

## Answers to Some Questions in Exercises

### UNIT 1

- 1.4 16.23 M  
1.6 157.8 mL  
1.8 17.95 m and 9.10 M  
1.15  $40.907 \text{ g mol}^{-1}$   
1.17 12.08 kPa  
1.19  $23 \text{ g mol}^{-1}$ , 3.53 kPa  
1.21 A = 25.58 u and B = 42.64 u  
1.24 KCl,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$ , Cyclohexane  
1.25 Toluene, chloroform; Phenol, Pentanol;  
Formic acid, ethylene glycol  
1.26 5 m  
1.28 1.424%  
1.30 4.575 g  
1.33  $i = 1.0753$ ,  $K_a = 3.07 \times 10^{-3}$   
1.35  $178 \times 10^5$   
1.38 0.6 and 0.4  
1.40 0.03 mol of  $\text{CaCl}_2$
- 1.5 0.617 m, 0.01 and 0.99, 0.67  
1.7 33.5%  
1.9  $1.5 \times 10^{-3}\%$ ,  $1.25 \times 10^{-4} \text{ m}$   
1.16 73.58 kPa  
1.18 10 g  
1.20 269.07 K  
1.22 0.061 M
- 1.27  $2.45 \times 10^{-8} \text{ M}$   
1.29 3.2 g of water  
1.32  $0.65^0$   
1.34 17.44 mm Hg  
1.36 280.7 torr, 32 torr  
1.39  $x(\text{O}_2) 4.6 \times 10^{-5}$ ,  $x(\text{N}_2) 9.22 \times 10^{-5}$   
1.41  $5.27 \times 10^{-3} \text{ atm}$

### UNIT 2

- 2.4 (i)  $E^0 = 0.34 \text{ V}$ ,  $\Delta_r G^0 = -196.86 \text{ kJ mol}^{-1}$ ,  $K = 3.124 \times 10^{34}$   
(ii)  $E^0 = 0.03 \text{ V}$ ,  $\Delta_r G^0 = -2.895 \text{ kJ mol}^{-1}$ ,  $K = 3.2$   
2.5 (i) 2.68 V, (ii) 0.53 V, (iii) 0.08 V, (iv) -1.298 V  
2.6 1.56 V  
2.8  $124.0 \text{ S cm}^2 \text{ mol}^{-1}$   
2.9  $0.219 \text{ cm}^{-1}$   
2.11  $1.85 \times 10^{-5}$   
2.12 3F, 2F, 5F  
2.13 1F, 4.44F  
2.14 2F, 1F  
2.15 1.8258g  
2.16 14.40 min, Copper 0.427g, Zinc 0.437 g

### UNIT 3

- 3.2 (i)  $8.0 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$ ;  $3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$   
3.4  $\text{bar}^{-1/2} \text{ s}^{-1}$   
3.6 (i) 4 times (ii)  $\frac{1}{4}$  times  
3.8 (i)  $4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$  (ii)  $1.98 \times 10^{-2} \text{ s}^{-1}$   
3.9 (i) rate =  $k[\text{A}][\text{B}]^2$  (ii) 9 times

- 3.10** Orders with respect to A is 1.5 and order with respect to B is zero.
- 3.11** rate law =  $k[A][B]^2$ ; rate constant =  $6.0 \text{ M}^{-2}\text{min}^{-1}$
- 3.13** (i)  $3.47 \times 10^{-3}$  seconds (ii) 0.35 minutes (iii) 0.173 years
- 3.14** 1845 years **3.16**  $4.6 \times 10^{-2}$  s
- 3.17** 0.7814  $\mu\text{g}$  and 0.227  $\mu\text{g}$ . **3.19** 77.7 minutes
- 3.20**  $2.20 \times 10^{-3} \text{ s}^{-1}$  **3.21**  $2.23 \times 10^{-3} \text{ s}^{-1}$ ,  $7.8 \times 10^{-4} \text{ atm s}^{-1}$
- 3.23**  $3.9 \times 10^{12} \text{ s}^{-1}$  **3.24** 0.135 M
- 3.25** 0.158 M **3.26** 232.79  $\text{kJ mol}^{-1}$
- 3.27** 239.339  $\text{kJ mol}^{-1}$  **3.28** 24°C
- 3.29**  $E_a = 76.750 \text{ kJ mol}^{-1}$ ,  $k = 0.9965 \times 10^{-2} \text{ s}^{-1}$
- 3.30** 52.8  $\text{kJ mol}^{-1}$

## UNIT 4

- 4.2** It is because  $\text{Mn}^{2+}$  has  $3d^5$  configuration which has extra stability.
- 4.5** Stable oxidation states.  
 $3d^3$  (Vanadium): +2, +3, +4, and +5  
 $3d^5$  (Chromium): +3, +4, +6  
 $3d^5$  (Manganese): +2, +4, +6, +7  
 $3d^8$  (Nickel): +2, +3 (in complexes)  
 $3d^4$  There is no  $d^4$  configuration in the ground state.
- 4.6** Vanadate  $\text{VO}_3^-$ , chromate  $\text{CrO}_4^{2-}$ , permanganate  $\text{MnO}_4^-$
- 4.10** +3 is the common oxidation state of the lanthanoids  
 In addition to +3, oxidation states +2 and +4 are also exhibited by some of the lanthanoids.
- 4.13** In transition elements the oxidation states vary from +1 to any highest oxidation state by one  
 For example, for manganese it may vary as +2, +3, +4, +5, +6, +7. In the nontransition elements the variation is selective, always differing by 2, e.g. +2, +4, or +3, +5 or +4, +6 etc.
- 4.18** Except  $\text{Sc}^{3+}$ , all others will be coloured in aqueous solution because of incompletely filled  $3d$ -orbitals, will give rise to  $d-d$  transitions.
- 4.21** (i)  $\text{Cr}^{2+}$  is reducing as it involves change from  $d^4$  to  $d^3$ , the latter is more stable configuration  
 $(t_{2g}^3)$  Mn(III) to Mn(II) is from  $3d^4$  to  $3d^5$  again  $3d^5$  is an extra stable configuration.
- (ii) Due to CFSE, which more than compensates the 3<sup>rd</sup> IE.
- (iii) The hydration or lattice energy more than compensates the ionisation enthalpy involved in removing electron from  $d^1$ .
- 4.23** Copper, because with +1 oxidation state an extra stable configuration,  $3d^{10}$  results.
- 4.24** Unpaired electrons  $\text{Mn}^{3+} = 4$ ,  $\text{Cr}^{3+} = 3$ ,  $\text{V}^{3+} = 2$ ,  $\text{Ti}^{3+} = 1$ . Most stable  $\text{Cr}^{3+}$
- 4.28** Second part 59, 95, 102.
- 4.30** Lawrencium, 103, +3
- 4.36**  $\text{Ti}^{2+} = 2$ ,  $\text{V}^{2+} = 3$ ,  $\text{Cr}^{3+} = 3$ ,  $\text{Mn}^{2+} = 5$ ,  $\text{Fe}^{2+} = 6$ ,  $\text{Fe}^{3+} = 5$ ,  $\text{CO}^{2+} = 7$ ,  $\text{Ni}^{2+} = 8$ ,  $\text{Cu}^{2+} = 9$
- 4.38**  $M\sqrt{n(n+2)} = 2.2$ ,  $n \approx 1$ ,  $d^2 \text{ sp}^3$ ,  $\text{CN}^-$  strong ligand  
 $= 5.3$ ,  $n \approx 4$ ,  $\text{sp}^3$ ,  $d^2$ ,  $\text{H}_2\text{O}$  weak ligand  
 $= 5.9$ ,  $n \approx 5$ ,  $\text{sp}^3$ ,  $\text{Cl}^-$  weak ligand.

## UNIT 5

- 5.5** (i) +3 (ii) +3 (iii) +2 (iv) +3 (v) +3
- 5.6** (i)  $[\text{Zn}(\text{OH})_4]^{2-}$  (ii)  $\text{K}_2[\text{PdCl}_4]$  (iii)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  (iv)  $\text{K}_2[\text{Ni}(\text{CN})_4]$   
 (v)  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$  (vi)  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$  (vii)  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$  (viii)  $[\text{Pt}(\text{NH}_3)_6]^{4+}$   
 (ix)  $[\text{CuBr}_4]^{2-}$  (x)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$
- 5.9** (i)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  - Nil  
 (ii)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^-$  - Two (*fac*- and *mer*-)
- 5.12** Three (two *cis* and one *trans*)
- 5.13** Aqueous  $\text{CuSO}_4$  solution exists as  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$  which has blue colour due to  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  ions.  
 (i) When  $\text{KF}$  is added, the weak  $\text{H}_2\text{O}$  ligands are replaced by  $\text{F}^-$  ligands, forming  $[\text{CuF}_4]^{2-}$  ions which is a green precipitate.  

$$[\text{Cu}(\text{H}_2\text{O})_4]^{2+} + 4\text{F}^- \rightarrow [\text{CuF}_4]^{2-} + 4\text{H}_2\text{O}$$
  
 (ii) When  $\text{KCl}$  is added,  $\text{Cl}^-$  ligands replace the weak  $\text{H}_2\text{O}$  ligands forming  $[\text{CuCl}_4]^{2-}$  ions which has bright green colour.  

$$[\text{Cu}(\text{H}_2\text{O})_4]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 4\text{H}_2\text{O}$$
- 5.14**  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} + 4\text{CN}^- \rightarrow [\text{Cu}(\text{CN})_4]^{2-} + 4\text{H}_2\text{O}$   
 As  $\text{CN}^-$  is a strong ligand, it forms a highly stable complex with  $\text{Cu}^{2+}$  ion. On passing  $\text{H}_2\text{S}$ , free  $\text{Cu}^{2+}$  ions are not available to form the precipitate of  $\text{CuS}$ .
- 5.23** (i) OS = +3, CN = 6, d-orbital occupation is  $t_{2g}^6 e_g^0$ .  
 (ii) OS = +3, CN = 6,  $d^3 (t_{2g}^3)$ ,  
 (iii) OS = +2, CN = 4,  $d^7 (t_{2g}^5 e_g^2)$ ,  
 (iv) OS = +2, CN = 6,  $d^5 (t_{2g}^3 e_g^2)$ .
- 5.28** (iii)
- 5.29** (ii)
- 5.30** (iii)
- 5.31** (iii)
- 5.32** (i) The order of the ligand in the spectrochemical series :  
 $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^-$   
 Hence the energy of the observed light will be in the order :  
 $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} < [\text{Ni}(\text{NH}_3)_6]^{2+} < [\text{Ni}(\text{NO}_2)_6]^{4-}$   
 Thus, wavelengths absorbed ( $E = hc/\lambda$ ) will be in the opposite order.

## NOTES

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