

## Answers to Some Questions in Exercises

### UNIT 1

- 1.11 106.57 u  
 1.13 143.1 pm  
 1.15  $8.97 \text{ g cm}^{-3}$   
 1.16  $\text{Ni}^{2+} = 96\%$  and  $\text{Ni}^{3+} = 4\%$   
 1.24 (i) 354 pm (ii)  $2.26 \times 10^{22}$  unit cells  
 1.25  $6.02 \times 10^{18}$  cation vacancies  $\text{mol}^{-1}$

### UNIT 2

- |      |   |      |  |
|------|---|------|--|
| 2.4  | 16.23 M   | 2.5  | 0.617 m, 0.01 and 0.99, 0.67   |
| 2.6  | 157.8 mL  | 2.7  | 33.5%  |
| 2.8  | 17.95 m and 9.10 M  | 2.9  | $1.5 \times 10^{-3}\%$ , $1.25 \times 10^{-4} \text{ m}$                 |
| 2.15 | $40.907 \text{ g mol}^{-1}$   | 2.16 | 73.58 kPa  |
| 2.17 | 12.08 kPa   | 2.18 | 10 g   |
| 2.19 | $23 \text{ g mol}^{-1}$ , 3.53 kPa                                  | 2.20 | 269.07 K   |
| 2.21 | A = 25.58 u and B = 42.64 u   | 2.22 | 0.061 M  |
| 2.24 | KCl, $\text{CH}_3\text{OH}$ , $\text{CH}_3\text{CN}$ , Cyclohexane  |      |  |
| 2.25 | Toluene, chloroform; Phenol, Pentanol; Formic acid, ethylene glycol |      |  |
| 2.26 | 5 m   | 2.27 | $2.45 \times 10^{-8} \text{ M}$  |
| 2.28 | 1.424%  | 2.29 | 3.2 g of water   |
| 2.30 | 4.575 g   | 2.32 | $0.65^0$   |
| 2.33 | $i = 1.0753$ , $K_a = 3.07 \times 10^{-3}$                          | 2.34 | 17.44 mm Hg  |
| 2.35 | $178 \times 10^{-5}$  | 2.36 | 280.7 torr, 32 torr  |
| 2.38 | 0.6 and 0.4   | 2.39 | $x(\text{O}_2) 4.6 \times 10^{-5}$ , $x(\text{N}_2) 9.22 \times 10^{-5}$ |
| 2.40 | 0.03 mol of $\text{CaCl}_2$   | 2.41 | $5.27 \times 10^{-3} \text{ atm}$  |

### UNIT 3

- 3.4 (i)  $E^\ominus = 0.34\text{V}$ ,  $\Delta_r G^\ominus = -196.86 \text{ kJ mol}^{-1}$ ,  $K = 3.124 \times 10^{34}$   
 (ii)  $E^\ominus = 0.03\text{V}$ ,  $\Delta_r G^\ominus = -2.895 \text{ kJ mol}^{-1}$ ,  $K = 3.2$   
 3.5 (i) 2.68 V, (ii) 0.53 V, (iii) 0.08 V, (iv) -1.298 V  
 3.6 1.56 V  
 3.8  $124.0 \text{ S cm}^2 \text{ mol}^{-1}$   
 3.9  $0.219 \text{ cm}^{-1}$   
 3.11  $1.85 \times 10^{-5}$   
 3.12 3F, 2F, 5F  
 3.13 1F, 4.44F  
 3.14 2F, 1F  
 3.15 1.8258g  
 3.16 14.40 min, Copper 0.427g, Zinc 0.437 g

## UNIT 4

- 4.2 (i)  $8.0 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$ ;  $3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$
- 4.4  $\text{bar}^{-1/2} \text{ s}^{-1}$
- 4.6 (i) 4 times (ii)  $\frac{1}{4}$  times
- 4.8 (i)  $4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$  (ii)  $1.98 \times 10^{-2} \text{ s}^{-1}$
- 4.9 (i)  $\text{rate} = k[\text{A}][\text{B}]^2$  (ii) 9 times
- 4.10 Orders with respect to A is 1.5 and order with respect to B is zero.
- 4.11  $\text{rate law} = k[\text{A}][\text{B}]^2$ ;  $\text{rate constant} = 6.0 \text{ M}^{-2} \text{ min}^{-1}$
- 4.13 (i)  $3.47 \times 10^{-3} \text{ seconds}$  (ii) 0.35 minutes (iii) 0.173 years
- 4.14 1845 years 4.16  $4.6 \times 10^{-2} \text{ s}$
- 4.17  $0.7814 \mu\text{g}$  and  $0.227 \mu\text{g}$ . 4.19 77.7 minutes
- 4.20  $2.20 \times 10^{-3} \text{ s}^{-1}$  4.21  $2.23 \times 10^{-3} \text{ s}^{-1}$ ,  $7.8 \times 10^{-4} \text{ atm s}^{-1}$
- 4.23  $3.9 \times 10^{12} \text{ s}^{-1}$  4.24 0.135 M
- 4.25 0.158 M 4.26  $232.79 \text{ kJ mol}^{-1}$
- 4.27  $239.339 \text{ kJ mol}^{-1}$  4.28  $24^\circ\text{C}$
- 4.29  $E_a = 76.750 \text{ kJ mol}^{-1}$ ,  $k = 0.9965 \times 10^{-2} \text{ s}^{-1}$
- 4.30  $52.8 \text{ kJ mol}^{-1}$

## UNIT 6

- 6.1 Zinc is highly reactive metal, it may not be possible to replace it from a solution of  $\text{ZnSO}_4$  so easily.
- 6.2 It prevents one of the components from forming the froth by complexation.
- 6.3 The Gibbs energies of formation of most sulphides are greater than that for  $\text{CS}_2$ . In fact,  $\text{CS}_2$  is an endothermic compound. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.
- 6.5 CO
- 6.6 Selenium, tellurium, silver, gold are the metals present in anode mud. This is because these are less reactive than copper.
- 6.9 Silica removes  $\text{Fe}_2\text{O}_3$  remaining in the matte by forming silicate,  $\text{FeSiO}_3$ .
- 6.15 Cast iron is made from pig iron by melting pig iron with scrap iron and coke. It has slightly lower carbon content ( $\approx 3\%$ ) than pig iron ( $\approx 4\%$  C)
- 6.17 To remove basic impurities, like  $\text{Fe}_2\text{O}_3$
- 6.18 To lower the melting point of the mixture.
- 6.20 The reduction may require very high temperature if CO is used as a reducing agent in this case.
- 6.21 Yes,  $2\text{Al} + \frac{3}{2}\text{O}_2 \rightarrow \text{Al}_2\text{O}_3$   $\Delta_r G^\ominus = -827 \text{ kJ mol}^{-1}$
- $2\text{Cr} + \frac{3}{2}\text{O}_2 \rightarrow \text{Cr}_2\text{O}_3$   $\Delta_r G^\ominus = -540 \text{ kJ mol}^{-1}$
- Hence  $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$   $-827 - (-540) = -287 \text{ kJ mol}^{-1}$
- 6.22 Carbon is better reducing agent.
- 6.25 Graphite rods act as anode and get burnt away as CO and  $\text{CO}_2$  during the process of electrolysis.
- 6.28 Above 1600K Al can reduce MgO.

## UNIT 7

- 7.10** Because of inability of nitrogen to expand its covalency beyond 4.
- 7.20** Freons
- 7.22** It dissolves in rain water and produces acid rain.
- 7.23** Due to strong tendency to accept electrons, halogens act as strong oxidising agent.
- 7.24** Due to high electronegativity and small size, it cannot act as central atom in higher oxoacids.
- 7.25** Nitrogen has smaller size than chlorine. Smaller size favours hydrogen bonding.
- 7.30** Synthesis of  $\text{O}_2\text{PtF}_6$  inspired Bartlett to prepare  $\text{XePtF}_6$  as Xe and oxygen have nearly same ionisation enthalpies.
- 7.31** (i) +3 (ii) +3 (iii) -3 (iv) +5 (v) +5
- 7.34** ClF, Yes.
- 7.36** (i)  $\text{I}_2 < \text{F}_2 < \text{Br}_2 < \text{Cl}_2$   
 (ii)  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$   
 (iii)  $\text{BiH}_3 \leq \text{SbH}_3 < \text{AsH}_3 < \text{PH}_3 < \text{NH}_3$
- 7.37** (ii)  $\text{NeF}_2$
- 7.38** (i)  $\text{XeF}_4$   
 (ii)  $\text{XeF}_2$   
 (iii)  $\text{XeO}_3$

## UNIT 8

- 8.2** It is because  $\text{Mn}^{2+}$  has  $3d^5$  configuration which has extra stability.
- 8.5** 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.
- 8.6** Vanadate  $\text{VO}_3^-$ , chromate  $\text{CrO}_4^{2-}$ , permanganate  $\text{MnO}_4^-$
- 8.10** +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.
- 8.13** 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.
- 8.18** 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.
- 8.21** (i)  $\text{Cr}^{2+}$  is reducing as it involves change from  $d^4$  to  $d^3$ , the latter is more stable configuration  
 ( $t_{2g}^3$ )  $\text{Mn(III)}$  to  $\text{Mn(II)}$  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  $d^1$ .
- 8.23** Copper, because with +1 oxidation state an extra stable configuration,  $3d^{10}$  results.
- 8.24** Unpaired electrons  $\text{Mn}^{3+} = 4$ ,  $\text{Cr}^{3+} = 3$ ,  $\text{V}^{3+} = 2$ ,  $\text{Ti}^{3+} = 1$ . Most stable  $\text{Cr}^{3+}$
- 8.28** Second part 59, 95, 102.
- 8.30** Lawrencium, 103, +3

**8.36**  $Ti^{2+} = 2, V^{2+} = 3, Cr^{3+} = 3, Mn^{2+} = 5, Fe^{2+} = 6, Fe^{3+} = 5, CO^{2+} = 7, Ni^{2+} = 8, Cu^{2+} = 9$

**8.38**  $M\sqrt{n(n+2)} = 2.2, n \approx 1, d^2 sp^3, CN^-$  strong ligand

$= 5.3, n \approx 4, sp^3, d^2, H_2O$  weak ligand

$= 5.9, n \approx 5, sp^3, Cl^-$  weak ligand.

## UNIT 9

**9.5** (i) +3 (ii) +3 (iii) +2 (iv) +3 (v) +3

**9.6** (i)  $[Zn(OH)_4]^{2-}$  (ii)  $K_2[PdCl_4]$  (iii)  $[Pt(NH_3)_2Cl_2]$  (iv)  $K_2[Ni(CN)_4]$

(v)  $[Co(NH_3)_5(ONO)]^{2+}$  (vi)  $[Co(NH_3)_6]_2(SO_4)_3$  (vii)  $K_3[Cr(C_2O_4)_3]$  (viii)  $[Pt(NH_3)_6]^{4+}$

(ix)  $[CuBr_4]^{2-}$  (x)  $[Co(NH_3)_5(NO_2)]^{2+}$

**9.9** (i)  $[Cr(C_2O_4)_3]^{3-}$  - Nil

(ii)  $[Co(NH_3)_3Cl_3]^-$  - Two (*fac*- and *mer*-)

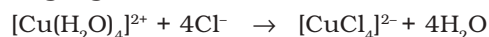
**9.12** Three (two *cis* and one *trans*)

**9.13** Aqueous  $CuSO_4$  solution exists as  $[Cu(H_2O)_4]SO_4$  which has blue colour due to  $[Cu(H_2O)_4]^{2+}$  ions.

(i) When KF is added, the weak  $H_2O$  ligands are replaced by  $F^-$  ligands, forming  $[CuF_4]^{2-}$  ions which is a green precipitate.



(ii) When KCl is added,  $Cl^-$  ligands replace the weak  $H_2O$  ligands forming  $[CuCl_4]^{2-}$  ions which has bright green colour.



**9.14**  $[Cu(H_2O)_4]^{2+} + 4CN^- \rightarrow [Cu(CN)_4]^{2-} + 4H_2O$

As  $CN^-$  is a strong ligand, it forms a highly stable complex with  $Cu^{2+}$  ion. On passing  $H_2S$ , free  $Cu^{2+}$  ions are not available to form the precipitate of  $CuS$ .

**9.23** (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)  $OS = +2, CN = 6, d^5 (t_{2g}^3 e_g^2)$ .

**9.28** (iii)

**9.29** (ii)

**9.30** (iii)

**9.31** (iii)

**9.32** (i) The order of the ligand in the spectrochemical series :



Hence the energy of the observed light will be in the order :



Thus, wavelengths absorbed ( $E = hc/\lambda$ ) will be in the opposite order.