

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 | 2.5 | 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 | $1.5 \times 10^{-3}\%$, 1.25×10^{-4} 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 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, ethylene glycol | | |
| 2.26 | 4 m | 2.27 | 2.45×10^{-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 | $i = 1.0753$, $K_a = 3.07 \times 10^{-3}$ | 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 | $x(\text{O}_2) 4.6 \times 10^{-5}$, $x(\text{N}_2) 9.22 \times 10^{-5}$ |
| 2.40 | 0.03 mol of CaCl_2 | 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) 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 = $6.0 \text{ M}^{-2} \text{ min}^{-1}$
- 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 μg and 0.227 μg . 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 kJ mol^{-1}
- 4.27 239.339 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 ($\approx 4\% \text{ C}$)
- 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
 $3d^8$ (Cobalt): +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 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

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 wavelength of the light observed will be in the order :



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

Elements, their Atomic Number and Molar Mass

Element	Symbol	Atomic Number	Molar mass/ (g mol ⁻¹)
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.22
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitneium	Mt	109	(268)
Mendelevium	Md	101	258.10

Element	Symbol	Atomic Number	Molar mass/ (g mol ⁻¹)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununbium	Uub	112	(277)
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

The value given in parenthesis is the molar mass of the isotope of largest known half-life.