Date: 22/10/2021

Q1. How can you increase the reduction potential of an electrode?

Q2. Why is the equilibrium constant K related to only E°_{cell} and not E_{cell}?

Q3. Why is it not possible to measure the voltage of an isolated half reaction?

Q4. When the silver electrode having reduction potential 0.80 V is attached to NHE, will it act as anode or cathode?

Q5. Two metals *A* and *B* have reduction potential values – 0.76 V and + 0.34 V respectively. Which of these will liberate H_2 from dil. H_2SO_4?

Q6. Can Fe^{3+} oxidise Br^- to Br under standard conditions?
$E^{\ominus}$ $Fe^{2+} | Fe = 0.771$ V, $E^{\ominus}$ $Br_2 | Br^- = 1.09$ V.

Q7. Is it safe to stir 1 M $AgNO_3$ solution with a copper spoon? Given $E^{\ominus}$ $Ag^+ | Ag = 0.80$ V, $E^{\ominus}$ $Cu^{2+} | Cu = 0.34$ V, Explain.

Q8. What is change in free energy for (a) galvanic cell and (b) electrolytic cell?

Q9. Given that the standard electrode potentials (E°) of metals are:
$K^+ | K = -2.93$ V, $Ag^+ | Ag = 0.80$ V, $Cu^{2+} | Cu = 0.34$ V, $Mg^{2+} | Mg = -2.37$ V, $Cr^{3+} | Cr = -0.74$ V, and $Fe^{2+} | Fe = -0.44$ V.
Arrange the metals in the increasing order of their reducing power.

Q10. Value of standard electrode potential for the oxidation of Cl^- ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl^- oxidised at anode instead of water?

Q11. Consider a cell given below
$Cu | Cu^{2+} || Cl | Cl_2$, Pt   Write the reactions that occur at anode and cathode.

Q12. Which reference electrode is used to measure the electrode potential of other electrodes?

Q13. Is e.m.f. extensive or intensive property?

Q14. Can we store copper sulphate in an iron vessel or not? Explain.

Q15. E° values for $Fe^{3+} | Fe^{2+}$ and $Ag^+ | Ag$ are respectively 0.771 V and 0.800 V. Is the reaction:
$Fe^{3+} + Ag \longrightarrow Fe^{2+} + Ag^+$ spontaneous or not?

Q16. The E° value of MnO_4^-, Cu^{4+} and Cl_2 are 1.507, 1.61 and 1.358 V respectively. Arrange these in order of increasing strength as oxidising agent.

Q17. A galvanic cell has electrical potential of 1.1 V. If an opposing potential of 1.1 V is applied to this cell, what will happen to the cell reaction and current flowing through the cell?

Q18. On the basis of the standard electrode potential values stated for acid solution, predict whether $Ti^{4\oplus}$ species may be used to oxidise Fe^{II} to Fe^{III}.

Reaction $\qquad\qquad$ E° / V

$$Ti^{4\oplus} + e^{\ominus} \longrightarrow Ti^{3\oplus};\ +0.01$$

$$Fe^{3\oplus} + e^{\ominus} \longrightarrow Fe^{2\oplus};\ +0.77$$

Q19. If $E^{\ominus}_{red}$ for copper electrode is + 0.34 V. How will you calculate its electrode potential when it is in contact with 0.1 M Cu^{2+} ions? How does electrode potential change if concentration of Cu^{2+} in solution is decreased?

Q20. What is the electrode potential of Mg^{2+}/Mg electrode in which conc. of Mg^{2+} is 0.01 M?

$$E^{\ominus}_{Mg^{2+}/Mg} = -2.36\ V.$$

Q21. For a cell, $Mg(s)/Mg^{2+}(aq) \,||\, Ag^{+}(aq)/Ag$; calculate the equilibrium constant at 250°C and also maximum work that can be obtained by operating the cell. $E^{\ominus}_{Mg^{2+}/Mg} = -2.37$ V and $E^{\ominus}_{Ag^{2+}/Ag} = +0.08$ V.

Q22. Calculate the maximum work that can be obtained from the Daniel cell $Zn/Zn^{2+}(aq)\,||\,Cu^{2+}(aq)/Cu$. Given that $E^{\ominus}_{Zn^{2+}/Zn}$ and $E^{\ominus}_{Cu^{2+}/Cu}$ are -0.76 and $+0.34$ V respectively.

Q23. Calculate the equilibrium constant for a reaction, $Ni(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Ni^{2+}(aq)$. Given the values of $E^{\ominus}_{Ni^{2+}/Ni}$ and $E^{\ominus}_{Cu^{2+}/Cu}$ as -0.25 and $+0.34$ V respectively.

Q24. Calculate the E_{red} of the following electrode:

$$Pt,\ Cl_2\,(1.5\ bar)/2\,Cl^-\,(0.01\ M); \qquad E^{\ominus}_{Cl_2/2Cl^-} = 1.36\ V.$$

Q25. Calculate the minimum voltage to cause the electrolysis of a solution of copper nitrate under standard condition. Given that $E^{\ominus}_{Cu^{2+}/Cu} = 0.34$ V and $E^{\ominus}_{H_2O/H^+} = -1.23$ V.

Q26. Given that standard potential of Cu^{2+}/Cu and Cu^{+}/Cu couples as 0.34 V and 0.52 V respectively, calculate the standard electrode potential of Cu^{2+}/Cu couple.

Q27. Using the standard electrode potentials given below, predict if the reaction between the following is feasible:

(a) $Fe^{3+}(aq)$ and $I^-(aq)$ $\qquad$ $E^{\ominus}_{I_2/I^-} = 0.541$ V, $\quad E^{\ominus}_{Cu^{2}/Cu} = 0.34$ V

(b) $Ag^{+}(aq)$ and $Cu(s)$ $\qquad$ $E^{\ominus}_{Br_2/Br^-} = 1.09$ V, $\quad E^{\ominus}_{Ag^+/Ag} = 0.80$ V

(c) $Fe^{3+}(aq)$ and $Br(aq)$ $\qquad$ $E^{\ominus}_{Fe^{3+}/Fe^{2+}} = +0.77$ V,

(d) $Ag(s)$ and $Fe^{3+}(aq)$

Q28. 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) An dilute solution of H_2SO_4 with platinum electrodes.

(d) An aqueous solution of $CuCl_2$ with platinum electrodes.

Q29. Calculate the equilibrium constant for the following reaction at 298 K:

$$Cu\,(s) + Cl_2\,(g) \longrightarrow CuCl_2\,(aq)$$

Given : R = 8.314 J K^{-1} Mol^{-1}, $E^\circ_{Cu^{2+}/Cu} = 0.34$ V, $E^\circ_{\frac{1}{2}Cl_2/Cl^{\ominus}} = 1.36$ V, 1 F = 96500 C mol^{-1}

Q30. Calculate the e.m.f. of the following cell:

$Mg\,(s)\ |\ Mg^{2\oplus}\,(0.2\ M)\ ||\ Ag^{\oplus}\,(1 \times 10^{-3}\ M)\ |\ Ag\,(s)$

$E^{\circ}_{Ag^{\oplus}} = 0.80\,V,\ E^{\circ}_{Mg^{2\oplus}/Mg} = -2.37\,V$

Q31. Calculate the cell e.m.f. and ΔG for the cell reaction at 25°C for the cell:

$Zn\,(s)\ |\ Zn^{2\oplus}\,(1\ M)\ ||\ Cd^{2\oplus}\,(1\ M)\ |\ Cd\,(s)$

Given : E° values at 25°C : $E^{\circ}_{Zn^{2\oplus}/Zn} = -0.76$ V and $E^{\circ}_{Cd^{2\oplus}/Cd} = -0.403$ V

1 F = 96500 C mol^{-1}, R = 8.314 J K^{-1} mol^{-1}.

Q32. In the button cell widely used in watches and other devices, the following reaction take place:

$$Zn\,(s) + Ag_2O\,(s) + H_2O\,(l) \longrightarrow Zn^{2+}(aq) + 2Ag\,(s) + OH^{-}(aq)$$

Determine $E^{\ominus}$ and $\Delta_r G^{\ominus}$ for the reaction.

Given $Zn \longrightarrow Zn^{2+} + 2e^{-},\quad E^{\ominus} = 0.76\,V$ **and** $AgE^{\ominus} = 0.80\,V$

$$Ag_2O + H_2O + 2e^{-} \longrightarrow 2Ag + 2OH^{-},\quad E^{\ominus} = 0.344\,V.$$

Q33. Calculate the standard cell potentials of galvanic cell in which the following reactions take place:

(a) $2Cr\,(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd$

(b) $Fe^{2+}(aq) + Ag^{+}(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

Calculate the $\Delta_r G^{\ominus}$ and equilibrium constant of the reactions.

Given, $E^{\ominus}_{Cr^{3+}/Cr} = -0.74\,V,\ E^{\ominus}_{Cd^{2+}/Cd} = 0.40\,V,\quad E^{\ominus}_{Ag^{+}/Ag} = 0.80\,V,\ E^{\ominus}_{Fe^{3+}/Fe^{2+}} = 0.77\,V$

Q34. The standard reduction potential for the half cell.

$$NO_3^{-} + 2H^{+} + e^{-} \longrightarrow NO_2(g) + H_2O \text{ is } 0.78\,V$$

(a) Calculate the reduction potential in 8M H^{+} solution.

(b) What will be the reduction potential of the half cell in a neutral solution?

Assume other species to be at unit concentration.

Q35. Given the following cell $Al/Al^{3+}(0.01\,M)\,||\,Fe^{2+}(0.02\,M)/Fe$ calculate the value of ΔG and E_{cell} at 298 K when $E^{\ominus}_{cAl^{3+}/Al}$ and $E^{\ominus}_{cFe^{2+}/Fe}$ are – 1.66 and – 0.44 respectively.

Q36. A galvanic cell is constructed with Ag^{+}/Ag and Fe^{3+}/Fe^{2+} electrodes. Find the concentration of Ag^{+} at which the e.m.f. of the cell is zero at equimolar concentrations of Fe^{2+} and Fe^{3+} ions.

$$(E^{\ominus}_{Ag^{+}/Ag} = 0.80\,V;\ E^{\ominus}_{Fe^{2+}/Fe^{3+}} = 0.77\,V).$$

Q37. Write Nernst equation and calculate the e.m.f. of the cell at 298 K

$$Cu\,(s)\,|\,Cu^{2+}\,(0.130\,M)\,||\,Ag^{+}(1.0 \times 10^{-4}\,M)/Ag(s)$$

Given the value of $E^{\ominus}_{Cu^{2+}/Cu}$ and $E^{\ominus}_{Ag^{+}/Ag}$ as 0.34 V and 0.80 V respectively.

Q38. Write the Nernst equation and the e.m.f. of the following cells at 298 K:

(a) $Sn\,(s)\,|\,Sn^{2+}_{(0.050\,M)}\,||\,2H^{+}_{(0.020\,M)}\,|\,H_2(g)_{(1\,bar)}\,|\,Pt\,(s)$

(b) $Pt\,(s)\,|\,Br_2(1)\,|\,Br^{-}_{(0.010\,M)}\,||\,H^{+}_{(0.030\,M)}\,|\,H_2(g)_{(1\,bar)}\,|\,Pt\,(s)$

Given: $E^{\ominus}_{Sn^{2+}/Sn} = -0.14\,V,\ E^{\ominus}_{Br^{2}/Br^{-}} = +1.08\,V.$

Q39. Write the Nernst equation and the e.m.f. of the following cells at 298 K:

(a) $Mg\,(s)\,|\,Mg^{2+}_{(0.001\ M)}\,||\,Cu^{2+}_{(0.0001\ M)}\,|\,Cu\,(s)$

(b) $Fe\,(s)\,|\,Fe^{2+}_{(0.001\ M)}\,||\,H^{+}\,|\,(1\ M)\ H_2(g)_{(1\ bar)}\,|\,Pt\,(s)$

Given: $E^{\ominus}_{Mg^{2+}/Mg} = -2.37\,V$, $E^{\ominus}_{Cu^{2+}/Cu} = +0.34\,V$, $E^{\ominus}_{Fe^{2+}/Fe} = -0.44\,V$.

Date: 22/10/2021

S1. By increasing the concentration of the ions.

S2. This because at equilibrium, $E_{cell} = 0$.

S3. It is not possible to measure the voltage of an isolated half reaction because neither the oxidation nor the reduction can occur by itself. Therefore, we can only calculate the relative electrode potential by connecting it to some standard electrode.

S4. It will act as cathode.

S5. Metal having higher oxidation potential (or lower reduction potential) will liberate H_2 from H_2SO_4. Thus, *A* will liberate H_2 from H_2SO_4.

S6. No, because for the reaction,

$$Fe^{3+} + Br^- \longrightarrow Fe^{2+} + \frac{1}{2}Br_2$$

$E^\ominus = 0.771 - 1.09 = -0.319$ V is negative.

S7. No, Copper spoon will dissolve as Cu^{2+} ions because copper has more tendency to get oxidised than silver.

S8. (a) For a galvanic cell, free energy decreases *i.e.*, $\Delta G < 0$.

(b) For electrolytic cell, free energy increases *i.e.*, $\Delta G > 0$.

S9. Higher is the value of oxidation potential (or lower the $E^\ominus_{red}$) greater is the tendency of element to oxidise and higher will be its reducing power. Thus, the correct arrangement in decreasing order of their $E^\ominus_{red}$ values is

Ag < Cu < Fe < Cr < Mg < K

S10. Under the conditions of electrolysis of aqueous sodium chloride, oxidation of water at anode requires over potential and therefore, Cl^- is oxidised instead of water.

S11. Anode : $Cu \longrightarrow Cu^{2+} + 2e^-$

Cathode : $Cl_2 + 2e^- \longrightarrow 2Cl^-$

Cu is anode because it is getting oxidised.

Cl_2 is cathode because it is getting reduced.

S12. The standard hydrogen electrode is used as a reference electrode whose electrode potential is taken to be zero. The electrode potential of other electrodes is measured with respect to it.

S13. Intensive property, it is independent of the size of electrode.

S14. The reduction potentials of $Cu^{2+} | Cu$ and $Fe^{2+} | Fe$ are + 0.34 V and – 0.44 V respectively. This means Cu^{2+} will be reduced to Cu and iron will be oxidised to Fe^{2+}. In other words, the vessel will dissolve. Therefore, it is not possible to store $CuSO_4$ in an iron vessel.

S15. E° for the reaction is 0.771 – 0.800 = – 0.029 V.

Therefore, the reaction is not spontaneous.

S16. $Cl_2 < MnO_4^- < Cu^{4+}$.

S17. When the opposing potential becomes equal to electrical potential, the cell reaction stops and no current flows through the cell. Thus, there is no chemical reaction.

S18. We shall find out the e.m.f. of the cell obtained by the combination of the two.

$$E^\circ_{cell} = E^\circ_{Fe^{3\oplus}/Fe^{2\oplus}} - E^\circ_{Ti^{4\oplus}/Ti^{3\oplus}} = +0.77 - 0.01\ V = +0.76\ V$$

As the e.m.f. of cell is positive, therefore, $Ti^{4\oplus}$ can be used to oxidise $Fe^{2\oplus}$ to $Fe^{3\oplus}$ ion.

$Ti^{4\oplus} + Fe^{2\oplus} \longrightarrow Ti^{3\oplus} + Fe^{3\oplus}$.

S19.

$$E_{Cu^{2+}/Cu} = E^\ominus_{Cu^{2+}/Cu} + \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Cu]}$$

$$[Cu] = 1,\ [Cu^{2+}] = 0.1\ M$$

$$\therefore \quad E_{Cu^{2+}/Cu} = E^\ominus_{Cu^{2+}/Cu} + \frac{0.059}{2} \log [Cu^{2+}]$$

$$= 0.34 + \frac{0.059}{2} \log 0.1 = \mathbf{0.3105\ V}.$$

If the concentration of $[Cu^{2+}]$ ion decreased, the value of electrode potential willl further decrease.

S20. $Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$

$$E_{Mg^{2+}/Mg} = E^\ominus_{Mg^{2+}/Mg} + \frac{0.059}{2} \log \frac{[Mg^{2+}]}{[Mg]}$$

$$[Mg^{2+}] = 0.01\ M; \quad [Mg] = 1$$

$$E_{Mg^{2+}/Mg} = -2.36 + \frac{0.059}{2} \log (0.01) = \mathbf{-2.42\ V}.$$

S21. Calculation of $E^\ominus_{cell}$

$$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode} = 0.80 - (-2.37) = 3.17\ V.$$

Calculation of $\Delta G^\ominus$ which gives the maximum work

The cell reaction is:

$$Mg(s) + 2Ag^{+}(aq) \longrightarrow 2Ag(s) + Mg^{2+}(aq)$$

Thus, value of $n = 2$

$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$$

$$= -2 \times 96500 \times 3.17 = -611810 \text{ C. V}$$

$$= \mathbf{-611810\ J}.$$

And, K_c is $\quad E^{\ominus}_{cell} = \frac{0.059}{n} \log K_c$

or $\quad 3.17 = \frac{0.059}{2} \log K_c$

or $\quad \log K_c = \frac{3.17 \times 2}{0.059} = 107.457$

$$K_c = \text{Antilog } 107.457$$

$$K_c = \mathbf{2.864 \times 10^{107}}.$$

S22. **Step 1:** Calculation of $E^{\ominus}_{cell}$

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$$

$$= 0.34 - (-0.76) = 1.10 \text{ V}.$$

Step 2: Calculation of $\Delta G^{\ominus}$

We know that maximum work is given by $\Delta G^{\ominus}$.

Now, the net cell reaction is

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

So, here the value of $n = 2$

$\therefore \quad \Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

$$= -(2 \text{ mol})(96500 \text{ C. mol}^{-1})(1.10 \text{ V})$$

$$= -212{,}300 \text{ Coulomb Volt}$$

$$= 212{,}300 \text{ J} = \mathbf{212.30\ kJ} \qquad (\because \text{ Coulomb} \times \text{Volt} = \text{Joule})$$

S23. **Step 1:** Calculation of $E^{\ominus}_{cell}$

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$$

$$= E^{\ominus}_{Cu^{2+}/Cu} - E^{\ominus}_{Ni^{2+}/Ni}$$

$$= 0.34 - (-0.25) = \mathbf{0.59\ V}.$$

Step 2: Calculation of K_c

$$\log K_c = \frac{2}{0.059} \times E^{\ominus}_{cell} \qquad \text{Here, } n = 2$$

$$\log K_c = \frac{2}{0.059} \times 0.59 = 20 \qquad = K_c = \text{Antilog } 20$$

$$K_c = \mathbf{1 \times 10^{20}}.$$

S24. The electrode reaction is

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-$$

$$E = E^{\ominus} + \frac{0.059}{2} \log \frac{[Cl_2]}{[Cl^-]^2}$$

$$= E^{\ominus} + \frac{0.059}{2} \log \frac{p_{Cl_2}}{[Cl^-]^2}$$

$$= 1.36 + 0.0295 \log \frac{1.5}{(0.01)^2}$$

$$= 1.36 + 0.0295 \times 4.1761$$

$$= 1.36 + 0.1231 = \mathbf{1.483\,V}.$$

S25. The electrode reaction during the electrolysis of copper nitrate are

Anodic reaction:

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s); \quad E^{\ominus}_{red} = 0.34\,V$$

Cathodic reaction:

$$H_2O(l) \longrightarrow 2H^+(aq) + \frac{1}{2} O_2(g) + 2e^-; \quad E^{\ominus}_{oxi} = -1.23\,V$$

Net reaction:

$$Cu^{+2}(aq) + H_2O(l) \longrightarrow Cu(s) + \frac{1}{2} O_2(g) + 2H^+(aq); \quad E^{\ominus}_{cell} = -0.89\,V$$

Thus, minimum voltage required to cause electrolysis is **0.89 V**.

S26. It is important to note that $E^{\ominus}$ values of the two given couples cannot be added directly as these are not extensive properties. Hence it is necessary to convert $E^{\ominus}$ values into $\Delta G^{\ominus}$ values, which can be added or subtracted

$$Cu^{2+} + 2e^- \longrightarrow Cu;$$

$$\Delta G_1^{\ominus} = -nFE_1^{\ominus} = 2F \times 0.34\,V = -0.68\,F$$

$$Cu^+ + e^- \longrightarrow Cu;$$

$$\Delta G_2^{\ominus} = -nFE_2^{\ominus} = -F \times (0.52\,V) = -0.52\,F$$

The required reaction is $Cu^{2+} + e \longrightarrow Cu^{+}$

Let E° be the standard electrode potential

$$\therefore \quad \Delta G_3^\ominus = -nFE^\ominus = -FE^\ominus$$

Now

$$\Delta G_3^\ominus = \Delta G_2^\ominus - \Delta G_1^\ominus$$

$$-FE^\ominus = -0.68\,F - (-0.52\,F) = -0.16\,F$$

$$E^\ominus = \mathbf{0.16\ V}.$$

S27. (a) $$Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2.$$

In this reaction Fe^{3+} ions are reduced by I^- ions. For this reaction to be feasible the $E^\ominus_{Fe^{3+}/Fe^{2+}}$ should be larger than $E^\ominus_{I_2/I^-}$. Since the given values agree with this requirement. Hence, this reaction is **feasible**.

(b) $$2Ag^+(aq) + Cu(s) \longrightarrow Cu^{2+} + 2Ag$$

In this reaction, Ag^+ inos being reduced. This is also **feasible** because $E^\ominus_{Ag^+/Ag}$ is greater than $E^\ominus_{Cu^2/Cu}$.

(c) $$Fe^{3+}(aq) + Br^-(aq) \longrightarrow Fe^{2+}(aq)\ \frac{1}{2}Br_2.$$

This reaction is **not feasible** because $E^\ominus_{Fe^{3+}/Fe^{2+}}$ is less than $E^\ominus_{Br_2/Br^-}$. Hence Br^- ions cannot reduce Fe^{3+} ions.

(d) This reaction is also **not feasible** because $E^\ominus_{Fe^{3+}/Fe^{2+}}$ is smaller than $E^\ominus_{Ag^+/Ag}$.

S28. (a) Here

$$AgNO_3(s) \longrightarrow Ag^+(aq) + NO_3^-(aq) + H_2O$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode: Ag^+ ions have lower potential then H^+ ions. So Ag^+ ions will deposited as preference to H^+ ions

At anode: Ag electrode will take part in the reaction and attacked by NO_3^- ions. Ag^+ ion releases from the anode and will go into solution

$$Ag \longrightarrow Ag^+ + e^-$$

(b) **At cathode:** Ag^+ ions have lower potential then H^+ ions. So Ag^+ ions will deposited as preference to H^+ ions

At anode: In this case silver do not take part in the reaction so out of OH^- and NO_3^-, OH^- ions have lower potential so it will discharge.

$$OH^-(aq) \longrightarrow OH + e^-$$

$$4OH \longrightarrow 2H_2O(l) + O_2(g)$$

(c) In elctrolysis of H_2SO_4

$$H_2O \longrightarrow 4H^+ + OH^- \quad \text{... (i)}$$

$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq) \quad \text{... (ii)}$$

At cathode: $H^+ + e^- \longrightarrow H$

$$H + H \longrightarrow H_2(g)$$

At anode: $OH^- \longrightarrow OH + e^-$

$$4OH \longrightarrow 2H_2O + O_2(g)$$

(d) Both $CuCl_2$ and H_2O will ionise into Cu^{2+}, Cl^- and H^+, OH^- respectively.

Cu^{2+} will reduced in preference to H^+

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

Cl^- will oxidised in preference to OH^-

At anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$.

S29.

$$E^\circ_{cell} = E^\circ_{\frac{1}{2}Cl_2/Cl^\ominus} - E^\circ_{Cu^{2\oplus}/Cu}$$

$$= +1.36\text{ V} - 0.34\text{ V}$$

$$= 1.02\text{ V}$$

Applying the following relation and substituting the values, we get

$$\log K = \frac{nE^\circ}{0.0591} = \frac{2 \times 1.02}{0.0591} = \frac{2.04}{0.0591}$$

$$= 34.5177$$

$$K = \text{Antilog } 34.5177$$

$$= 3.294 \times 10^{34}$$

Thus, equilibrium constant = 3.294×10^{34}

S30. The electrode reactions may be represented as:

$$Mg\ (s) \longrightarrow Mg^{2\oplus}\ (aq) + 2e^\ominus$$

$$2Ag^\oplus(aq) + 2e^\ominus \longrightarrow 2Ag\ (s)$$

$$Mg\ (s) + 2Ag^\oplus\ (aq) \longrightarrow Mg^{2\oplus}\ (aq) + Ag\ (s)$$

Thus, $n = 2$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Mg^{2\oplus}]}{[Ag^\oplus]^2}$$

$$= \left(E^\circ_{Ag^{\oplus}/Ag} - E^\circ_{Mg^{2\oplus}/Mg}\right) - \frac{0.0591}{2}\log\frac{0.2}{(10^{-3})^2}$$

$$= \left[+0.80\text{ V} - (-2.37\text{ V}) - \frac{0.0591}{2}\log(2\times10^5)\right]$$

$$= +3.17\text{ V} - \frac{0.0591}{2}[\log 2 + \log 10^5]$$

$$= +3.17\text{ V} - \frac{0.0591}{2}\times 5.3010$$

$$= +3.17\text{ V} - 0.1566\text{ V}$$

$$= 3.0134\text{ V}$$

e.m.f. of the cell = 3.0134 V

S31. Electrode reactions may be represented as under:

$$Zn\ (s) \longrightarrow Zn^{2\oplus}\ (aq) + 2e^{\ominus}$$

$$Cd^{2\oplus}\ (aq) + 2e^{\ominus} \longrightarrow Cd\ (s)$$

$$E^\circ_{cell} = E^\circ_{Cd^{2\oplus}/Cd} - E^\circ_{Zn^{2\oplus}/Zn}$$

$$= [-0.403\text{ V} - (-0.76\text{ V})] = +0.357\text{ V}$$

To calculate ΔG, use the following relation:

$$\Delta G^\circ = -n E^\circ F$$

$$= -2\times 0.357\text{ V}\times 96500\text{ C} = -68901\text{ J mol}^{-1} = -68.901\text{ kJ mol}^{-1}$$

ΔG for the cell reaction = – 68.901 kJ mol^{-1}.

S32. Electrode reactions taking place in the button cell are as under :

$$Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^-$$

$$2Ag^+\ (aq) + 2e^- \longrightarrow 2Ag\ (s)$$

$$Zn\ (s) + 2Ag^+\ (aq) \longrightarrow Zn^{2+}\ (aq) + 2Ag\ (s)$$

Thus, $n = 2$

$E^\ominus$ for the reaction can be obtained as under:

$$E^\ominus_{cell} = (E^\ominus_{cathode} - E^\ominus_{anode})$$

$$= +0.80\text{ V} - (-0.76\text{ V}) = +1.56\text{ V}$$

Use the following relation to calculate $\Delta_r G^\ominus$

$$\Delta_r G^\ominus = -nE^\ominus F$$

or $$\Delta_r G^\ominus = -2\times 1.56\times 96500 = -301080\text{ J mol}^{-1} = -301.080\text{ kJ mol}^{-1}$$

S33. (a)

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$$

$$= -0.40\,V - (-0.74\,V) = +0.34\,V$$

$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell} = -6 \times 96500\,(C\,mol^{-1}) \times 0.34\,(V)$$

$$= -196860\,CV\,mol^{-1}$$

or $$= -196860\,J\,mol^{-1}$$

or $$= -196.86\,kJ\,mol^{-1}$$

$$\Delta G^{\ominus} = -2.303\,RT \log K - 196860 = -2.303 \times 8.314 \times 298 \log K$$

or $$\log K = 34.5014$$

$$K = \text{Antilog}\,(34.5014) = \mathbf{3.192 \times 10^{34}}.$$

(b)

$$E^{\ominus}_{cell} = +0.80\,V - 0.77\,V = +0.03\,V.$$

$$\Delta G^{\ominus} = -nFEe_{cell} = 1 \times 96500\,(C\,mol^{-1}) \times 0.03\,(V)$$

$$= -2895\,(CV\,mol^{-1}) = -2895\,(J\,mol^{-1})$$

$$= -2.895\,kJ\,mol^{-1}$$

$$\Delta G^{\ominus} = -2.303\,RT \log K$$

$$-2895 = 2.303 \times 8.314 \times 298 \times \log K$$

$$\log K = 0.5074$$

$$K = \text{Antilog}\,(0.5074) = \mathbf{3.22}.$$

S34. The given half cell is $NO_3^-(aq) + 2H^+(aq) + e^- \longrightarrow NO_2(g) + H_2O(l)$

According to nernst equation

$$E_{cell} = E^{\ominus}_{cell} + \frac{0.059}{1} \log \frac{[NO_3^-][H^+]^2}{[NO_2]}$$

(a) Electrode potential at 8M H^+ solution

$[NO_3^-] = [NO_2] = 1$ (As per given conditions)

$[H^+] = 8M$

$$\therefore \quad E = 0.78 + \frac{0.059}{1} \log (8)^2 = 0.78 + 0.059 \log 64$$

$$= 0.78 + (0.059)(1.8062) = 0.886\,V.$$

(b) Electrode potential in neutral solution

In neutral solution, $[H^+] = 1 \times 10^{-7}$

$$\therefore \quad E = 0.78 + \frac{0.059}{1} \log (1 \times 10^{-7})^2$$

$$= 0.78 + 0.059 \log (1 \times 10^{-14})$$

$$= 0.78 + 0.059 \times (-14)$$

$$= 0.78 - (0.826) = \mathbf{-0.046\,V}.$$

S35. **Step 1:** Calculation of $E^{\ominus}_{cell}$

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{canode}$$

$$= -0.44 - (1.66) = 1.22\,V$$

Step 2: Calculate of E_{cell}

The net cell reaction is

$$2Al\,(s) + 3Fe^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Fe\,(s)$$

Since 6 moles of electrons are involved $\therefore\ n = 6$.

Now, applying Nernst equation

$$E_{cell} = E^{\ominus}_{cell} + \frac{0.059}{n} \log \frac{[Fe^{2+}]^3}{[Al^{3+}]^2}$$

$$= 1.22 + \frac{0.059}{n} \log \frac{(0.02)^3}{(0.01)^2} = 1.22 + \frac{0.059}{6} \log \frac{(2 \times 10^{-2})^3}{(1 \times 10^{-2})^2}$$

$$= 1.22 + \frac{0.059}{6} \log (8 \times 10^{-2}) = 1.22 + \frac{0.059}{6} (\log (8) - 2)$$

$$= 1.22 + \frac{0.059}{6} (0.9031 - 2) = 1.22 - 0.0197 = \mathbf{1.209\,V}.$$

And, $\Delta G = -nFE_{cell}$

$$= -(6\ \text{mol})(96500\ \text{C. mol}^{-1})(1.209\ \text{V})$$

$$= -700{,}011\ \text{CV} = -700{,}011\ \text{J} = \mathbf{-700.01\ kJ}.$$

S36. Since $E^{\ominus}_{Ag^+/Ag}$ is larger than $E^{\ominus}_{Fe^{3+}/Fe^{2+}}$. Hence reduction will occur at silver electrode and the cell is

$$Fe^{2+}/Fe^{3+} \,||\, Ag^+/Ag.$$

The cell reaction is

$$Fe^{2+} + Ag^+ \rightarrow Fe^{3+} + Ag$$

According to Nernst equation,

$$E_{cell} = E^{\ominus}_{cell} + \frac{0.059}{1} \log \frac{[Fe^{2+}][Ag^+]}{[Fe^{3+}][Ag]}$$

Now, $[Fe^{2+}] = [Fe^{3+}]$ and $[Ag] = 1$

i.e., $[Fe^{2+}]$ $[Fe^{3+}]$ is equimolar and [Ag] is solid.

$\therefore \quad E_{cell} = 0.80 - 0.77 + \frac{0.059}{1} \log [Ag^+]$

or $\quad 0 = 0.03 + \frac{0.059}{1} \log [Ag^+]$

[Antilog of –0.5084]

$$\log [Ag^+] = \frac{-0.03}{0.059} = -0.5084$$

or $\quad [Ag^+]$ = Antilog (–0.5084) = **0.3102 M**.

S37. The given cell is

$$Cu/Cu^{2+}(0.130\ M) \,||\, Ag^+(1.0 \times 10^{-4}\ M)/Ag$$

(Anode) (Cathode)

The net cell reaction is

$$Cu\,(s) + 2Ag^+(aq) \longrightarrow 2Ag\,(s) + Cu^{2+}(aq)$$

and it involves the transfer of 2 electrons: Thus n = 2 the Nernst equation for the above cell reaction is

$$E_{cell} = E^{\ominus}_{cell} + \frac{0.059}{2} \log \frac{[Cu][Ag^{2+}]^2}{[Cu^{2+}][Ag]^2} \quad \text{... (i)}$$

Now, $\quad [Ag] = [Cu] = 1$ being solids.

Also, $\quad E^{\ominus}_{cell} = E^{\ominus}_{Ag^+/Ag} - E^{\ominus}_{Cu^{2+}/Cu}$

$= 0.80 - 0.34 = 0.46\,V.$

Substituting the value of $E^{\ominus}_{cell}$ in Eq. (i),

$$E_{cell} = 0.46 + \frac{0.059}{2} \log \frac{[Ag^+]^2}{[Cu^{2+}]}$$

$$= 0.46 + \frac{0.059}{2} \log \frac{[1 \times 10^{-4}]^2}{[0.130]}$$

$$= 0.46 + \frac{0.059}{2} \log \frac{1 \times 10^{-8}}{[0.130]}$$

$$= 0.46 + \frac{0.059}{2} \log (7.6 \times 10^{-8})$$

$= \mathbf{0.250\,V}$.

S38. (a) Cell reaction is $Sn + 2H^+ \longrightarrow Sn^{2+} + H_2$ (n = 2)

According to Nernst eqn.

$$E_{cell} = E^{\ominus}_{cell} + \frac{0.0591}{2} \log \frac{[H^+]^2}{[Sn^{2+}]}$$

$$= 0 - (-0.14) + \frac{0.0591}{2} \log \frac{(0.02)^2}{0.05}$$

$$= 0.14 + \frac{0.0591}{2} \log (8 \times 10^{-3})$$

$$= 0.14 - \frac{0.0591}{2} (2.0969) = \mathbf{0.078\,V}.$$

(b) According to given cell, the net cell reaction, is

$$2Br^- + 2H^+ \longrightarrow Br_2 + H_2$$

it involves the transference of $2e^-$

Applying Nernst equation we have

$$E_{cell} = E^{\ominus}_{cell} + \frac{0.0591}{2} \log [Br^-]^2/[H^+]^2$$

$$E_{cell} = (0 - 1.08) + \frac{0.0591}{2} \log (0.01)^2/(0.03)^2$$

$$= -1.08 + \frac{0.0591}{2} \log (0.11)$$

$$= -1.08 + \frac{0.0591}{2} (-0.95)$$

$$= -1.08 - 0.028 = \mathbf{-1.108\,V}.$$

Since E_{cell} is –ve, it means that the representation of the cell is wrong. For cell to show +ve e.m.f. it should be Pt, He (1 bar)/H^+(0.03 M) || $Br_2(l)$/Br^-(0.01 M).

S39. (a) Cell reaction is

$$Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu\ (n = 2)$$

Applying Nernst equation,

$$E_{cell} = E^{\ominus}_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Mg^{2+}]}$$

$$\therefore \quad E_{cell} = 0.34 - (-2.37) + \frac{0.0591}{2} \log \frac{10^{-4}}{10^{-3}}$$

$$= 2.71 - 0.02955 = \mathbf{2.68\,V}.$$

(b) Cell reaction is $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\ (n = 2)$

According to Nernst eqn.

$$E_{cell} = E^{\ominus}_{cell} + \frac{0.0591}{2}\log\frac{[H^+]^2}{[Fe^{2+}]}$$

$\therefore$

$$E_{cell} = 0 - (-0.44) + \frac{0.0591}{2}\log\frac{(1)^2}{10^{-3}}$$

$$= 0.44 + \frac{0.0591}{2}(+3)$$

$$= 0.44 + 0.0887 = \mathbf{0.523\ V}.$$

Date: 22/10/2021

Q1. Which of 0.1 M HCl and 0.1 M NaCl do you expect to have greater Λ_m° and why?

Q2. Why is alternating current used in place of direct current in measuring the electrolytic conduction?

Q3. Which will have greater molar conductivity?
(a) Solution containing 1 mol of KCl in 200 cc or 1 mol of KCl in 500 cc.
(b) Solution containing 1 mol of LiCl in 500 cc or 1 mol of KCl in 500 cc.

Q4. Electrolytic conductivity of 0.30 M solution of KCl at 298 K is 3.72×10^{-2} S cm^{-1}. Calculate its molar conductivity.

Q5. Solutions of two electrolytes 'A' and 'B' are diluted. The Λ_m of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte? Justify your answer.

Q6. How will the pH of brine (aq. NaCl solution) be affected when it is electrolysed?

Q7. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}?

Q8. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

Q9. Express the relation between conductivity and molar conductivity of a solution.

Q10. Calculate the limiting molar conductivity of $CaSO_4$ if limiting molar conductivities of calcium and sulphate ions are 119.0 and 106.0 S cm^2 mol^{-1} respectively.

Q11. What is the effect of temperature on the electrical conductance of
(a) metallic conductor (b) electrolytic conductor

Q12. Give relationship between molar conductance and equivalent conductance?

Q13. The value of Λ_m° of $Al_2(SO_4)_3$ is 858 S cm^2 mol^{-1}, while $\lambda^\circ_{SO_4^{-2}}$ is 160 S cm^2 mol^{-1}. Calculate the limiting ionic conductivity of Al^{3+}.

Q14. The electrical resistance of a column of 0.05 M caustic soda solution of diameter 1 cm and length 50 cm is 5.55×10^3 Ω. Calculate its resistivity, conductivity and molar conductivity.

Q15. Calculate Λ°_m for NH_4OH, given the values of Λ°_m for Ba (OH_2), $BaCl_2$ and NH_4Cl are 523.28, 280.0 and 129.8 S cm^2 mol^{-1} respectively.

Q16. Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually?

Q17. The values of Λ_m° for NH_4Cl, NaOH and NaCl at infinite dilution are respectively 129.8, 248.1 and 126.4 ohm^{-1} cm^2 mol^{-1}. Calculate Λ_m° of NH_4OH.

Q18. The molar conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001 M are 5.20 and 49.2 S cm^2 mol^{-1} respectively. Calculate the degree dissociation of acetic acid at these concentrations. Given that, $\lambda°(H^+)$ and $\lambda°(CH_3COO^-)$ are 349.8 and 40.9 ohm^{-1} cm^2 mol^{-1} respectively.

Q19. The conductivity of saturated solution of silver chloride is $1.24 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. The iconic conductivities of Ag^+ and Cl^{-1} ions at infinite dilution are 53.8 and 65.3 Ω^{-1} cm^2 mol^{-1}. Calculate the solubility of AgCl in gL^{-1}. (Molar mass of AgCl = 143.5 g mol^{-1}).

Q20. At 25°C, the specific conductance (κ) of saturated solution of AgCl is 2.68×10^{-6} and that of a water in which the solution is made is $0.86 \times 10^{-6}\ \Omega^{-1}$. If limiting molar conductivities of $AgNO_3$, HNO_3 and HCl are respectively 133.0, 421.0 and 426.0 Ω^{-1} cm^2 mol^{-1}. Calculate the solubility of AgCl in water at a given temperature.

Q21. Conductivity of 0.00241 M acetic is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity and if Λ_m° for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

Q22. What is meant by 'molar conductivity' of a solution? The specific conductivity of 0.40 M solution of KCl at 298 K is 4.96×10^{-2} S cm^{-1}. Calculate its molar conductivity.

Q23. What is meant by specific conductivity of a solution? The specific conductance of a 0.12 N solution of an electrolyte is 2.4×10^{-2} S cm^{-1}. Calculate its equivalent conductance.

Q24. Define conductivity and molar conductivity for the solution of an electrolyte.

Q25. How does molar conductivity vary with concentration for (a) weak electrolyte and for (b) strong electrolyte? Give reasons for these variations.

Q26. The conductivity of a solution containing 1.0 g of anhydrous $BaCl_2$ (barium chloride) in 200 cm^3 of the solution has been found to be 0.0058 S cm^{-1}. Calculate the molar and equivalent conductivity of the solution. (Atomic masses: Ba = 137 and Cl = 35.5).

Q27. The resistance of a conductivity cell when filled with 0.02 M KCl solution is 164 ohm at 298 K. However, when it is filled with 0.05 M $AgNO_3$ solution its resistance is found to be 78.50 ohms. If conductivity of 0.02 M KCl is 2.768×10^{-3} ohm^{-1} cm^{-1}, calculate

(a) The conductivity of 0.05 M $AgNO_3$ (b) the molar conductivity of $AgNO_3$ solution.

Q28. The resistance of 0.01 M acetic acid solution when measured in a conductivity of cell constant 0.366 cm^{-1}, is found to be 2220 Ω. Calculate degree of dissociation of acetic acid. given that values of $\lambda^{\ominus}_{H^+}$ and $\lambda^{\ominus}_{CH_3COO^-}$ are 349.1 and 40.9 Ω^{-1} cm^2 mol^{-1} respectively.

Q29. The conductivity of NaCl at 298 K has been determined at different concentrations and the results are given as under:

Concentration (M):	0.001	0.010	0.020	0.050	0.100
k (S m^{-1}) $\times 10^2$:	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° from the graph.

Date: 22/10/2021

S1. 0.1 M HCl will have greater Λ°_m value because H^+ ions are smaller than Na^+ ions and hence have greater ionic mobility.

S2. Direct current result in the electrolysis of the electrolytic solution. As a result, concentration of the electrolyte near the electrodes changes and these results change in the resistance of the solution.

S3. (a) 1 mol of KCl in 500 cc

(b) 1 mol of KCl in 500 cc.

S4. Using the following relation and substituting the values, we get

$$\Lambda_m = \frac{1000\kappa}{M} = \frac{1000\,\text{cm}^3 \times 3.72 \times 10^{-2}\,\text{S cm}^{-1}}{0.30\,\text{M}} = 124\ \text{S cm}^2\ \text{mol}^{-1}.$$

S5. Electrolyte 'B' is strong because on dilution there is small increase in Λ_m.

S6. Since NaOH is formed during electrolysis, pH of the brine solution will increase.

S7.

$$\text{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}}$$
$$= \text{Conductivity} \times \text{Resistance}$$
$$= 0.146 \times 10^{-3}\,\text{S cm}^{-1} \times 1500\,\Omega = \mathbf{0.219\,cm^{-1}}.$$

S8.

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0248\,(\text{S cm}^{-1}) \times 1000\,(\text{cm}^3)}{0.20\,(\text{mol})}$$
$$= \mathbf{124\ S\ cm^2\ mol^{-1}}.$$

S9. Molar conductivity (Λ_m) is related to conductivity (κ) as:

$$\Lambda_m = \frac{\kappa \times 1000}{\text{M}}$$, where M is the molarity of the solution.

S10.

$$\Lambda^\circ_m(CaSO_4) = \lambda^\circ_m(Ca^{2+}) + \lambda^\circ_m(SO_4^{2-})$$
$$= 119.0 + 106.0$$
$$= 225.0\ \text{S cm}^2\ \text{mol}^{-1}$$

S11. With increase in temperature, the electrical conductance of ***metallic conductor decreases*** whereas that of ***electrolytic conductor increases***.

S12. $\Lambda_m = \dfrac{\kappa \times 1000}{\text{Molarity}}$ and $\Lambda_e = \dfrac{\kappa \times 1000}{\text{Normality}}$

$\therefore$ $\dfrac{\Lambda_m}{\Lambda_e} = \dfrac{\text{Normality}}{\text{Molarity}}$

S13. According to Kohlrausch's law,

$$\Lambda_m^\circ (Al_2(SO_4)_3) = 2\lambda^\circ_{(Al^{3+})} + 3\lambda^\circ_{(SO_4^{2-})}$$

$$858 = 2\lambda^\circ_{(Al^{3+})} + 3 \times 160$$

$$2\lambda^\circ_{(Al^{3+})} = 858 - 3 \times 160 = 378 \text{ S cm}^2 \text{ mol}^{-1}$$

or $\lambda^\circ_{(Al^{3+})} = \dfrac{378}{2} = \mathbf{189 \text{ S cm}^2 \text{ mol}^{-1}}$.

S14. $a = \pi r^2 = 3.14 \times (0.5)^2 \text{ cm}^2 = 0.785 \text{ cm}^2$

Now, $R = \rho \times \dfrac{l}{a}$ or $\rho = \dfrac{Ra}{l}$

$$= \frac{5.55 \times 10^3 \times 0.785}{50} = \mathbf{87.135\ \Omega \text{ cm}}$$

$$\kappa = \frac{1}{\rho} = \frac{1}{87.135} = \mathbf{0.01148 \text{ S cm}^{-1}}$$

$$\Lambda_m = \frac{\kappa \times 1000}{\text{molarity}} = \frac{0.01148 \times 1000}{0.05}$$

$$= \mathbf{229.6 \text{ S Cm}^2 \text{ mol}^{-1}}.$$

S15. According to Kohlrauch's law,

$$\Lambda^\circ_m (NH_4OH) = \lambda^\circ_{(NH_4^+)} + \lambda^\circ_{(OH^{-1})}$$

Now, add and subtract $\frac{1}{2}\lambda^\circ_{(Ba^{2+})}$ and also $\lambda^\circ_{(cl^-)}$ in R.H.S.

$\therefore$ $\Lambda^\circ_m (NH_4OH) = \lambda^\circ_{NH_4^+} + \lambda^\circ_{(OH^-)} + \frac{1}{2}\lambda^\circ_{(Ba^{2+})} - \frac{1}{2}\lambda^\circ_{(Ba^{2+})} + \lambda^\circ_{(Cl^-)} - \lambda^\circ_{(Cl^-)}$

On rearranging, we get

$$\Lambda^\circ_m (NH_4OH) = \left[\lambda^\circ_{(NH_4^+)} + \lambda^\circ_{(Cl^-)}\right] + \left[\frac{1}{2}\lambda^\circ_{(Ba^{2+})} + \lambda^\circ_{(OH^-)}\right] - \left[\frac{1}{2}\lambda^\circ_{(Ba^{2+})} + \lambda^\circ_{(Cl^-)}\right]$$

$$= \Lambda^\circ_m (NH_4Cl) + \frac{1}{2}\Lambda^\circ_m (Ba(OH)_2) - \frac{1}{2}\Lambda^\circ_m (BaCl_2)$$

$$= 129.8 + \frac{1}{2} \times 523.28 - \frac{1}{2} \times 280$$

$$= \mathbf{251.44 \text{ S cm}^2 \text{ mol}^{-1}}.$$

S16. In the case of CH_3COOH, which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

In the case of strong electrolyte such as CH_3COONa, the number of ions remains the same but the interionic attraction decreases.

S17. According to Kohlrausch's law,

$$\Lambda_m^\circ(NH_4OH) = \lambda^\circ_{(NH_4^+)} + \lambda^\circ_{(OH^-)}$$

Add and subtract $\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$ in R.H.S.

$$= \lambda^\circ_{(NH_4^+)} + \lambda^\circ_{(OH^-)} + \lambda^\circ_{(Cl^-)} - \lambda^\circ_{(Cl^-)} + \lambda^\circ_{(Na^+)} - \lambda^\circ_{(Na^+)}$$

$$= \lambda^\circ_{(NH_4^+)} + \lambda^\circ_{(Cl^-)} + \lambda^\circ_{(Na^+)} + \lambda^\circ_{(OH^-)} - \lambda^\circ_{(Na^+)} - \lambda^\circ_{(Cl^-)}$$

$$= \Lambda_m^\circ(NH_4Cl) + \Lambda_m^\circ(NaOH) - \Lambda_m^\circ(NaCl)$$

$$= 129.8 + 248.1 - 126.4 = 251.5$$

Thus, $\Lambda_m^\circ(NH_4OH) = \mathbf{251.5\ ohm^{-1}\ cm^2\ mol^{-1}}$.

S18. Degree of dissociation is given by $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m}$.

Step 1: To calculate $\Lambda^\circ_{m\,(CH_2COOH)}$.

$$\Lambda^\circ_m(CH_3COOH) = \lambda^\circ_{(CH_3COO^-)} + \lambda^\circ_{(H^+)}$$

$$= 40.9 + 349.8 = 390.7\ ohm^{-1}\ cm^2\ mol^{-1}.$$

Step 2: Calculation of degree of dissociation.

At $C = 0.1\ M$, $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m} = \dfrac{5.20}{390.7} = 0.013$ or **1.3%**.

At $C = 0.001\ M$, $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m} = \dfrac{49.2}{390.7} = 0.125$ or **12.5%**.

S19.

$$\Lambda^\circ_{(AgCl)} = \lambda^\circ_{(Ag^+)} + \lambda^\circ_{(Cl^-)}$$

$$= 53.8 + 65.3 = 119.1\ \Omega^{-1}\ cm^2\ mol^{-1}$$

Now solubility ($mol\ L^{-1}$)

$$= \frac{\kappa \times 1000}{\Lambda^\circ_m} = \frac{1.24 \times 10^{-6} \times 1000}{119.1}$$

$$= 1.04 \times 10^{-5}\ mol\ L^{-1}$$

$$= 1.04 \times 10^{-5} \times 143.5 = 1.49 \times 10^{-3}\ gL^{-1}.$$

S20.

$$\kappa_{solution} = \kappa_{AgCl} + \kappa_{water}$$

$$\therefore \quad \kappa_{AgCl} = \kappa_{solution} - \kappa_{water}$$

$$= (2.68 - 0.86) \times 10^{-6} = 1.82 \times 10^{-6}$$

Calculation of Λ°_m for AgCl using Kohlrausch law

$$\Lambda^\circ_m(\text{AgCl}) = \Lambda^\circ_m(\text{AgNO}_3) + \Lambda^\circ_m(\text{HCl}) - \Lambda^\circ_m(\text{HNO}_3)$$

$$= 133 + 426 - 421 = 138.0\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Now, solubility

$$= \frac{\kappa_{\text{AgCl}} \times 1000}{\Lambda^\circ_m(\text{AgCl})} = \frac{1.82 \times 10^{-6} \times 1000}{138.0}$$

$$= 1.32 \times 10^{-5}\ \text{mol L}^{-1}$$

Solubility in gL^{-1}

$$= 1.32 \times 10^{-5} \times 143.5 = \mathbf{1.89 \times 10^{-3}\ gL^{-1}}.$$

S21.

$$\Lambda_m^c = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{7.896 \times 10^{-5}(\text{S cm}^{-1}) \times 1000(\text{cm}^3 L^{-1})}{0.00241(\text{mol} L^{-1})}$$

$$= 32.76\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

$$K_a = \frac{c\alpha^2}{1-\alpha} = \frac{0.00241 \times (8.4 \times 10^{-2})^2}{1 - 0.084} = \mathbf{1.86 \times 10^{-5}}.$$

S22. It is defined as the conducting power of all the ions produced by one gram mole of an electrolyte in a solution. It is denoted by Λ_m.

$$\Lambda_m = \frac{\kappa}{C} \times 1000\ \text{S cm}^2\ \text{mol}^{-1}$$

Where 'k' is electrolytic conductivity of solution and 'C' is concentration of the solution expressed in mol L^{-1} (or mol dm^{-3}). The unit of Λ_m is $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ or $\text{S cm}^2\ \text{mol}^{-1}$.

To find out molar conductivity, use the following equation:

$$\Lambda_m = \frac{1000\,\kappa}{M} = \frac{1000\ \text{cm}^3 \times 4.96 \times 10^{-2}\ \text{S cm}^{-1}}{0.4\,\text{M}}$$

$$\Lambda_m = \frac{496}{4} = 124\ \text{S cm}^2\ \text{mol}^{-1}.$$

S23. Specific conductivity is defined as conductivity of solution when electrodes are unit distance apart and have area of cross-section equal to unity, i.e., when cell constant is equal to unity.

To calculate equivalent conductance, using the following relation and substituting the values, we get

$$\Lambda_{eq} = \frac{1000\kappa}{N} = \frac{1000\,cm^3 \times 2.4 \times 10^{-2}\,S\,cm^{-1}}{0.12}$$

$$= \frac{2400}{12} = 200\ S\ cm^2\ eq^{-1}$$

S24. Conductivity is defined as the conductance of a solution of 1cm length and having 1 sq cm as the area of cross section.

It is denoted by Kappa(κ).

Conducting (k) is reciprocal of resistivity

$$\kappa = \frac{1}{\rho} \text{ unit is Ohm}^{-1}\ cm^{-1}$$

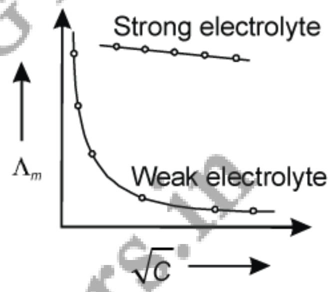
Molar Conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution. It is denoted by λm.

$$\lambda_m = \frac{\kappa \times 1000}{M},$$

where k is conducting power and M is molarity.

S25. Molar conductivity increases sharply for weak electrolyte with decrease in concentration as shown in diagram because both number of ions as well as mobility of ions increases with dilution, *i.e.*, decrease in concentration.

In case of strong electrolyte, Λ_m increases slightly on dilution because number of ions do not increase much whereas mobility of ions increases.



S26. Conductivity (κ) = 0.0058 S cm^{-1}

Molar mass of $BaCl_2$ = 137 + 2 × 35.5 = 208 g mol^{-1}

Number of moles of $BaCl_2$ in 200 cm^3 of solution

$$= \frac{1}{208} \text{ mol}$$

Volume of solution that contains 1 mol of $BaCl_2$(V)

$$= 200 \times 208\ cm^3$$

Molar conductivity, $\Lambda_m = \kappa \mathbf{V}$

or $\Lambda_m = 0.0058 \times 200 \times 208$

$= \mathbf{241.28\ S\ cm^2\ mol^{-1}}$.

Equivalent mass of $BaCl_2$

$$= \frac{\text{Molecular mass}}{2} = \frac{208}{2} = 104$$

Volume of solution containing one equivalent (*i.e.*, 104 g) of $BaCl_2$)

$$= 200 \times 104 \text{ cm}^3$$

Equivalent conductivity,

$$\Lambda_{eq} = 0.0058 \text{ S cm}^{-1} \times 200 \times 104 \text{ cm}^3$$

$$= \mathbf{120.6 \text{ S cm}^2 \text{ equivalent}^{-1}}.$$

S27. Step 1: Calculation of cell constant.

$$\text{Conductivity of } 0.02 \text{ M KCl} = 2.768 \times 10^{-3} \times \Omega^{-1} \text{ cm}^{-1}$$

$$\text{Resistance} = 164 \text{ ohm}$$

We know, $\text{Conductivity } (\kappa) = \frac{1}{R} \times \text{Cell constant } (G^*)$

or Cell constant $(G^*) = R \times \kappa = 164 \times 2.768 \times 10^{-3}$

$$= \mathbf{0.4539 \text{ cm}^{-1}}.$$

Step 2: Calculation of conductivity of $AgNO_3$.

$$\text{Conductivity } (\kappa) = \frac{1}{R} \times G^* = \frac{1}{78.50} \times 0.4539$$

$$= \mathbf{0.00578 \text{ ohm}^{-1} \text{ cm}^{-1}}.$$

Step 3: Calculation of Λ_m of 0.05 M $AgNO_3$.

$$\Lambda_m = \frac{1000\,\kappa}{M} = \frac{1000 \times 0.00578}{0.05}$$

$$= \mathbf{115.6 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}.$$

S28. Step 1: Calculation of conductivity (κ) of 0.01 M acetic acid.

$$\kappa = \frac{1}{R} \times (\text{cell constant}) = \frac{1}{2220\,\Omega} \times 0.366 \text{ cm}^{-1}$$

$$= 1.648 \times 10^{-4} \, \Omega^{-1} \text{ cm}^{-1}.$$

Step 2: Calculation of Λ_m.

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.648 \times 10^{-4} \times 1000}{0.01}$$

$$= 16.48 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}.$$

Step 3: Calculation of $\Lambda^{\ominus}_m$.

$$\Lambda^{\ominus}_{m\,(CH_3COOH)} = \lambda^{\ominus}_{H^+} + \lambda^{\ominus}_{CH_3COO^-}$$

$$= 349.1 + 40.9 = 390 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}.$$

Step 4: Calculation of dissociation of acetic acid.

$$\alpha = \frac{\Lambda_m}{\Lambda^{\ominus}_m} = \frac{16.48\,\Omega^{-1}\,cm^2\,mol^{-1}}{390\,\Omega^{-1}\,cm^2\,mol^{-1}} = 0.0422.$$

Step 5: Calculation of dissociation constant (K). Dissociation of acetic acid can be represented as

	$CH_3COOH \rightleftharpoons$	CH_3COO^-	$+ H^+$
Initial conc.	c mol L^{-1}	—	—
Equilibrium conc.	$c - c\alpha$	$c\alpha$	$c\alpha$

Dissociation constant K is given as K

$$= \frac{c\alpha \times c\alpha}{c - c\alpha} = \frac{c\alpha^2}{1-\alpha}$$

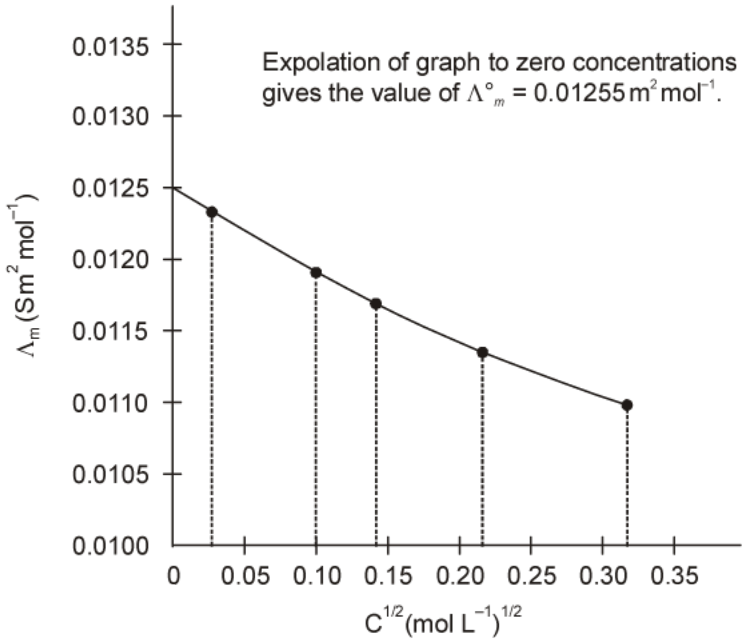
Substituting the value of c (0.01 M) and α (0.0422).

$$\therefore \quad K = \frac{0.01 \times (0.0422)^2}{1 - 0.0422} = \mathbf{1.86 \times 10^{-5}}.$$

S29.

Concentration (C) (M0l L^{-1})	*$C^{1/2}$ ($Mol^{1/2}$ $L^{1/2}$)*	*k (S m^{-1})*	$\Lambda_m = \frac{\kappa\,(S\,m^{-1})}{10^3 \times M\,(mol\,L^{-1})}$
0.001	0.031	1.237×10^{-2}	$\frac{1.237 \times 10^{-2}}{10^3 \times 0.001} = 0.01237$
0.010	0.1	11.85×10^{-2}	$\frac{11.85 \times 10^{-2}}{10^3 \times 0.01} = 0.0118$
0.020	0.141	23.15×10^{-2}	$\frac{23.15 \times 10^{-2}}{10^3 \times 0.02} = 0.0115$
0.050	0.224	55.53×10^{-2}	$\frac{55.53 \times 10^{-2}}{10^3 \times 0.05} = 0.0111$
0.10	0.316	106.74×10^{-2}	$\frac{106.74 \times 10^{-2}}{10^3 \times 0.1} = 0.0107$

Plot between Λ_m and $C^{1/2}$



Date: 22/10/2021

Q1. How many coulombs of electricity are required for reduction of 1 mol of Al^{3+} to Al?

Q2. How many coulombs of electricity are required for reduction of 1 mol of Cu^{2+} to Cu?

Q3. How many coulombs of electricity are required for reduction of 1 mol MnO_4^- to Mn^{2+} ?

Q4. How many coulombs of electricity are required for oxidation of 1 mol of FeO to Fe_2O_3?

Q5. How many coulombs of electricity are required for oxidation of 1 mol of H_2O to O_2?

Q6. What mass of Zn (II) ion will be reduced by 1 mole of electrons?

Q7. From the following data calculate the value of the Avogadro constant. Charge of an electron $= 1.6 \times 10^{-19}$ coulomb. (1 faraday = 96500 coulombs).

Q8. From the values of 1 faraday and Avogadro constant, show that 1 faraday may be called 1 mole of electricity.

Q9. A metal wire carries a current of 1 ampere. How many electrons pass a point in the wire in 1 second?

Q10. For how long a current of 1.5 ampere has to be passed through the electrolyte in order to deposit 1 mole of Al when the electrode reaction is

$$Al^{+3} + 3e^- \longrightarrow Al \text{ (At. mass of Al = 27)}$$

Q11. Calculate the mass of hydrogen evolved by passing a current of 0.5 ampere for 40 minutes through acidified water.

Q12. The electrolysis of a metal salt solution was carried out by passing a current of 4 amp for 45 minutes. It resulted in deposition of 2.977 g of a metal. If atomic mass of the metal is 106.4 g mol^{-1}, calculate the charge on the metal cation.

Q13. How much electricity is required in coulomb for the oxidation of

(a) 1 mol of H_2O to O_2 (b) 1 mol of FeO to Fe_2O_3.

Q14. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode? (At. mass of Ni = 58.7 u)

Q15. How many faradays of charge are required to convert

(a) 1 mole of $MnO_4^{\ominus}$ to $Mn^{2\oplus}$ ions (b) 1 mole of $Cr_2O_7^{2\ominus}$ to $Cr^{3\oplus}$

Q16. How many electrons are lost and gained by 2 g of Cl^- ions and 1 g of Zn^{2+} ions as the result of electrolysis respectively? (Cl = 35.5; Zn = 65)

Q17. How much copper is deposited on the cathode of an electrolytic cell if a current of 5 ampere is passed through a solution of copper sulphate for 45 minutes? [Cu = 63.5 g mol^{-1}, 1 F = 96500 C mol^{-1}]

Q18. How much time would it take in minutes to deposit 1.18 g of metallic copper on a metal object when a current of 2.0 A is passed through the electrolytic cell containing $Cu^{2\oplus}$ ions? [Cu = 63.5 g mol^{-1}, 1 F = 96,500 C mol^{-1}]

Q19. Calculate the quantity of ferrous and ferric ions that would be deposited by 1 faraday. (Fe = 56)

Q20. 0.2864 g of Cu was deposited on passage of a current of 0.5 ampere for 30 minutes through a solution of copper sulphate. What is the electrochemical equivalent of copper? (1 F = 96500 coulombs)

Q21. Three electrolytic cells *A*, *B*, *C*, containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell *B*. How long did the current flow? What mass of copper and of zinc were deposited? At. masses of Ag, Cu, Zn are 108 u, 63.5 u and 65 u respectively.

Q22. A current of 1.70 amp was passed through 300 ml of 0.160 M solution of $ZnSO_4$ for 230 sec with a current efficiency of 90%. Find the molarity of zinc (Zn^{+2}) after the deposition of zinc. Assume that volume of solution remains constant during electrolysis.

Q23. A current of 4 amp was passed for 1.5 hours through a solution of copper sulphate when 3.0 g of copper was deposited. Calculate the current efficiency.

Q24. How much electricity in terms of Faraday is required to produce
(a) 20.0 g of Ca from molten $CaCl_2$ (b) 40.0 g of Al from molten Al_2O_3.

Q25. How much charge is required for the following reduction of
(a) 1 mol of Al^{3+} to Al. (b) 1 mol of Cu^{2+} of Cu (c) 1 mol of MnO^{4-} to Mn^{2+}

Q26. Silver is electrodeposited on a metallic vessel of surface area 900 cm^2 by passing a current of 0.5 ampere for 2 hours. Calculate the thickness of the silver deposited. Given the density of silver as 10.50 g/cc (Atomic mass of Ag =108 u).

Q27. How many coulombs of electricity are required for
(a) Oxidation of 90 g of water. (b) Reduction of 0.2 mols of CrO_7^{2-} to Cr^{3+}.
(c) Complete reduction of MnO_4^- ions in 500 ml of 0.5 M solution to Mn^{2+} ions.

Date: 22/10/2021

S1. Reduction of 1 mol of Al^{3+} to Al

$Al^{3+} + 3e^- \longrightarrow Al$

Reduction of 1 mol of Al^{3+} requires $= 3 \times 96500$ C

$= 2.895 \times 10^5$ C

S2. Reduction of 1 mol of Cu^{2+} to Cu

$Cu^{2+} + 2e^- \longrightarrow Cu$

Reduction of 1 mol of Cu^{2+} requires $= 2 \times 96500$ C

$= 1.93 \times 10^5$ C

S3. Reduction of 1 mol MnO_4^- to Mn^{2+}

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

Reduction of 1 mol of MnO_4^- requires $= 5 \times 96500$ C

$= 4.825 \times 10^5$ C

S4. Oxidation of 1 mol of FeO to Fe_2O_3

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

Oxidation of 1 mol of Fe^{2+} require $= 1 \times 96500$ C

$= 96500$ C

S5. Oxidation of H_2O to O_2

$2H_2O \rightleftharpoons 4H^+ + O_2 + 4e^-$

Oxidation of 2 mol of H_2O require $= 4 \times 96500$ C

Oxidation of 1 mol of H_2O requires $= 2 \times 96500$ C

$= 1.93 \times 10^5$ C

S6. 1 mole of electrons means 1 faraday of electricity

$Zn^{2\oplus} (aq) + 2e^{\ominus} \longrightarrow Zn\ (s)$
(65 g)

2 faradays of charge deposit = 65 g of zinc

1 faraday of charge deposit = 32.5 g of zinc.

S7. Since 1 faraday, i.e. 96500 coulombs, is the charge of 1 mole of electrons, i.e., Av. no. of electrons.

$$\therefore \quad \text{Av. constant} = \frac{\text{charge of 1 mole of electrons}}{\text{charge of one electron}}$$

$$= \frac{96500}{1.6 \times 10^{-19}} = 6.03 \times 10^{23}$$

S8. Since 1 faraday = 96500 coulombs

$$\therefore \quad \frac{1\,\text{F}}{\text{Av. no.}} = \frac{96500}{6 \cdot 022 \times 10^{23}}$$

$$= 1.6 \times 10^{-19} \text{ coulomb}$$

= charge of an electron

$$\therefore \quad 1\text{ F} = \text{charge of an electron} \times \text{Av. no.}$$

Since 1 F of electricity is the charge of Av. no. of electrons, 1 faraday may be called 1 mole of electricity.

S9. Charge in coulomb = current in ampere $\times$ time(s)

$$= 1 \times 1 = 1$$

Since 1 F (96500 coulombs) of electricity is carried out by 1 mole of electrons, i.e., 6.022×10^{23} electrons, therefore, 1 coulomb shall involve $6.022 \times 10^{23}/96500$, *i.e.*, 6.24×10^{18} electrons. Thus, 6.24×10^{18} electrons pass a point in the wire in 1 second.

S10. Step 1: Calculation of number of coulomb required.

From the electrode reaction, it is clear that

For depositing one mole of Al atoms the electrons required = 3 mol

Charge on 3 mol of electrons = 3×96500 C

Now 1 mol of Al = 27 g

$\therefore$ Deposition of 27 g of Al requires charge

$$= \frac{3 \times 96500}{27} \times 1.0 = \mathbf{10722.2\,C}. \quad \text{... (i)}$$

Step 2: Calculation of time

Current strength =1.5 amp.

Let the time required by t sec

$$\therefore \quad \text{No. of coulombs} = 1.5 \times t\,\text{C} \quad \text{... (ii)}$$

Equate (i) and (ii), $1.5\,t = 10722.2$

$$t = \frac{10722.2}{1.5} = 7148 \text{ sec}$$

$$= \frac{7148}{60 \times 60} = \mathbf{1.98 \ hrs}.$$

S11. Current strength = 0.5 amp.

Time = 40 minutes = 40×60 = 2400 sec.

Total quantity of electricity passed = 0.5×2400 = 1200 coulombs

Now the electrode reaction is $H^+ + e^- \longrightarrow \frac{1}{2} H_2$

Thus, formation of $\frac{1}{2}$ of hydrogen requires electrons = 1 mol.

$\therefore$ Formation of 1.008 g of H_2 requires charge = 96500 C.

Now 96500 coulombs of electricity produces hydrogen = 1.008 g

1200 coulombs of electricity will produce hydrogen

$$= \frac{1.008 \times 1200}{96500} = \mathbf{0.0126 \ g}.$$

S12. Let the charge on the metal ion be n^+

$\therefore$ The reduction half reaction is

$$\underset{(1 \text{ mol})}{M^{n+}} + \underset{(n \text{ mol})}{ne^-} \longrightarrow \underset{(106.4\text{g})}{M}$$

Quantity of electricity required for depositing 106.4 g of metal = $n \times 96500$ C

Quantity of electricity required for depositing of metal

$$= \frac{n \times 96500 \times 2.977}{106.4} = n \times 2700 \text{ C}$$

Quantity of electricity actually passed

$$= 4 \times 45 \times 60 = 10800 \text{ C}$$

Now, $10800 = n \times 2700$

$\therefore$ $n = \frac{10800}{2700} = 4$

Hence, charge on metal ion = **+4**.

S13. (a) The reaction involved is

$$2H_2O \longrightarrow O_2 + 4H^+ + 4\bar{e}$$

Electricity required for oxidation of 1 mol of

$$H_2O = 2\,F \quad \text{or} \quad 2 \times 96500 = \mathbf{193000\,C}.$$

(b) The electrode reaction is

$$\overset{(+2)}{2\,FeO} \longrightarrow \overset{(+3)}{Fe_2O_3} + 2\bar{e}$$

Electricity required for oxidation of 1 mol of

$$FeO = \mathbf{1\,F \quad or \quad 96500\,C}.$$

S14. Quantity of electricity passed

$$= 5\,(A) \times 20 \times 60\,(s) = 6000\,C$$

The electrode reaction is $Ni^{2+} + 2e \longrightarrow \underset{58.7\,g}{Ni}$

$2 \times 96500\,C$ of electricity produce $Ni = 58.7\,g$

6000 C of electricity produce $\quad Ni = \dfrac{58.7 \times 6000}{2 \times 96500} = \mathbf{1.825\,g}$.

S15. (a) $MnO_4^{\ominus}$ to $Mn_2^{\oplus}$ means $Mn^{7\oplus} + 5e^{\ominus} \longrightarrow Mn^{2\oplus}$

5 faradays of charge is required.

(b) $Cr_2O_7^{2\ominus}$ to $Cr^{3\oplus}$ means $2Cr^{6\oplus} + 6e^{\ominus} \longrightarrow 2Cr^{3\oplus}$

Thus, 6 faradays of charge is required.

S16.

$$\text{Number of equivalents of } Cl^- \text{ ions} = \frac{\text{weight}}{\text{eq. wt.}}$$

$$= \frac{2}{35.5}$$

$$\text{Number of equivalent of } Zn^{2+} \text{ ions} = \frac{1}{65/2} = \frac{2}{65}.$$

Now, 1 mole (1 F) of electric charge discharge 1 equivalent of matter.

$$\text{Mole of electric charge involved in case of } Cl^- = \frac{2}{35.5}.$$

$$\text{Mole of electric charge involved in case of } Zn^{2+} = \frac{2}{65}.$$

As 1 mole of electric charge corresponds to Av. no. of electrons, thus,

$$\text{no. of electrons lost by } Cl^- = \frac{2}{35.5} \times 6.022 \times 10^{23} = \mathbf{3.39 \times 10^{22}}$$

$$\text{and no. of electrons gained by } Zn^{2+} = \frac{2}{65} \times 6.022 \times 10^{23} \quad = \mathbf{1.85 \times 10^{22}}$$

S17. $Cu^{2\oplus}(aq) + 2e^{\ominus} \longrightarrow Cu(s)$

Using the following relation and substituting the values, we get

$$m = Z \times I \times t = \frac{63.5}{2 \times 96500} \times 5\text{A} \times (45 \times 60)\,s$$

or $$m = \frac{857250}{193000} = \frac{85725}{19300} = 4.44\,\text{g}$$

Copper deposited = 4.44 g

S18. $Cu^{2\oplus} + 2e^{\ominus} \longrightarrow Cu(s)$

Using the following relation and substituting the values, we get

$$m = Z \times I \times t$$

or $$1.18 = \frac{63.5}{2 \times 96500} \times 2 \times t$$

or $$t = \frac{1.18 \times 2 \times 96500}{2 \times 63.5} = 1793.23\text{ s}$$

$$= \frac{1793.23}{60} = 29.88\text{ minutes}$$

Thus, time taken = 29.88 minutes.

S19. 1 mole of electricity (*i.e.*, 1 faraday) produces 1 eq. of matter.

Mole of electric charge = 1 faraday

$\therefore$ $$\text{wt. of } Fe^{2+} = 1 \times \frac{56}{2} = 28\text{ g} \qquad [\text{wt.} = \text{mole of electricity} \times \text{eq. wt.}]$$

and $$\text{wt. of } Fe^{3+} = 1 \times \frac{56}{3} = 18.6\text{ g}$$

S20. Electrochemical equivalent (z) is defined as the weight of the substance deposited by the passage of 1 coulomb of electricity.

$\therefore$ $$z = \frac{\text{wt. of Cu deposited}}{\text{charge in coulombs}}$$

$$= \frac{\text{wt. of Cu}}{\text{current in ampere} \times \text{time in seconds}}$$

$$= \frac{0.2864}{0.5 \times 30 \times 60} = 0.00032 \text{ g/coulomb}$$

S21. Electrode reaction involving deposition of Ag

$$Ag^{+} + e^{-} \longrightarrow \underset{108\,g}{Ag}$$

Electricity required for deposition of 1.45 g of

$$Ag = \frac{96500 \times 1.45}{108} = 1295.6\,C$$

Now, $1295.6 = 1.5\,(A) \times t\,(s)$

$\therefore$ $t = \frac{1295.6}{1.5} = 863.73\,s = \frac{863.73}{60}$ min

= **14.4 min**.

Reaction for deposition of Cu and Zn are respectively

$$Cu^{2+} + 2e^{-} \longrightarrow \underset{63.5\,g}{Cu} \qquad Zn^{2+} + 2e^{-} \longrightarrow \underset{65\,g}{Zn}$$

Copper deposited by 1295.6 C

$$= \frac{63.5 \times 1295.6}{2 \times 96500} = \mathbf{0.426\,g}.$$

Zn deposited by 1295.6 C

$$= \frac{65 \times 1295.6}{2 \times 96500} = \mathbf{0.436\,g}.$$

S22. Calculation of theoretical amount of zinc

Quantity of electricity = 1.70 A $\times$ 230 sec = 391 C

The electrode reaction is

$$Zn^{2+} + \underset{(2\text{ mol})}{2e^{-}} \longrightarrow \underset{(1\text{ mol})}{Zn}$$

2×96500 C of electricity produces Zn = 1 mol

391 C of electricity produces

$$Zn = \frac{391}{2 \times 96500}\text{ mol} = 0.0020\text{ mol}$$

Since current efficiency is 90%

$\therefore$ Amount of Zn actually deposited

$$= \frac{0.0020}{100} \times 90 = 0.0018 \text{ mol}$$

Amount of Zn^{2+} ions initially present in 300 mL of solution

$$= V_{(mL)} \times M \times 10^{-3} \text{ mol}$$

$$= 300 \times 0.160 \times 10^{-3} \text{ mol} = 0.048 \text{ mol}$$

Amount of Zn^{2+} ion left after deposit in 300 ml of solution

$$= 0.048 - 0.0018 = 0.0462 \text{ mol}$$

Molarity of Zn^{2+} after deposition

$$= \frac{0.0462}{300} \times 1000 = \mathbf{0.154\,M}.$$

S23. The current efficiency is given by the relation

$$\text{Current efficiency} = \frac{\text{Mass of metal actually deposited}}{\text{Theoretical mass that can be deposited}}$$

Calculation of theoretical mass $I = 4$ amp

$t = 1.5$ hr.

Quantity of electricity passed $= 4 \times 1.5 \times 60 \times 60\, C$

$$\underset{}{Cu^{2+}} + \underset{(2\text{ mol})}{2e^-} \longrightarrow \underset{(63.5)}{Cu}$$

$2 \times 96500\, C$ of electricity produces Cu = 63.5 g

$4 \times 1.5 \times 60 \times 60\, C$ electricity produces Cu

$$= \frac{63.5 \times 4 \times 1.5 \times 60 \times 60}{2 \times 96500} \text{ g} = 7.106 \text{ g}$$

Mass of Cu actually obtained = 3 g

$\therefore$ Current efficiency $= \frac{3}{7.106} =$ **0.422** or **42.2%**.

S24. (a) The electrode reaction is

$$Ca^{2+} + 2e^- \longrightarrow \underset{40\text{ g}}{Ca}$$

Electricity required for production of 40 g of Ca = 2 F

Electricity required for production of 20 g of Ca = 1 F

or 96500 C

(b) The electrode reaction is

$$Al^{3+} + 3e^- \longrightarrow \underset{27\,g}{Al}$$

Electricity required for producing of 27g of Al = 3F

Electricity required for producing of 40 g of

$$Al = \frac{3F \times 40}{27} = \frac{3 \times 96500 \times 40}{27}$$

$$= \mathbf{4.4\,F} \quad \textbf{or} \quad \mathbf{428888.9\,C}.$$

S25. (a) The electrode reaction is

$$Al^{3+} + 3e^- \longrightarrow Al$$

Quantity of charge required for reduction of

$$1 \text{ mol of } Al^{3+} = 3\,F = 3 \times 95600\,C = 289500\,C$$

(b) The electrode reaction is

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Charge required for reducing 1 mol of

$$Cu^{2+} = 2\,F = 2 \times 96500\,C = 193000\,C$$

(c) The reaction involved is

$$MnO_4^- + 5e^- \longrightarrow Mn^{2+} \quad \text{(O.N. of Mn changes from + 7 to + 2)}$$

Charge required for reduction of 1 mol of MnO_4^- = 5 F

$= 5 \times 96500\,C = 482500\,C.$

S26. Calculation the mass of Ag deposited

The electrode reaction is $Ag^+ + e^- \longrightarrow Ag$

The quantity of electricity passed = Current $\times$ Time

$= 0.5\ \text{(amp.)} \times 2 \times 60 \times 60\ \text{(sec)} = 3600\,C.$

From the electrode reaction, it is clear that

96500 C of electricity deposit Ag = 108 g

3600 C of electricity deposit Ag = $\frac{108}{96500} \times 3600 = 4.03\,g$

Calculation of thickness

Let the thickness of deposit be x cm.

$\therefore$ Mass = Volume $\times$ density

= Area $\times$ thickness $\times$ density ($\because$ Volume = Area $\times$ thickness)

$\therefore$ $4.03\,g = 900\,(cm^2) \times x\,(cm) \times 10.5\,(g\ cm^{-3})$

$\therefore$ $x = \dfrac{4.03}{900 \times 10.5}\,cm$ = $\mathbf{4.26 \times 10^{-4}\ cm}$.

S27. (a) $2H_2O \rightleftharpoons 4H^+ + O_2 + 4e^-$

36 g 4 mol

Oxidation of 36 g water require electricity

$= 4 \times 96500\,C$

Oxidation of 90 g water require electricity

$= \dfrac{4 \times 96500 \times 90}{36} = \mathbf{9.65 \times 10^5\ C}$.

(b) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

1mol 6 mol

1 mol of $Cr_2O_7^{2-}$ ions require electricity

$= 6 \times 96500\,C$

0.2 mol of $Cr_2O_7^{2-}$ ions require electricity

$= 6 \times 96500 \times 0.2 = \mathbf{19300\ C}$.

(c) Moles of MnO_4^- in 500 ml

$= 500 \times 10^{-3} \times 0.5 = 0.25\,mol$

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

1 mol 5 mol

1 mol of MnO_4^- require electricity

$= 5 \times 96500\,C$

0.25 mol of MnO_4^- require electricity

$= 5 \times 96500\,C \times 0.25 = 120625\,C$.

Date: 22/10/2021

Q1. Unlike dry cell, the mercury cell has a constant cell potential throughout its life. Why?

Q2. What advantage do the fuel cells have over primary and secondary batteries?

Q3. Write the cell reaction of a lead storage battery when it is discharged. How does the density of the electrolyte change when the battery is discharged?

Q4. What is a primary cell? Give an example.

Q5. State two advantages of H_2 — O_2 fuel cell over ordinary cells.

Q6. What is name of cell which were used in Apollo space program?

Q7. Why does a dry cell become dead after a long time, even if it has not been used?

Q8. What is the role of $ZnCl_2$ in a dry cell?

Q9. How does concentration of sulphuric acid change in lead storage battery when current is drawn from it?

Q10. What are fuel cells? Write the electrode reactions of a fuel cell which uses the reaction of hydrogen with oxygen.

Q11. What type of a battery is lead storage battery? Write the anode and the cathode reactions and the overall reactions occurring in a lead storage battery.

Q12. Write the cell reactions which occur in lead storage battery (a) when the battery is in use and (b) when the battery is on charging.

Q13. What are secondary cells? Give the anode and cathode reaction of Nckel-Cadmium storage cell.

Q14. What is the Mercury cell?

Q15. Describe the composition of anode and cathode in a mercury cell. Write the electrode reactions for this cell.

Date: 22/10/2021

S1. Because ions are not involved in the overall cell reaction of mercury cells.

S2. Primary batteries contain a limited amount of reactants and are discharged when the reactants have been consumed. Secondary batteries can be recharged but take a long time to recharge. Fuel cell runs continuously as long as the reactants are supplied to it and products are removed continuously.

S3.
$$Pb + PbO_2 + 2H_2SO_4 \xrightarrow{\text{Discharge}} 2PbSO_4 + 2H_2O$$

Density of electrolyte decreases because water is formed and sulphuric acid is consumed as the product during discharge of the battery.

S4. A cell in which the reaction occurs only once and after use over a time period becomes dead.

For example: Leclanche cell or dry cell.

S5. (a) It does not create pollution.

(b) It has much higher efficiency.

S6. Hydrogen-oxygen fuel cell.

S7. A dry cell becomes dead after a long time because the acidic NH_4Cl corrodes the zinc container.

S8. $ZnCl_2$ combines with the NH_3 produced to form the complex $[Zn(NH_3)_2Cl_2]$ otherwise the pressure developed due to NH_3 would crack the seal of the cell.

S9. Concentration of sulphuric acid decreases.

S10. Those cells in which chemical energy of fuel is converted into electrical energy are called fuel cells.

Electrode reactions:

At anode: $[H_2(g) + 2OH^{\ominus}(aq) \longrightarrow 2H_2O(l) + 2e^{\ominus}] \times 2$ ... (i)

At cathode: $O_2(g) + 2H_2O(l) + 4e^{\ominus} \longrightarrow 4OH^{\ominus}(aq)$ ... (ii)

Net cell reaction: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

S11. It is a secondary cell.

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

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

Overall reaction: $Pb(s) + PbO_2(s) + 2H_2SO_4 \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

S12. (a) When the battery is in use

$$Pb\ (s) + PbO_2\ (s) + 2H_2SO_4\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$$

At anode: $Pb(s) + SO_4^{2\ominus}\ (aq) \longrightarrow PbSO_4\ (s) + 2e^{\ominus}$

At cathode: $PbO_2\ (s) + SO_4^{2\ominus}\ (aq) + 4H^{\oplus}\ (aq) + 2e^{\ominus} \longrightarrow PbSO_4\ (s) + 2H_2O\ (l)$

(b) When the battery is on charging

$$2PbSO_4\ (s) + 2H_2O_4\ (l) \longrightarrow Pb\ (s) + PbO_2\ (s) + 2H_2SO_4(aq)$$

At anode: $PbSO_4\ (s) + 2e^{\ominus} \longrightarrow Pb(s) + SO_4^{2\ominus}\ (aq)$

At cathode: $PbSO_4\ (s) + 2H_2O\ (l) \longrightarrow PbO_2\ (s) + SO_4^{2\ominus}\ (aq) + 4H^{\oplus}\ (aq) + 2e^{\ominus}$

S13. Secondary cells are those cells which can be recharged by passing a direct current through them and can be used again as a source of electric current.

Nickel-Cadmium storage cell:

At anode:

$$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^- \quad \text{(Oxidation)}$$

At cathode:

$$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^- \quad \text{(Reduction)}$$

overall $Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$

S14. These cells are new type of dry cell suitable for low current devices like hearing aids, cameras

Anode $\longrightarrow$ Zinc-mercury amalgam

Cathode $\longrightarrow$ Carbon rod and Paste of HgO

Electrolyte $\longrightarrow$ KOH + ZnO Paste

Net reaction:

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The e.m.f. of cell is independent of the concentration of KOH.

S15. It consists of zinc mercury amalgam as anode, a paste of HgO and carbon as cathode.

The electrolyte is paste of KOH and ZnO.

Electrode reactions are given as under:

At anode: $Zn(Hg) + 2OH^{\ominus} \longrightarrow ZnO\ (s) + H_2O(l) + 2e^{\ominus}$

At cathode: $HgO\ (s) + H_2O + 2e^{\ominus} \longrightarrow Hg(l) + 2OH^{\ominus}$

Net reaction: $Zn(Hg) + HgO\ (s) \longrightarrow ZnO\ (s) + Hg(l)$

Date: 22/10/2021

Q1. **Give reasons for the following:**
- **(a)** **Rusting of iron is quicker in saline water than in ordinary water.**
- **(b)** **Aluminium metal cannot be produced by the electrolysis of aqueous solution of aluminium salt.**

Q2. **What are antirust solutions? Give one example.**

Q3. **What is the chemical formula of rust?**

Q4. **What is the effect of carbon dioxide in water on corrosion?**

Q5. **Can tin coating on iron act as sacrificial anode in protecting iron against corrosion?**

Date: 22/10/2021

S1. (a) Rusting of iron is quicker in saline water than in ordinary water because conductivity of saline water is more than that of ordinary water.

(b) Aluminium metal is highly reactive and cannot be reduced easily. As compared to aluminium ion, water is reduced easily.

S2. The antirust solutions are those which retard the corrosion of iron. For example, solutions of alkaline phosphates.

S3. The chemical formula of rust is $Fe_2O_3 \cdot xH_2O$.

S4. The presence of carbon dioxide in water increases rusting of iron. Water containing CO_2 acts as an electrolyte and increases the flow of electrons from one place to another.

S5. No, because tin is less readily oxidised in comparison to iron ($E^{\ominus}\ Fe^{2+} | Fe = -0.44$ V, $E^{\ominus}\ Sn^{2+} | Sn = -0.14$ V). Tin protects iron only as a cover.

Date: 23/10/2021

Q1. How is the presence of SO_2 detected?

Q2. Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water?

Q3. Write main differences between the properties of white phosphorus and red phosphorus.

Q4. Why are halogens strong oxidising agents?

Q5. What are the oxidation states of phosphorus in the following?
(a) H_3PO_3 (b) PCl_3 (c) Ca_3P_2 (d) Na_3PO_4 (e) POF_3

Q6. What inspired Neil Barlett for carrying out reaction between Xe and PtF_6?

Q7. Knowing the electron gain enthalpy values for $O \rightarrow O^{\ominus}$ and $O \rightarrow O_2$ as –141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having $O^{2\ominus}$ species and not $O^{\ominus}$?

Q8. Which aerosols deplete ozone?

Q9. Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation, state and hydride formation.

Q10. Comment the following:
(a) NO_2 readily forms a dimer, explain.
(b) H_3PO_3 is diprotic, explain.
(c) How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure?

Q11. Account the following:
(a) Give reason SF_6 is not easily hydrolysed though thermodynamically it should be, why?
(b) The bond energy of F_2 is less than Cl_2, explain.
(c) Draw the structure of XeO_3.
(d) Complete the reaction $XeF_6 + KF \longrightarrow$
(e) Arrange the following decreasing boiling point H_2O, H_2S, H_2Se and H_2Te.

Q12. (a) Write the chemical equations involved in the preparation of the following:
(i) XeF_4 (ii) H_3PO_3
(b) Account for the following:
(i) Thermal stability of water is much higher than that of H_2S.
(ii) White phosphorous is more reactive than red phosphorus.
(c) Draw the structure of $XeOF_4$.

Q13. Account the following
(a) Xenon show Fluorides but Xenon chloride not known, explain.
(b) How are XeF_2 and XeF_4 prepared.
(c) Give shape and hybridization of $XeOF_2$ and XeO_2F_2.

Q14. Account the following

(a) Give equation to Lab. preparation of dioxygen.

(b) Give equation to Lab preparation of PH_3.

(c) Name two compounds in which oxygen has oxidation state different from – 2. Given oxidation state also.

(d) Oxygen molecule has formula O_2 whilest sulphur is S_8. Explain why?

(e) SF_6 is known but SH_6 is not known.

Date: 23/10/2021

S1. SO_2 is pungent smelling gas. Following two tests can be performed to detect SO_2.

(a) SO_2 turns the pinck violet colour of $KMnO_4$ solution to colourless due to reduction of $MnO_4^{\ominus}$ to $Mn^{2\oplus}$ ions.

$$SO_2 + 2H_2O \longrightarrow SO_4^{2\ominus} + 4H^{\oplus} + e^{\ominus}] \times 5$$
$$MNO_4^{\ominus} + 8H^{\oplus} + 5e^{\ominus} \longrightarrow Mn^{2\oplus} + 4H_2O] \times 2$$
$$\underset{\text{(pink violet)}}{2MnO_4^{\ominus} + 5SO_2 + 2H_2O} \longrightarrow \underset{\text{(colourless)}}{2Mn^{2\oplus} + 5SO_4^{2\ominus} + 4H^{\oplus}}$$

(b) SO_2 turns acidified $K_2Cr_2O_7$ solution green due to reduction of $Cr_2O_7^{2\ominus}$ to $Cr^{3\oplus}$ ions.

$$SO_2 + 2H_2O \longrightarrow SO_4^{2\ominus} + 4H^{\oplus} + 2e^{\ominus}] \times 3$$
$$Cr_2O_7^{2\ominus} + 14H^{\oplus} + 6e^{\ominus} \longrightarrow 2Cr^{3\oplus} + 7H_2O$$
$$\underset{\text{(orange)}}{Cr_2O_7^{2\ominus} + 3SO_2 + 2H^{\oplus}} \longrightarrow \underset{\text{(green)}}{2Cr^{3\oplus} + 3SO_4^{2\ominus} + H_2O}$$

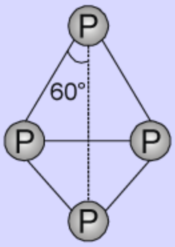
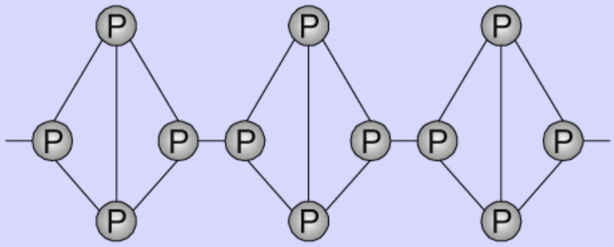
S2. H_2SO_4 is a dibasic acid, it ionises in two stages and hence has low dissociation constants as given below :

(a) $H_2SO_4\,(aq) + H_2O\,(l) \longrightarrow H_3O^{\oplus}\,(aq) + HSO_4^{\ominus}\,(aq);\ K_{a_1} > 10$

(b) $HSO_4^{\ominus}\,(aq)\ H_2O\,(l) \longrightarrow H_3O^{\oplus}\,(aq) + SO_4^{2\ominus}\,(aq);\ K_{a_2} = 1.2 \times 10^{\ominus 2}$

K_{a_2} is less then K_{a_1} *i.e.*, tendency to move towards the products is much less in (ii) than (i). This is because the negativity charged $HSO_3^{\ominus}$ ion has much less tendency to donate a proton to H_2O as compared to neutral H_2SO_4.

S3. Differences between properties of white and red phosphorus.

White phosphorus	Red phosphorus
1. White phosphorus has the structure as given below :  It consists of discrete tetrahedral P_4 soluble.	Red phosphorus has the structure as given below :  It is polymeric, consisting chains of P_4 tetrahedra linked together.
2. It is poisonous, insoluble in water but soluble in carbon disulphide.	2. It is odourless, non-poisonous, insoluble in water as well as carbon disulphide.
3. It glows in the dark (chemiluminiscence).	3. It does not glow in the dark.
4. It is more reactive. It catches fire in the air to give dense white fumes of P_4O_{10}. $P_4 + 5O_2 \longrightarrow P_4O_{10}$	4. It is much less reactive.

S4. Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy, halogens have a strong tendency to accept electrons and thus get reduced.

$$X + e^{\ominus} \longrightarrow X^{\ominus}$$

In other words, halogens act as strong oxidising agents. Their oxidizing power, however, decreases from F_2 to I_2 as evident from their electrode potentials :

$$E^\circ_{F_2/F^\ominus} = +2.87\ V, \qquad E^\circ_{Cl_2/Cl^\ominus} = +1.36\ V,$$

$$E^\circ_{Br_2/Br^\ominus} = +1.09\ V \quad \text{and} \quad E^\circ_{I_2/I^\ominus} = +0.54\ V$$

Thus, F_2 is the strongest while I_2 is the weakest oxidizing agent.

S5. Let the oxidation state of P be taken as *x*. Substituting the oxidation states of other elements, we can calculate the oxidation state of P as done below :

(a) $\overset{+1}{H_3}\ \overset{x}{P}\ \overset{-2}{O_3}$ or $3(+1) + x + 3(-2) = 0$ or $x = +3$

(b) $\overset{x}{P}\ \overset{-1}{Cl_3}$ or $x + 3(-1) = 0$ or $x = +3$

(c) $\overset{+2}{Ca_3}\ \overset{x}{P_2}$ or $3(+2) + 2 \times x = 0$ or $x = -3$

(d) $\overset{+1}{Na_3}\ \overset{x}{P}\ \overset{-2}{O_4}$ or $3(+1) + x + 4(-2) = 0$ or $x = +5$

(e) $\overset{x}{P}\ \overset{-2}{O}\ \overset{-1}{F_3}$ or $x + 1(-2) + 3(-1) = 0$ or $x = +5$.

S6. Neil Bartlett observed that PtF_6 reacts with O_2 to yield an ionic solid, $O_2^{\oplus}$, $PtF_6^{\ominus}$.

$O_2\,(g) + PtF_6\,(g) \longrightarrow O_2^{\oplus}\,[PtF_6]^{\ominus}$

In this reaction, O_2 gets oxidised to $O_2^{\oplus}$ by PtF_6.

He thought since the first ionisation enthalpy of Xe (1170 kJ mol^{-1}) is fairly close to that of O_2 molecule (1175 kJ mol^{-1}), PtF_6 should also oxidise Xe to $Xe^{\oplus}$. This inspired Barlett to carry out the reaction between Xe and PtF_6. When Xe and PtF_6 were mixed, actually a rapid reaction took place and a red solid with the formula, $Xe^{\oplus}\,PtF_6^{\ominus}$ was obtained.

$$Xe + PtF_6 \xrightarrow{278\ K} \underset{red}{Xe^{\oplus}\,[PtF_6]^{\ominus}}$$

S7. Consider the reaction of a divalent metal (M) with oxygen. The formation of M_2O and MO involves the following steps:

$$M(g) \xrightarrow{\Delta_i H_1} M^{\oplus}\,(g) \xrightarrow{\Delta_i H_2} M^{2\oplus}\,(g)$$

$\Delta_i H_1$ and $\Delta_i H_2$ are first and second ionisation enthalpies of the metal M.

$$O\,(g) \xrightarrow{\Delta_{eg} H_1} O^{\ominus}\,(g) \xrightarrow{\Delta_{eg} H_2} O^{2\ominus}\,(g)$$

$\Delta_{eg} H_1$ and $\Delta_{eg} H_2$ are first and second electron gain enthalpies

$$2M^{\oplus}(g) + O^{\ominus}(g) \xrightarrow{\text{Lattice energy}} M_2O(s)$$

$$M^{2\oplus}(g) + O_2^{\ominus}(g) \xrightarrow{\text{Lattice energy}} MO\,(s)$$

Although $\Delta_i H_2$ is much more than $\Delta_i H_1$ and $\Delta_{eg} H_2$ is much higher than $\Delta_{eg} H_1$, yet the lattice energy of formation of MO (*s*) due to higher charges is much more than that of M_2O (s). In other words, formation MO is energetically more favourable than M_2O. It is due to this reason that oxygen forms preferably oxides having the $O_2^{\ominus}$ species and not $O^{\ominus}$.

S8. Aerosols such as chlorofluorocarbons (CFC's) depletes the O_3 layer by supplying Cl free radical which convert O_3 to O_2 in the following sequence of reactions :

$$\underset{Freon}{Cl_2CF_2\,(g)} \xrightarrow{hv} \bullet Cl\,(g) + \bullet CClF_2\,(g)$$

$$\bullet Cl(g) + O_3\,(g) \longrightarrow ClO\bullet\,(g) + O_2\,(g)$$

$$ClO\bullet\,(g) \longrightarrow Cl\bullet\,(g) + \bullet O\,(g)$$

$$ClO\bullet\,(g) + \bullet O\,(g) \longrightarrow \bullet Cl\,(g) + O_2\,(g)$$

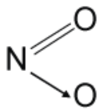
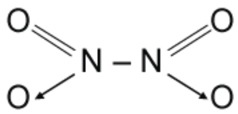
S9. (a) ***Electronic configuration:*** All these elements have the common ns^2np^4 (n = 2 to 6) valence shell electronic configuration.

$$_8O = [He]2s^2\,2p^4; \quad _{16}S = [Ne]\,3s^2\,3p^4; \quad _{34}Se = [Ar]\,3d^{10}\,4s^2\,4p^4$$
$$_{52}Te = [Kr]\,4d^{10}\,5s^2\,5p^4 \quad \text{and} \quad _{84}Po = [Xe]\,4f^{14}\,5d^{10}\,6s^2\,6p^4$$

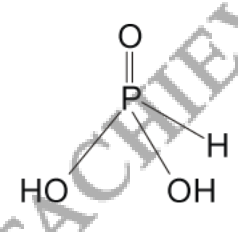
Hence, it is justified to place them in Group 16 of the periodic table.

(b) ***Oxidation states:*** They need two more electrons to form dinegative ions and acquire the nearest inert gas configuration. Thus, the minimum oxidation state of these elements should be –2. Oxygen, sulphur being electronegative show an oxidation state of –2. Other elements of this group, being more electropositive than O and S, do not show negative oxidation states. Since these elements have six electrons in the valence shell, therefore, at the maximum they can show an oxidation state +6. Other positive oxidation states shown by these elements are +2 and +4. However, due to the absence of *d*-orbitals, oxygen does not show oxidation states of +4 and +6. Thus, on the basis of minimum and maximum oxidation states, these elements are justified to be placed in the same group.

(c) ***Formation of hydrides:*** All the elements complete their respective octets by sharing two of their valence electrons with 1*s*-orbital of hydrogen to form hydrides of the general formula EH_2, i.e., H_2O, H_2S, H_2Se, H_2Te and H_2Po. Thus, on the basis of formation of hydrides of the general formula EH_2, these elements are justified to be placed in Group 16 of the period table.

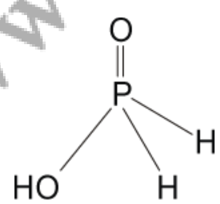
S10. (a)  has one unpaired electron, therefore, it is unstable and forms dimer, i.e., N_2O_4 whose structure is 

(b) H_3PO_3 has three H atoms and therefore, it is expected to be tribasic. However, in its structure, two hydrogen atoms are joined through oxygen atoms and are ionisable. The third H atom is linked to P and is non-ionisable.



$$H_3PO_3 \rightleftharpoons HPO_3^{2\ominus} + 2H^{\oplus}$$

(c) H_3PO_2 has one P $=$ O, one P — OH and two P — H bonds as. Phosphorous has +1 oxidation state.



Since two H atoms are bonded directly to P atom which impart reducing character to the acid.

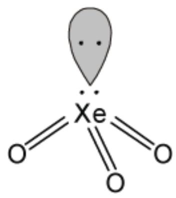
S11. (a) Due to sterically protection of six F atom, which donot allow to water molecules to attack on sulphur and due to steric repulsion of F at SF_6 thermodynamically unstable.

(b) Due to higher electron-density on F, the bond length of F–F increase due to electron-electron repulsion and B.d.E. decrease while Cl is bigger in size and has less electron-density and has not electron-electron repulsion in Cl_2 and bond length is comparatively shorter than F_2.

(c) Shape of XeO_3

Hybridization sp^3

Shape - Bent pyramidal



(d) $XeF_6 + KF \longrightarrow K^{\oplus}[XeF_7]^{\ominus}$

(e) $H_2O > H_2Te > H_3Se > H_2S$

S12. (a) (i) $$Xe(g) + 2F_2(g) \xrightarrow[7\ bar]{873\ K} XeF_4(s)$$

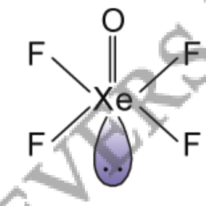
1 : 5

(ii) $$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl.$$

(b) (i) Due to high electronegativity of oxygen, the O — H in H_2O forms strong intermolecular H — bonds. While other hydrides of group of 16 like H_2S do not form H — bonds. So, water has high stability as compared to H_2S.

(ii) It is because white phosphorus is a discrete P_4 molecule whereas red phosphorus is polymeric.

(c) Structure $XeOF_4$.



S13. (a) Xe is noble gas, its ionization energy is much higher. F is highly electronegativity element it can unpair the paired electron of Xe to form covalence bond.

(b) XeF_2 is prepared in Lab in Nickel tube at 673 and 1 bar pressure.

$$Xe + F_2 \xrightarrow[673\ K,\ 1\ bar]{Nickel\ tube} XeF_2$$

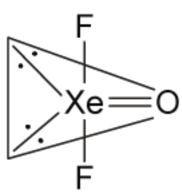
XeF_4 is prepared in Lab in nickel tube at 673 K and 7 bar pressure.

$$Xe + 2F_2 \xrightarrow[673\ K,\ 7\ bar]{Nickel\ tube} XeF_4$$

(c) $XeOF_2$

hybridization – sp^3d

shape – T–shape

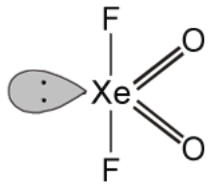


$XeOF_2$

XeO_2F_2

hybridization — sp^3d

shape — see-saw shape



XeO_2F_2

S14. (a) $2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$

MnO_2 lower the B.P. of $KClO_3$

(b) $P_4 + 3\ NaOH + 3H_2O \longrightarrow 3\ NaH_2PO_2 + PH_3$

Sodiumhydrophosphite   phosphine

(c) Oxygen Floride OF_2 oxygen has +2 oxidation state. Hydrogen peroxide H_2O_2 oxygen has –1 oxidation state.

(d) Oxygen is smaller in size and has ability to form $P\pi - P\pi$ multiple bond, and satisfy its octate forming (O ═ O) O_2 molecule.

While S is bigger in size and has not ability to form $P\pi - P\pi$ multiple bond, satisfy its octate by forming (Puckered shape) S_8 molecule.

(e) F is highly electronegative hence F unpair the paired electron of sulphate to form SF_6 while H is electropositive in respect to sulphur and it cannot unpair to paired electron of sulphur to expained S oxidation state.