Answers to Some Questions in Exercises

UNIT 1

1.4	16.23 M	**1.5**	0.617 m, 0.01 and 0.99, 0.67
1.6	157.8 mL	**1.7**	33.5%
1.8	17.95 m and 9.10 M	**1.9**	1.5×10^{-3}%, 1.25×10^{-4} m
1.15	40.907 g mol^{-1}	**1.16**	73.58 *k*Pa
1.17	12.08 *k*Pa	**1.18**	10 g
1.19	23 g mol^{-1}, 3.53 kPa	**1.20**	269.07 *K*
1.21	A = 25.58 u and B = 42.64 u	**1.22**	0.061 M
1.24	KCl, CH_3OH, CH_3CN, Cyclohexane		
1.25	Toluene, chloroform; Phenol, Pentanol; Formic acid, ethylelne glycol		
1.26	5 m	**1.27**	$2.45\text{x}10^{-8}$ M
1.28	1.424%	**1.29**	3.2 g of water
1.30	4.575 g	**1.32**	0.65^0
1.33	i = 1.0753, $K_a = 3.07\times10^{-3}$	**1.34**	17.44 mm Hg
1.35	178×10^{-5}	**1.36**	280.7 torr, 32 torr
1.38	0.6 and 0.4	**1.39**	$x\,(O_2)$ $4.6\text{x}10^{-5}$, $x\,(N_2)$ 9.22×10^{-5}
1.40	0.03 mol of $CaCl_2$	**1.41**	$5.27\text{x}10^{-3}$ atm.

UNIT 2

2.4	(i) $E^o = 0.34V$, $\Delta_rG^o = -196.86$ kJ mol^{-1}, $K = 3.124 \times 10^{34}$ (ii) $E^o = 0.03V$, $\Delta_rG^o = -2.895$ 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 S cm^2 mol^{-1}
2.9	0.219 cm^{-1}
2.11	1.85×10^{-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) 8.0×10^{-9} mol L^{-1} s^{-1}; 3.89×10^{-9} mol L^{-1} s^{-1}	
3.4	$bar^{-1/2}s^{-1}$	
3.6	(i) 4 times	(ii) ¼ times
3.8	(i) 4.67×10^{-3} mol $L^{-1}s^{-1}$	(ii) 1.98×10^{-2} s^{-1}
3.9	(i) rate = $k[A][B]^2$	(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 M^{-2}min^{-1}

3.13 (i) 3.47 x 10^{-3} seconds (ii) 0.35 minutes (iii) 0.173 years

3.14 1845 years

3.16 4.6 × 10^{-2} s

3.17 0.7814 μg and 0.227 μg.

3.19 77.7 minutes

3.20 2.20 × 10^{-3} s^{-1}

3.21 2.23 × 10^{-3} s^{-1}, 7.8 ×10^{-4} atm s^{-1}

3.23 3.9 × 10^{12} s^{-1}

3.24 0.135 M

3.25 0.158 M

3.26 232.79 kJ mol^{-1}

3.27 239.339 kJ mol^{-1}

3.28 24°C

3.29 E_a = 76.750 kJ mol^{-1}, k = 0.9965 × 10^{-2} s^{-1}

3.30 52.8 kJ mol^{-1}

UNIT 4

4.2 It is because 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 VO_3^-, chromate CrO_4^{2-}, permanganate 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 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) 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.

4.23 Copper, because with +1 oxidation state an extra stable configuration, 3d^{10} results.

4.24 Unpaired electrons Mn^{3+} = 4, Cr^{3+} = 3, V^{3+} = 2, Ti^{3+} = 1. Most stable Cr^{3+}

4.28 Second part 59, 95, 102.

4.30 Lawrencium, 103, +3

4.36 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

4.38 $M\sqrt{n(n+2)}$ = 2.2, n ≈ 1, d^2 sp^3, CN^- strong ligand

= 5.3, n ≈ 4, sp^3, d^2, H_2O weak ligand

= 5.9, n ≈ 5, sp^3, Cl^- weak ligand.

UNIT 5

5.5 (i) + 3 (ii) +3 (iii) +2 (iv) +3 (v) +3

5.6 (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) $[Co(NH_3)_5(NO_2)]^{2+}$

5.9 (i) $[Cr(C_2O_4)_3]^{3-}$ – Nil
(ii) $[Co(NH_3)_3Cl_3]$ – Two (*fac*- and *mer*-)

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

5.13 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.

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

5.14 $[Cu(H_2O)_4]^{2+} + 4\,CN^- \rightarrow [Cu(CN)_4]^{2-} + 4H_2O$

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.

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 :

$H_2O < NH_3 < NO_2^-$

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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