

Answers to Some Questions in Exercises

UNIT 1

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

UNIT 2

- 2.4 16.23 M
2.6 157.8 mL
2.8 17.95 m and 9.10 M
2.15 $40.907 \text{ g mol}^{-1}$
2.17 12.08 kPa
2.19 23 g mol^{-1} , 3.53 kPa
2.21 A = 25.58 u and B = 42.64 u
2.24 KCl, CH_3OH , CH_3CN , Cyclohexane
2.25 Toluene, chloroform; Phenol, Pentanol; Formic acid, ethylene glycol
2.26 5 m
2.28 1.424%
2.30 4.575 g
2.33 $i = 1.0753$, $K_a = 3.07 \times 10^{-3}$
2.35 178×10^{-5}
2.38 0.6 and 0.4
2.40 0.03 mol of CaCl_2
2.5 0.617 m, 0.01 and 0.99, 0.67
2.7 33.5%
2.9 $1.5 \times 10^{-3}\%$, 1.25×10^{-4} m
2.16 73.58 kPa
2.18 10 g
2.20 269.07 K
2.22 0.061 M
2.27 2.45×10^{-8} M
2.29 3.2 g of water
2.32 0.65°
2.34 17.44 mm Hg
2.36 280.7 torr, 32 torr
2.39 $x(\text{O}_2) 4.6 \times 10^{-5}$, $x(\text{N}_2) 9.22 \times 10^{-5}$
2.41 5.27×10^{-3} 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 cm^{-1}
3.11 1.85×10^{-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 rate law = $k[\text{A}][\text{B}]^2$; rate constant = $6.0 \text{ M}^{-2} \text{ min}^{-1}$
- 4.13 (i) 3.47×10^{-3} 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°C
- 4.29 $E_a = 76.750 \text{ kJ mol}^{-1}$, $k = 0.9965 \times 10^{-2} \text{ s}^{-1}$
- 4.30 52.8 kJ mol^{-1}

UNIT 6

- 6.1 Zinc is highly reactive metal, it may not be possible to replace it from a solution of 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 CS_2 . In fact, 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 Fe_2O_3 remaining in the matte by forming silicate, 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 Fe_2O_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, $2\text{Al} + \frac{3}{2}\text{O}_2 \rightarrow \text{Al}_2\text{O}_3 \quad \Delta_r G^\ominus = -827 \text{ kJ mol}^{-1}$
- $2\text{Cr} + \frac{3}{2}\text{O}_2 \rightarrow \text{Cr}_2\text{O}_3 \quad \Delta_r G^\ominus = -540 \text{ kJ mol}^{-1}$
- Hence $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr} \quad -827 - (-540) = -287 \text{ kJ mol}^{-1}$
- 6.22 Carbon is better reducing agent.
- 6.25 Graphite rods act as anode and get burnt away as CO and 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 O_2PtF_6 inspired Bartlett to prepare $XePtF_6$ 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) $I_2 < F_2 < Br_2 < Cl_2$
(ii) $HF < HCl < HBr < HI$
(iii) $BiH_3 \leq SbH_3 < AsH_3 < PH_3 < NH_3$
- 7.37** (ii) NeF_2
- 7.38** (i) XeF_4
(ii) XeF_2
(iii) XeO_3

UNIT 8

- 8.2** It is because 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 VO_3^- , chromate CrO_4^{2-} , permanganate 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 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) 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^{rd} 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 $Mn^{3+} = 4$, $Cr^{3+} = 3$, $V^{3+} = 2$, $Ti^{3+} = 1$. Most stable 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*-)

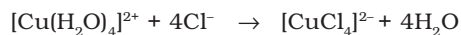
9.12 Three (two *cis* and one *trans*)

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.

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NOTES

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