PHYSICAL / INORGANIC CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

DPP No. 27

Total Marks : 42

Max. Time : 44 min.

Topic : Electro Chemistry

Type of Questions		M.M., Min.
Single choice Objective ('–1' negative marking) Q.1 to Q.10	(3 marks, 3 min.)	[30, 30]
Multiple choice objective ('–1' negative marking) Q.11	(4 marks, 4 min.)	[4, 4]
Subjective Questions ('–1' negative marking) Q.12 to Q.13	(4 marks, 5 min.)	[8, 10]

1. E° for $F_2 + 2e^- \rightleftharpoons 2F^-$ is 2.8 V, E° for $\frac{1}{2} F_2 + e^- = F^-$ is -

(A) 2.8 V (B) 1.4 V (C) –2.8 V (D) –1.4 V

2. The standard reduction potential of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0.337 and 0.153 respectively. The standard electrode potential of Cu^+/Cu half-cell is -

(A) 0.184 V (B) 0.827 V (C) 0.521 V (D) 0.490 V

3. $E^0_{Fe^{3+}/Fe^{+2}} = +0.77$ V ; $E^0_{Fe^{+3}/Fe} = -0.036$ V. What is $E^0_{Fe/Fe^{+2}}$ and is Fe^{+2} stable to disproportionation in aqueous solution under standard conditions

(A) +0.44 V, yes (B) – 0.44 V, No (C) + 0.44 V, No (D) – 0.44 V, yes

4. Given that $E^\circ_{Fe^{2+}/Fe} = -0.44$ V ; $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ V if Fe^{2+}, Fe^{3+} and Fe solid are kept together then

(A) Fe^{3+} increases (B) Fe^{3+} decreases

(C) Fe^{2+}/Fe^{3+} remains unchanged (D) Fe^{2+} decreases

5. The spontaneous redox reaction/s among the following is/are

(a) $2Fe^{3+} + Fe \longrightarrow 3Fe^{++}$

(b) $Hg_2^{++} \longrightarrow Hg^{++} + Hg$

(c) $3\,AgCl + NO + 2H_2O \longrightarrow 3\,Ag + 3\,Cl^- + NO_3^- + 4H^+$

Given that

$E^\circ_{Fe^{+++}/Fe^{++}} = 0.77$ V $E^\circ_{Fe^{++}/Fe} = -0.44$ V

$E^\circ_{Hg_2^{++}/Hg} = 0.85$ V $E^\circ_{Hg^{++}/Hg_2^{++}} = 0.92$ V

$E^\circ_{AgCl/Ag} = 0.22$ V $E^\circ_{NO_3^-/NO} = 0.96$ V

(A) a (B) a, b, c (C) a, b (D) a, c

6. ΔG° of the cell reaction $AgCl(s) + \frac{1}{2} H_2(g) \rightleftharpoons Ag(s) + H^+ + Cl^-$ is –21.52 kJ.

ΔG° of $2AgCl(s) + H_2(g) = 2Ag(s) + 2H^+ + 2Cl^-$ is -

(A) –21.52 kJ (B) –10.76 kJ (C) –43.04 kJ (D) 43.04 kJ

7. In a concentration cell, $Zn \mid Zn^{2+}\ (1.0M) \,||\, Zn^{2+}\ (0.15\ M) \mid Zn$ as the cell discharges,

(A) reaction proceeds to the right

(B) the two solutions approach each other in concentration

(C) no reaction takes place

(D) water gets decomposed

8. In a half-cell contaning $[Tl^{3+}] = 0.1$ M and $[Tl^{+}] = 0.01$M, the cell potential is –1.2496 V for the reaction $Tl^{+} \longrightarrow Tl^{3+} + 2e^{-}$. The standard reduction potential of the $T\ell^{+3}/T\ell^{+1}$ couple at 25°C is

(A) 144 V (B) 0.61 V (C) 2.44 V (D) 1.22 V

9. A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. In which of the following solutions should the other electrode be immersed to get maximum e.m.f. ($K_a = 10^{-5}$ for acetic acid and $K_a = 10^{-3}$ for phosphoric acid)

(A) 0.1 M HCl (B) 0.1 M CH_3COOH (C) 0.1 M H_3PO_4 (D) 0.1 M H_2SO_4

10. The standard electrode potential for the reactions,

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

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

at 25°C are 0.80 volt and –0.14 volt, respectively. The emf of the cell $Sn|Sn^{2+}$ (1 M) $||Ag^{+}$ (1M)|Ag is-

(A) 0.66 volt (B) 0.80 volt (C) 1.08 volt (D) 0.94 volt

11. For the cell Tl | Tl^{+} (0.001 M) | | Cu^{2+} (0.1 M) | Cu. E_{cell} at 25°C is 0.83 V, which can be increased-

(A) by increasing $[Cu^{2+}]$ (B) by increasing $[Tl^{+}]$

(C) by decreasing $[Cu^{2+}]$ (D) by decreasing $[Tl^{+}]$

12. Given the standard reduction potentials $T\ell^{+} + e^{-} \longrightarrow T\ell$, E° = – 0.34V and $T\ell^{3+} + 2e^{-} \longrightarrow T\ell^{+}$, E° = 1.25V. Examine the spontaneity of the reaction, $3T\ell^{+} \longrightarrow 2T\ell + T\ell^{3+}$. Also find E° for this disproportionation.

13. What is the electrode potential of Mg^{2+} | Mg electrode at 25°C, in which the concentration of Mg^{2+} is 0.01M. E° (Mg^{2+} | Mg) = – 2.36V.

Answer Key

DPP No. # 27

1.	(A)	**2.**	(C)	**3.**	(A)	**4.**	(B)	**5.**	(A)
6.	(C)	**7.**	(B)	**8.**	(D)	**9.**	(B)	**10.**	(D)
11.	(A,D)	**12.**	E° = – 1.59 V, non-spontaneous			**13.**	E = – 2.4191 V.		

Hints & Solutions

PHYSICAL / INORGANIC CHEMISTRY

DPP No. # 27

1. E° is intensive property.

2.

$Cu^{2+} + 2e^- \longrightarrow Cu$	$E^\circ = 0.337$ V	$\Delta G^\circ = -2F \times 0.337.$
$Cu^{2+} + e^- \longrightarrow Cu^+$	$E^\circ = 0.153$ V	$\Delta G^\circ = -1F \times 0.153.$
$Cu^{2+} + 2e^- \longrightarrow Cu$	$E_1^0 = 0.337$ V	$\Delta G_1^0 = -2F \times 0.337.$
$Cu^+ \longrightarrow Cu^{2+} + e^-$	$E_2^0 = 0.153$ V	$\Delta G_2^0 = 1 \times F \times 0.153.$
$Cu^+ + e^- \longrightarrow Cu$	$E_3^0 = ?$	$\Delta G_3^0 =$

$$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0.$$

$$-F \times E_3^0 = -2F \times 0.337 + F \times 0.153.$$

$$E_3^0 = 2 \times 0.337 - 0.153 = \mathbf{0.521\ V.}$$

3.
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ (1) $E^\circ_1 = 0.77V$ $\Delta G_1{}^\circ = -1 \times F \times 0.77$
$Fe^{3+} + 3e^- \longrightarrow Fe$ (2) $E^\circ_2 = -0.036V$ $\Delta G_2{}^\circ = 3 \times F \times 0.036$
$Fe \longrightarrow Fe^{2+} + 2e^-$ (3) $E_3{}^\circ$ $_=$ $\Delta G_3{}^\circ = -2 \times F \times E_3{}^\circ$
(1) – (2) = 3
$\Delta G_1{}^\circ - \Delta G_2{}^\circ = \Delta G_3{}^\circ$
$\Rightarrow -F \times 0.77 - 3F - 0.036 = -2 \times F \times E_3{}^\circ$
$\Rightarrow (0.77 \times 0.108) = 2 \times E_3{}^\circ$
$\Rightarrow E_3{}^\circ \simeq 0.44V$ **Ans.**
Disproportionation reaction.
$3Fe^{2+} \longrightarrow Fe + 2Fe^{3+}$ (4)
$Fe^{2+} + 2e^- \longrightarrow Fe$
$E^\circ = -0.44V$ $\Delta G^\circ = -2 \times F \times (-0.44)$ (5)
$Fe^{2+} \longrightarrow Fe^{3+} + e^-$
$E^\circ = -0.77V$ $\Delta G^\circ = -1 \times F \times (-0.77)$ (6)
(5) + 2 × (6) = (4)
$\Rightarrow \Delta G^\circ_4 = -2 \times F \times (-0.44) + 2(-1 \times F \times (-0.77))$

$= +ve$

$\because \Delta G_4^o > 0,$

$\Rightarrow$ Reaction is not spontaneous.

Hence, Fe^{2+} is stable to disproportionation.

4. From the given data, we see that Fe^{3+} reduces to Fe^{2+} as $E^o_{(Fe^{3+}/Fe^{2+})}$ is positive and Fe oxidises to Fe^{2+} are $E^o_{(Fe^{2+}/Fe)}$ is negative.

So, Fe^{3+} decreases, Fe^{2+} increases.

5. Only for this reaction E^0 will come out to be positive, calculate using relation

$$\Delta G^\circ = \Delta G_1^0 + \Delta G_2^0 \qquad \text{and} \qquad \Delta G^0 = -nFE^\circ_{cell}$$

6. $AgCl\ (s) + \frac{1}{2}H_2\ (g) \rightleftharpoons Ag\ (s) + H^+ + Cl^-.$

$\Delta G^o = -nF\,E^o_{cell} = -21.52\text{ KJ} = -1 \times F\,E^o_{cell}.$

$2AgCl\ (s) + H_2\ (g) \rightleftharpoons 2Ag\ (s) + 2H^+ + 2Cl^-.$

$\Delta G^o = -2 \times F \times E^o_{cell} = -21.52 \times 2 = \mathbf{-43.04\ kJ.}$

7. At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$

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

As cell discharges, $[Zn^{2+}]$ increase in anode compartment and decrease in cathode compartment, finally becoming equal at equilibrium. Hence, they approach each other.

8. $T\ell^{3+} + 2e^- \longrightarrow T\ell^+ \qquad E_{Cell} = +1.2496\text{ V}$

$$E_{Cell} = 1.2496\text{ V} = E^o_{Cell} - \frac{0.0591}{2}\log\frac{0.01}{0.1}$$

$E^o_{Cell} = 1.22\text{ V}.$

9. $$E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{1}{[H^+]^2}.$$

$H_2 \longrightarrow 2H^+ + 2e^-.$

$$E_{cell} = -\frac{0.0591}{2}\log[H^+]^2.$$

Higher the $[H^+]$ conc ; less will be emf.

or $$E_{cell} = 0 - \frac{0.0591}{2}\log\frac{(C)^2}{(\sqrt{KC})^2}$$

$$E_{cell} = 0 - \frac{0.0591}{2}\log\frac{(1)^2}{(0.1)^2}$$

$$= -\frac{0.0591}{2} \times 2 = -0.0591.$$

10. $$E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2}. = 0.8 - (-0.14) - \frac{0.0591}{2}\log\frac{1}{1^2} = \mathbf{0.94\ V.}$$

11. E_{cell} increases by increasing concentration of oxidised species at cathode and by increasing concentration of reduced species at anode.

Or by decreasing concentration of reduced species at cathode on decreasing concentration of oxidixed species at anode.

12. $\Delta G^o = (2 \times 0.34 + 2 \times 1.25)$

$-2 \times E^o = (2 \times 0.34 + 2 \times 1.25)$

$E^o = -1.59$ V non-spontanous $\quad E^o = -ve$

13. $$E_{cell} = -2.36 - \frac{0.0591}{2}\log\frac{1}{10^{-2}} = -2.4191\text{ V}.$$