂

(C) MgCl₂

(D) BeCl₂

Solution

(A) Equivalent conductance is the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution. In SrCl₂, gram equivalent mass is larger as a result of which the compound shows maximum value of equivalent conductance in a fused state.

18. Emf of the cell $\text{Ni}|\text{Ni}^{2+}(0.1 \text{ M})||\text{Au}^{3+}(1.0 \text{ M})|\text{Au}$ will be (Given $E^\circ_{\text{Ni}/\text{Ni}^{2+}} = 0.25 \text{ V}$, $E^\circ_{\text{Au}/\text{Au}^{3+}} = 1.5 \text{ V}$)

(A) 1.75 V

(B) +1.7795 V

(C) +0.7795 V

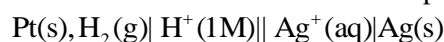
(D) -1.7795 V

Solution

(B) Cell reaction: $3\text{Ni} + 2\text{Au}^{3+} \rightarrow 3\text{Ni}^{2+} + 2\text{Au}$

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0591}{6} \log \frac{[\text{Ni}^{2+}]^3}{[\text{Au}^{3+}]^2} = (0.25 + 1.5) - \frac{0.0591}{6} \log \frac{(0.1)^3}{(1)^2} \\ &= 1.75 + \frac{0.0591}{2} \times \log(1) = 1.75 + 0.295 = +1.7795 \text{ V} \end{aligned}$$

19. An alloy of Pb–Ag weighing 1.08 g was dissolved in dilute HNO₃ and the volume made to 100 mL. A silver electrode was dipped in the solution and the emf of the cell setup as



was 0.62 V. If E°_{cell} is 0.80 V, what is the percentage of Ag in the alloy? (At 25°C, $RT/F = 0.06$)

(A) 25

(B) 2.50

(C) 10

(D) 50

Solution

(C) $0.62 = 0.8 - \frac{0.06}{1} \log \frac{[\text{H}^+]}{[\text{Ag}^+]} \Rightarrow -0.18 = 0.06 \log \frac{1}{[\text{Ag}^+]} \Rightarrow [\text{Ag}^+] = 10^{-3} \text{ M}$.

Weight of Ag = $10^{-3} \times 108 = 0.108 \text{ g}$

Therefore, weight% of Ag = $\frac{0.108}{1.08} \times 100 = 10\%$

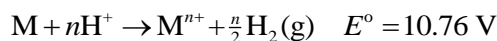
20. The emf of the cell $M|M^{n+}(0.02M)||H^+(1M)|H_2(g)(1\text{ atm}),Pt$ at 25°C is 0.81 V. Find the valency of the metal if the standard oxidation potential of the metal is 0.76 V?

- (A) 5 (B) 2 (C) 4 (D) 3

Solution

(B) At the anode: $M - ne^- \rightarrow M^{n+}_{(0.02M)} \quad E^\circ = +0.76$

At the cathode: $nH^+_{(1M)} + ne^- \rightarrow \frac{n}{2}H_2(g) \quad E^\circ = 0$



$$E_{\text{cell}} = 0.81 = +0.76 - \frac{0.0591}{n} \log \frac{[M^{n+}]}{[H^+]^n} = 0.81 = +0.76 - \frac{0.0591}{n} \log \frac{[M^{n+}]}{[H^+]^n}$$

$$\frac{0.0591}{n} \times 1.7 = 0.81 - 0.76 \Rightarrow n = \frac{0.0591 \times 1.7}{0.05} = 2.$$

21. An electrochemical cell stops working after some time because

- (A) one of the electrodes is eaten away.
 (B) electrode potentials of both the electrodes become equal in magnitude.
 (C) electrode potentials of both the electrodes go on decreasing.
 (D) electrode potentials of both the electrodes go on increasing.

Solution

(B) Concept based

22. Conductivity (units Siemens, S) is directly proportional to the area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is

- (A) S m mol^{-1} (B) $\text{S m}^2\text{mol}^{-1}$ (C) $\text{S}^{-2}\text{m}^2\text{mol}$ (D) $\text{S}^2\text{m}^2\text{mol}^{-2}$

Solution

(B) Conductivity $\propto \frac{\text{Area} \times \text{Concentration}}{\text{Length}}$

or Conductivity = $\kappa \times \frac{\text{Area} \times \text{Concentration}}{\text{Length}}$

or $\kappa = \frac{\text{Conductivity} \times \text{Length}}{\text{Area} \times \text{Concentration}} = \frac{\text{S} \times \text{m}}{\text{m}^2 \times \text{mol m}^{-3}} = \text{S m}^2 \text{mol}^{-1}$

23. If the standard half-cell reduction potentials are 0.522 V for Cu^+/Cu and 0.3402 V for Cu^{2+}/Cu . The standard half-cell reduction potential for $\text{Cu}^+/\text{Cu}^{2+}$ is

- (A) 0.20 V (B) 0.158 V (C) 0.40 V (D) 0.80 V

Solution

(B) Given that $\text{Cu}^+ + e^- \rightarrow \text{Cu} \quad E_1^\circ = 0.522 \text{ V} \quad n = 1 \quad (1)$

$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad E_2^\circ = 0.3402 \text{ V} \quad n = 2 \quad (2)$

$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \quad E_3^\circ = ? \quad n = 1 \quad (3)$

Equation (2) – (1) gives Eq. (3), therefore,

Since $E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3} = 1 \times \frac{(-0.522) + 2 \times 0.3402}{1} = -0.522 + 0.6802 = 0.1584 \text{ V}$

24. A solution containing one mole per liter of each $\text{Cu}(\text{NO}_3)_2$; AgNO_3 ; $\text{Hg}_2(\text{NO}_3)_2$; $\text{Mg}(\text{NO}_3)_2$ is being electrolyzed using inert electrodes. The values of standard electrode potentials (reduction potentials in volts) are $\text{Ag}/\text{Ag}^+ = 0.80 \text{ V}$, $\text{Hg}/\text{Hg}_2^{2+} = 0.79 \text{ V}$, $\text{Cu}/\text{Cu}^{2+} = -0.34 \text{ V}$, $\text{Mg}/\text{Mg}^{2+} = +2.37 \text{ V}$. With increasing voltage, the sequence of deposition of metals on the cathode will be

- (A) Ag, Hg, Cu (B) Cu, Hg, Ag (C) Ag, Hg, Cu, Mg (D) Mg, Cu, Hg, Ag

Solution

(A) Greater the value of standard reduction potential, greater will be its tendency to undergo reduction. So the sequence of deposition of metals on cathode will be Ag, Hg, Cu. Here, magnesium will not be deposited because its standard reduction potential is negative. So it is a strong tendency to undergo oxidation. Therefore, on electrolysis of $\text{Mg}(\text{NO}_3)_2$ solution, H_2 gas will be evolved at cathode.

25. In passing 3 F of electricity through the three electrolytic cells connected in series containing Ag^+ , Ca^{2+} , and Al^{3+} ions, respectively. The molar ratio in which the three metal ions are liberated at the electrodes is

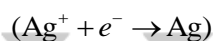
- (A) 1:2:3 (B) 3:2:1 (C) 6:3:2 (D) 3:4:2

Solution

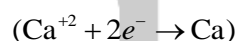
(C) Faraday's second law states that $\frac{W}{E} = \text{constant}$

So, g equiv. of $\text{Ag}^+ = \text{g equiv. of Ca}^{2+} = \text{g equiv. of Al}^{3+} = a$ (say)

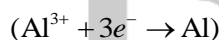
Now, mole of $\text{Ag}^+ = a^+$



$$\text{Mole of Ca}^{+2} = \frac{W}{E}$$

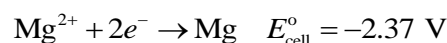
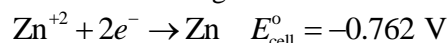


$$\text{Mole of Al}^{3+} = \frac{a}{3}$$



So, mole ratio of $\text{Ag}^+ : \text{Ca}^{+2} : \text{Al}^{+3} = a : \frac{W}{E} : \frac{W}{E} = 6 : 3 : 2$

26. The standard potentials at 25°C for the following half-cell reactions are given as



When zinc dust is added to a solution of magnesium chloride,

- (A) no reaction will take place. (B) zinc chloride is formed.
(C) zinc dissolve in solution. (D) magnesium is precipitated.

Solution

(A) The reaction is $\text{Zn} + \text{MgCl}_2 \rightarrow \text{ZnCl}_2 + \text{Mg}$. Therefore,

$$E_{\text{cell}}^\circ = E_{\text{Zn}/\text{Zn}^{+2}}^\circ + E_{\text{Mg}^{+2}/\text{Mg}}^\circ = +0.762 - 2.37 = -1.608 \text{ V}$$

Therefore $E_{\text{cell}}^\circ = E_{\text{Zn}/\text{Zn}^{2+}}^\circ + E_{\text{Mg}^{2+}/\text{Mg}}^\circ$ is negative so no reaction will take place.

27. Four alkali metals A, B, C, and D have standard electrode potentials, respectively, as -3.05 , -1.66 , -0.40 , and 0.80 V . Which one will be the most reducing?

- (A) A (B) B (C) C (D) D

Solution

(A) Best reducing agent is one which is itself oxidized most easily, namely, A.

28. $\text{Zn(s)} + \text{Cl}_2(1\text{atm}) \rightarrow \text{Zn}^{2+} + 2\text{Cl}^-$. The E° of the cell is 2.12V. To increase E ,

- (A) Zn^{2+} concentration should be increased.
 (B) Zn^{2+} concentration should be decreased.
 (C) Cl^- concentration should be increased.
 (D) partial pressure Cl_2 should be decreased.

Solution

$$(B) E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}][\text{Cl}^-]^2}{p_{\text{Cl}_2}}$$

29. $\text{Cr}_2\text{O}_7^{2-} + \text{I}^- \rightarrow \text{I}_2 + \text{Cr}^{3+}$, $E_{\text{cell}}^\circ = 0.79 \text{ V}$, $E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^\circ = 1.33 \text{ V}$, $E_{\text{I}_2/\text{I}^-}^\circ = ?$

- (A) 0.54 V (B) -0.054 V (C) +0.18 V (D) -0.18 V

Solution

(A) In the given reaction, I⁻ has been oxidized to I₂ and Cr₂O₇²⁻ ions have been reduced to Cr³⁺. Therefore,

$$E_{\text{cell}}^\circ = E_{\text{Cr}_2\text{O}_7^{2-}}^\circ - E_{\text{I}_2}^\circ \Rightarrow 0.79 = 1.33 - E_{\text{I}_2}^\circ \text{ or } E_{\text{I}_2}^\circ = 0.54 \text{ V}.$$

30. Value of $E_{\text{H}_2\text{O}/\text{H}_2(1\text{atm})}^\circ$ at 298 K would be

- (A) -0.207V (B) +0.207V (C) -0.414 V (D) +0.414 V

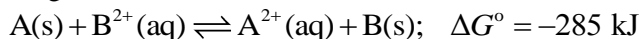
Solution

(C) For water at 298 K, $[\text{H}^+] = 10^{-7} \text{ M}$

Reduction reaction is $\text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2$

$$\text{Therefore, } E_{\text{cell}} = -\frac{RT}{F} \ln \frac{(\text{pH})^{1/2}}{[\text{H}^+]} = -0.591 \log \frac{(\text{pH})^{1/2}}{[\text{H}^+]} = -0.0591 \log \frac{1}{10^{-7}} = -0.4137 \approx 0.414 \text{ V}.$$

31. Efficiency of the following cell is 84%



then the standard electrode potential of the cell will be

- (A) 1.20 V (B) 2.40 V (C) 1.10 V (D) 1.24 V

Solution

(D) Given $\text{A(s)} + \text{B}^{2+}(\text{aq}) \rightleftharpoons \text{A}^{2+}(\text{aq}) + \text{B(s)}; \Delta G^\circ = -285 \text{ kJ}$

$$\text{But } \Delta G^\circ = -nFE^\circ \Rightarrow -285 \times 1000 = -2 \times 96500 E^\circ \Rightarrow E^\circ = 1.48 \text{ V}$$

$$\text{Since efficiency is 84\%, actual } E^\circ = 1.48 \times \frac{84}{100} = 1.24 \text{ V}.$$

32. The standard emf of the cell $\text{Cd(s)}|\text{CdCl}_2(0.1\text{M})||\text{AgCl(s)}|\text{Ag(s)}$ in which the cell reaction is

$\text{Cd(s)} + 2\text{AgCl(s)} \rightarrow 2\text{Ag(s)} + \text{Cd}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$ is 0.6915 V at 0°C and 0.6753 V at 25°C.

- (A) -176kJ (B) -334.7kJ (C) +123.5 kJ (D) -167 kJ

Solution

$$(D) \Delta G = -nFE_{\text{cell}} = -2 = -2 \times 96500 \times 0.6753 \text{ (at } 25^\circ\text{C)} = -130333 \text{ J}$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right) \text{ where } \left[\frac{\partial E}{\partial T} \right] \text{ is called temperature coefficient of emf.}$$

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{E_2 - E_1}{T_2 - T_1} = \frac{0.6753 - 0.6915}{298 - 273} = -6.48 \times 10^{-4}$$

Therefore, $\Delta S = 2 \times 96500 \times (-6.48 \times 10^{-4}) = -125.064 \text{ JK}^{-1} \text{ mol}^{-1}$.

Substituting the values in $\Delta G = \Delta H - T\Delta S$, we get $\Delta H = -167.6 \text{ kJ}$.

33. Calculate the emf of the cell

Pt, H_2 (1.0 atm) | CH_3COOH (0.1 M) || NH_3 (aq, 0.01 M) | H_2 (1.0 atm), Pt

Pt, $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$, $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

(A) -0.92 V (B) -0.46 V (C) -0.35 V (D) -0.20 V

Solution

(B) Pt, H_2 (1 atm) | CH_3COOH (0.1 M) || NH_3 (or, 0.01 M) | H_2 (1 atm), Pt

Given that $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ and $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$. Now,

At the anode: $\frac{1}{2}\text{H}_2(\text{g}) - e^- \rightarrow \text{H}^+$; $E^\circ = 0$

At the cathode: $\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2(\text{g})$; $E^\circ_{\text{cell}} = 0 \text{ V}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.06}{1} \log \frac{[\text{H}^+]_{\text{anode}}}{[\text{H}^+]_{\text{cathode}}}$$

Now, $[\text{OH}^-]^2 = 0.01 \times 1.8 \times 10^{-5} = 4.2 \times 10^{-4} \text{ M}$

We have $[\text{H}^+][\text{OH}^-] = 10^{-14}$, therefore,

$$[\text{H}^+]_{\text{cathode}} = \frac{10^{-14}}{4.2 \times 10^{-4}}$$

Similarly, $[\text{OH}^-]^2 = 1.8 \times 10^{-5} \times 0.1 = 1.34 \times 10^{-3} \text{ M}$

We have $[\text{H}^+][\text{OH}^-] = 10^{-14}$, therefore,

$$[\text{H}^+]_{\text{anode}} = \frac{10^{-14}}{1.34 \times 10^{-3}}$$

$E_{\text{cell}} = -0.0591 \times 7.78 = -0.46 \text{ V}$.

34. An aqueous solution containing Na^+ , Sn^{2+} , Cl^- , and SO_4^{2-} ions, all at unit concentration, is electrolyzed between a silver anode and a platinum cathode. What changes occur at the electrodes when current passed through the cell? Given that $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.799 \text{ V}$, $E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}$, $E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$, $E^\circ_{\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}} = 0.13 \text{ V}$.

- (A) Si^{2+} is reduced and Cl^- is oxidized. (B) Ag is oxidized and Sn^{2+} is reduced.
(C) Sa^{2+} is reduced and Sn^{2+} is oxidized. (D) H^+ is reduced and Sn^{2+} is oxidized.

Solution

(C) At anode, either Ag can get oxidized to Ag^+ or Sn^{2+} to Sn^{4+} or Cl^- to Cl_2 or SO_4^{2-} to $\text{S}_2\text{O}_8^{2-}$. Their respective oxidation potential values are -0.799 V , -0.13 V , -1.36 V , and -2 V . From these values, it is evident that Sn^{2+} would be oxidized first, followed by Ag at anode. At cathode, either Na^+ can get reduced to Na or Sn^{2+} to Sn or H^+ to H_2 . The reduction potential value of Na^+ is highly negative while for Sn^{2+} | Sn is -0.14 V and for $\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$ $\left(E_{\text{H}^+/\text{H}_2} = -0.059 \log \frac{1}{10^{-7}}\right)$ is -0.413 V . Thus, Sn^{2+} will get reduced at cathode followed by H^+ .

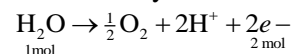
35. Dal lake has $8.2 \times 10^{12} \text{ L}$ of water, approximately. A power reactor produces electricity at the rate $1.5 \times 10^6 \text{ C s}^{-1}$ at an appropriate voltage. How many years would it take to electrolyze the lake?

- (A) 2.4 million years (B) 5.3 million years (C) 1.9 million years (D) 4.6 million years

Solution

(C)

The electrolysis reaction is



So electrolysis of one mole of water will lead to discharge of half mole of oxygen. Given that volume of water is $8.2 \times 10^{12}\text{L} = 8.2 \times 10^{15}\text{g} = 0.45 \times 10^{15}\text{ mol}$. The number of moles of oxygen liberated is $0.225 \times 10^{15}\text{ mol}$. The volume of oxygen liberated is $0.225 \times 10^{15} \times 22.4 = 5.04 \times 10^{15}\text{ L}$.

For electrolysis that leads to formation of gaseous products, Faraday's law can be expressed as

$$V = \frac{ItV_e}{96500}$$

Where V is the volume of gas liberated, I is the current passed for time t (in seconds) and V_e (= 5.6 L for oxygen) is the equivalent volume (volume of gas evolved at an electrode at STP by 1 faraday charge). Substituting values in the equation we get

$$5.04 \times 10^{15}\text{ L} = \frac{1.5 \times 10^6\text{ C s}^{-1} t\text{ (s)} 5.6 \times \text{L}}{96500}$$

Solving we get,

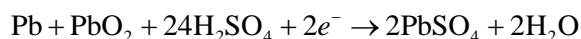
$$t = 57900 \times 10^9\text{ s} = 1.836\text{ million years}$$

36.In lead storage battery, during discharging process

- (A) PbO_2 gets oxidized. (B) H_2SO_4 is produced.
 (C) density of H_2SO_4 solution decreases. (D) density of H_2SO_4 solution increases.

Solution(C)

The following reactions take place in a lead storage battery during discharging process:



In the overall reaction, H_2SO_4 is consumed and water is formed (Pb , PbSO_4 , and PbO_2 are solids). Therefore, the density of H_2SO_4 solution decreases.

37.The conductivity of a saturated solution of BaSO_4 is $3.06 \times 10^{-6}\text{ S cm}^{-1}$ and its equivalent conductance is $1.53\text{ S cm}^2\text{equiv.}^{-1}$. The K_{sp} for BaSO_4 will be

- (A) 4×10^{-12} (B) 2.5×10^{-9} (C) 2.5×10^{-13} (D) 4×10^{-6}

Solution

(D) The reaction involved is $\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$

Given that $\kappa(\text{BaSO}_4) = 3.06 \times 10^{-6}\text{ S cm}^{-1}$ and $\lambda(\text{BaSO}_4) = 1.53\text{ S cm}^2\text{equiv.}^{-1}$

Let the solution contain x mol of Ba^{2+} and x mol of SO_4^{2-} and they are produced from $x\text{ mol L}^{-1}$ of BaSO_4

$$\lambda = \kappa \times V = 3.06 \times 10^{-6} \times \frac{1000}{x} = 1.53$$

where $x = 2 \times 10^{-3}$, $[\text{Ba}^{2+}] = 2 \times 10^{-3}$; $K_{\text{sp}} = 4 \times 10^{-6}$.

38.The emf of the standard Weston cadmium cell is



is 1.0180 V at 25°C and the temperature coefficient of the cell emf, $\left(\frac{\partial E}{\partial T}\right)_p = -4.0 \times 10^{-5} \text{ V deg}^{-1}$. Calculate

ΔG , ΔH , and ΔS for the reaction in the cell when $n = 2$.

(A) $\Delta G = -196.5 \text{ kJ}$, $\Delta H = 198.8 \text{ kJ}$, $\Delta S = -7.72 \text{ J deg}^{-1}$

(B) $\Delta G = 196.5 \text{ kJ}$, $\Delta H = 198.8 \text{ kJ}$, $\Delta S = -7.72 \text{ J deg}^{-1}$

(C) $\Delta G = 196.5 \text{ kJ}$, $\Delta H = -198.8 \text{ kJ}$, $\Delta S = -7.72 \text{ J deg}^{-1}$

(D) $\Delta G = -196.5 \text{ kJ}$, $\Delta H = 198.8 \text{ kJ}$, $\Delta S = 7.72 \text{ J deg}^{-1}$

Solution(A)

Given that $\left(\frac{\partial E}{\partial T}\right)_p = -4.0 \times 10^{-5} \text{ V deg}^{-1}$, $n = 2$ and $E_{\text{cell}}^{\circ} = 1.0181 \text{ V}$. Hence,

$$\Delta G^{\circ} = -2FE_{\text{cell}}^{\circ} = -2 \times 96500 \times 1.018 = -196474 \text{ J} = -196.5 \text{ kJ}$$

$$\Delta S^{\circ} = nF\left(\frac{\partial E}{\partial T}\right)_p = 2 \times 96500 \times (-4.0 \times 10^{-5}) = -7.72 \text{ J deg}^{-1}$$

$$\Delta H^{\circ} = nF\left(T\left(\frac{\partial E}{\partial T}\right)_p + E_{\text{cell}}^{\circ}\right) = 198.8 \text{ kJ}$$

39. If the molar conductance values of Ca^{2+} and Cl^{-} at infinite dilution are, respectively, 118.88×10^{-4} and $77.33 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$, then that of CaCl_2 is ($\text{S mm}^2 \text{ mol}^{-1}$).

(A) 118.88×10^{-4} (B) 154.66×10^{-4} (C) 273×10^{-4} (D) 196.21×10^{-4}

Solution

(B) $\Lambda_m^{\circ}(\text{CaCl}_2) = \lambda_m^{\circ}(\text{Ca}^{2+}) + 2\lambda_m^{\circ}(\text{Cl}^{-}) = 118.88 \times 10^{-4} + 2(77.33 \times 10^{-4}) = 273.54 \times 10^{-4} \text{ S mm}^2 \text{ mol}^{-1}$

40. Best way to prevent rusting of iron is by

- (A) making iron cathode. (B) putting it in saline water.
(C) both A and B. (D) none of these.

Solution

(A) Iron loses electrons to form Fe^{2+} only when it acts as anode.

41. A current of 9.65 A is drawn from a Daniell cell for exactly 1 h. The loss in mass at anode and gain in mass at cathode, respectively, are

(A) 11.43 g, 11.77 g (B) 11.77 g, 11.43 g (C) 22.86 g, 23.54 g (D) 23.54, 22.86 g

Solution

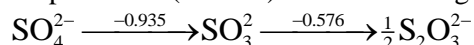
(B) Number of farads passed = $\frac{9.65 \times 1 \times 3600}{96500}$

Let W_{Zn} grams of zinc be discharged at anode and W_{Cu} grams of copper be discharged at cathode.

$$\text{Therefore } \frac{W_{\text{Zn}}}{65.4} \times \frac{W_{\text{Cu}}}{63.5} \times = \frac{9.65 \times 3600 \times 1}{96500}$$

$$W_{\text{Zn}} = 11.77, W_{\text{Cu}} = 11.43 \text{ g.}$$

42. Consider the standard reduction potentials (in volts) as shown in Fig. 11.6. Find E°



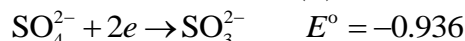
(A) 0.326 V

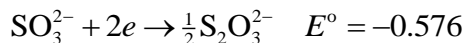
(B) 0.425 V

(C) 0.756 V

(D) 0.512V

Solution(C)





$$\text{SO}_4^{2-} + 4e \rightarrow \frac{1}{2}\text{S}_2\text{O}_3^{2-}$$

$$E^\circ = \frac{-2 \times 0.936 - 2 \times 0.576}{4} = -756 \text{ V}$$

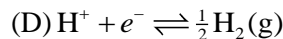
43. The correct order of equivalent conductance at infinite dilution of (i) LiCl, (ii) NaCl, and (iii) KCl
 (A) i>ii>iii (B) iii>ii>i (C) ii>iii>i (D) i>iii>ii

Solution(B) Concept based

44. How much potential of a hydrogen electrode will change when its solution initially at pH = 0 is neutralized to pH = 7?

- (A) It will increase by 0.0591 V. (B) It will decrease by 0.0591 V.
 (C) It will increase by 0.413 V. (D) It will decrease by 0.413 V.

Solution



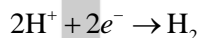
$$E = E^\circ - \frac{0.0591}{n} \log Q = 0.0 - \frac{0.0591}{1} \log \frac{[\frac{1}{2}\text{H}_2]}{[\text{H}^+]} = \frac{0.591}{1} \log \frac{1}{10^{-7}} = -0.0591 \times 7 \times \log 10 = -0.413 \text{ V}$$

45. In an electrolysis of acidulated water, 4.48 L of hydrogen was produced by passing a current of 2.14 A. For how many hours was the current passed?

- (A) 4 (B) 3 (C) 6 (D) 5

Solution

(D) The reaction occurring is



Thus, 1 mol of H_2 , that is, 22400 cm^3 at NTP requires $2F = 2 \times 96500 \text{ C}$

Therefore, 4480 cm^3 requires = $\frac{2 \times 96500 \times 4480}{22400} = 38600 \text{ C}$

As $Q = I \times t \Rightarrow t = \frac{Q}{I} = \frac{38600}{2.14} = 18037.38 \text{ s} = 5 \text{ h}$

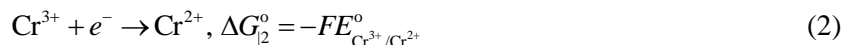
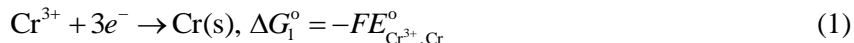
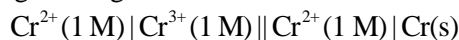
46. Construct the cell corresponding to the reaction: $3\text{Cr}^{2+}(\text{1M}) \rightarrow 2\text{Cr}^{3+}(\text{1M}) + \text{Cr}(\text{s})$ and predict if the reaction is spontaneous. Also calculate the following ΔH and ΔS of the reaction at 25°C .

Given $E_{\text{Cr}^{3+}, \text{Cr}}^\circ = 0.5 \text{ V}$, $E_{\text{Cr}^{3+}, \text{Cr}^{2+}}^\circ = -0.41 \text{ V}$, and ΔG of the reaction at $35^\circ\text{C} = -270.50 \text{ kJ}$

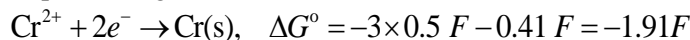
- (A) $\Delta H = -51.05 \text{ kJ}$, $\Delta S = 700 \text{ kJ K}^{-1}$ (B) $\Delta H = -31.05 \text{ kJ}$, $\Delta S = -700 \text{ kJ K}^{-1}$
 (C) $\Delta H = -51.05 \text{ kJ}$, $\Delta S = 706 \text{ kJ K}^{-1}$ (D) $\Delta H = -53.05 \text{ kJ}$, $\Delta S = 706 \text{ kJ K}^{-1}$

Solution

(D) The cell corresponding to the given reaction is as follows.



Subtracting Eq. (2) from Eq. (1), we get



Now, $\Delta G^\circ = -2FE_{\text{Cr}^{2+}/\text{Cr}}^\circ = -1.91F$. Therefore, $E_{\text{Cr}^{2+}/\text{Cr}}^\circ = \frac{1.91}{2} = 0.955 \text{ V}$.

$$E_{\text{cell}}^\circ = E_{\text{Cr}^{2+}/\text{Cr}}^\circ - E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^\circ = 0.955 + 0.41 = 1.365 \text{ V}$$

E_{cell}° is positive so ΔG° is negative, and hence, the given reaction is spontaneous

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -2 \times 96500 \times 1.365 \text{ J} = -263.44 \text{ kJ}$$

From Gibbs-Helmholtz equation,

$$\Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_p$$

$$-263.44 = \Delta H + 298 \frac{(-270.50 + 263.44)}{10} = \Delta H - 298 \times 0.706$$

Solving, we get $\Delta H = -53.05 \text{ kJ}$. Hence, entropy can be determined as

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-53.05 + 263.44}{298} = +0.706 \text{ kJ K}^{-1} = +706 \text{ J K}^{-1}$$

47. Electrolysis of a solution of HSO_4^- ions produces $\text{S}_2\text{O}_8^{2-}$. Assuming 75% current efficiency, what current should be employed to achieve a production rate of 1 mol $\text{S}_2\text{O}_8^{2-}$ per hour?

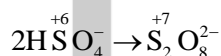
- (A) 43.3 A (B) 71.5 A (C) 35.2 A (D) 58.3 A

Solution

(B) From Faraday's law,

$$W = \frac{EIt}{96500} \times n \quad (1)$$

Where $W = 1 \text{ mol}$, $n = 0.75$, $t = 1 \text{ h} = 3600 \text{ s}$. The reaction involved is



The molecular weight of $\text{S}_2\text{O}_8^{2-} = 192 \text{ g mol}^{-1}$, and equivalent weight, $E = 192/2 \text{ g equiv}$.

Substituting these values in Eq. (1), we get

$$I = \frac{W \times 96500}{E \times t \times n} = \frac{192 \times 96500 \times 2}{192 \times 3600 \times 0.75} = 71.5 \text{ A}$$

48. By how much would the oxidizing power of the $(\text{MnO}_4^- | \text{Mn}^{2+})$ couple change if the H^+ ions concentration is decreased 100 times at 25°C ?

- (A) It will increase by 189 mV. (B) It will decrease by 189 mV.
(C) It will increase by 19 mV. (D) It will decrease by 19 mV.

Solution

(B) The reaction involved is $\text{MnO}_4^- + 5e^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

According to Nernst equation,

$$E_{\text{red}} = E_{\text{red}}^\circ - \frac{0.059}{5} \log \left[\frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8} \right]$$

Let $[\text{H}^+]_{\text{initial}} = x/100 = x/10^2$, therefore,

$$E_{\text{red(initial)}} = E_{\text{red}}^\circ - \frac{0.0591}{5} \log \left[\frac{[\text{Mn}^{2+}] \times 10^{16}}{[\text{MnO}_4^-][X]^8} \right]$$

$$= \frac{-0.0591}{5} \log 1016 = -0.1891 \text{ V}$$

This $E_{\text{red(initial)}}$ decreases by 0.189 V. The tendency of the half-cell to get reduced is its oxidizing power. Hence, the oxidizing power decreases by 0.189 V.

49. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing Ag(l) for a period of 8.0 h at a current of 8.46 A? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? (Density of silver is 10.5 g cm^{-3} .)

- (A) 124.18g, $1.02 \times 10^{-5} \text{ cm}^2$ (B) 124.18g, $1.02 \times 10^{-2} \text{ cm}^2$
 (C) 272.18g, $1.02 \times 10^{-4} \text{ cm}^2$ (D) 272.18g, $1.02 \times 10^{-2} \text{ cm}^2$

Solution

$$(C) W_{\text{Ag}} = \frac{Eit}{96500} = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500} = 272.18 \text{ g}$$

$$\text{Volume of Ag} = \frac{272.18}{10.5} = 25.92 \text{ mL}$$

$$\text{Surface area} = \frac{25.92}{0.00254} = 1.02 \times 10^4 \text{ cm}^2$$

50. For HCl solution at 25°C , the equivalent conductivity at infinite dilution is $425 \text{ S cm}^{-1} \text{ equiv}^{-1}$. The specific conductance of a solution of HCl is 3.825 S cm^{-1} . If the apparent degree of dissociation is 90%, the normality of solution is

- (A) 0.9 (B) 10.00 (C) 1.1 (D) 1.2

Solution

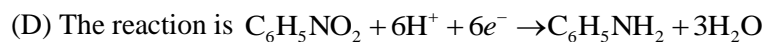
$$(B) \alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{\Lambda_m}{425} = 0.9 \Rightarrow \Lambda_m = 382.5 \text{ S cm}^{-1} \text{ g. equiv}^{-1}$$

$$\text{Therefore, } \Lambda_m = \kappa \times N \Rightarrow N = \frac{382.5}{3.825} = 10 \text{ N}$$

51. The number of coulombs required to reduce 12.3 g of nitrobenzene to aniline is

- (A) 96500 C (B) 5790 C (C) 95700 C (D) 57900 C

Solution



6 F is required to reduce 1 mol of nitrobenzene to aniline. So, $6 \times 96500 = 57900 \text{ C}$.

52. Molar conductances of BaCl_2 , H_2SO_4 , and HCl at infinite dilutions are x_1 , x_2 , and x_3 , respectively, equivalent conductance of BaSO_4 at infinite dilution will be

- (A) $(x_1 + x_2 - x_3)/2$ (B) $x_1 + x_2 - 2x_3$
 (C) $(x_1 - x_2 - x_3)/2$ (D) $(x_1 + x_2 - 2x_3)/2$

Solution

(B) Using Kohlrausch's law

$$\Lambda_{\text{mBaCl}_2}^0 = \lambda^0 \text{Ba}^{2+} + 2\lambda^0 \text{Cl}^- = x_1 \quad (1)$$

$$\Lambda_{\text{mH}_2\text{SO}_4}^0 = 2\lambda^0 \text{H}^+ + \lambda^0 \text{SO}_4^{2-} = x_2 \quad (2)$$

$$\Lambda_{\text{mHCl}}^0 = \lambda^0 \text{H}^+ + \lambda^0 \text{Cl}^- = x_3 \quad (3)$$

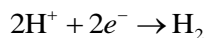
Adding the Eqs (1) and (2) and subtracting $2 \times \text{Eq}(3)$, we get

$$\Lambda_{\text{mBaSO}_4}^0 = x_1 + x_2 - 2x_3 \langle \rangle$$

53. Which among the following has maximum potential for the half-cell reaction: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$?
 (A) 1.0 M HCl (B) 1.0 M NaOH (C) Pure water (D) A solution with pH = 4

Solution

(A) HCl is a strong electrolyte. The reactions involved are



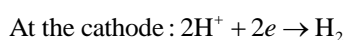
54. If the hydrogen electrodes in two solutions of pH = 3 and pH = 6 are connected by a salt bridge, the emf of the resulting cell is

- (A) 0.177 V (B) 0.3 V (C) 0.052 V (D) 0.104 V

Solution

(A)

The half-cell reactions in the cell are:



The EMF of the cell is given by

$$\begin{aligned} E_{\text{cell}} &= \frac{0.0591}{2} \log \frac{[\text{H}^+]_{\text{cathode}}^2}{[\text{H}^+]_{\text{anode}}^2} \\ &= \frac{0.0591}{2} (2 \log[\text{H}^+]_{\text{cathode}} - 2 \log[\text{H}^+]_{\text{anode}}) \\ &= \frac{0.0591}{2} (-2\text{pH}_{\text{cathode}} + 2\text{pH}_{\text{anode}}) \\ &= \frac{0.0591}{2} \times 6 = 0.177\text{V} \end{aligned}$$

Multiple Correct Choice Type

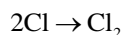
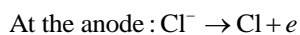
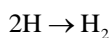
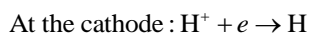
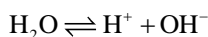
1. Which of the following aqueous solution turn(s) alkaline after electrolysis?

- (A) NaCl (B) CuCl_2 (C) CH_3COONa (D) K_2SO_4

Solution

(A, B, C, D)

The reactions involved in the electrolysis of aqueous sodium chloride solution are:



At the cathode H^+ ions are discharged in preference to Na^+ as discharge potential of ions H^+ is lower than that of Na^+ . Similarly Cl^- ions are discharged at anode in preference to OH^- ions. The solution contains Na^+ and OH^- ions, so it is alkaline in nature.

For CuCl_2 solution: Cu^{2+} is discharged at the cathode as it has lower discharge potential than H^+ ions and Cl^- ions are discharged at anode in preference to OH^- ions. So the solution contains OH^- and H^+ ions and is neutral.

For CH_3COONa , CO_2 and CH_3-CH_3 are liberated at the anode and H_2 at the anode:

At the anode: $2\text{CH}_3\text{COO}^- \rightarrow \text{CH}_3-\text{CH}_3 + 2\text{CO}_2 + 2e$

At the cathode: $2\text{H}_3\text{O}^+ + 2e \rightarrow 2\text{H}_2\text{O} + \text{H}_2$

The solution will contain Na^+ ions and OH^- and will be alkaline in nature.

In electrolysis of K_2SO_4 , H^+ ions are discharged in preference to K^+ ions at the cathode as they have lower discharge potential. Also OH^- ions are discharged at the anode as they have lower discharge potential than sulphate ions.

2. For the cell $\text{Tl} | \text{Tl}^+ (0.001 \text{ M}) || \text{Cu}^{2+} (0.1 \text{ M}) | \text{Cu}$. Given that E_{cell} is 0.83 V, which can be increased

- (A) by increasing $[\text{Cu}^{2+}]$. (B) by increasing $[\text{Tl}^+]$.
(C) by decreasing $[\text{Cu}^{2+}]$. (D) by decreasing $[\text{Tl}^+]$.

Solution

(A, D) The reaction involved is $2\text{Tl} + \text{Cu}^{2+} \rightarrow 2\text{Tl}^+ + \text{Cu}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Tl}^+]^2}{[\text{Cu}^{2+}]}$$

3. We observe blue color if

- (A) Cu electrode is placed in the AgNO_3 solution.
(B) Cu electrode is placed in the ZnSO_4 .
(C) Cu electrode is placed in the dil. HNO_3 .
(D) Cu electrode is placed in the NiSO_4 .

Solution

(A, C) Due to the formation of Cu^{2+} ions in the solution.

4. In which of the following, $(E_{\text{cell}} - E_{\text{cell}}^{\circ}) = 0$?

- (A) $\text{Zn} | \text{Zn}^{2+} (0.01 \text{ M}) || \text{Ag}^+ (0.1 \text{ M}) | \text{AgO}(\text{s})$ (B) $\text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{pH}=1 || \text{Zn}^{2+} (0.01 \text{ M}) | \text{Zn}$
(C) $\text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{pH}=1 || \text{Zn}^{2+} (1 \text{ M}) | \text{Zn}$ (D) $\text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{H}^+ (0.01 \text{ M}) || \text{Zn}^{2+} (0.01 \text{ M}) | \text{Zn}$

Solution

(A, B)

(A)

$$E_{\text{cell}} - E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]} = \frac{0.0591}{2} \log \frac{[0.1]^2}{[0.01]} = 0$$

(B)

$$E_{\text{cell}} - E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = \frac{0.0591}{2} \log \frac{[0.01]}{[0.1]^2} = 0$$

(C)

$$E_{\text{cell}} - E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = \frac{0.0591}{2} \log \frac{[1]}{[0.1]^2} = \frac{0.0591}{2} \log 100 = 0.0591 \text{ V}$$

(D)

$$E_{\text{cell}} - E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = \frac{0.0591}{2} \log \frac{[0.01]}{[0.01]^2} = \frac{0.0591}{2} \log 100 = 0.0591 \text{ V}$$

5. Process inside the cell is exothermic when

- (A) $\left[\frac{\partial E}{\partial T} \right] < 0$ (B) $\left[\frac{\partial E}{\partial T} \right] = 0$ (C) $\Delta H > nFE$ (D) $\Delta H = nFE$

Solution

(A), (C)

$$\text{If } \left[\frac{\partial E}{\partial T} \right] < 0$$

that means

$$\Delta H > nFE$$

It means the process inside the cell is exothermic.

6. Equal quantity of electricity is passed through three electrolytic cells containing aqueous solutions of FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, and $\text{Fe}(\text{NO}_3)_3$. Regarding the electrolytic process which of the following is/are correct, assuming at cathode only iron is reduced.

- (A) The amount of iron deposited in the three cases is equal.
- (B) The amount of iron deposited in $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Fe}(\text{NO}_3)_3$ is equal.
- (C) Same gas is evolved at anode in all three electrolytic processes.
- (D) Amount of the iron deposited in $\text{Fe}_2(\text{SO}_4)_3$ is double to that of iron deposited in case of $\text{Fe}(\text{NO}_3)_3$.

Solution

(B,C)

7. Which of the following statements is (are) correct?

- (A) The reactivity of metals decreases in going down the electrochemical series.
- (B) A metal can displace any other metal placed above it in the electrochemical series from its salt solution.
- (C) The oxidizing power of the substances decrease from the top to the bottom in the electrochemical series.
- (D) A redox reaction is feasible when the substance having higher reduction potential gets reduced and the one having lower reduction potential gets oxidized.

Solution

(A,D) Reduction potential means the ability of the species to accept electrons. Metals are good contributors of electrons. That is why down the group (which is arranged in order of increasing reduction potential) reactivity decreases

8. Hydrogen gas will reduce

- (A) heated cupric oxide.
- (B) heated silver oxide.
- (C) heated zinc oxide.
- (D) heated aluminum oxide.

Solution

(A, B) The standard reduction potential of copper and silver is greater than the standard reduction potential of hydrogen. So hydrogen gas reduces cupric oxide and silver oxide.

9. Which of the following statements is (are) not correct?

- (A) Metallic conduction is due to the movement of electrons whereas the electrolytic conduction is due to the movement of ions.
- (B) Both metallic and electrolytic conduction involve transfer of matter.
- (C) Electrolytic conduction decreases with rise in temperature.
- (D) Metallic conduction involves no chemical change.

Solution

(A,B)

10. Select the correct statements if 9.65 A current is passed for 1 h through the cell $\text{Ag} | \text{Ag}^+ (1 \text{ M}) || \text{Cu}^{2+} (1 \text{ M}) | \text{Cu}$

- (A) Ag will oxidize to Ag^+ and new $[\text{Ag}^+] = 1.36 \text{ M}$.
 (B) Ag^+ will reduce to Ag and new $[\text{Ag}^+] = 0.64 \text{ M}$.
 (C) Cu^{2+} will reduce to Cu and new $[\text{Cu}^{2+}] = 0.82 \text{ M}$.
 (D) Cu will oxidize to Cu^{2+} and new $[\text{Cu}^{2+}] = 0.82 \text{ M}$.

Solution

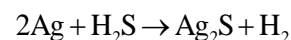
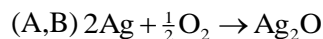
$$(A,C) \frac{w}{E} = \frac{It}{n \times 96500} = \frac{9.65 \times 3600}{96500n} = 0.36 \text{ equiv. of } \text{Ag}^+ = 0.36 \text{ mol of } \text{Ag}^+ (n = 1) \text{ and } 0.18 \text{ mol of } \text{Cu}^{2+} (n = 2).$$

Now, Ag will oxidize to Ag^+ and Cu^{2+} will reduce to Cu.

11. The tarnishing of silver ornaments in atmosphere is due to

- (A) Ag_2O (B) Ag_2S (C) Ag_2CO_3 (D) Ag_2SO_4

Solution.



12. Which of the following statements are correct?

- (A) Ionic mobility is directly proportional to the velocity of the ion.
 (B) Ionic mobility of an ion decreases if potential gradient increases.
 (C) Conductance of an electrolyte solution decreases if the interionic forces of attraction are high.
 (D) Conductance = $F \times$ Ionic mobility

Solution

(A,B,D) Conductance of an electrolyte solution increases if the interionic forces of attraction are high.

13. In the electrolysis of which of the following aqueous solutions, pH remains constant (assuming no change in volume)

- (A) K_2SO_4 (B) AgNO_3 (B) CuCl_2 (D) NaCl

Solution

(A,C)

In electrolysis of K_2SO_4 , H^+ ions are discharged in preference to K^+ ions at the cathode as they have lower discharge potential. Also OH^- ions are discharged at the anode as they have lower discharge potential than sulphate ions. So the pH of solution will not change. >

In electrolysis of AgNO_3 : At the cathode Ag^+ ions are discharged due to lower discharge potential than H^+ ions. At the anode, OH^- ions are discharged as they have lower discharge potential than nitrate ions. So the solution will contain H^+ and the pH of the solution will change.

For CuCl_2 solution: Cu^{2+} is discharged at the cathode as it has lower discharge potential than H^+ ions and Cl^- ions are discharged at anode in preference to OH^- ions. So the pH of the solution will not change.

In electrolysis of NaCl : At the cathode H^+ ions are discharged in preference to Na^+ as discharge potential of ions H^+ is lower than that of Na^+ . Similarly Cl^- ions are discharged at anode in preference to OH^- ions. The solution contains Na^+ and OH^- ions, so it is alkaline in nature (change in pH).

14. The standard emf of the cell, $\text{Cd(s)}|\text{CdCl}_2(\text{aq})||\text{AgCl(s)}|\text{Ag(s)}$ in which the cell reaction is 0.6195 V at 0°C and 0.6753 V at 25°C . The value of ΔH of the reaction at 25°C is

- (A) $167.26 \text{ kJ mol}^{-1}$ (B) $-167.26 \text{ kJ mol}^{-1}$ (C) 40 kJ mol^{-1} (D) -40 kJ mol^{-1}

Solution

$$(B,D) \frac{dE}{dT} = \frac{0.6753 - 0.6195}{298 - 273} = 0.002232 \text{ V K}^{-1}$$

$$\text{Hence, } \Delta H = nF \left(T \left(\frac{dE}{dT} \right) - E \right)$$

15. Which are true for a standard hydrogen electrode?

- (A) The hydrogen ion concentration is 1 M.
 (B) Temperature is 25°C .
 (C) Pressure of hydrogen is 1 atm.
 (D) It contains a metallic conductor which does not adsorb hydrogen.

Solution

(A,B,C) It contains platinum electrode which is inert.

16. In which of the following electrolytes, KCl cannot be used in salt bridge?

- (A) Solution of silver (B) Solution of mercurous ion
 (C) Solution of thallos salt (D) Solution of Zn^{2+} ions

Solution

(A,D) With silver, lead and zinc ions present in electrolyte, KCl cannot be used as these ions are insoluble in water and precipitation will take place.

17. Which of the following are concentration cells?

- (A) $\text{Pt}, \text{H}_2(\text{g})(p_1)|\text{HCl}|\text{H}_2(\text{g})(p_2), \text{Pt}$
 (B) $\text{Cd}(\text{Hg})(a_1)|\text{Cd}^{2+}(\text{C})|(\text{Hg})\text{Cd}(a_2)$
 (C) $\text{Zn(s)}|\text{Zn}^{2+}(\text{C}_1)||\text{Cu}^{2+}(\text{C}_2)|\text{Cu}$
 (D) $\text{Ag}|\text{AgCl}|\text{Cl}^-(\text{aq})(\text{C}_1)||\text{Br}^-(\text{aq})(\text{C}_2)|\text{AgBr}|\text{Ag}$

Solution

(A,B,D)

Concept based. Concentration cells have the same electrodes with different concentrations of metal-ion, or gas-ion or different electrode pressure.

18. When a nickel spatula is used to stir an aqueous copper sulphate solution,

- (A) the solution is stirred well without any chemical change.
 (B) nickel spatula gets partly oxidized into Ni^{2+} ions.
 (C) Cu^{2+} ions present in the solution get partly reduced into Cu.
 (D) copper gets deposited on the spatula.

Solution

(B,C,D) The reactions involved are $\text{CuSO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-}$ and $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$

At the cathode: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu(s)}$

At the anode: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu(s)}$

At the cathode: $\text{Ni} - 2e^- \rightarrow \text{Ni}^{2+}(\text{aq})$

19. Select the wrong relations.

$$(A) \Delta S = \left(\frac{\partial E}{\partial T} \right)_p \times nF$$

$$(B) -\Delta S = \left(\frac{\partial E}{\partial T} \right)_p \times nF$$

$$(C) \left(\frac{\partial E}{\partial T} \right)_p = \left(\frac{\partial \Delta S}{\partial T} \right)$$

$$(D) \left(\frac{\partial E}{\partial T} \right)_p = \frac{\Delta H + nEF}{T}$$

Solution

$$(A, D) \Delta G = \Delta H - T\Delta S \text{ and } \Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_p$$

$$\text{Therefore, } \left(\frac{\partial \Delta G}{\partial T} \right)_p = \frac{\Delta G - \Delta H}{T} = -\frac{T\Delta S}{T} = -\Delta S$$

$$\text{Also, } -nEF = \Delta H + T \times \left(\frac{\partial E}{\partial T} \right)_p$$

$$\text{Therefore, } \left(\frac{\partial E}{\partial T} \right)_p = \frac{\Delta H + nEF}{T}$$

20. Saturated solution of KNO_3 is used to make salt bridge because

(A) velocity of K^+ greater than that of NO_3^- .

(B) velocity of NO_3^- is greater than that of K^+ .

(C) velocity of both K^+ and NO_3^- are nearly the same.

(D) K^+ has very low reduction potential and NO_3^- has very low oxidation potential.

Solution

(A, C, D)

21. In which of the following salt bridge is not needed

(A) $\text{Pb}|\text{PbSO}_4(\text{s})|\text{H}_2\text{SO}_4(\text{aq})|\text{PbO}_2(\text{s})|\text{Pb}$

(B) $\text{Cd}|\text{CdO}(\text{s})|\text{KOH}(\text{aq})|\text{NiO}_2(\text{s})|\text{Ni}$

(C) $\text{Fe}(\text{s})|\text{FeO}(\text{s})|\text{KOH}(\text{aq})|\text{Ni}_2\text{O}_3(\text{s})|\text{Ni}$

(D) $\text{Zn}|\text{ZnSO}_4|\text{CuSO}_4(\text{aq})|\text{Cu}$

Solution

(A, B, C) Salt bridge is used to eliminate liquid junction potential arising due to different speed of ions present in cathodic and anodic compartments.

Assertion-Reasoning Type

Choose the correct option from the following:

(A) Statement 1 and Statement 2 are True; Statement 2 is the correct explanation of the Statement 1.

(B) Statement 1 and Statement 2 are True; Statement 2 is NOT a correct explanation of the Statement 1.

(C) Statement 1 is True, Statement 2 is False.

(D) Statement 1 is False, Statement 2 is True.

1. Statement 1: If an aqueous solution of NaCl is electrolyzed, the product obtained at the cathode is H_2 gas and not Na .

Statement 2: Gases are liberated faster than the metals.

Solution

(C) The reactions involved are $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$ and $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$

At the cathode: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2(\text{g})$

At the anode: $2\text{Cl}^- - 2e^- \rightarrow \text{Cl}_2(\text{g})$

2. Statement 1: Specific conductance decreases with dilution ion, whereas equivalent conductance increases.

Statement 2: On dilution, the number of ions per milliliter decreases, but the total number of ions increases considerably.

Solution

(A) For specific conduction, the number of charge-carrying particles is less compared to the increases in area. For equivalent conductance the increases in volume is more comparable to the decrease in specific conductance.

3. Statement 1: On increasing dilution, the specific conductance keeps on increasing.

Statement 2: On increasing dilution, degree of ionization of weak electrolyte increases and mobility of ions also increases.

Solution

(D) On dilution, the number of ions per unit volume decreases degree of ionization of weak electrolyte increases and mobility of ions increases.

4. Statement 1: For the Daniell cell, $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$ with $E_{\text{cell}} = 1.1 \text{ V}$, the application of opposite potential greater than 1.1 V results into flow of electrons from cathode to anode.

Statement 2: Zn is deposited at anode and Cu is dissolved at cathode.

Solution

(B) On applying potential greater than 1.1 V, reaction proceeds in opposite direction and the cell now behaves as electrolytic cell.

5. Statement 1: Zinc displaces copper from copper sulphate solution.

Statement 2: Lesser number of ions are available per gram equivalent at higher concentration.

Solution

(A) Standard reduction potential of zinc electrode is less than that of copper electrode.

6. Statement 1: Calomel electrode especially with saturated KCl solution is used as a reference electrode, that is, secondary standard electrode.

Statement 2: The potential of calomel electrode depends upon the concentration of Cl^- ions.

Solution

(B) Assertion is correct and reason is correct but not the proper explanation. Assertion is convention based but reason is related to Nernst equation.

7. Statement 1: Salt bridge maintains electrical neutrality in two half-cells.

Statement 2: Salt bridge transfer ions from one solution to other.

Solution

(C) Salt bridge electrolytes maintain the electrical neutrality without mixing with the solution.

Comprehension Type

Read the paragraphs and answer the questions that follow:

Paragraph I: Molar conductance of NaCl varies with concentration according to the equation $\Lambda_m = \Lambda_m^0 - b\sqrt{C}$ where Λ_m is molar specific conductance, Λ_m^0 is molar specific conductance at infinite dilution, and C is the molar concentration. The variation is shown in the following table:

Molar Concentration of NaCl	Molar Conductance in $\text{S cm}^2\text{mol}^{-1}$
-----------------------------	---

4×10^4	107
9×10^4	97
16×10^{-4}	87

1. When a certain conductivity cell (C) was filled with 25×10^{-4} (M) NaCl solution. The resistance of the cell was found to be 1000Ω . At infinite dilution, conductance of Cl^- and SO_4^{2-} are $80 \text{ S cm}^2 \text{ mol}^{-1}$ and $160 \text{ S cm}^2 \text{ mol}^{-1}$, respectively. What is the molar conductance of NaCl at infinite dilution?

- (A) $147 \text{ S cm}^2 \text{ mol}^{-1}$ (B) $107 \text{ S cm}^2 \text{ mol}^{-1}$ (C) $127 \text{ S cm}^2 \text{ mol}^{-1}$ (D) $157 \text{ S cm}^2 \text{ mol}^{-1}$

Solution

(C) Given that $R = 1000 \Omega$, $\Lambda_m^0(\text{Cl}^-) = 80 \text{ S cm}^2 \text{ mol}^{-1}$; $\Lambda_m^0(\text{SO}_4^{2-}) = 160 \text{ S cm}^2 \text{ mol}^{-1}$. Applying the equation

$\Lambda_m^0 = \Lambda_m + b\sqrt{C}$, we get

$$\Lambda_{m(\text{NaCl})}^0 = 107 + b\sqrt{4 \times 10^{-4}} \quad (1)$$

$$\Lambda_{m(\text{NaCl})}^0 = 97 + b\sqrt{9 \times 10^{-4}} \quad (2)$$

Subtracting Eq. (2) from Eq. (1), we get

$$0 = 10 + b(2 \times 10^{-2}) - b(3 \times 10^{-2})$$

Solving, we get $b = 10^3$. Hence, $\Lambda_{m(\text{NaCl})}^0 = 107 + 10^3 \sqrt{4 \times 10^{-4}} = 107 + 20 = 127 \text{ S cm}^2 \text{ mol}^{-1}$

2. What is the cell constant of the conductivity cell (C)?

- (A) 0.385 cm^{-1} (B) 3.85 cm^{-1} (C) 38.5 cm^{-1} (D) 0.1925 cm^{-1}

Solution

(D) We have $\Lambda_m^0 = \Lambda_m - b\sqrt{C} = 127 - 10^3 \sqrt{25 \times 10^{-4}} = 127 - 10^3 \times 5 \times 10^{-2} = 77$

$$\Lambda_m^0 = \kappa \times C = 77 = K \times V = K \times \frac{1000}{25 \times 10^{-4}}$$

Hence, $\kappa = 77 \times 25 \times 10^{-7} = 1925 \times 10^{-7}$

Now, $\kappa = \frac{1}{R} \times \frac{l}{A} \Rightarrow \frac{l}{A} = 1925 \times 10^{-7} \times 1000 = 0.1925 \text{ cm}^{-1}$

3. If the cell (C) is filled with 5×10^{-3} (N) Na_2SO_4 , the observed resistance was 400Ω . What is the molar conductance of Na_2SO_4 ?

- (A) $19.25 \text{ S cm}^2 \text{ mol}^{-1}$ (B) $96.25 \text{ S cm}^2 \text{ mol}^{-1}$ (C) $385 \text{ S cm}^2 \text{ mol}^{-1}$ (D) $192.5 \text{ S cm}^2 \text{ mol}^{-1}$

Solution

(D) We know that $N = M \times 2 \Rightarrow M = \frac{5 \times 10^{-3}}{2}$. We found that $\frac{l}{A} = 0.1925 \text{ cm}^{-1}$

$$\Lambda = \kappa \times V = \kappa \times \frac{1000 \times 2}{5 \times 10^{-3}} = \frac{1}{R} \times \frac{l}{A} \times \frac{1000 \times 2}{5 \times 10^{-3}}$$

$$= \frac{1}{400} \times 0.1925 \times \frac{1000 \times 2}{5 \times 10^{-3}}$$

$$= 0.009625 \times 10^4 = 96.25 \text{ S cm}^2 \text{ mol}^{-1}$$

Paragraph II:

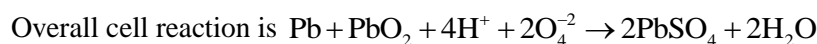
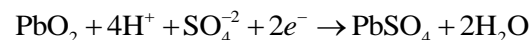
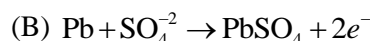
Pb is used at anode and PbO_2 at cathode in a lead storage battery, while concentrated H_2SO_4 is used as electrolyte. The battery holds 3.5 L acid with it. During the discharge process, the density of acid

falls from 1.294 to 1.139 gL⁻¹. Given that the sulphuric acid of density 1.294 g mL⁻¹ is 39% by mass and that of density 1.139 gL⁻¹ is 20% by mass.

4. Equivalent mass of sulphuric acid in lead storage battery is

- (A) 49 (B) 98 (C) 24.5 (D) none of these.

Solution



From the above equation, it is clear that $E_{\text{H}_2\text{SO}_4} = \frac{98}{1}$

5. Normalities of sulphuric acid before and after discharge are

- (A) 5.15, 2.32 (B) 2.32, 5.15 (C) 5.15, 5.15 (D) 2.32, 2.32

Solution

$$(A) \text{Weight of } \text{H}_2\text{SO}_4 \text{ before discharging} = 1.294 \times \frac{39}{100} \times 3500 = 1766.31 \text{ g}$$

$$\text{Weight of } \text{H}_2\text{SO}_4 \text{ after discharging} = 1.139 \times \frac{20}{100} \times 3500 = 797.3 \text{ g}$$

$$\text{Normality of } \text{H}_2\text{SO}_4 \text{ before discharging} = \frac{1766.31}{98} \times \frac{1}{3.5} = 5.15 \text{ N}$$

$$\text{Normality of } \text{H}_2\text{SO}_4 \text{ after discharging} = \frac{797.3}{98} \times \frac{1}{3.5} = 2.32 \text{ N}$$

6. The number of ampere-hours for which the battery must have been used is

- (A) 26504 Ah (B) 2650.4 Ah (C) 265.04 Ah (D) 26.504 Ah

Solution

$$(C) \text{ Ampere hour} = \frac{\text{Coulomb}}{3600 \text{ s}} = \frac{954178}{3600} = 265.05$$

7. The amount of charge which the battery must have been used is

- (A) 9.88 F (B) 8.98 F (C) 8.89 F (D) 7.88 F

Solution

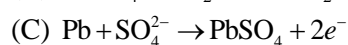
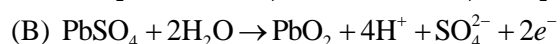
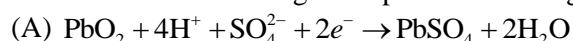
$$(A) 1766.31 - 797.3 = 969.01 \text{ g}$$

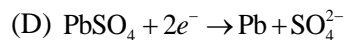
$$\text{Moles of } \text{H}_2\text{SO}_4 \text{ lost during discharge} = \frac{969.01}{98} = 9.88786$$

During the discharge reaction, 4 mol of H⁺ ions, that is, 2 mol of H₂SO₄ require 2F, 2 × 96500 coulombs.

$$\text{Therefore, } 9.88786 \text{ mol will require} = \frac{2 \times 96500 \times 9.88786}{2} = 954178 \text{ C}$$

8. Which of the following takes place in discharge process at anode?



**Solution****Paragraph III:**

At equilibrium, the driving force ΔG is equal to zero, just as in any other spontaneous process. Both ΔG and E_{cell} are zero when the redox reaction is at equilibrium. The Nernst equation for the redox process of the cell is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log Q$$

Where Q is the reaction quotient and the standard cell potential E° is derived from the standard Gibbs energy change as

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

At equilibrium, the Nernst equation is

$$E_{\text{cell}}^{\circ} = \frac{0.059}{n} \log K_c$$

9. On the basis of information available for the reaction



the minimum emf required to carry out an electrolysis of Al_2O_3 is (Given $1 \text{ F} = 96500 \text{ C}$)

- (A) 2.14V (B) 4.28V (C) 6.42 V (D) 8.56 V

Solution

$$(A) \Delta G = -nFE^{\circ} \Rightarrow -827 \times 1000 = -4 \times 96500 E^{\circ} \Rightarrow E^{\circ} = 2.14\text{V}.$$

10. The nature of graph of E_{cell}° against $\log K_c$ is a/an

- (A) straight line. (B) parabola. (C) hyperbola. (D) elliptical curve.

Solution

$$(A) E^{\circ} = \frac{0.059}{n} \log K. \text{ This represents a straight line passing through origin}$$

11. The equilibrium constant K_c for the reaction $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$ ($E_{\text{cell}}^{\circ} = 0.46 \text{ V}$) will be

- (A) antilog 15.6 (B) antilog 2.5 (C) antilog 1.5 (D) antilog 12.2

Solution

$$(A) 0.46 = \frac{0.059}{2} \log K \Rightarrow \log K = 15.6 \Rightarrow K = \text{antilog } 15.6.$$

Integer Answer Type

The answer to each question is a **non-negative integer**.

1. For the Mg–Ag cell, if concentration of Mg^{2+} ions is changed from 0.1 M to 0.01 M and that of Ag^+ ions is changed from 0.5 M to 0.25 M, the number of times the difference between the emf of the cell and its standard emf will change is ____.

Solution

(2) The original emf is $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{0.1}{0.5}$

Now, changed or new emf is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{0.01}{0.25}$$

Solving only the log terms, we get

In the first case $\log 0.1/0.5 = -0.6989$

In the second case $\log 0.01/0.25 = -1.3979$

Taking their ratios, we get $1.3979/0.6989 = 2$.

2. Calculate the volume of Cl_2 at NTP produced during electrolysis of MgCl_2 which produces 6.50 g Mg. (atomic weight of Mg = 24.3 amu).

Solution

(6) At cathode: $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$

At anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$

Therefore, the equivalent of Mg at cathode = Equivalent of Cl_2 at anode

Therefore, $\frac{6.5}{24.3/2} = \frac{w_{\text{Cl}_2}}{35.5} \Rightarrow w_{\text{Cl}_2} = 18.99 \text{ g}$

At NTP, $pV = \frac{w}{m}RT$. Substituting values, we get

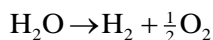
$$1 \times V = \frac{18.99}{71} \times 0.0821 \times 273$$

Solving, we get volume of $\text{Cl}_2 = 5.99 \text{ L}$.

3. When water is electrolyzed, hydrogen and oxygen gases are produced. If 1.008 g of H_2 is liberated at cathode, the mass of O_2 formed at the anode is ____.

Solution

(8) When water is electrolyzed, gram equivalent mass is liberated at cathode and anode.



Mass of H_2 formed = 1.008 g

Number of moles of $\text{H}_2 = \frac{1.008}{2} = 0.504$

Mass of O_2 formed = x g

Number of moles of $\text{O}_2 = x/32$

According to the law of conservation of mass,

Number of moles of $\text{H}_2 \times 2 =$ Number of moles of O_2

$$0.504 = \frac{1}{2} \left(\frac{x}{32} \right) \Rightarrow x = \frac{32.256}{4} = 8.064 \text{ g}$$

4. At equimolar concentration of Fe^{2+} and Fe^{3+} what must $[\text{Ag}^+]$ be so that the voltage of the galvanic cell made from Ag^+/Ag and $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrodes equals zero? The reaction is $\text{Fe}^{2+} + \text{Ag}^+ \rightleftharpoons \text{Fe}^{3+} + \text{Ag}$.

Determine the equilibrium constant at 25°C for the reaction. Given: $E_{\text{Ag}^+/\text{Ag}}^{\circ} = 0.799 \text{ V}$ and $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.771 \text{ V}$.

Solution

(3) $E_{\text{cell}}^{\circ} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + E_{\text{Ag}^+/\text{Ag}}^{\circ} = -0.771 + 0.799 = 0.028 \text{ V}$

At equilibrium, $E_{\text{cell}} = 0$, so

$$0 = E_{\text{cell}}^{\circ} - \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^+]}$$

$$E_{\text{cell}}^{\circ} = 0.0591 \log \frac{1}{[\text{Ag}^+]} \Rightarrow [\text{Ag}^+] = 0.34 \text{ M}$$

Now, $\log K = \frac{nE^{\circ}}{0.0591} \Rightarrow K = 3.0$.

5. Cd amalgam is prepared by the electrolysis of a solution of CdCl_2 using a mercury cathode. Find how long should a current of 5 A be passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2.56 g mercury? (Atomic weight of Cd = 112.40 amu).

Solution

(2) 88 g Hg has 12 g Cd. Therefore, 2.56 g Hg require $= \frac{12 \times 2}{88} \text{ g Cd} = 0.349$

Since $\text{Cd}^{2+} + 2e \rightarrow \text{Cd}$, hence the equivalent weight of Cd is $E_{\text{Cd}} = \frac{112.40}{2}$

Now, $w = \frac{Eit}{96500} \Rightarrow 0.349 = \frac{112.4 \times 5 \times t}{2 \times 96500} \Rightarrow t = 120 \text{ s} = 2 \text{ min}$

6. The equilibrium constant for the following reaction at 298 K is expressed as $x \times 10^y$. $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$, $E_{\text{cell}}^{\circ} = 0.235 \text{ V}$. The value of y is ____.

Solution

(7) $E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log K_c \Rightarrow K_c = \text{antilog} \left(\frac{2 \times 0.235}{0.0591} \right) = 8.966 \times 10^7$

7. The standard oxidation potential of Ni/Ni^{2+} electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured emf be zero at 25°C ? (Assume $[\text{Ni}^{2+}] = 1 \text{ M}$ and $p_{\text{H}_2} = 1 \text{ atm}$)

Solution

(4) $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e$; $E_{\text{ox}}^{\circ} = 0.236 \text{ V}$

$2\text{H}^+ + 2e \rightarrow \text{H}_2$; $E_{\text{red}}^{\circ} = 0$

Therefore, $E_{\text{cell}} = 0$ so $E_{\text{cell}}^{\circ} + \frac{0.059}{2} \log_{10} \frac{[\text{H}^+]^2}{[\text{Ni}^{2+}]} = 0 = 0.236 + \frac{0.059}{2} \log_{10} [\text{H}^+]^2$

Solving, we get $-\log \text{H}^+ = 4$ therefore $\text{pH} = 4$.

Matrix–Match Type

1. Match the cell with its applications

Column I	Column II
(A) Nickel–Cadmium cell	(p) Used in auto vehicles
(B) Lithium battery	(q) Secondary cell

(C) H ₂ -O ₂ cell	(r) Fuel cell
(D) Lead storage battery	(s) Used in Apollo spacecraft

Solution

(A) → (q); (B) → (q); (C) → (r, s); (D) → (p, q)
 Concept based

2. Match the cell with its characteristics

Column I	Column II
(A) Concentration cell	(p) Fe is oxidised by Ni ₂ O ₃
(B) Edison cell	(q) Zinc anode
(C) Mercury cell	(r) Hg cathode
(D) Dry cell	(s) E° = 0

Solution

(A) → (s); (B) → (p); (C) → (q, r); (D) → (q)
 Concept based

3. For the galvanic cell Ag|Ag⁺(aq, 0.1 M)||Cd²⁺(aq, 0.1 M)|Cd, E°_{Ag⁺/Ag} = 0.80 V, E°_{Cd²⁺/Cd} = -0.40 V.
 Match the quantities with their values.

Column I	Column II
(A) The cell reaction	(p) -1.17 V
(B) Reaction quotient	(q) -1.20 V
(C) The cell potential	(r) Non-spontaneous
(D) The standard cell potential	(s) 1/10
	(t) E° _{cell} = E° _{cathode} - E° _{anode}

Solution

(A) → (p, r); (B) → (s); (C) → (p); (D) → (t, q)

(A) $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \frac{[\text{Ag}^+]^2}{[\text{Cd}^{2+}]} = -1.20 - \frac{0.0591}{2} (-1) = -1.17 \text{ V}$$

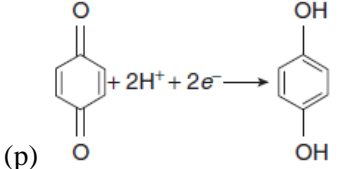
As E_{cell} is negative, $\Delta G = -nFE$ is positive, so the reaction should be non-spontaneous

(B) $[\text{Ag}^+]^2 / [\text{Cd}^{2+}] = (0.1)^2 / 0.1 = 1/10$

(C) $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

(D) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.40 - 0.80 = -1.20 \text{ V}$

4. Match the electrode with its composition.

Column I	Column II
(A) Concentration cell	 <p>(p)</p>
(B) Electrode reversible with	(q) Pt Hg ₂ Cl ₂ , KCl

respect to anion	
(C) Quinhydrone electrode	(r) $\text{Na(Hg)} \mid \text{NaCl} \mid \text{Na (Hg)}$
(D) Redox electrode	(s) Ag/AgCl, Cl^-

Solution

(A) \rightarrow (r); (B) \rightarrow (q); (C) \rightarrow (p); (D) \rightarrow (s)

Concept based.

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