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 Ni^{2+} = 96% and 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	**2.5**	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**	1.5×10^{-3} %, 1.25×10^{-4} m
2.15	40.907 g mol^{-1}	**2.16**	73.58 *k*Pa
2.17	12.08 *k*Pa	**2.18**	10 g
2.19	23 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, CH_3OH, CH_3CN, Cyclohexane		
2.25	Toluene, chloroform; Phenol, Pentanol; Formic acid, ethylelne glycol		
2.26	5 m	**2.27**	$2.45\text{x}10^{-8}$ 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, $K_a = 3.07\times10^{-3}$	**2.34**	17.44 mm Hg
2.35	178×10^{-5}	**2.36**	280.7 torr, 32 torr
2.38	0.6 and 0.4	**2.39**	$x(O_2)$ $4.6\text{x}10^{-5}$, $x(N_2)$ 9.22×10^{-5}
2.40	0.03 mol of $CaCl_2$	**2.41**	$5.27\text{x}10^{-3}$ atm.

UNIT 3

3.4 (i) $E^{\ominus}$ = 0.34V, $\Delta_rG^{\ominus}$ = – 196.86 kJ mol^{-1}, $K = 3.124 \times 10^{34}$
(ii) $E^{\ominus}$ = 0.03V, $\Delta_rG^{\ominus}$ = – 2.895 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 S cm^2 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

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UNIT 4

4.2 (i) 8.0×10^{-9} mol L^{-1} s^{-1}; 3.89×10^{-9} mol L^{-1} s^{-1}

4.4 $bar^{-1/2}s^{-1}$

4.6 (i) 4 times (ii) ¼ times

4.8 (i) 4.67×10^{-3} mol $L^{-1}s^{-1}$ (ii) 1.98×10^{-2} s^{-1}

4.9 (i) rate = $k[A][B]^2$ (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 = $k[A][B]^2$; rate constant = 6.0 $M^{-2}min^{-1}$

4.13 (i) $3.47 \text{ x } 10^{-3}$ seconds (ii) 0.35 minutes (iii) 0.173 years

4.14 1845 years

4.16 4.6×10^{-2} s

4.17 0.7814 μg and 0.227 μg.

4.19 77.7 minutes

4.20 2.20×10^{-3} s^{-1}

4.21 2.23×10^{-3} s^{-1}, 7.8×10^{-4} atm s^{-1}

4.23 3.9×10^{12} s^{-1}

4.24 0.135 M

4.25 0.158 M

4.26 232.79 kJ mol^{-1}

4.27 239.339 kJ mol^{-1}

4.28 24°C

4.29 E_a = 76.750 kJ mol^{-1}, $k = 0.9965 \times 10^{-2}$ 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 (» 3%) than pig iron (» 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, $2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 \quad \Delta_r G^\ominus = -827 \text{ kJ mol}^{-1}$

$$2Cr + \frac{3}{2}O_2 \rightarrow Cr_2O_3 \quad \Delta_r G^\ominus = -540 \text{ kJ mol}^{-1}$$

Hence $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr \quad -827-(-540) = -287 \text{ kJ mol}^{-1}$

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.

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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 3*d*-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 3rd 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

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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.

$$[Cu(H_2O)_4]^{2+} + 4F^- \rightarrow [CuF_4]^{2-} + 4H_2O$$

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

$$[Cu(H_2O)_4]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 4H_2O$$

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

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 :

$H_2O < NH_3 < NO_2^-$

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

$[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$

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

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NOTES

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