competishun — Power of real gurus	CAPS – 10
CHEMISTRY TARGET : JEE Advanced – 2021	**Electrochemistry**

Answer Key

1.	(D)	**2.**	(B)	**3.**	(D)	**4.**	(D)	**5.**	(A)
6.	(B)	**7.**	(C)	**8.**	(B)	**9.**	(B)	**10.**	(ABC)
11.	(BC)	**12.**	(AD)	**13.**	(ABCD)	**14.**	(C)	**15.**	(A)
16.	(D)	**17.**	(1144)	**18.**	(265)	**19.**	(3.00)	**20.**	(4.00)
21.	(B)	**22.**	(A)q	**23.**	(B)	**24.**	(C)	**25.**	(B)
26.	(0571)	**27.**	(2×10^5 dm^3)						

Solution

1. D is not reacted with HCl, So not easily oxidized at compare to A, B to C.

C is reduced B as well as D, but unable to reduce A.

So A is obidized easily as compare to other metals.

∴ ability to act as easily as compare to other metals.

2. $E^o_{Cell} = \frac{0.0591}{2}\log K_{eq}$

$$0.003 = \frac{0.0591}{2}\log\frac{[D^+]^2}{[H^+]^2} = \frac{[D^+]}{[H^+]} = 1.123$$

3. $$E_{Cr_2O_7^{2-}|Cr^{3+}} = E^o_{Cr_2O_7^{2-}|Cr^{3+}} - \frac{0.0591}{6}\times\left(\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}]}\times\frac{1}{[H^+]^{14}}\right)$$

$$E_{Cr_2O_7^{2-}|Cr^{3+}} = 1.33 - \frac{0.0591}{6}\log\frac{1}{(0.01)^{14}}$$

$\Rightarrow$ 1.0542 V

4. Equivalents of CO_2 produced = $\frac{(I\times\eta)\times t}{96500}$

$$= \frac{0.5\times0.8\times96.5\times60}{96500} = 0.024$$

Moles of CO_2 (n = 1) produced = 0.024

moles of C_2H_6 (n = 2) produced = $\frac{0.024}{2} = 0.012$

Total moles of gases produced $\Rightarrow$ 0.036

$$V_{gases} = \frac{nRT}{p} = \frac{0.036\times0.0821\times300}{(740/760)} = 0.91 \text{ litre}$$

5. Initial m moles of Cu^{2+} = 5 ;

m-eq. or m-moles of H^+ produced = 100 × 10^{-2} = 1

$\Rightarrow$ m-moles of Cu^{2+} converted into

$$Cu = \frac{1}{2} = 0.5$$

m-moles of Cu^{2+} remaining in solution = 5 – 0.5 = 4.5

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2O_2 + I_2$$

and $$I_2 + 2NaS_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

m moles of Cu^{2+} remaining = m moles of $Na_2S_2O_3$

4.5 = 0.04 × V

$\Rightarrow$ V = 112.5 mL

6.

	HBr	+	NaOH	→	NaBr	+	H2O
Initial	10 Mmol		-		-		-
At eq. Point	-		-		10 mmol		-

At equivalence point, the concentration of NaBr = $\frac{10}{100} = 0.1\,M$

In mole m^{-3}, concentration of NaBr = 100 mole m^{-3}

Now, $\lambda_m^o(NaBr) = \lambda_m^o(Na^+) + \lambda_m^o(Br^-) = 12 \times 10^{-13}\,S\ m^2\ mol^{-1}$

Now, $\lambda_m^o(S\ m^2\ mol^{-1}) = \frac{K(sm^{-1})}{C(mol\ m^{-3})}$

$$12 \times 10^{-3} = \frac{k}{100}$$

K = 1.2 m^{-1}

7. For strong electrolytes,

$$\lambda_m = \lambda_m^o - A\sqrt{C}$$

$282 = \lambda_m^o - A(0.4)$ .....(1)

$240 = \lambda_m^o - A$ .....(2)

Substituting the value of λ_m^o from equation (2) to equation (1),

$$282 = \lambda_m^o - 0.4\left(\lambda_m^o - 240\right)$$

$$\lambda_m^o = 310$$

8. $AgCl + e^- \rightarrow Ag + Cl^-$ $E^o = 0.2$ V

$Ag \rightarrow Ag^+ + e^-$ $E^o = -0.79$ V

$AgCl \rightarrow Ag^+ + Cl^-$ $E^o = -0.59$ V

$$E^o = \frac{0.059}{n}\log K \Rightarrow -0.59 = \frac{0.059}{1}\log K_{SP}$$

$K_{SP} = 10^{-10}$

Now solubility of AgCl in 0.1 M $AgNO_3$

$S(S + 0.1) = 10^{-10} \Rightarrow S = 10^{-9}$ mol/L

Hence, 1 mole dissolves in 10^9 L solution.

Hence, in 10^6 L amount that dissolve is 1 mmol.

9. The concentration of Fe^{3+} decreases due to conversion to Fe^{+2}.

10. **(ABC)**

11. At Anode

$H_2(g) \rightarrow 2H^+ + 2e^-$

P_1 C_1

At Cathode

$2H^+ + 2e^- \rightarrow H_2$

C_2 P_2

Net:

$H_2(g) + 2H^+ \rightarrow 2H^+ + H_2$

P_1 C_2 C_1 P_2

$$E_{cell} = \frac{-0.0591}{2}\log\frac{(H^+)^2_{LHS}(P_{H_2})_{RHS}}{(H^+)^2_{RHS}(P_{H_2})_{LHS}}$$

$Pt|H_2(P_1)|H^+(C_1)||H^+(C_2)|H_2(P_2)|Pt$

So, here $[H^+]LHS = x_1$, $[H^+]_{RHS} = x_2$

12. Substance with More positive value of E^0 has more tendency to get reduced.

13. Refer theory of corrosion

14. Equivalent of Zn^{2+} produced = 0.1 or Moles of $Zn^{2+} = \frac{0.1}{2} \Rightarrow 0.05$

+ve charge increases in first compartment so due to interaction and maintain electrical neutrality Zn^{2+} move toward II compartment and NO_3^- move towards first compartment. Solution is always electrically neutral so charge of 1 Zn^{2+} is neutralized by $2NO_3^-$.

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Concentration of NO_3^- in second compartment = 1 – 0.05 = 0.95 M

16. In third compartment moles of Cu^{2+} reduced = $\frac{0.05}{2} = 0.025$

Relatively –ve charge increased so SO_4^{2-} and Na^+ move toward opposite direction to maintain electrical neutrality

$$\left[SO_4^{2-}\right]_{ramaining} = 1 - \frac{0.025}{2} \Rightarrow 0.975M$$

17. $K_a = \frac{C\alpha}{1-\alpha} \Rightarrow \frac{1}{6} = \frac{\alpha^2}{1-\alpha}$

$\Rightarrow \quad \alpha = \frac{-1 \pm \sqrt{(1)^2 + 4 \times 6 \times 1}}{12} = \frac{-1 \pm \sqrt{1+24}}{12} = \frac{1}{3}$

$\therefore \quad [IO_3] = 1 \times \frac{1}{3} = \frac{1}{3}M$

$\Rightarrow \quad \left[Ag^+\right] = \frac{3 \times 10^{-8}}{\frac{1}{3}} = 9 \times 10^{-8}M$

Now $2Ag + Zn^{+2} \xrightarrow{2e^-} 2Ag^+ + Zn$

Give $E = -1.56 + \frac{0.059}{2} \log \frac{1}{\left(9 \times 10^{-8}\right)^2} = -1.144V = -1144mV$

18. $Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$

$NH_2SO_4 = M_{H_2SO_4} \left(\text{since } 2SO_4^{2-} \text{ requires } 2e^-\right)$

i.e., Normality = Molarity

Now, $M_1(H_2SO_4)$ before electrolysis = $\frac{39 \times 1.294 \times 1000}{98 \times 100} = 5.15$

$M_2(H_2SO_4)$ after electrolysis = $\frac{20 \times 1.139 \times 1000}{98 \times 100} = 2.325$

Now, moles of H_2SO_4 before electrolysis = 5.15 × 3.5 = 18.025

Moles of H_2SO_4 after electrolysis = 2.235 × 3.5 = 8.1375

$\therefore$ Molos of equivalents of H_2SO_4 used

Weight of H_2SO_4 used up = 3.5 ∗ (1.294 ∗ 0.39 − 1.139 ∗ 0.2) ∗ 1000g = 969g

Equivalences of H_2SO_4 = 1*969/98

Ampere hour = 1*969/98*96500/3600 = 265

19. $\Lambda = \frac{K}{C} \times 1000 = \frac{2.19 \times 10^{-4}}{0.1} \times 1000 = 2.19 Scm^2 mol^{-1}$

$\alpha = \frac{\Lambda}{\Lambda_o} = \frac{2.19}{400} = 5.475 \times 10^{-3}$

$K_\alpha = \frac{C\alpha^2}{1-\alpha} = \frac{0.1(5.475 \times 10^{-3})^2}{1-5.475 \times 10^{-3}} = 2.99 \times 10^{-6}$

20. $\wedge_M^\infty(MA) = \wedge_M^\infty(HCl) + \wedge_M^\infty(NaA) - \wedge_M^\infty(NaCl)$

= 425 + 100 – 125 – 400 S cm^2 mol^{-1}

pH = 4, $[H^+] = 10^{-4} = \alpha C$

$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{200}{400} = 0.5;$

$K_a = \frac{(C\alpha).\alpha}{(1-\alpha)} = \frac{10^{-4}(0.5)}{(1-\alpha)} = 10^{-4}; pK_a = 4$

21. (A) The reduction tendency of $AuCl_4^-$ is more than reduction tendency of Li^+

(B) The tendency of reduction of Zn^{2+} is more than that of Al^{3+}, while the given representation shows the reverse order, thus, the cell is non-spontaneous and $E^o_{cell} < 0$.

(C) For a spontaneous concentration cell, the concentration of anode compartment should be less than the concentration of cathode compartment.

(D) The tendency of reduction of Cu^{2+} is more than that of Ni^{2+} and the given representation shows the same order, thus, the cell is spontaneous and $E^o_{cell} > 0$. Such cells act as galvanic cells.

22. Electrolysis of dilute solution of NaCl: Water is reduced at cathode to give hydrogen gas and chloride ion is oxidized at anode (due to overpotential of oxygen) to give chlorine gas.

Electrolysis of concentrated solution of $AgNO_3$: Silver ion is reduced at cathode to deposit silver and water is oxidized at anode to give oxygen gas.

23. No. of equivalent of aluminum, $\frac{W}{E} = \frac{I \times \eta \times t}{96500}$

$\frac{24 \times 5}{27} \times 3 = \frac{9650 \times 0.9 \times t}{96500}$

t = 148.14 sec

24. $3Cu(s) + 8H^+ + 2NO_3^- \rightarrow 3Cu^{2+} + 2NO + 4H_2O$ .....(1)

$Cu(s) + 4H^+ + 2NO_3^- \rightarrow Cu^{2+} + 2NO_2 + 2H_2O$ .....(2)

Let concentration of HNO_3 is x so $[H^+] = x$, and $[NO_3^-] = x$

$E_{NO_3^-|NO} - E_{Cu^{2+}|Cu} = E_{NO_3^-|NO_2} - E_{Cu^{2+}|Cu}$

or $E_{NO_3^-|NO} = E_{NO_3^-|NO_2}$

$(0.96 - 0.34) - \frac{0.06}{6}\log\frac{[Cu^{2+}]^3(P^2_{NO})}{[NO_3^-]^2[H^+]^8}$

$= (0.79 - 0.34) - \frac{0.06}{2}\log\frac{[Cu^{2+}](P^2_{NO_2})}{[NO_3^-]^2[H^+]^4} \Rightarrow 0.62 - \frac{0.06}{6}\log\frac{10^{-9}}{x^{10}} = 0.45 - \frac{0.06}{2}\log\frac{10^{-7}}{x^6}$

log x = 0.657 = 0.66 or x = $10^{+0.66}$

25. $$E_{cell} = \frac{0.06}{1}\log\frac{\left[H^+\right]_{RHS}}{\left[H^+\right]_{LHS}}$$

or $$E_{cell} = 0.06\left[(pH)_{LHS} - (pH)_{RHS}\right]$$

$$(pH)_{LHS} = pK_a + \log\frac{\left[A^-\right]}{[HA]}$$

$$= 4 + \log\left(\frac{1}{0.1}\right) = 5; (pH)_{RHS} = 4$$

E_{cell} = 0.06(5 − 4) = + 0.06 V

26. **(0571)**

27. For KCl,

$$\lambda_M = \frac{k \times 1000}{M} \quad \Rightarrow \quad 138 = \frac{k \times 1000}{0.02}$$

$$k = 2.76 \times 10^{-3} = \frac{1}{R}\left(\frac{l}{a}\right) = \frac{1}{85}\left(\frac{l}{a}\right)$$

(l/a) = 0.2346

For $H_2O : k_{H_2O} = \frac{1}{9200}(l/a)$

For $NaCl : k_{NaCl} = \frac{1}{7600}(l/a)$

$$\lambda_M = \frac{\left(k_{NaCl} - k_{H_2O}\right) \times 1000}{M}$$

$$126.5 = \frac{\left(\frac{1}{7600} - \frac{1}{9200}\right) \times 0.2346 \times 1000}{M}$$

M = 4.2438 × 10^{-5}M = $\frac{500}{58.5 \times V} = 4.2438 \times 10^{-5}$

V = 201400 V

V = 2.014×10^5 L