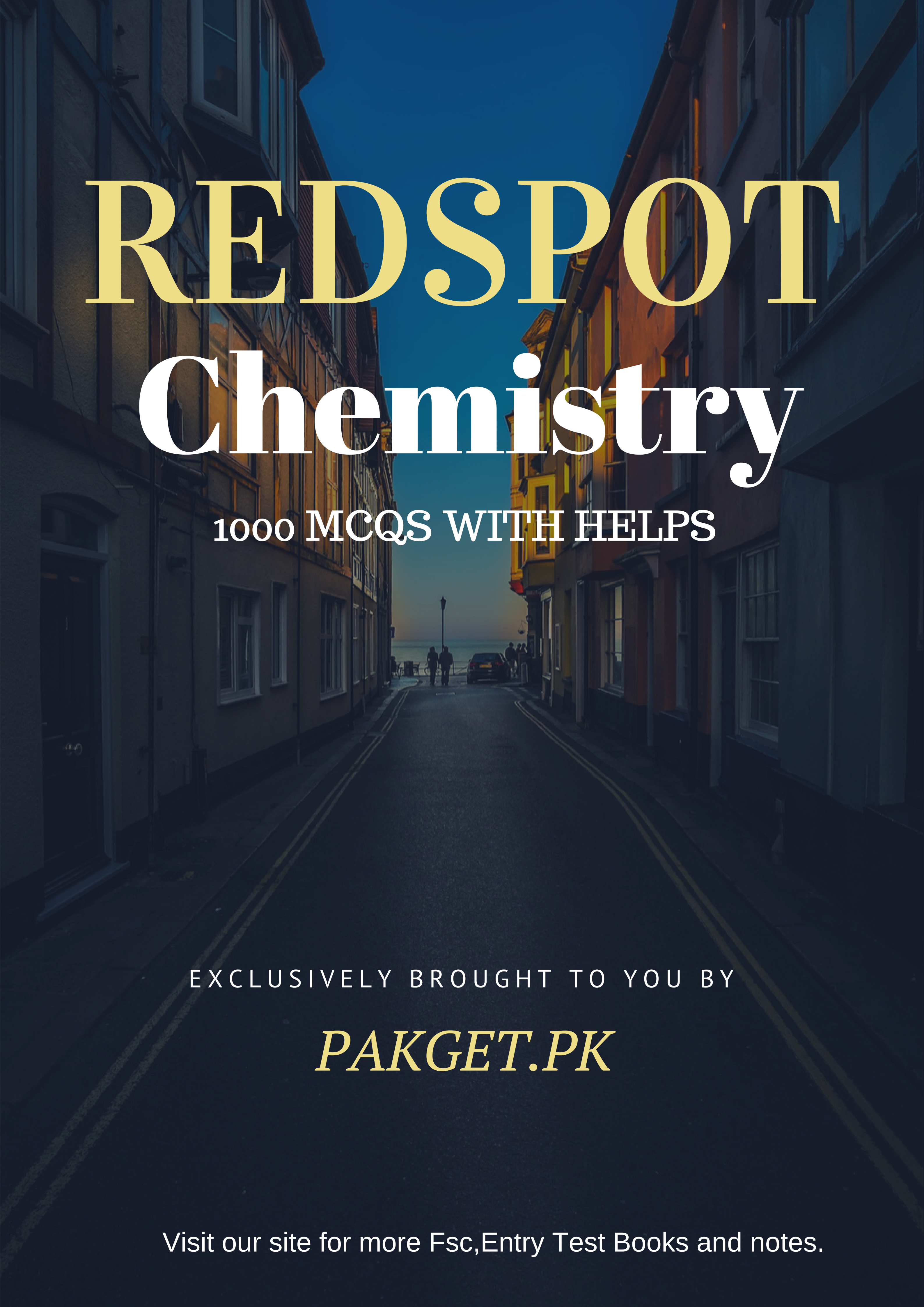

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Contents

Data Booklet

for

Chemistry (Advanced Level)

TABLES OF CHEMICAL DATA

Important values, constants and standards

molar gas constant	R	$= 8.31\ J\ K^{-1}\ mol^{-1}$
the Faraday constant	F	$= 9.65 \times 10^{4}\ C\ mol^{-1}$
the Avogadro constant	L	$= 6.02 \times 10^{23}\ mol^{-1}$
the Planck constant	h	$= 6.63 \times 10^{-34}\ J\ s$
speed of light in a vacuum	c	$= 3.00 \times 10^{8}\ m\ s^{-1}$
rest mass of proton, ${}^{1}_{1}H$	m_p	$= 1.67 \times 10^{-27}\ kg$
rest mass of neutron, ${}^{1}_{0}n$	m_n	$= 1.67 \times 10^{-27}\ kg$
rest mass of electron, ${}^{0}_{-1}e$	m_e	$= 9.11 \times 10^{-31}\ kg$
electronic charge	e	$= -1.60 \times 10^{-19}\ C$
molar volume of gas	V_m	$= 22.4\ dm^{3}\ mol^{-1}$ at s.t.p.
	V_m	$= 24\ dm^{3}\ mol^{-1}$ under room conditions

(where s.t.p. is expressed as 101 kPa, approximately, and 273 K (0 °C))

ionic product of water	K_w	$= 1.00 \times 10^{-14}\ mol^{2}\ dm^{-6}$ (at 298 K [25 °C])
specific heat capacity of water		$= 4.18\ kJ\ kg^{-1}\ K^{-1}$ ($= 4.18\ J\ g^{-1}\ K^{-1}$)

Ionisation energies (1st, 2nd, 3rd and 4th) of selected elements, in kJ mol^{-1}

	Proton Number	First	Second	Third	Fourth
H	1	1310	-	-	-
He	2	2370	5250	-	-
Li	3	519	7300	11800	-
Be	4	900	1760	14800	21000
B	5	799	2420	3660	25000
C	6	1090	2350	4610	6220
N	7	1400	2860	4590	7480
O	8	1310	3390	5320	7450
F	9	1680	3370	6040	8410
Ne	10	2080	3950	6150	9290
Na	11	494	4560	6940	9540
Mg	12	736	1450	7740	10500
Al	13	577	1820	2740	11600
Si	14	786	1580	3230	4360
P	15	1060	1900	2920	4960
S	16	1000	2260	3390	4540
Cl	17	1260	2300	3850	5150
Ar	18	1520	2660	3950	5770
K	19	418	3070	4600	5860
Ca	20	590	1150	4940	6480
Sc	21	632	1240	2390	7110
Ti	22	661	1310	2720	4170
V	23	648	1370	2870	4600
Cr	24	653	1590	2990	4770
Mn	25	716	1510	3250	5190
Fe	26	762	1560	2960	5400
Co	27	757	1640	3230	5100
Ni	28	736	1750	3390	5400
Cu	29	745	1960	3350	5690
Zn	30	908	1730	3828	5980
Ga	31	577	1980	2960	6190
Ge	32	762	1540	3300	4390
Br	35	1140	2080	3460	4850
Sr	38	548	1060	4120	5440
Sn	50	707	1410	2940	3930
I	53	1010	1840	2040	4030
Ba	56	502	966	3390	-
Pb	82	716	1450	3080	4080

Bond energies

(a) Diatomic molecules

Bond	Energy/kJ mol^{-1}
H—H	436
D—D	442
N≡N	994
O=O	496
F—F	158
Cl—Cl	244
Br—Br	193
I—I	151
H—F	562
H—Cl	431
H—Br	366
H—I	299

(b) Polyatomic molecules

Bond	Energy/kJ mol^{-1}
C—C	350
C=C	610
C≡C	840
C⋯C (benzene)	520
C—H	410
C—Cl	340
C—Br	280
C—I	240
C—O	360
C=O	740
C—N	305
C=N	610
C≡N	890
N—H	390
N—N	160
N=N	410
O—H	460
O—O	150
Si—Cl	359
Si—H	320
Si—O	444
Si—Si	222
S—Cl	250
S—H	347
S—S	264

Standard electrode potential and redox potentials, $E^\ominus$ at 298 K (25 °C)

For ease of reference, two tabulations are given:

(a) an extended list in alphabetical order;

(b) a shorter list in decreasing order of magnitude, i.e. a redox series.

(a) $E^\ominus$ in alphabetical order

Electrode reaction			$E^\ominus$/V
$Ag^+ + e^-$	⇌	Ag	+0.80
$Al^{3+} + 3e^-$	⇌	Al	−1.66
$Ba^{2+} + 2e^-$	⇌	Ba	−2.90
$Br_2 + 2e^-$	⇌	$2Br^-$	+1.07
$Ca^{2+} + 2e^-$	⇌	Ca	−2.87
$Cl_2 + 2e^-$	⇌	$2Cl^-$	+1.36
$2HOCl + 2H^+ + 2e^-$	⇌	$Cl_2 + 2H_2O$	+1.64
$Co^{2+} + 2e^-$	⇌	Co	−0.28
$Co^{3+} + e^-$	⇌	Co^{2+}	+1.82
$[Co(NH_3)_6]^{2+} + 2e^-$	⇌	$Co + 6NH_3$	−0.43
$Cr^{2+} + 2e^-$	⇌	Cr	−0.91
$Cr^{3+} + 3e^-$	⇌	Cr	−0.74
$Cr^{3+} + e^-$	⇌	Cr^{2+}	−0.41
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	⇌	$2Cr^{3+} + 7H_2O$	+1.33
$Cu^+ + e^-$	⇌	Cu	+0.52
$Cu^{2+} + 2e^-$	⇌	Cu	+0.34
$Cu^{2+} + e^-$	⇌	Cu^+	+0.15
$[Cu(NH_3)_4]^{2+} + 2e^-$	⇌	$Cu + 4NH_3$	−0.05
$F_2 + 2e^-$	⇌	$2F^-$	+2.87
$Fe^{2+} + 2e^-$	⇌	Fe	−0.44
$Fe^{3+} + 3e^-$	⇌	Fe	−0.04
$Fe^{3+} + e^-$	⇌	Fe^{2+}	+0.77
$[Fe(CN)_6]^{3-} + e^-$	⇌	$[Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_3 + e^-$	⇌	$Fe(OH)_2 + OH^-$	−0.56
$2H^+ + 2e^-$	⇌	H_2	0.00
$I_2 + 2e^-$	⇌	$2I^-$	+0.54
$K^+ + e^-$	⇌	K	−2.92
$Li^+ + e^-$	⇌	Li	−3.04
$Mg^{2+} + 2e^-$	⇌	Mg	−2.38
$Mn^{2+} + 2e^-$	⇌	Mn	−1.18
$Mn^{3+} + e^-$	⇌	Mn^{2+}	+1.49
$MnO_2 + 4H^+ + 2e^-$	⇌	$Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + e^-$	⇌	MnO_4^{2-}	+0.56
$MnO_4^- + 4H^+ + 3e^-$	⇌	$MnO_2 + 2H_2O$	+1.67
$MnO_4^- + 8H^+ + 5e^-$	⇌	$Mn^{2+} + 4H_2O$	+1.52
$NO_3^- + 2H^+ + e^-$	⇌	$NO_2 + H_2O$	+0.81
$NO_3^- + 3H^+ + 2e^-$	⇌	$HNO_2 + H_2O$	+0.94
$NO_3^- + 10H^+ + 8e^-$	⇌	$NH_4^+ + 3H_2O$	+0.87

$Na^+ + e^-$	$\rightleftharpoons$	Na	–2.71
$Ni^{2+} + 2e^-$	$\rightleftharpoons$	Ni	–0.25
$[Ni(NH_3)_6]^{2+} + 2e^-$	$\rightleftharpoons$	$Ni + 6NH_3$	–0.51
$H_2O_2 + 2H^+ + 2e^-$	$\rightleftharpoons$	$2H_2O$	+1.77
$O_2 + 4H^+ + 4e^-$	$\rightleftharpoons$	$2H_2O$	+1.23
$O_2 + 2H_2O + 4e^-$	$\rightleftharpoons$	$4OH^-$	+0.40
$O_2 + 2H^+ + 2e^-$	$\rightleftharpoons$	H_2O_2	+0.68
$2H_2O + 2e^-$	$\rightleftharpoons$	$H_2 + 2OH^-$	–0.83
$Pb^{2+} + 2e^-$	$\rightleftharpoons$	Pb	–0.13
$Pb^{4+} + 2e^-$	$\rightleftharpoons$	Pb^{2+}	+1.69
$PbO_2 + 4H^+ + 2e^-$	$\rightleftharpoons$	$Pb^{2+} + 2H_2O$	+1.47
$SO_4^{2-} + 4H^+ + 2e^-$	$\rightleftharpoons$	$SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^-$	$\rightleftharpoons$	$2SO_4^{2-}$	+2.01
$S_4O_6^{2-} + 2e^-$	$\rightleftharpoons$	$2S_2O_3^{2-}$	+0.09
$Sn^{2+} + 2e^-$	$\rightleftharpoons$	Sn	–0.14
$Sn^{4+} + 2e^-$	$\rightleftharpoons$	Sn^{2+}	+0.15
$V^{2+} + 2e^-$	$\rightleftharpoons$	V	–1.20
$V^{3+} + e^-$	$\rightleftharpoons$	V^{2+}	–0.26
$VO^{2+} + 2H^+ + e^-$	$\rightleftharpoons$	$V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^-$	$\rightleftharpoons$	$VO^{2+} + H_2O$	+1.00
$VO_3^- + 4H^+ + e^-$	$\rightleftharpoons$	$VO^{2+} + 2H_2O$	+1.00
$Zn^{2+} + 2e^-$	$\rightleftharpoons$	Zn	–0.76

All ionic states refer to aqueous ions but other state symbols have been omitted.

(b) $E^{\ominus}$ in decreasing order of oxidising power

(see also the extended alphabetical list on the previous pages)

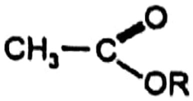
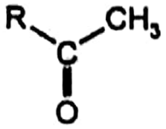
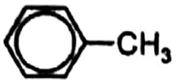
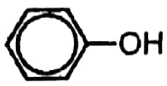
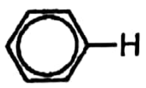
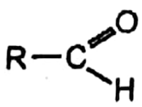
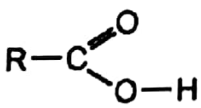
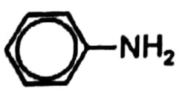
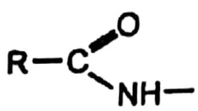
Electrode reaction			$E^{\ominus}$/V
$F_2 + 2e^-$	$\rightleftharpoons$	$2F^-$	+2.87
$S_2O_8^{2-} + 2e^-$	$\rightleftharpoons$	$2SO_4^{2-}$	+2.01
$H_2O_2 + 2H^+ + 2e^-$	$\rightleftharpoons$	$2H_2O$	+1.77
$MnO_4^- + 8H^+ + 5e^-$	$\rightleftharpoons$	$Mn^{2+} + 4H_2O$	+1.52
$PbO_2 + 4H^+ + 2e^-$	$\rightleftharpoons$	$Pb^{2+} + 2H_2O$	+1.47
$Cl_2 + 2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightleftharpoons$	$2Cr^{3+} + 7H_2O$	+1.33
$Br_2 + 2e^-$	$\rightleftharpoons$	$2Br^-$	+1.07
$NO_3^- + 2H^+ + e^-$	$\rightleftharpoons$	$NO_2 + H_2O$	+0.81
$Ag^+ + e^-$	$\rightleftharpoons$	Ag	+0.80
$Fe^{3+} + e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77
$I_2 + 2e^-$	$\rightleftharpoons$	$2I^-$	+0.54
$O_2 + 2H_2O + 4e^-$	$\rightleftharpoons$	$4OH^-$	+0.40
$Cu^{2+} + 2e^-$	$\rightleftharpoons$	Cu	+0.34
$SO_4^{2-} + 4H^+ + 2e^-$	$\rightleftharpoons$	$SO_2 + 2H_2O$	+0.17
$Sn^{4+} + 2e^-$	$\rightleftharpoons$	Sn^{2+}	+0.15
$S_4O_6^{2-} + 2e^-$	$\rightleftharpoons$	$2S_2O_3^{2-}$	+0.09
$2H^+ + 2e^-$	$\rightleftharpoons$	H_2	0.00
$Pb^{2+} + 2e^-$	$\rightleftharpoons$	Pb	–0.13
$Sn^{2+} + 2e^-$	$\rightleftharpoons$	Sn	–0.14
$Fe^{2+} + 2e^-$	$\rightleftharpoons$	Fe	–0.44
$Zn^{2+} + 2e^-$	$\rightleftharpoons$	Zn	–0.76
$Mg^{2+} + 2e^-$	$\rightleftharpoons$	Mg	–2.38
$Ca^{2+} + 2e^-$	$\rightleftharpoons$	Ca	–2.87
$K^+ + e^-$	$\rightleftharpoons$	K	–2.92

Atomic and ionic radii

		atomic/nm		ionic/nm	
(a) Period 3					
metallic		Na	0.186	Na^{+}	0.095
		Mg	0.160	Mg^{2+}	0.065
		Al	0.143	Al^{3+}	0.050
single covalent		Si	0.117	Si^{4+}	0.041
		P	0.110	P^{3-}	0.212
		S	0.104	S^{2-}	0.184
		Cl	0.099	Cl^{-}	0.181
van der Waals		Ar	0.192		
(b) Group II					
metallic		Be	0.112	Be^{2+}	0.031
		Mg	0.160	Mg^{2+}	0.065
		Ca	0.197	Ca^{2+}	0.099
		Sr	0.215	Sr^{2+}	0.113
		Ba	0.217	Ba^{2+}	0.135
		Ra	0.220	Ra^{2+}	0.140
(c) Group IV					
single covalent		C	0.077		
		Si	0.117	Si^{4+}	0.041
		Ge	0.122	Ge^{2+}	0.093
metallic		Sn	0.162	Sn^{2+}	0.112
		Pb	0.175	Pb^{2+}	0.120
(d) Group VII					
single covalent		F	0.072	F^{-}	0.136
		Cl	0.099	Cl^{-}	0.181
		Br	0.114	Br^{-}	0.195
		I	0.133	I^{-}	0.216
		At	0.140		
(e) First row transition elements					
single covalent		Sc	0.144	Sc^{3+}	0.081
		Ti	0.132	Ti^{2+}	0.090
		V	0.122	V^{3+}	0.074
		Cr	0.117	Cr^{3+}	0.069
		Mn	0.117	Mn^{2+}	0.080
		Fe	0.116	Fe^{2+}	0.076
				Fe^{3+}	0.064
		Co	0.116	Co^{2+}	0.078
		Ni	0.115	Ni^{2+}	0.078
		Cu	0.117	Cu^{2+}	0.069
		Zn	0.125	Zn^{2+}	0.074

Bond		Characteristic ranges Wavenumber (reciprocal wavelength) /cm^{-1}
C—Cl		700 to 800
C—O	alcohols, ethers, esters	1000 to 1300
C=C		1610 to 1680
C=O	aldehydes, ketones, acids, esters	1680 to 1750
C≡C		2070 to 2250
C≡N		2200 to 2280
O—H	'hydrogen-bonded' in acids	2500 to 3300
C—H	alkanes, alkenes, arenes	2840 to 3095
O—H	'hydrogen-bonded' in alcohols, phenols	3230 to 3550
N—H	primary amines	3350 to 3500
O—H	'free'	3580 to 3650

Typical proton chemical shift value (δ) relative to T.M.S.=0

Type of proton	Chemical shift (ppm)
$R-CH_3$	0.9
$R-CH_2-R$	1.3
R_3CH	1.4–1.7
	2.0
	2.1
	2.3
$R-C\equiv C-H$	1.8–3.1
$R-CH_2-Hal$	3.2–3.7
$R-O-CH_3$	3.3–4.0
$R-O-H$	0.5–6.0*
$R_2C=CH-$	4.5–6.0
	4.5–7.0*
	6.0–9.0
	9.0–10.0
	9.0–13.0*
$R-NH_2$	1.0–5.0*
	3.0–6.0*
	5.0–12.0*

* : sensitive to solvent, concentration

TOPIC

1

Atoms, Molecules and Stoichiometry

Key content that you will be examined on:

1. Relative masses of atoms and molecules
2. The mole, the Avogadro constant
3. The calculation of empirical and molecular formulae
4. Reacting masses and volumes (of solutions and gases)

Atoms, Molecules and Stoichiometry

Topic 1

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. The relative atomic mass of boron, which consists of the isotopes $^{10}_{5}B$ and $^{11}_{5}B$ is 10.8. What is the percentage of $^{11}_{5}B$ atoms in the isotopic mixture?

   A 0.8% **B** 8.0%
   C 20% **D** 80%

Helping Concepts *Exam Favourite Rating* ★★★

Let x be the percentage of $^{11}_{5}B$ atoms in the isotopic mixture.

$$10(1-x)+11x=10.8$$
$$x=0.8 \text{ (or 80\%)}$$

2. In the absence of a catalyst, ammonia burns in an excess of oxygen to produce steam and nitrogen. What is the volume of oxygen remaining when 60 cm^3 of ammonia is burnt in 100 cm^3 of oxygen, all volumes being measured at the same temperature and pressure?

   A 35 cm^3 **B** 40 cm^3
   C 45 cm^3 **D** 55 cm^3

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$$4NH_3(g)+3O_2(g) \rightarrow 2N_2(g)+6H_2O(g)$$

60 cm^3 of NH_3 requires $\frac{3}{4}\times 60=45\ cm^3$ of O_2.

$\therefore$ Volume of excess $O_2=100-45=55\ cm^3$

3. For complete oxidation, 1 mol of an organic compound requires 3 mol of oxygen gas. What could be the formula of the compound?

   A CH_3CHO **B** CH_3CH_2OH
   C CH_3CH_3 **D** CH_3CO_2H

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$$CH_3CH_2OH+3O_2 \rightarrow 2CO_2+3H_2O$$

A: $CH_3CHO+\frac{5}{2}O_2 \rightarrow 2CO_2+2H_2O$

C: $CH_3CH_3+\frac{7}{2}O_2 \rightarrow 2CO_2+3H_2O$

D: $CH_3CO_2H+2O_2 \rightarrow 2CO_2+2H_2O$

4. *Use of the Data Booklet is relevant to this question.*

   What is the number of molecules in 500 cm^3 of oxygen under room conditions?

   A 1.25×10^{22} **B** 1.34×10^{22}
   C 3.0×10^{22} **D** 3.0×10^{26}

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Under room conditions, 1 mole of gas occupies 24000 cm^3.

Hence, $n=\dfrac{500}{24000}=2.083\times10^{-2}$ mol

$\therefore N=2.083\times10^{-2}\times6.02\times10^{23}$
$=1.25\times10^{22}$

5. ^{9}Be is used in the production of 'fast neutrons'. How many neutrons are present in 0.09 g of ^{9}Be? [L = Avogadro constant]

   A 0.04L **B** 0.05L
   C 0.09L **D** 0.45L

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In $^{9}_{4}Be$, there are 4 protons and $9-4=5$ neutrons.

$n_{Be}=\dfrac{0.09}{9}=0.01$ mol

$n_{neutrons}=5\times0.01=0.05$ mol

$\therefore N_{neutrons}=0.05L$

6. Which of these samples of gas contains the same number of atoms as 1 g of hydrogen (M_r: H_2, 2)?

A 22 g of carbon dioxide (M_r: CO_2, 44)
B 8 g of methane (M_r: CH_4, 16)
C 20 g of neon (M_r: Ne, 20)
D 8 g of ozone (M_r: O_3, 48)

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A: $n = \frac{22}{44} \times 3 = 1.5$ mol

B: $n = \frac{8}{16} \times 5 = 2.5$ mol

C: $n = \frac{20}{20} = 1$ mol

D: $n = \frac{8}{48} \times 3 = 0.5$ mol

---

7. Which statement about one mole of metal is always correct?

A It contains the same number of atoms as 1 mol of hydrogen atoms.
B It contains the same number of atoms as $\frac{1}{12}$ mol of ^{12}C.
C It has the same mass as 1 mol of hydrogen atoms.
D It is liberated by 1 mol of electrons.

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1 mol of a substance contains 6.02×10^{23} of that substance. Hence, 1 mol of a metal contains the same number of atoms as 1 mol of hydrogen atoms.

---

8. How many atoms of carbon are present in 18 g of glucose, $C_6H_{12}O_6$?

A 6.0×10^{22}
B 3.6×10^{23}
C 6.0×10^{23}
D 3.6×10^{24}

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Molar mass of $C_6H_{12}O_6 = 6\times12+12\times1+6\times16$
$= 180$ g mol^{-1}

Amount of $C_6H_{12}O_6 = \frac{18}{180} = 0.1$ mol

Amount of C atoms $= 6\times0.1 = 0.6$ mol

Number of C atoms $= 0.6\times6\times10^{23} = 3.6\times10^{23}$

---

9. What volume of oxygen is required for the complete combustion of a mixture of 5 cm^3 of CH_4 and 5 cm^3 of C_2H_4?

A 10 cm^3
B 15 cm^3
C 20 cm^3
D 25 cm^3

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$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$
$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(\ell)$$

Volume of O_2 required to burn 5 cm^3 of $CH_4 = 2\times5$
$= 10$ cm^3

Volume of O_2 required to burn 5 cm^3 of $C_2H_4 = 3\times5$
$= 15$ cm^3

Total volume of O_2 required $= 10+15 = 25$ cm^3

---

10. *Use of the Data Booklet is relevant to this question.*

A substance **X** was found to contain 72% carbon, 12% hydrogen and 16% oxygen.

What is the empirical formula of **X**?

A C_2H_4O
B C_3H_6O
C $C_6H_{12}O$
D $C_6H_{12}O_2$

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	C		H		O
% mass	72		12		16
A_r	12		1		16
Molar ratio	$\frac{72}{12}$	:	$\frac{12}{1}$	:	$\frac{16}{16}$
	$= 6$	:	12	:	1

---

11. What volume of 0.10 mol dm^{-3} aqueous silver nitrate reacts with 20 cm^3 of 0.20 mol dm^{-3} barium chloride?

A 10 cm^3
B 20 cm^3
C 40 cm^3
D 80 cm^3

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$$2AgNO_3(aq) + BaCl_2(aq)$$
$$\rightarrow 2AgCl(s) + Ba(NO_3)_2(aq)$$

Amount of $BaCl_2$ = concentration × volume
$= 0.20$ mol $dm^{-3} \times \frac{20}{1000}$ dm^3
$= 4\times10^{-3}$ mol

Amount of $AgNO_3 = 2 \times (4 \times 10^{-3})$
$= 8 \times 10^{-3}$ mol

Volume of $AgNO_3 = \dfrac{8 \times 10^{-3}}{0.10}$
$= 0.08\ dm^3$
$= 80\ cm^3$

---

12. When 20 cm^3 of a gaseous hydrocarbon were completely burnt in an excess of oxygen, 60 cm^3 of carbon dioxide and 40 cm^3 of water vapour were formed, all volumes being measured at the same temperature and pressure.

What is the formula of the hydrocarbon?

A C_2H_6 **B** C_3H_4
C C_3H_6 **D** C_3H_8

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$$C_xH_y + (x+\tfrac{y}{4})O_2 \rightarrow xCO_2 + \tfrac{y}{2}H_2O$$

1 volume of C_xH_y produces x volumes of CO_2 and $\frac{y}{2}$ volumes of H_2O vapour. Therefore from the data, $x = 3$ and $\frac{y}{2} = 2$. Hence, the hydrocarbon is C_3H_4.

---

13. Naturally occurring silicon is a mixture of three isotopes, ^{28}Si, ^{29}Si and ^{30}Si. The relative atomic mass of silicon is 28.109.

What could be the relative abundance of each of the three isotopes?

A 91.1% ^{28}Si, 7.9% ^{29}Si and 1.0% ^{30}Si
B 92.2% ^{28}Si, 4.7% ^{29}Si and 3.1% ^{30}Si
C 95.0% ^{28}Si, 3.2% ^{29}Si and 1.8% ^{30}Si
D 96.3% ^{28}Si, 0.3% ^{29}Si and 3.4% ^{30}Si

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A: $A_r = (0.911 \times 28) + (0.079 \times 29) + (0.01 \times 30)$
$= 28.099$

C: $A_r = 28.068$

D: $A_r = 28.071$

2nd method

---

14. A 0.20 g sample of a monobasic acid requires 8.0 cm^3 of 0.40 mol dm^{-3} sodium hydroxide for complete reaction.

What is the relative molecular mass of the acid?

A 62.5 **B** 250
C 625 **D** 640

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$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(\ell)$$

Amount of NaOH used = concentration × volume
$= 0.4\ mol\ dm^{-3} \times \frac{8}{1000}\ dm^3$
$= 3.2 \times 10^{-3}$ mol

Amount of HA $= 3.2 \times 10^{-3}$ mol

Molar mass of HA $= \dfrac{0.20\ g}{3.2 \times 10^{-3}\ mol}$
$= 62.5\ g\ mol^{-1}$

---

15. On collision, airbags in cars inflate rapidly due to the production of nitrogen.

The nitrogen is formed according to the following equations.

$$2NaN_3 \rightarrow 2Na + 3N_2$$
$$10Na + 2KNO_3 \rightarrow K_2O + 5Na_2O + N_2$$

How many moles of nitrogen gas are produced from 1 mol of sodium azide, NaN_3?

A 1.5 **B** 1.6
C 3.2 **D** 4.0

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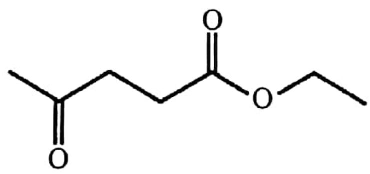
1 mol of NaN_3 produces 1 mol of Na and 1.5 mol of N_2.

1 mol of Na produces 0.1 mol of N_2.

Hence, total amount of $N_2 = 1.5 + 0.1 = 1.6$ mol

---

16. Compound G is a diesel fuel additive which reduces the amount of soot formed when the fuel burns.



compound G

How many moles of oxygen gas are needed to completely burn 1 mole of compound G?

A 8.5 B 9.0
C 9.5 D 10.0

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G is $C_7H_{12}O_3$.

$$C_7H_{12}O_3 + \frac{17}{2}O_2 \rightarrow 7CO_2 + 6H_2O$$

---

17. Self-igniting flares contain Mg_3P_2. With water this produces diphosphane, P_2H_4, which is spontaneously flammable in air.

Which equation that includes the formation of diphosphane is balanced?

A $Mg_3P_2 + 6H_2O \rightarrow 3Mg(OH)_2 + P_2H_4$
B $Mg_3P_2 + 6H_2O \rightarrow 3Mg(OH)_2 + P_2H_4 + H_2$
C $2Mg_3P_2 + 12H_2O \rightarrow 6Mg(OH)_2 + P_2H_4 + 2PH_3$
D $2Mg_3P_2 + 12H_2O \rightarrow 6Mg(OH)_2 + 3P_2H_4$

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A: H is not balanced.
C: H is not balanced.
D: P is not balanced.

---

18. A gaseous organic compound, *X*, was burnt in an excess of oxygen. A 0.112 dm^3 sample of *X*, measured at s.t.p., produced 0.88 g of carbon dioxide.

How many carbon atoms are there in one molecule of *X*?

A 1 B 2
C 3 D 4

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Let *x* be the number of C atoms per molecule of *X*. Therefore, 1 mole of *X* will produce *x* moles of CO_2 when completely burnt in O_2.

$$\text{Amount of } X \text{ used} = \frac{0.112}{22.4} = 5.00\times10^{-3} \text{ mol}$$

$$\text{Amount of } CO_2 \text{ produced} = \frac{0.88}{12+2(16)} = 2.0\times10^{-2} \text{ mol}$$

$$\therefore (5.00\times10^{-3})x = 2.0\times10^{-2} \Rightarrow x = 4$$

---

19. Ethanedioate ions, $C_2O_4^{2-}$, are oxidised by hot acidified, aqueous potassium manganate(VII) according to the following equation.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(\ell)$$

What volume of 0.020 mol dm^{-3} potassium manganate(VII) is required to oxidise completely 1.0×10^{-3} mol of the salt $KHC_2O_4.H_2C_2O_4$?

A 20 cm^3 B 40 cm^3
C 50 cm^3 D 125 cm^3

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In 1 mole of $KHC_2O_4.H_2C_2O_4$, there are 2 moles of $C_2O_4^{2-}$.

$$n_{C_2O_4^{2-}} = 2.0\times10^{-3} \text{ mol}$$

$$n_{MnO_4^-} = \tfrac{2}{5}\times n_{C_2O_4^{2-}} = 8\times10^{-4} \text{ mol}$$

$$V_{MnO_4^-} = \frac{n_{MnO_4^-}}{c_{MnO_4^-}} = \frac{8\times10^{-4}}{0.020} = 4\times10^{-2} \text{ dm}^3 = 40 \text{ cm}^3$$

---

20. Nervous disorders resulting from mercury poisoning occur because mercury forms a 1:1 complex with lipoyl groups which are vital for glucose metabolism.

If the average concentration of lipoyl groups in the body fluid is 1.0×10^{-8} mol kg^{-1}, what mass of mercury could complex all the lipoyl groups in a human containing 5.0 kg of body fluid?

[Relative atomic mass: Hg, 200]

A 2.5×10^{-9} g B 4.0×10^{-8} g
C 1.0×10^{-7} g D 1.0×10^{-5} g

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Amount of lipoyl groups in 5.0 kg of body liquid

$$= (1.0\times10^{-8})\times5.0 = 5.0\times10^{-8} \text{ mol}$$

$$\text{Mass of Hg} = (5.0\times10^{-8})\times200 = 1.0\times10^{-5} \text{ g}$$

---

21. A mixture of 10 cm^3 of oxygen and 50 cm^3 of hydrogen is sparked continuously.

What is the maximum theoretical decrease in volume?

[All gas volumes are recorded at 298 K and standard atmospheric pressure.]

A $10\ cm^3$ B $15\ cm^3$
C $20\ cm^3$ D $30\ cm^3$

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$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$

O_2 is the limiting agent.

Volume of H_2 used $= 2 \times 10 = 20\ cm^3$

$\therefore$ Maximum decrease in volume
$=$ volume of gases reacted
$= 10 + 20 = 30\ cm^3$

---

22. Which of the following contains two moles of solute particles?

A $1.0\ dm^3$ of $0.50\ mol\ dm^{-3}$ $Na_2SO_4(aq)$
B $1.0\ dm^3$ of $0.20\ mol\ dm^{-3}$ $Al_2(SO_4)_3(aq)$
C $4.0\ dm^3$ of $0.25\ mol\ dm^{-3}$ $CH_3CO_2Na(aq)$
D $8.0\ dm^3$ of $0.125\ mol\ dm^{-3}$ $CH_3CO_2H(aq)$

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Amount of $CH_3CO_2Na = 0.25 \times 4.0$
$= 1.0$ mol

Each CH_3CO_2Na gives 2 particles, Na^+ and $CH_3CO_2^-$.

$\therefore$ Amount of particles present $= 2 \times 1.0 = 2.0$ mol

A: 1.5 mol
B: 1.0 mol
D: Between 1.0 mol and 2.0 mol

---

23. The reaction of hydrogen sulfide with sulfur dioxide gives sulfur as one of the products.

$$H_2S(aq) \rightleftharpoons S(s) + 2H^+(aq) + 2e^-$$

$$SO_2(aq) + 4H^+(aq) + 4e^- \rightleftharpoons S(s) + 2H_2O(\ell)$$

How many moles of hydrogen sulfide are needed to react with sulfur dioxide to produce 1 mol of sulfur?

A $\frac{1}{3}$ mol B $\frac{2}{3}$ mol
C $\frac{3}{2}$ mol D 2 mol

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$$2H_2S(aq) + SO_2(aq) \rightarrow 3S(s) + 2H_2O(\ell)$$

From the equation, it can be seen that 2 moles of H_2S react to give 3 moles of S.

Hence, to give 1 mole of S, $\frac{2}{3}$ mole of H_2S is required.

---

24. Group I and Group II ionic hydrides react with water:

$$H^-(s) + H_2O(\ell) \rightarrow OH^-(aq) + H_2(g)$$

In an experiment, 1 g samples of each of the following five ionic hydrides are treated with an excess of water.

Which sample produces the greatest mass of hydrogen?

A CaH_2 B LiH
C MgH_2 D NaH

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1 mol of H^- gives 1 mol of H_2. The salt with the greatest amount of H^- will therefore give the highest amount of H_2.

A: Amount of $H^- = \frac{1}{40.1+2} \times 2 = 0.0475$ mol
B: 0.127 mol
C: 0.0760 mol
D: 0.0417 mol

---

25. *Use of the Data Booklet is relevant to this question.*

How many molecules are present in $1\ cm^3$ of oxygen gas under room conditions?

A $\dfrac{1 \times 24000}{6.02 \times 10^{23}}$

B $\dfrac{1 \times 6.02 \times 10^{23}}{24000}$

C $1 \times 6.02 \times 10^{23} \times 32$

D $\dfrac{6.02 \times 10^{23} \times 24000}{1 \times 1000}$

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Under room conditions, $V_m = 24000\ cm^3\ mol^{-1}$.

Volume of 1 mol of $O_2 = 1\ mol \times 24000\ cm^3\ mol^{-1}$

Amount in $1\ cm^3 = \dfrac{1\ mol}{1\ mol \times 24000\ cm^3\ mol^{-1}}$

Topic 1 Atoms, Molecules and Stoichiometry

There are 6.02×10^{23} molecules in 1 mol of oxygen.

$\therefore$ Number of molecules in $1\ cm^3 = \frac{1 \times 6.02 \times 10^{23}}{1 \times 24000}$.

---

26. Equimolar amounts of ClO_2 and OH^- ions react to produce three products; water, chlorate(III) ions ClO_2^- and another chloro-oxy anion Q.

What is the oxidation state of chlorine in the ion Q?

A +1 B +2

C +5 D +7

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There is a disproportionation reaction.

ClO_2 is oxidised to ClO_2^- (oxidation state of Cl decreases from +4 to +3).

Hence, in the chloro-oxy anion, the oxidation state of Cl should have increased to either +5 or +7.

For +5: $2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$

For +7: $4ClO_2 + 4OH^- \rightarrow 3ClO_2^- + ClO_4^- + 2H_2O$

Note: Both balanced equations fit the information provided (equimolar amounts of ClO_2 and OH^-). Hence, both (C) and (D) are acceptable answers.

---

27. Sodium azide, NaN_3, is made for use in car 'airbags'. When this compound is heated to 300 °C, it rapidly decomposes into its elements.

Which volume of gas, at room temperature and pressure, would be produced by the decomposition of one mole of sodium azide?

A $24\ dm^3$ B $36\ dm^3$

C $48\ dm^3$ D $72\ dm^3$

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$$2NaN_3 \rightarrow 2Na + 3N_2$$

2 mol of NaN_3 give 3 mol of N_2.

$\therefore$ 1 mol of NaN_3 give $\frac{3}{2}$ mol of N_2.

Volume of $\frac{3}{2}$ mol of $N_2 = \frac{3}{2} \times 24 = 36\ dm^3$

---

28. A mixture of $10\ cm^3$ of methane and $10\ cm^3$ of ethane was sparked with an excess of oxygen. After cooling to room temperature, the residual gas was passed through aqueous potassium hydroxide. What volume of gas was absorbed by the alkali?

A $15\ cm^3$ B $20\ cm^3$

C $25\ cm^3$ D $30\ cm^3$

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$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$C_2H_6(g) + \tfrac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

The gas absorbed by KOH is CO_2.

$$CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$$

Volume of CO_2 produced by $CH_4 = 10\ cm^3$

Volume of CO_2 produced by $C_2H_6 = 20\ cm^3$

$\therefore$ Total volume of CO_2 produced $= 10 + 20 = 30\ cm^3$

---

29. *Use of the Data Booklet is relevant to this question.*

Most modern cars are fitted with airbags. These work by decomposing sodium azide to liberate nitrogen gas, which inflates the bag.

$$2NaN_3 \rightarrow 3N_2 + 2Na$$

A typical driver's airbag contains 50 g of sodium azide.

Calculate the volume of nitrogen this will produce at room temperature.

A $9.2\ dm^3$ B $13.9\ dm^3$

C $27.7\ dm^3$ D $72.0\ dm^3$

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$M_r(NaN_3) = 23.0 + 3(14.0) = 65$

$n_{NaN_3} = \frac{50}{65} = 0.769$ mol

$n_{N_2} = \frac{2}{3} \times n_{NaN_3} = 1.154$ mol

$V_{N_2} = n_{N_2} \times 24 = 27.7\ dm^3$

---

30. *Use of the Data Booklet is relevant to this question.*

Burning sodium reacts with carbon dioxide to produce sodium carbonate and carbon only.

$$4Na + 3CO_2 \rightarrow 2Na_2CO_3 + C$$

If all the 1.1×10^7 dm^3 carbon dioxide, measured at standard temperature and pressure, produced by each person in a year, could be reacted with sodium, what would be the mass in grams of sodium carbonate produced?

A 3.2×10^7 B 3.5×10^7
C 7.3×10^7 D 7.8×10^7

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$$n_{CO_2} = \frac{1.1\times10^7}{22.4} = 4.91\times10^5 \text{ mol}$$

$$n_{Na_2CO_3} = \tfrac{2}{3}\times n_{CO_2}$$
$$= \tfrac{2}{3}\times(4.91\times10^5)$$
$$= 3.274\times10^5 \text{ mol}$$

$$M_{Na_2CO_3} = 2(23)+12+3(16) = 106$$

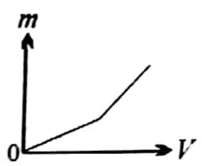
$$m_{Na_2CO_3} = n\times M$$
$$= (3.274\times10^5)\times106$$
$$= 3.47\times10^7 \text{ g}$$

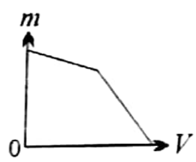
---

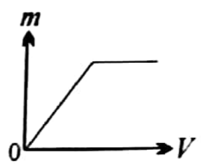
31. When an excess of aqueous potassium iodide is gradually added to aqueous mercury(II) chloride, the following reaction occur:

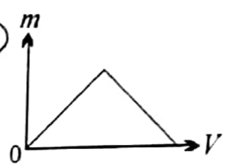
$$HgCl_2(aq) + 2KI(aq) \rightarrow HgI_2(s) + 2KCl(aq)$$
$$HgI_2(s) + 2KI(aq) \rightarrow K_2HgI_4(aq)$$

Which diagram shows how the mass m of the precipitate varies with the volume V of aqueous potassium iodide added?

A


B


C


D


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When KI is gradually added, HgI_2 precipitates out and therefore m increases. After reaching the maximum, additional KI added is in excess and the precipitate dissolves to form the complex, K_2HgI_4. Hence, m decreases to zero.

---

32. When Fe is reacted with Fe^{3+}(aq) ions, Fe^{2+}(aq) ions are formed.

Assuming the reaction goes to completion, how many moles of Fe and Fe^{3+}(aq) would result in a mixture containing equal numbers of moles of Fe^{3+}(aq) and Fe^{2+}(aq) once the reaction had taken place?

	moles of Fe	moles of Fe^{3+} (aq)
A	1	2
B	1	3
C	1	5
D	2	3

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$$Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$$

1 mole of Fe react with 2 moles of Fe^{3+} to form 3 moles of Fe^{2+}. There will be no more Fe^{3+} at the end of the reaction.

Hence, to have 3 moles of Fe^{2+}, we will have to use 1 mole of Fe and (2 + 3) moles of Fe^{3+}. This will result in an excess of 3 moles of Fe^{3+}.

---

33. In 1892, Lord Rayleigh made 'atmospheric nitrogen' by removing carbon dioxide, water vapour and oxygen from a sample of air. He found the density of this nitrogen to be 1.2572 g dm^{-3} at s.t.p. Chemically pure nitrogen has a density of 1.2505 g dm^{-3} at s.t.p.

Which gas present in 'atmospheric nitrogen' caused this discrepancy?

A argon B helium
C methane D neon

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The density of 'atmospheric nitrogen' is denser than pure N_2. The impurity in 'atmospheric nitrogen' is denser than N_2.

Comparing M_r: M_r of $N_2 = 28.0$
M_r of Ar = 39.9
M_r of He = 4.0
M_r of $CH_4 = 16.0$
M_r of Ne = 20.2

---

34. Since 1850, most books have been printed on acidic paper, which eventually becomes brittle and disintegrates. These books can be preserved by treatment with diethylzinc vapour, $Zn(C_2H_5)_2$, which reacts both with acid residues and also with small amounts of water retained in the paper.

Diethylzinc reacts with an acid to give ethane.

$$Zn(C_2H_5)_2 + 2HX \rightarrow ZnX_2 + 2C_2H_6$$

Which products are likely to result from the reaction of diethylzinc with water?

A $ZnH_2 + C_2H_6$

B $ZnH_2 + C_2H_5OH$

C $Zn(OH)_2 + C_2H_6$

D $Zn(OH)_2 + C_2H_5OH$

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When H_2O is used, $X = OH$.

$\therefore Zn(C_2H_5)_2 + H_2O \rightarrow Zn(OH)_2 + C_2H_6$

35. A sample of 0.025 mol of the chloride of an element Z was dissolved in distilled water and the solution made up to 500 cm^3. 12.5 cm^3 of this solution reacted with 25 cm^3 of 0.1 mol dm^{-3} silver nitrate solution. What is the most likely formula of the chloride?

A Z_2Cl B ZCl

C ZCl_2 D ZCl_4

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Silver(I) nitrate reacts with chloride ion to give silver(I) chloride precipitate:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

Amount of Ag^+ used = concentration × volume

$= 0.1 \text{ mol dm}^{-3} \times \frac{25}{1000} \text{ dm}^3$

$= 2.5 \times 10^{-3}$ mol

Since 1 mole of Ag^+ reacts with 1 mole of Cl^-,

amount of Cl^- present in 12.5 $cm^3 = 2.5 \times 10^{-3}$ mol.

$\therefore$ Amount of Cl^- present in 500 $cm^3 = \frac{2.5 \times 10^{-3}}{12.5} \times 500$

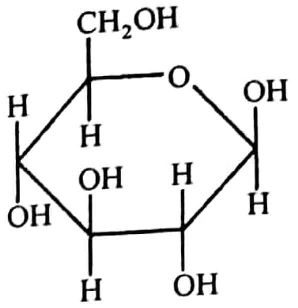
$= 0.1$ mol

Since 0.025 mole of the compound contain 0.1 mole of chloride, 1 mole of the compound therefore contain $\frac{0.1}{0.025} = 4$ moles of chloride.

The formula of the compound is ZCl_4.

36. In the body, cellular respiration produces energy from the oxidation of glucose.

The diagram shows the structure of glucose.



A new artificial sweetener has been produced by replacing all of the hydroyl groups attached directly to the ring carbon atoms in glucose with chlorine atoms.

What is the empirical formula of this chlorinated glucose?

A CHClO B CH_2Cl

C $C_3H_4Cl_2O$ D $C_6H_7Cl_5O$

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The molecular formula of glucose is $C_6H_{12}O_6$.

In the sweetener, 4 –OH groups are replaced by Cl. The molecular formula of the sweetener is thus $C_6H_8O_2Cl_4$. Hence, its empirical formula is $C_3H_4OCl_2$.

37. A sample of 10 dm^3 of polluted air is passed through lime water so that all the carbon dioxide present is precipitated as calcium carbonate. The mass of calcium carbonate formed is 0.05 g. What is the percentage, by volume, of carbon dioxide in the air sample?

[Relative atomic masses: C, 12; O, 16; Ca, 40; 1 mol of gas under experimental conditions has a volume of 24 dm^3.]

A 0.03% B 0.05%

C 0.12% D 0.3%

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$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(\ell)$$

Amount of $CaCO_3$ precipitated $= \frac{0.05}{40 + 12 + 3 \times 16}$

$= 5.0 \times 10^{-4}$ mol

$\therefore$ % by volume of $CO_2 = \frac{1.2 \times 10^{-2}}{10} \times 100 = 0.12$

38. In a pathology laboratory, a sample of urine containing 0.120 g of urea, NH_2CONH_2, ($M_r = 60$) was treated with an excess of nitrous acid. The urea reacted according to the following equation.

$$NH_2CONH_2 + 2HNO_2 \rightarrow CO_2 + 2N_2 + 3H_2O$$

The gas produced was passed through aqueous sodium hydroxide and the final volume measured. What was this volume at room temperature and pressure?

[Molar volume of a gas at r.t.p. is 24000 $cm^3\ mol^{-1}$.]

A 9.6 cm^3 B 14.4 cm^3
C 48.0 cm^3 D 96.0 cm^3

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Aqueous NaOH absorbs CO_2 and the remaining gas is N_2.

Amount of urea used $= \frac{0.120}{60} = 2.00\times10^{-3}$ mol

Amount of N_2 produced $= 2\times(2.00\times10^{-3})$
$= 4.00\times10^{-3}$ mol

Volume of N_2 produced $= (4.00\times10^{-3})\times24000$
$= 96.0\ cm^3$

39. A pure hydrocarbon is used in bottled gas for cooking and heating.

When 10 cm^3 of the hydrocarbon is burned in 70 cm^3 of oxygen (an excess), the final gaseous mixture contains 30 cm^3 of carbon dioxide and 20 cm^3 of unreated oxygen. All gaseous volumes were measured under identical conditions.

What is the formula of the hydrocarbon?

A C_2H_6 B C_3H_6
C C_3H_8 D C_4H_{10}

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$$C_xH_y + (x+\tfrac{y}{4})O_2 \rightarrow xCO_2 + \tfrac{y}{2}H_2O$$

By Avogadro's law,

$$\frac{n_{CO_2}}{n_{C_xH_y}} = \frac{V_{CO_2}}{V_{C_xH_y}} \Rightarrow \frac{x}{1} = \frac{30}{10} \Rightarrow x = 3$$

$$\frac{n_{O_2}}{n_{C_xH_y}} = \frac{V_{O_2}}{V_{C_xH_y}} \Rightarrow \frac{x+\frac{y}{4}}{1} = \frac{70-20}{10} \Rightarrow 3+\frac{y}{4} = 5$$

$\Rightarrow y = 8$

40. A condensation reaction involves eliminating a molecule of water between two molecules.

Two molecules of phosphoric acid, H_3PO_4, can undergo a condensation reaction producing diphosphoric acid, $H_4P_2O_7$.

When three molecules of phosphoric acid undergo a similar condensation reaction, triphosphoric acid is produced.

What is the molecular formula of triphosphoric acid?

A $H_5P_3O_8$ B $H_5P_3O_{10}$
C $H_7P_3O_{10}$ D $H_7P_3O_{11}$

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The formula of the triphosphoric acid should be that of $3\times H_3PO_4$ with the elimination of $2\times H_2O$.
Hence, the triphosphoric acid should contain:

H: $3\times3-2\times2=5$
P: $3\times1=3$
O: $3\times4-2\times1=10$

i.e. the formula is $H_5P_3O_{10}$.

41. *Use of the Data Booklet is relevant to this question.*

Sodium percarbonate, $(Na_2CO_3)_x.y(H_2O_2)$, is an oxidising agent in some home and laundry cleaning products.

10.0 cm^3 of 0.100 mol dm^{-3} sodium percarbonate releases 48.0 cm^3 of carbon dioxide at room conditions on acidification.

An identical sample, on titration with 0.0500 mol dm^{-3} $KMnO_4$, requires 24.0 cm^3 before the first pink colour appears. $KMnO_4$ reacts with H_2O_2 in the mole ratio 2 : 5.

What is the ratio $\frac{y}{x}$?

A $\frac{1}{3}$ B $\frac{2}{3}$
C $\frac{3}{2}$ D $\frac{3}{1}$

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$n_{percarbonate} = 0.100\times\frac{10}{1000} = 1\times10^{-3}$ mol

$n_{CO_2} = \frac{48}{24000} = 2\times10^{-3}$ mol

Since 1 mol of percarbonate contain x mol of C, therefore, $x = 2$.

$n_{MnO_4^-} = 0.0500 \times \frac{24}{1000} = 1.2 \times 10^{-3}$ mol

$n_{H_2O_2} = \frac{5}{2} \times 1.2 \times 10^{-3} = 3 \times 10^{-3}$ mol

Since 1 mol of precarbonate contain y mol of H_2O_2, $y = 3$.

---

42. When iron is reacted with aqueous iron(III) ions, iron(II) ions are formed.

Assuming the reaction goes to completion, how many moles of Fe and of Fe^{3+}(aq) would result in a mixture containing equal numbers of moles of Fe^{3+}(aq) and Fe^{2+}(aq) once the reaction had taken place?

	moles of Fe	moles of Fe^{3+} (aq)
A	1	2
B	1	3
C	1	5
D	2	3

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$$Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$$

To form x mole of Fe^{2+}, $\frac{2x}{3}$ mole of Fe^{3+} would have reacted with $\frac{x}{3}$ mole of Fe.

Therefore, initial $n_{Fe^{3+}} = \frac{2x}{3} + x = \frac{5x}{3}$

$n_{Fe} = \frac{x}{3}$

$\therefore\ n_{Fe} : n_{Fe^{3+}} = \frac{x}{3} : \frac{5x}{3} = 1 : 5$

---

43. In an experiment, 50 cm^3 of a 0.1 mol dm^{-3} solution of a metallic salt reacted exactly with 25 cm^3 of 0.1 mol dm^{-3} aqueous sodium sulfite.

The half-equation for oxidation of sulfite ion is shown below.

$$SO_3^{2-}(aq) + H_2O(\ell) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

If the original oxidation number of the metal in the salt was 3, what would be the new oxidation number of the metal?

A 0 **B** 1

C 2 **D** 4

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Amount of sulfite used = concentration × volume

$= 0.1 \text{ mol dm}^{-3} \times \frac{25}{1000} \text{ dm}^3$

$= 2.5 \times 10^{-3}$ mol

Amount of electrons lost $= 2 \times (2.5 \times 10^{-3})$

$= 5 \times 10^{-3}$ mol

Amount of electrons gained by metallic salt

= amount of electrons lost by sulfite

$= 5 \times 10^{-3}$ mol

Amount of metallic salt used

$= 0.1 \text{ mol dm}^{-3} \times \frac{50}{1000} \text{ dm}^3$

$= 5 \times 10^{-3}$ mol

Amount of electrons gained per mole of metallic salt

$= \frac{5 \times 10^{-3}}{5 \times 10^{-3}}$

= 1 mol

Hence, oxidation state of the metal decreases by 1 unit.

Therefore, its new oxidation state is +2.

---

44. Carbon disulfide, CS_2, is a volatile flammable liquid used in the manufacture of cellophane.

On combustion, CS_2 is oxidised as follows.

$$CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$$

A 20 cm^3 sample of carbon disulfide vapour is ignited with 100 cm^3 of oxygen. The final volume of gas after burning is treated with an excess of aqueous alkali.

Which percentage of this final volume dissolves in the alkali?

[All volumes measured at the same temperature and pressure, conditions under which CS_2 is a gas.]

A 20% **B** 40%

C 60% **D** 80%

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	$CS_2(g)$	$+ 3O_2(g)$	$\rightarrow CO_2(g)$	$+ 2SO_2(g)$
Initial Vol/cm^3	20	100	0	0
Change in Vol/cm^3	−20	−60	+20	+40
Final Vol/cm^3	0	40	20	40

The final volume of gas after burning

$= 40 + 20 + 40$

$= 100\ cm^3$

Treatment with aqueous alkali removes the acidic CO_2 and SO_2, so that volume of gases that dissolves in alkali $= 20 + 40 = 60\ cm^3$.

Percentage that dissolves in alkali $= \frac{60}{100} \times 100\%$

$= 60\%$

---

45. In an attempt to establish the formula of an oxide of nitrogen, a known volume of the pure gas was mixed with hydrogen and passed over a catalyst at a suitable temperature. 100% conversion of the oxide to ammonia and water was shown to have taken place.

$$N_xO_y \xrightarrow[\text{catalyst}]{H_2(g)} xNH_3 + yH_2O$$

2400 cm^3 of the nitrogen oxide, measured at room temperature and pressure (r.t.p.), produced 7.20 g of water. The ammonia produced was neutralised by 200 cm^3 of 1.0 mol dm^{-3} HCl.

[Molar volume of gas at r.t.p. $= 24000\ cm^3\ mol^{-1}$; A_r: H, 1; O, 16.]

What was the oxidation number of the nitrogen in the nitrogen oxide?

A +1 **B** +2

C +3 **D** +4

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Amount of $H_2O = \frac{7.20}{18} = 0.40$ mol

$$NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

Amount of HCl = concentration × volume

$= 1.0\ mol\ dm^{-3} \times \frac{200}{1000}\ dm^3$

$= 0.2$ mol

$\therefore$ Amount of $NH_3 = 0.2$ mol

Hence, $\frac{x}{y} = \frac{\text{amount of } NH_3}{\text{amount of } H_2O} = \frac{0.2}{0.4} = \frac{1}{2}$

Empirical formula of the nitrogen oxide is NO_2.

Amount of nitrogen oxide $= \frac{2400}{24000} = 0.1$ mol

Since 0.1 mol of nitrogen oxide produce 0.2 mol of NH_3, $x = 2$.

$\therefore$ The molecular formula of the nitrogen oxide is N_2O_4.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

46. Three organic molecules each have
- three elements;
- the composition, by mass, C, 54.5%; H, 9.1%.

What could these molecules be?

1 $CH_3CH_2CH_2CO_2H$
2 $OHCCH_2CH_2CH_2OH$
3 $CH_3CH{=}CHCH_2SH$

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*1,*2,*3. $M_r = 88$

$$\% \, C = \frac{4 \times 12}{88} \times 100\% = 54.5\%$$

$$\% \, H = \frac{8 \times 1}{88} \times 100\% = 9.1\%$$

---

47. In an experiment, 10 cm^3 of an organic compound in the gaseous state were sparked with an excess of oxygen. 20 cm^3 of carbon dioxide and 5 cm^3 of nitrogen were obtained among the products. All gas volumes were measured at the same temperature and pressure.

Which of the following molecular formulae would fit these data?

1 C_2H_7N
2 C_2H_3N
3 $C_2H_6N_2$

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$$C_xH_yN_z + O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2$$

10 cm^3 of $C_xH_yN_z$ when burnt in O_2, gives $10x$ cm^3 of CO_2 and $10 \times \frac{z}{2} = 5z$ cm^3 of N_2.

Hence, $x = 2$ and $z = 1$ (any reasonable value of y is possible).

---

48. Which statements about a 12.0 g sample of ^{12}C are correct?

1 The number of atoms is 6.02×10^{23}.
2 The number of atoms is the same as the number of atoms in 4.0 g of ^4He.
3 The number of atoms is the same as the number of atoms in 2.0 g of $^1H_2$.

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*1. 12.0 g of ^{12}C contains 1 mole or 6.02×10^{23} carbon atoms.

*2. 4.0 g of ^4He also contains 1 mole of He atoms.

3. 2.0 g $^1H_2$ contains 1 mole of H_2 molecules but 2 moles of H atoms.

---

49. Which of the following statements will be true for the complete combustion of an akene in oxygen?

1 The volume of oxygen required is directly proportional to the number of carbon atoms present in the molecule.
2 The volume of gas produced at 25 °C is the same as for the complete combustion of an alkane with the same number of carbon atoms under the same conditions.
3 At 120 °C, the volume of steam produced is always twice the volume of carbon dioxide.

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*1. $$C_nH_{2n} + \frac{3n}{2}O_2 \rightarrow nCO_2 + nH_2O$$

The volume of O_2 requires is $\frac{3n}{2}$ and hence it is directly proportional to n, the number of carbon in the alkene.

*2. $$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + (n+1)H_2O$$

The volume of CO_2 produced in both cases are the same if the alkene have the same number of carbon atoms per molecule (H_2O is a liquid at 25 °C).

3. The volume of steam produced is the same as that of CO_2.

---

50. Which statements about relative molecular mass are correct?

1 It is the sum of the relative atomic masses of all the atoms within the molecule.

2 It is the ratio of the average mass of a molecule to the mass of a ^{12}C atom.

3 It is the ratio of the mass of 1 mol of molecules to the mass of 1 mol of ^{1}H atoms.

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*1. $$M_r = \sum A_r$$

In fact, this is what we use to compute the M_r of a substance given the A_r of the elements (atoms) that constitute the substance.

E.g. $M_r(C_2H_6) = 2 \times A_r(C) + 6 \times A_r(H)$
$= 2 \times 12 + 6 \times 1$
$= 30$

*2. M_r is defined as the ratio of the average mass of 1 molecule to the mass of a ^{12}C atom.

3. It should be 1 mol of ^{12}C atoms instead of ^{1}H atoms.

---

51. Given weighed samples of the same mixture of magnesium carbonate and barium carbonate, how can the mole fraction of magnesium carbonate in the mixture be estimated?

1 Add a known volume of 0.1 mol dm^{-3} HCl(aq), in excess, and back titrate the excess of acid.

2 Add an excess of HCl(aq) and measure, at known temperature and pressure, the volume of CO_2 liberated.

3 Add an excess of HCl(aq) followed by an excess of H_2SO_4(aq); filter, dry and weigh the precipitate.

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*1,*2. Through back titration or measuring the volume of CO_2 evolved, the total amount of carbonate in the mixture can be determined. The mass of each carbonate can then be calculated and hence the mole fraction.

Let m be the total mass and m_B be the mass of $BaCO_3$.

$$nCO_3^{2-} = \frac{m_B}{M_B} + \frac{m - m_B}{M_M}$$

where M_B = molar moass of $BaCO_3$,
M_M = molar mass of $MgCO_3$.

*3. The ppt. is $BaSO_4$. From the mass of the ppt., $n_{Ba^{2+}}$ can be calculated. Hence, the mass of $BaCO_3$ can also be determined.

---

52. A group of students attempted to estimate the concentration of a solution of Fe^{2+} by pipetting fixed volumes of the solution into a flask, adding an excess of dilute sulfuric acid, and then titrating with a standard solution of potassium manganate (VII) from a burette. The volume of $KMnO_4$ solution required by one student was 0.2 cm^3 higher than that of the other students.

Which of the following are possible explanations for this discrepancy?

1 The titration flask was rinsed with the solution of Fe^{2+} instead of water before titration.

2 The last drop of Fe^{2+} solution was blown from the pipette into the flask.

3 The burette was rinsed with water instead of the solution of $KMnO_4$ before titration.

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*1. Rinsing the flask with solution of Fe^{2+} gives rise to more Fe^{2+} than the intended quantity. Hence, more $KMnO_4$ is required for titration.

*2. Pipettes are designed in such a way that with the last drop, the equipment is calibrated to the specified volume. Blowing out the last drop from the pipette gives rise to more Fe^{2+} than the intended quantity.

*3. Rinsing the burette with water causes the concentration of $KMnO_4$ in the burette to be lower. Hence, a larger volume is required to give the correct amount of $KMnO_4$ for titration.

TOPIC 2

Atomic Structure

Key content that you will be examined on:

1. The nucleus of the atom: neutrons and protons, isotopes, proton and nucleon numbers
2. Electrons: electronic energy levels, ionisation energies, atomic orbitals, extranuclear structure

Atomic Structure

Topic 2

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which one of the following has the same number of electrons as an alpha particle?

   A H B H^+
   C H_2 D He

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An alpha particle is a helium necleus, i.e. He^{2+} and it does not have any electron. The number of electrons in the species are (A) 1, (B) 0, (C) 2 and (D) 2.

2. Which of the following elements has the largest second ionisation energy?

   A O B F
   C Ne D Na

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Second ionisation energy corresponds to

$$X^+(g) \rightarrow X^{2+}(g) + e^-$$

The highest value is given by one where the X^+ has a noble gas electronic configuration, i.e. Na^+: 2,8.

3. Which one of the following represents the configuration of the three electrons of highest energy for the ground state of an element in Group III?

   A $1s^1\ 2s^1\ 2p^1$ B $2s^1\ 2p^2$
   C $3p^3$ D $4s^2\ 4p^1$

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Group III element has 3 valence electrons, $ns^2\ np^1$. These electrons therefore are the 3 electrons with the highest energy.

4. Which one of the following determines the position of an element in the Periodic Table.

   A chemical reactivity
   B first ionisation energy
   C number of electrons in outer orbital
   D number of protons in the nucleus of its atom

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The atomic number (or number of protons) of an element determines its position in the Periodic Table.

5. Which of the following electronic configurations represents an element that forms a simple ion with a charge of –3?

   A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
   B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
   C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$
   D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

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The element is in Group V. It can take in 3 electrons (forming X^{3-}) to form a stable octet configuration.

6. In which species are the numbers of electrons and neutrons equal?

   A ${}^{9}_{4}Be$ B ${}^{19}_{9}F$
   C ${}^{23}_{11}Na^+$ D ${}^{18}_{8}O^{2-}$

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In ${}^{18}_{8}O^{2-}$, there are 8 protons and $18 - 8 = 10$ neutrons. The number of electrons $= 8 + 2 = 10$ since there are 2 electrons more than the number of protons (charge is –2).

7. *Use of the Data Booklet is relevant to this question.*
Which particle would, on gaining an electron, have a half-filled set of p orbitals?

A C^+ **B** N
C Si^- **D** P^+

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C^+ : $1s^2\ 2s^2\ 2p^1$ C : $1s^2\ 2s^2\ 2p^2$
N : $1s^2\ 2s^2\ 2p^3$ N^- : $1s^2\ 2s^2\ 2p^4$
Si^- : $1s^2\ 2s^2\ 2p^3$ Si^{2-} : $1s^2\ 2s^2\ 2p^4$
P^+ : $1s^2\ 2s^2\ 2p^2$ P : $1s^2\ 2s^2\ 2p^3$

8. Which of the following ions contains an unpaired electron?

A Ca^{2+} **B** Cu^{2+}
C K^+ **D** Ti^{4+}

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Cu : [Ar] $3d^{10}\ 4s^1$
Cu^{2+}: [Ar] $3d^9$

1l	1l	1l	1l	1

9. What is the order of increasing energy of the listed orbitals in the atom of titanium?

A 3s 3p 3d 4s
B 3s 3p 4s 3d
C 3s 4s 3p 3d
D 4s 3s 3p 3d

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Ti : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$

Note: 4s is at a higher level and 4s electrons are removed before 3d electrons when Ti ionises.

10. Which of the following formulae represents a particle with the composition 1 proton, 1 neutron and 2 electrons?
[D represents deuterium, ^2H]

A D **B** D^-
C H^- **D** He

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The presence of only 1 proton means that the species is hydrogen (H or D). With 1 neutron, it is D. An excess of 1 electron over the proton indicates that it is D^-.

species	protons	neutrons	electrons
D	1	1	1
D^-	1	1	2
H^-	1	0	2
He	2	2	2

11. Which one of the following does **not** contain either an unpaired s electron or an unpaired p electron?

A Cr **B** Ge
C S^- **D** Sc

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Particle	Electronic Configurations	Remarks
Cr	[Ar] $3d^5\ 4s^1$	unpaired s electron
Ge	[Ar] $3d^{10}\ 4s^2\ 4p^2$	unpaired p electron
S	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	unpaired p electron
Sc	[Ar] $3d^1\ 4s^2$	unpaired d electron

12. Which of the following ions contains five unpaired d-electrons?

A Cr^{3+} **B** Fe^{3+}
C Mn^{3+} **D** Ni^{2+}

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Fe : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Fe^{3+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
Cr^{3+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
Mn^{3+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
Ni^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3d^7$

13. Which of the following particles would, on losing an electron, have a half-filled set of p orbitals?

A C^- B N

C N^- D O^+

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$$N^- \rightarrow N + e^-$$
$$N : 1s^2\,2s^2\,2p^3$$

A: $C^-\ (1s^2\,2s^2\,2p^3) \rightarrow C\ (1s^2\,2s^2\,2p^2) + e^-$
B: $N\ (1s^2\,2s^2\,2p^3) \rightarrow N^+\ (1s^2\,2s^2\,2p^2) + e^-$
D: $O^+\ (1s^2\,2s^2\,2p^3) \rightarrow O^{2+}\ (1s^2\,2s^2\,2p^2) + e^-$

---

14. What kind of orbital must an electron with the principal quantum number $n = 2$ occupy?

A a spherically-shaped orbital
B either an s or p orbital
C the orbital closest to the nucleus
D a dumb-bell-shaped orbital

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With principal quantum number $n = 2$, the orbitals present are 2s and 2p orbitals.

---

15. What is the electronic configuration of the atom of the element which is isoelectronic with H_2S?

A $1s^2\,2s^2\,2p^6\,3s^2$
B $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$
C $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$
D $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

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The electronic configuration of a sulfur atom is

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^4$$

However, in H_2S, there are 2 more electrons, each from a hydrogen atom in forming covalent bonds. Hence, the electronic configuration of S in H_2S is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ (octet configuration).

---

16. The first ionisation energies, in kJ mol^{-1}, of a sequence of elements of increasing proton (atomic) number are given below.

548 620 660 660 680

Where in the Periodic Table is this sequence of elements likely to be located?

A Group I
B Group II
C from Li to N inclusive
D from Sr to Mo inclusive

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The differences in the IE's are small, indicating that the elements are transition elements.

---

17. Which equation relates to the first ionisation energy of bromine?

A $Br(g) \rightarrow Br^-(g) - e^-$
B $Br(g) \rightarrow Br^+(g) + e^-$
C $\frac{1}{2}Br_2(g) \rightarrow Br^-(g) - e^-$
D $\frac{1}{2}Br_2(g) \rightarrow Br^+(g) + e^-$

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First ionisation energy is the energy required for 1 mole of gaseous M atoms at ground state, to lose 1 mole of electrons to form 1 mole of gaseous M^+ ions at ground state.

---

18. Why is the first ionisation energy of Ne higher than that of F?

A Fluorine is more electronegative than neon.
B Neon has a complete octet, but fluorine does not.
C The atomic radius of fluorine is less than that of neon.
D The nuclear charge in neon is greater than that in fluorine.

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Ne, having a complete octet electronic configuration, is very stable. Hence, a lot of energy is required to remove an electron since this will destroy the stable octet configuration.

---

19. In the radioactive decay of an isotope of lead to an isotope of bismuth, a particle ${}^{0}_{-1}X$ is emitted. Which particle is ${}^{0}_{-1}X$?

A electron
B ion
C neutron
D proton

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An electron has a −1 charge and it is represented as ${}_{-1}X$. Since its mass is close to 0 compared to a proton, it can be represented as ${}^{0}X$. Hence, ${}^{0}_{-1}X$ is electron.

---

20. Which isotope of an element in the third period of the Periodic Table contains the same number of neutrons as ${}^{32}_{16}S$?

A ${}^{23}_{11}Na$
B ${}^{24}_{12}Mg$
C ${}^{28}_{14}Si$
D ${}^{31}_{15}P$

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Number of neutron in ${}^{32}_{16}S = 32 - 16 = 16$

Number of neutron in ${}^{31}_{15}P = 31 - 15 = 16$

A: $23 - 11 = 12$

B: $24 - 12 = 12$

C: $28 - 14 = 14$

---

21. Carbon-14 is radioactive and is used by archaeologists in carbon dating.

Which species has both the same number of neutrons and the same number of electrons as an atom of carbon-14?

A ${}^{14}N^{+}$
B ${}^{16}O^{2+}$
C ${}^{17}F^{+}$
D ${}^{28}Si$

Helping Concepts *Exam Favourite Rating* ★★

Number of electrons and number of neutrons in carbon-14 are 6 and 8 respectively, which are same as those of ${}^{16}O^{2+}$.

---

22. The following ideas were those underlying John Dalton's atomic theory, published in 1803.

Which idea is known to be correct?

A Atoms are indivisible.
B Atoms are very small.
C Atoms of an element are identical.
D Atoms of one element always differ in mass from those of another element.

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A: Atoms contain sub-atomic particle, e.g. ${}^{1}_{0}n$, ${}^{1}_{1}p$, ${}^{0}_{-1}e$.

C: Isotopes of an element are not identical.

D: Isotopes of different elements **may** have the same mass, e.g. ${}^{32}_{16}S$, ${}^{32}_{15}P$.

---

23. An ion Q^{2+} contains 44 protons.

What is the electronic configuration Q^{2+}?

[The symbol [Ar] represents $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.]

A [Ar] $3d^{10}\ 4s^2\ 4p^5\ 4d^5$
B [Ar] $3d^{10}\ 4s^2\ 4p^6\ 4d^2$
C [Ar] $3d^{10}\ 4s^2\ 4p^6\ 4d^6$
D [Ar] $3d^{10}\ 4s^2\ 4p^6\ 4d^8$

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In Q, there are 44 electrons and its electronic configuration is [Ar] $3d^{10}\ 4s^2\ 4p^6\ 4d^6\ 5s^2$.

Hence, Q^{2+} has 42 electrons and its electronic configuration is [Ar] $3d^{10}\ 4s^2\ 4p^6\ 4d^6$.

Note: The 2 electrons lost in forming Q^{2+} are from the outermost 5s orbital.

---

24. *Use of the Data Booklet is relevant to this question.*

In the gas phase, aluminum and a transition element require the same amount of energy to form one mole of an ion with a 2+ charge.

What is the transition element?

A Co
B Cr
C Cu
D Ni

Helping Concepts *Exam Favourite Rating* ★

$$Al(g) \rightarrow Al^{2+}(g) + 2e^-$$
$$\Delta H = 577 + 1820 = 2397 \text{ kJ mol}^{-1}$$
$$Co(g) \rightarrow Co^{2+}(g) + 2e^-$$
$$\Delta H = 757 + 1640 = 2397 \text{ kJ mol}^{-1}$$

25. Gallium has the electronic configuration [Ar] $3d^{10}$ $4s^2$ $4p^1$, where [Ar] represents the configuration of argon.

In which order are the electrons lost in forming the Ga^{4+} ion?

	1st	2nd	3rd	4th
A	3d	4p	4s	4s
B	3d	4s	4s	4p
C	4s	4s	4p	3d
D	4p	4s	4s	3d

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Electrons furthest away from the nucleus are removed first. Hence, the electrons in Ga are removed in the order: 4p 4s 4s 3d.

---

26. *Use of the Data Booklet is relevant to this question.*

The successive ionisation energies, in kJ mol^{-1}, of an element **X** are given below.

870 1800 3000 3600 5800 7000 13200

What is **X**?

A $_{33}As$ **B** $_{53}I$

C $_{8}O$ **D** $_{52}Te$

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There is a large difference between the 6th and 7th ionisation energies, indicating that the 6th and 7th electrons are from different principal quantum shells. Hence, **X** is a Group VI element, i.e. O or Te. However, from the data booklet, the data do not fit into O. Hence, **X** is Te.

---

27. The first six ionisation energies of four elements, **A** to **D**, are given.

Which elements is most likely to be in Group IV of the Periodic Table?

I.E./kJ mol^{-1}	1st	2nd	3rd	4th	5th	6th
A	494	4560	6940	9540	13400	16600
B	736	1450	7740	10500	13600	18000
C	1090	2350	4610	6220	37800	47000
D	1400	2860	4590	7480	9400	53200

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There is a large increase from 4th I.E. to 5th I.E. This shows that the 5th electrons is removed from an inner principal quantum shell. Hence, there are 4 valence electrons and it is therefore a Group IV element.

---

28. Which property is the same for the two nuclides $^{40}_{18}Ar$ and $^{40}_{19}K$?

A the number of electrons

B the number of neutrons

C the number of nucleons

D the number of protons

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Given a nuclide $^{n}_{m}X$,

where n = mass number or nucleon number
= number of protons and neutrons
m = atomic number or proton number
= number of protons

Since both $^{40}_{18}Ar$ and $^{40}_{19}K$ have the same value of n, they have the same nucleon number.

---

29. The elements radon (Rn), francium (Fr) and radium (Ra) are consecutive in the Periodic Table. What is the order of their first ionisation energies?

	least endothermic → most endothermic		
A	Fr	Ra	Rn
B	Fr	Rn	Ra
C	Ra	Fr	Rn
D	Rn	Ra	Fr

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Rn is in Group 0 (octet configuration) and it has the highest first ionisation energy, i.e. most endothermic. Being in the same period, Ra is smaller and has 1 proton more than Fr since Ra is in Group II and Fr is in Group I. Consequently, the valence electrons in Ra are more tightly bound and it has a more endothermic first ionisation energy than does Fr.

---

30. In 1999, chemists claimed to be the first to identify atoms of a new element of proton number 114. This was produced by bombarding atoms of plutonium, Pu, with atoms of an isotope of a Group II element, X. The reaction taking place is the following.

$^{244}_{94}Pu + X \rightarrow ^{289}_{114}[\text{new element}] + 3 \text{ neutrons } (^{1}_{0}n)$

What is X?

A Mg **B** Ca
C Sr **D** Ba

Helping Concepts *Exam Favourite Rating* ★

The total number of protons and neutrons must balance. Hence, the proton number of **X** is $114 - 94 = 20$ and hence, **X** is Ca.

---

31. The first six ionisation energies of an element, M, in kJ mol^{-1} are shown.

660; 1267, 2218, 3313, 7863, 9500

M forms its only chloride by heating M with chlorine.

What is the equation for the formation of the chloride of M?

A $2M + Cl_2 \rightarrow 2MCl$
B $M + Cl_2 \rightarrow MCl_2$
C $M + 2Cl_2 \rightarrow MCl_4$
D $M + 3Cl_2 \rightarrow MCl_6$

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There is a large increase from IE_4 to IE_5. Therefore, M is likely a Group IV element. Hence, M forms MCl_4 on reacting with Cl_2.

---

32. *Use of the Data Booklet is relevant to this question.*

The sunlight-induced photolysis of water is being investigated as a useful source of the pollution-free fuel hydrogen.

$$2H_2O \rightarrow 2H_2 + O_2$$

It has been found that anatase, one of the three crystalline forms of the ionic compound TiO_2, is a good catalyst for this reaction.

How many electrons are associated with each titanium ion in the anatase lattice?

A 18 **B** 19
C 20 **D** 22

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$_{22}Ti^{4+}$

Number of electrons $= 22 - 4 = 18$

---

33. The second ionisation energy of calcium is 1150 kJ mol^{-1}. Which of the following correctly represents this statement?

A $Ca(g) \rightarrow Ca^{2+}(g) + 2e^-$ $\Delta H^\ominus = +1150$ kJ mol^{-1}
B $Ca^{+}(g) \rightarrow Ca^{2+}(g) + e^-$ $\Delta H^\ominus = +1150$ kJ mol^{-1}
C $Ca^{+}(g) \rightarrow Ca^{2+}(g) + e^-$ $\Delta H^\ominus = -1150$ kJ mol^{-1}
D $Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$ $\Delta H^\ominus = +1150$ kJ mol^{-1}

Helping Concepts *Exam Favourite Rating* ★★★

Second I.E. is defined as the energy required (endothermic) to remove one mole of electrons from one mole of gaseous M^+ ion to form one mole of gaseous M^{2+} ions.

A: First I.E. + Second I.E.

C: $\Delta H^\ominus$ should be positive.

---

34. The orbitals of a nitrogen atom may be represented as shown

1s	2s	2p		
[ ]	[ ]	[ ]	[ ]	[ ]

Which diagram represents the arrangement of electrons in the ground state of the atom?

	1s	2s	2p		
A	↑	↑	↑	↑	↑
B	↑↓	↑↓	↑		
C	↑↓	↑↓	↑↓	↑	
D	↑↓	↑↓	↑	↑	↑

Helping Concepts *Exam Favourite Rating* ★★★

The atomic number of N is 7. In a neutral atom, there would be 7 electrons and the electronic configuration is $1s^2\ 2s^2\ 2p^3$. The 3 electrons in the 2p orbital are singly filled.

35. *Use of the Data Booklet is relevant to this question.*

The ^{68}Ge isotope of the Group IV element germanium is medically useful because it undergoes a natural radioactive process to give a gallium isotope, ^{68}Ga, which can be used to detect tumours. This transformations of germanium occurs when an electron enters the nucleus, changing a proton into a neutron.

Which statement about the composition of an atom of the gallium isotope is correct?

A It has 37 neutrons.

B Its proton number is 32.

C It has a total of 32 electrons.

D It has 4 electrons in its outer shell.

Helping Concepts *Exam Favourite Rating* ★★

From the Periodic Table, gallium-68 may be represented as $^{68}_{31}Ga$. Hence, number of neutron = 68 − 31 = 37.

36. *Use of the Data Booklet is relevant to this question.*

Which particle has more protons than electrons and more protons than neutrons? ($D = {}^{2}_{1}H$)

A D_3O^+ **B** H_3O^+

C NH_2^- **D** OD^-

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particles	proton	neutron	electron
H	1	0	
D	1	1	
N	7	7	
O	8	8	
D_3O^+	3×1+8=11	3×1+8=11	11−1=10
H_3O^+	3×1+8=11	0+8=8	11−1=10
NH_2^-	7+2×1=9	7+0=7	9+1=10
OD^-	8+1=9	8+1=9	9+1=10

37. Oxygen reacts with platinum(VI) fluoride, PtF_6, as follows:

$$O_2 + PtF_6 \rightarrow O_2^+PtF_6^-$$

It was suggested that xenon should react similarly and, in this way, the first noble gas compound was produced.

$$Xe + PtF_6 \rightarrow Xe^+PtF_6^-$$

What is the most likely reason for the suggestion being made?

A O and Xe have similar atomic radii.

B O and Xe have similar electron affinities.

C O and Xe have similar electron configurations.

D O_2 and Xe have similar first ionisation energies.

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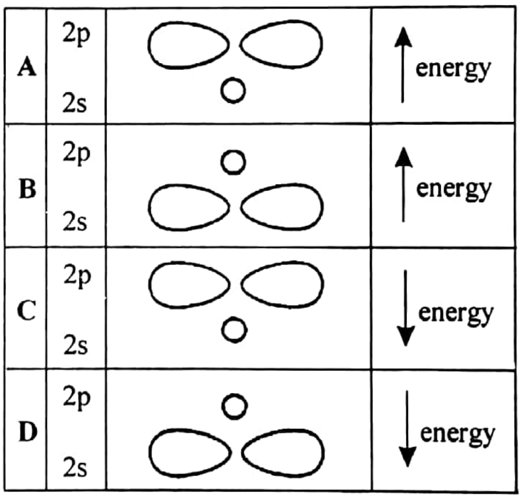
In the reactions, both O_2 and Xe ionise to give O_2^+ and Xe^+ respectively. They should have similar first ionisation energy.

Note: This is similar to saying that both O_2 and Xe '*belong to the same group*' and they form similar ionic compounds.

38. Which diagram best shows the shapes and relative energies of 2s and 2p orbitals in carbon?



Helping Concepts *Exam Favourite Rating* ★★★

The energy level of a 2p orbital is higher than that of a 2s orbital.

39. *Use of the Data Booklet is relevant to this question.*

How many electrons have to be removed to ionise 1.0×10^{-6} mol of Ne atoms to Ne^+ ions in a neon advertising tube?

A $\dfrac{6.02\times10^{23}}{1.0\times10^{-6}}$

B $1.0\times10^{-6}\times6.02\times10^{23}$

C $\dfrac{1.0\times10^{-6}\times6.02\times10^{23}}{20.2}$

D $\dfrac{1.0\times10^{-6}\times6.02\times10^{23}}{9.65\times10^{4}}$

Helping Concepts *Exam Favourite Rating* ★★★

$$Ne(g) \rightarrow Ne^{+}(g) + e^{-}$$

From the data booklet,

$L = 6.02\times10^{23}\ mol^{-1}$

$= $ number of particles in 1 mol

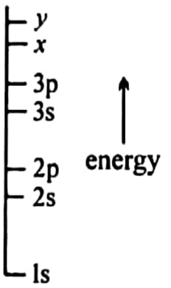
Since 1 mol of electron is removed to ionise 1 mol of Ne atoms (from the equation),

number of electron removed

$= (1.0\times10^{-6}\ mol^{-1})\times(6.02\times10^{23}\ mol^{-1})$

---

40. The diagram shows the energy levels of various electronic sub-shells of an atom of a transition element in the fourth period of the Periodic table.



What are sub-shells x and y?

A $x = 3d$, $y = 4s$

B $x = 4s$, $y = 3d$

C $x = 4s$, $y = 4p$

D $x = 4p$, $y = 3d$

Helping Concepts *Exam Favourite Rating* ★★★

For an element before the transition elements in the 4th period, the 3d orbital has higher energies than the 4s orbital. However, for the transition elements in the 4th period, the 3d orbital is at lower energies than the 4s orbital.

---

41. The radioactive isotope $^{210}_{84}Po$ was said to be the agent that poisoned the former Russian security agent L. Alexander in London in November 2006. $^{210}_{84}Po$ decays to give an element **X** and emits a high energy α-particle (which is a helium nucleus, $^{4}_{2}He$). No other particle is produced. α-particle cause irreparable damage to the tissues of internal organs.

$$^{210}_{84}Po \rightarrow {}^{4}_{2}He + X$$

Which row in the table correctly describes the nuclear make-up of $^{210}_{84}Po$ and element **X**?

	$^{210}_{84}Po$	X	
	no. of neutrons	no. of protons	no. of neutrons
A	126	80	122
B	126	82	124
C	210	80	206
D	210	82	208

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No. of neutron in $Po = 210 - 84 = 126$

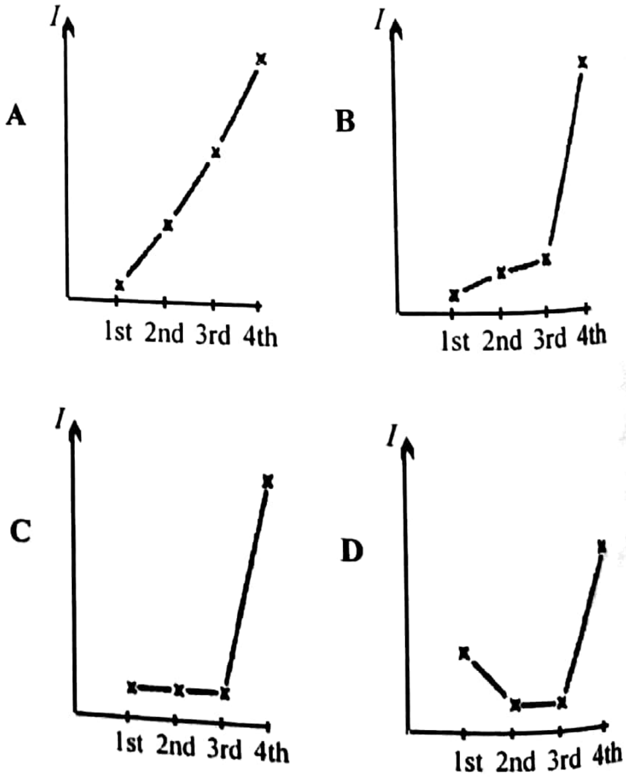
No. of proton in $X = 84 - 2 = 82$

Mass number of $X = 210 - 4 = 206$

No. of neutron in $X = 206 - 82 = 124$

---

42. Which of the following diagrams represents the first four ionisation energies, I, of a Group III element?



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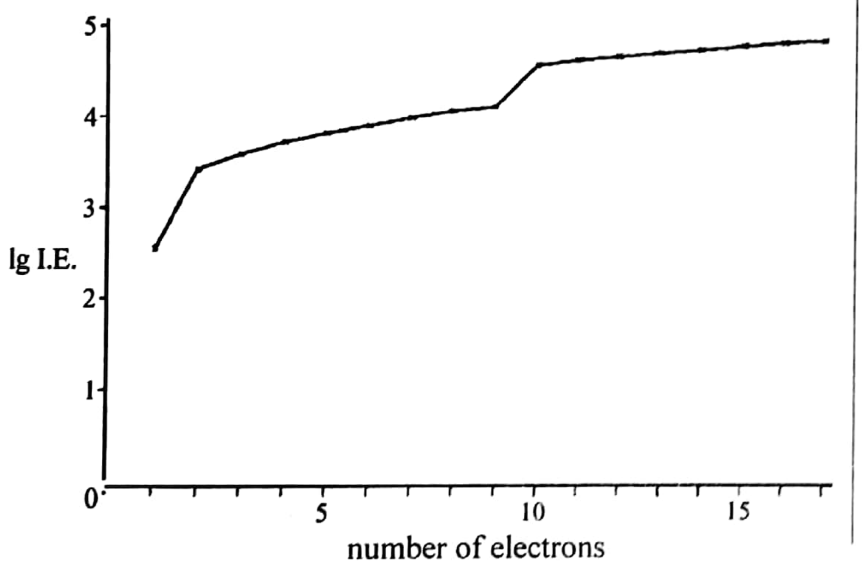
As electrons are progressively removed from an atom, the removal becomes more *difficult* due to the contraction in size and also increase in the positive charge of the species. Therefore, there is an increase in the ionisation energies. However, being a Group III element, a sudden increase in the 4th ionisation energy is expected because an electron is removed from the *inner* shell of the species that has an *octet configuration.*

---

43. *Use of the Data Booklet is relevant to this question.*

The graph shows the logarithm, lg, of the ionisation energies for the outermost seventeen electrons in an atom of an element X.



Which of the following could be X?

A argon **B** calcium

C chlorine **D** potassium

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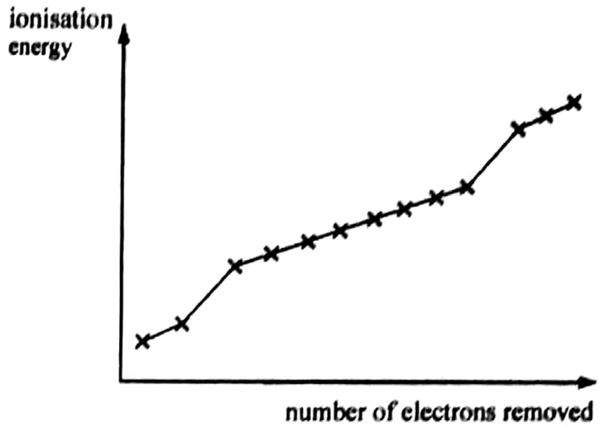
The graph shows a Group I element since there is a large jump between the first ionisation energy and the second ionisation energy, signifying that the first electron removed is not in the same principal quantum shell as the subsequent electron, i.e. it is in the outermost shell.

---

44. The graph shows the first thirteen ionisation energies for element X.



What can be deduced about element X from the graph?

A It is a d-block element.

B It is in Group II of the Periodic Table.

C It is in Group III of the Periodic Table.

D It is in the second period (Li to Ne) of the Periodic Table.

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There is a large difference between the IE_2 and IE_3, followed by IE_{10} and IE_{11}. This shows that the 2nd and 3rd electrons are in different quantum shell. Hence, we can deduce that the element has 2 valence electrons.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

45. A species **Z** has the following electronic configuration.

[↑↓] [↑↓] [↑↓|↑↓|↑↓] [↑↓] [↑↓|↑ |↑]

What could **Z** be?

1 Cl^{+} ion
2 S atom
3 Ar^{2-} ion

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*1. $_{17}Cl$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
$_{17}Cl^{+}$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

*2. $_{16}S$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

3. $_{18}Ar$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
$_{18}Ar^{2-}$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

Note: Ar^{2+} would be an answer.

---

46. Which statements about atomic particles are correct?

1 The nucleon number of an element is the number of neutrons in one atom of the element.
2 The proton number of an element is the number of protons in one atom of the element.
3 The size of the charge on an electron is the same as that on a proton.

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1. The nucleon number, or mass number, is the number of protons and neutrons in the nucleus. The neutron number is the number of neutrons in the nucleus.

*2. The proton number, or atomic number, is the number of protons in the nucleus.

*3. For a neutral atom, the number of electrons is equal to the number of protons.

---

47. The isotope cobalt-60 ($^{60}_{27}Co$) is used to destroy cancer cells in the human body.

Which statements about an atom of cobalt-60 are correct?

1 It contains 33 neutrons.
2 Its nucleus has a relative charge of 27+.
3 It has a different number of neutrons from the atoms of other isotopes of cobalt.

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*1. Number of neutrons = 60 − 27 = 33

*2. Number of protons = 27

*3. Isotopes have the same number of proton but different number of neutrons.

---

48. Which of the following statements about the two isotopes $^{32}_{15}P$ and $^{32}_{16}S$ are correct?

1 The phosphorus atom has more neutrons than the sulfur atom.
2 If a neutron is added to the nucleus of $^{32}_{15}P$, $^{32}_{16}S$ is produced.
3 Both contain 32 electrons.

Helping Concepts *Exam Favourite Rating* ★★★

*1. Number of neutrons in $^{32}_{15}P = 32 - 15 = 17$
Number of neutrons in $^{32}_{16}S = 32 - 16 = 16$

2. Adding a neutron to $^{32}_{15}P$ still gives a phosphorus isotope because the number of protons (which gives the identity of an element) is still the same.

$$^{32}_{15}P + ^{1}_{0}n \rightarrow ^{33}_{15}P$$

3. $^{32}_{15}P$ contains 15 electrons and $^{32}_{16}S$ contains 16 electrons. The number of electrons in a neutral atom is equal to the atomic number.

49. Which of the following statements about the s, p and d orbitals of principal quantum numbers 1, 2 and 3 are true?

1 Each s orbital can contain a maximum of two electrons.

2 A series of transition elements arises from the filling of d orbitals.

3 A p orbital has a higher energy than the s orbital of the same principal quantum number.

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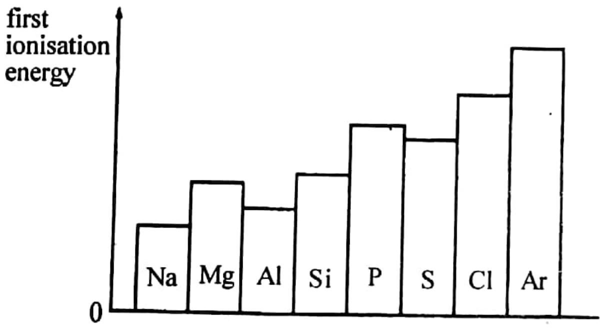
*1. Every orbital (not only the s orbital) can accomodate a maximum of 2 electrons with opposite spins.

*2. Transition elements arise from the filling of d orbitals.

*3. In the *same* principal quantum number, the energy of the orbitals increases from s < p < d.

---

50. The first ionisation energies of elements in the third period are shown.



Which factors explain why the value of the first ionisation energy of sulfur is lower than that of phosphorus?

1 repulsion between the pair of 3p electrons

2 greater shielding by inner electrons

3 increase of principal quantum number

Helping Concepts *Exam Favourite Rating* ★★

*1. S has a p^4 configuration so that its first I.E. is lower than that of P due to electronic repulsion between the two 3p electrons in the same orbital.

2. Both P and S have the same number of inner electrons.

3. Both P and S have the same principal quantum number ($n = 3$).

---

51. Gaseous particle **X** has a proton (atomic) number n and a charge of +1.

Gaseous particle **Y** has a proton (atomic) number of $(n + 1)$ and is isoelectronic with (has the same number of electrons as) **X**.

Which of the following statements corrrectly describe **X** and **Y**?

1 **X** has a larger radius than **Y**.

2 **X** requires more energy than **Y** when a further electron is removed from each particle.

3 **X** releases more energy than **Y** when an electron is added to each particle.

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Let **X** be ${}_{n}M^{+}$ (it has $(n-1)$ number of electrons). Then **Y** will be ${}_{n+1}N^{2+}$ so that it also has a $(n-1)$ number of electrons.

*1. Since **X** has a lower nuclear charge, the electrons are more loosely bound and hence it has a larger radius.

2. **X** requires less energy because it is larger and it has a lower positive cationic charge.

3. **Y** releases more energy because it has a stronger attraction for electron than does **X** due to its smaller radius and higher cationic charge.

TOPIC 3

Chemical Bonding

Key content that you will be examined on:

1. Ionic (electrovalent) bonding
2. Covalent bonding and co-ordinate (dative covalent) bonding
   (i) The shapes of simple molecules
   (ii) Bond energies, bond lengths and bond polarities
3. Intermolecular forces, including hydrogen bonding
4. Metallic bonding
5. Bonding and physical properties
6. The solid state

Chemical Bonding

Topic 3

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which ion is most polarising?

   A Al^{3+} B Ba^{2+}
   C Mg^{2+} D Na^{+}

Helping Concepts *Exam Favourite Rating* ★★★

A cation with a high charge and small size has a high charge density and hence a high polarising power.

Al^{3+} has the highest charge and smallest size among the 4 options.

---

2. Which solid exhibits more than one kind of chemical bonding?

   A brass B copper
   C diamond D ice

Helping Concepts *Exam Favourite Rating* ★★★

There are covalent bonds between H and O in a molecule, and hydrogen bonds between H and O of different molecules.

---

3. Which of the following solids consists of atoms or molecules held together only by van der Waals' forces?

   A CO_2 B Cu
   C H_2O D MgO

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CO_2 is simple molecular. Even in the solid state, the molecules are still held together only by van der Waals' forces. The forces of attraction in the other solids are (B) metallic bonds; (C) hydrogen bonds; (D) ionic bonds.

---

4. Which of the following solids has a simple molecular lattice?

   A magnesium oxide
   B sodium
   C silicon(IV) oxide
   D sulfur

Helping Concepts *Exam Favourite Rating* ★★★

Sulfur exists as S_8 molecules.

A: giant ionic lattice

B: giant metallic lattice

C: giant covalent lattice

---

5. Magnesium oxide is used to line industrial furnaces because it has a very high melting point.

   Which type of bond needs to be broken for magnesium oxide to melt?

   A co-ordinate B covalent
   C ionic D metallic

Helping Concepts *Exam Favourite Rating* ★★★

$Mg^{2+}O^{2-}$ is an ionic compound. It has a giant ionic lattice with strong ionic bonds between Mg^{2+} and O^{2-}.

---

6. Why does copper wire conduct electricity when a potential difference is applied?

   A Bonding electrons in the crystal lattice move.
   B Copper(II) ions move to the cathode.
   C The atoms of copper become ionised.
   D The crystal lattice breaks down.

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Being a metal, Cu has a sea of delocalised electrons.

When a potential difference is applied, these electrons move towards the positive potential.

---

7. Which of the following molecules is not planar?

A benzene

B boron trifluoride

C ethene

D phosphorus trichloride

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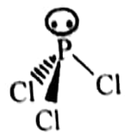
PCl_3 is trigonal pyramidal.



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8. Which of the following molecules contains six bonding electrons?

A C_2H_4 B CO_2

C H_2S D NCl_3

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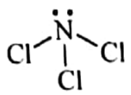
6 bonding electrons is equivalent to 3 bond pairs of electrons.



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9. Which of the following best describes the change in the bond angle in water when the ion H_3O^+ is formed?

A decreases to approximately 90°

B decreases to approximately 109°

C increases slightly

D increases to approximately 120°

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In H_2O, the bond angle is 104.5° (2 lone pairs, 2 bond pairs). In H_3O^+, there are 3 bond pairs and only 1 lone pair. Since bond pair exerts less repulsion, the bond angle in H_3O^+ become bigger (but still less than 109.5°).

---

10. In which one of the following compounds does the underlined element not have eight electrons in the outer shell?

A $\underline{Li}_2O$ B $H_2\underline{O_2}$

C $\underline{P}Cl_3$ D $\underline{P}Cl_5$

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Li has an electronic configuration of $1s^2\ 2s^1$. On losing an electron to O, Li^+ acquires a duplet configuration (NOT octet).

---

11. As the number of carbon atoms in the homologous series of alkane molecules **increases**, for which property of the alkanes does the numerical value **decrease**?

A density

B ethalpy change of vaporisation

C number of isomers

D vapour pressure

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As number of carbon atoms of the homologues increases, the van der Waals' forces increases so that the homologues vaporise less readily. Hence, vapour pressure decreases.

---

12. Which type of bond is responsible for intermolecular forces in liquid tetrachloromethane, CCl_4?

A covalent bonding

B hydrogen bonding

C induced dipole - induced dipole attractions

D permanent dipole - permanent dipole attractions

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CCl_4 exists as discrete molecules and its molecules are non-polar. The forces operating between its molecules are id-id interactions.

---

13. Which one of the following molecules will have no permanent dipole?

A C_2Cl_4 B CF_2Cl_2

C C_2H_5Cl D $CHCl_3$

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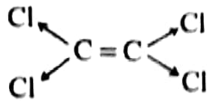
Although there is a permanent dipole in each C–Cl bonds, the effect of each cancels one another vectorically due to the symmetrical distribution of the 4 Cl atoms.



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14. Which equation defines the lattice energy of the ionic compound XY?

A $X(s) + Y(s) \rightarrow XY(s)$

B $X(g) + Y(g) \rightarrow XY(s)$

C $X^{+}(s) + Y^{-}(s) \rightarrow XY(s)$

D $X^{+}(g) + Y^{-}(g) \rightarrow XY(s)$

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By definition, lattice energy is the energy released when 1 mole of an ionic compound is formed from its constituent **gaseous ions** (infinitely apart) combine together.

---

15. The lattice energies of the compounds caesium chloride, caesium fluoride, sodium chloride and sodium fluoride are given below.

Which value corresponds to the lattice energy of caesium chloride?

A -661 kJ mol^{-1} B -747 kJ mol^{-1}

C -780 kJ mol^{-1} D -918 kJ mol^{-1}

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$$\text{L.E.} \propto -\left|\frac{q_{+}q_{-}}{r_{+}+r_{-}}\right|$$

CsCl has the largest r_{+} and r_{-} among the ionic compounds. Hence, it has the least exothermic L.E.

---

16. Which of the following isomers is likely to have the highest boiling point?

A $(CH_3)_2CHCH(CH_3)_2$

B $(CH_3)_2CHCH_2CH_2CH_3$

C $CH_3CH_2CH(CH_3)CH_2CH_3$

D $CH_3CH_2CH_2CH_2CH_2CH_3$

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All the 5 compounds are isomers of hexane but (D) is unbranched. It has the greatest surface area of contact for VDW interaction and hence, the highest boiling point.

---

17. What is the approximate value of the O–C–O bond angle in ethanoic acid?

A 45° B 90°

C 109° D 120°

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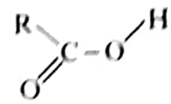

There are only 3 regions of electron clouds around C. To minimise electronic repulsion, they are directed in a trigonal planar manner and the bond angles are about 120°.

---

18. Which one of the following structural features is common to both diamond and graphite?

A a carbon-carbon bond length equal to that in ethane

B covalent bonds between carbon atoms

C delocalised electrons

D each carbon atom bonded to four others

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In diamond and graphite, covalent bonds operate between carbon atoms and the extension of these bonds throughout the lattices gives rise to macromolecular structure.

---

19. A mixture of aqueous silver nitrate and aqueous potassium cyanide, KCN, is used for electroplating.

The mixture contains the complex ion $[Ag(CN)_2]^-$.

What is the carbon-silver-carbon bond angle?

A 104° B 109.5°

C 120° D 180°

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$$[NC \rightarrow Ag \leftarrow CN]^-$$

The 2 CN^- ligands arrange themselves as far away from each other as possible to minimise electronic repulsion. Hence, it is linear (bond angle = 180°).

---

20. Which of the following is a property of a solution of dry hydrogen chloride in dry methylbenzene?

A It has a pH less than 7.

B It is a non-conductor of electricity.

C It reacts with magnesium to give hydrogen.

D It reacts with dry copper(II) oxide on warming to give a blue solution.

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Dry HCl does not dissociate in non-polar solvents such as methylbenzene. Since there is no free ions or electrons, it does not conduct electricity.

---

21. Predict the most likely bond angle at each nitrogen atom in diimine, HN=NH.

A 107° **B** 118°

C 120° **D** 180°

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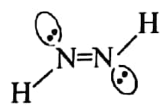

The molecular is planar w.r.t. each N, with bond angle about 120°. The lone pair of electrons exert a greater electronic repulsion and makes the H–N–N angle less than 120°.

---

22. Graphite can be used as a lubricant; diamond cannot. This is because graphite has

A delocalised electrons.

B a hexagonal arrangement of atoms in the layers.

C covalent bonds between atoms in the layers.

D van der Waals' forces between the layers of atoms.

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The weak van der Waals' forces between the layers of C atoms allow the layers to slide over one another without shattering the lattice.

---

23. In which one of the following does ionic bonding occur between the named atoms?

A aluminium and chlorine in the tetrachloroaluminate ion

B boron and fluorine in boron trifluoride

C hydrogen and chlorine in hydrogen chloride

D hydrogen and sodium in sodium hydride

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Ionic bond is formed between a metal and a non-metal, e.g. Na^+H^-. In (A) and (B), both Al^{3+} and B^{3+} are too highly polarising so much so that the bonds between Al and Cl and that between B and F are predominantly covalent. In (C), the bonds are formed between non-metals and are hence covalent.

---

24. The C_2H_2 molecule is linear.

What can be deduced from this about the numbers of σ and π bonds present in the molecule?

	σ	π
A	2	2
B	2	3
C	3	1
D	3	2

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$$H-C\equiv C-H$$

The $C\equiv C$ triple contains 1 σ and 2 π bonds. Hence, there are 2 π bonds and 3 σ bonds (1 $C\equiv C$ and 2 C–H bonds).

---

25. The atoms X and Y have the electronic configurations shown below.

X: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2$; Y: $1s^2\,2s^2\,2p^4$

Which one of the following compounds are they likely to form?

A XY B XY_2
C X_2Y D XY_4

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X has a completely filled d-subshell (d^{10} s^2) and it behaves like a Group II element. Y has 6 valence electrons and therefore is in Group VI. It is expected that X will lose 2 electrons to Y so that both have stable electronic configurations.

i.e. $X^{2+}Y^{2-}$.

---

26. Which one of the following is a linear molecule?

A H_2O B HCN
C SO_2 D C_2H_4

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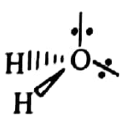
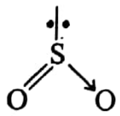
$$H-C\equiv N:$$

There are 2 regions of electron clouds around carbon. To minimise electronic repulsion, they are directed linearly.

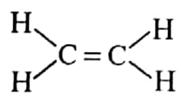
The shapes of the other molecules are



bent



bent



planar
(trigonal planar w.r.t. each carbon atom)

---

27. Which molecule is planar?

A NF_3 B C_2Cl_4
C C_3H_6 D C_3H_8

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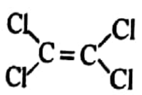
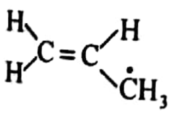
trigonal pyramidal



trigonal planar w.r.t. each C



tetrahedral w.r.t. $\dot{C}$

$CH_3-CH_2-CH_3$ tetrahedral w.r.t. each C

---

28. Which of the following statements describes a phenomenon which can be explained by intermolecular hydrogen-bonding.

A The boiling points of the alkanes increase with increasing relative molecular mass.

B CH_3OCH_3 ($M_r=46$) has a higher boiling point than $CH_3CH_2CH_3$ ($M_r=44$).

C Hydrogen chloride forms an acidic solution when dissolved in water.

D Ice has a lower density than water at 0 °C.

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Due to the presence of hydrogen-bonding in ice, the H_2O molecules take up an open structure and hence, ice becomes less dense than water at 0 °C.

---

29. The gecko, a small lizard, can climb up a smooth glass window. The gecko has millions of microscopic hairs on its toes and each hair has thousands of pads at its tip. The result is that the molecules in the pads are extremely close to the glass surface on which the gecko is climbing.

What is the attraction between the gecko's toe pads and the glass surface?

A co-ordinate bonds

B covalent bonds

C ionic bonds

D van der Waals' forces

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The extreme close proximity allows VDW interaction and the many pad-glass VDW interactions allow gecko to be able to stick on glass surface.

---

30. Solid carbon dioxide, CO_2(s) (dry ice), is used as a refrigerating agent because it readily changes directly from the solid into the vapour state at a low temperature.

What does this indicate the main intermolecular bonding in CO_2(s) to be?

A covalent bonding

B hydrogen bonding

C ionic bonding

D van der Waals' forces

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This shows that the forces acting between CO_2 molecules are very weak (VDW) such that when enough energy is supplied, these forces are readily overcome and the molecules become very far apart from each other, i.e. gas is formed.

---

31. Which feature is present in the ions carbonate, ethanoate, nitrate and phenoxide (phenate)?

A all bond angles are 120°

B dative covalent bonds

C delocalised electrons

D hydrogen bonds

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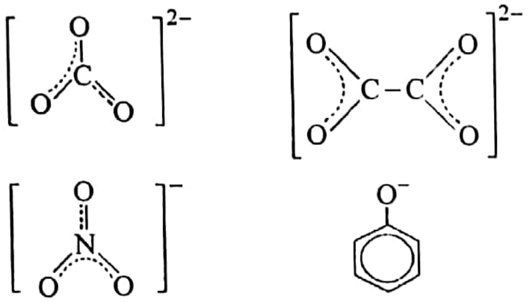

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32. Which set of properties could apply to a non-ionic compound which has a giant lattice?

	physical state at room temp.	electrical conductivity of the molten compound	m.p./°C
A	liquid	does not conduct	−114
B	liquid	does not conduct	melts over a temp. range
C	solid	conducts well	808
D	solid	does not conduct	1610

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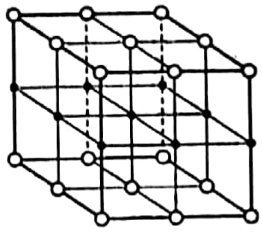
A non-ionic compound which has a giant lattice has strong covalent bonds. Thus, it has a high melting point. Since it does not contain mobile charges (e.g. electron), it does not conduct electricity.

Note: It is not a mixture and thus does not melt over a range of temperatures.

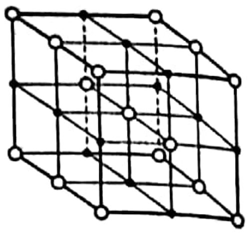
---

33. Which diagram best represents the structure of solid magnesium oxide?

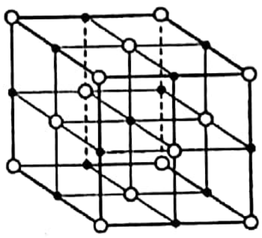
A



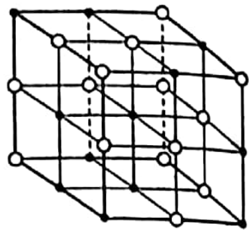
B



C



D



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In an ionic lattice, the cations and anions occupy alternate positions to maximise attraction and minimise repulsion. Only structure C satisfies this condition.

---

34. Which of the following molecules will **not** form a hydrogen bond with another of its own molecules?

A CH_3CHO **B** CH_3NH_2

C CH_3OH **D** NH_3

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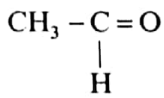
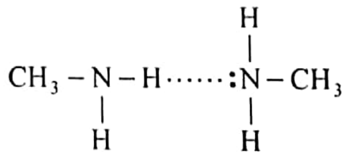
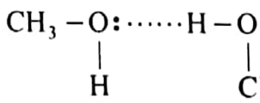


There is no H bonded directly to a small and highly electronegative atom, e.g. N, O, F.

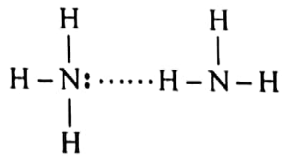
B:



C:



D:



35. Why is the boiling point of methane greater than that of neon? [Ar: H, 1; C, 12; Ne, 20]

A A molecule of methane has a greater mass than a molecule of neon.

B A molecule of methane has more electrons than a molecule of neon.

C Molecules of methane have stronger intermolecular forces than those of neon.

D Molecules of methane from hydrogen bonds, but those of neon do not.

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Since both methane and neon are simple molecular, their boiling points are determined by the strength of their intermolecular forces (van der Waals' forces). Stronger intermolecular forces (due to larger surface area of contact of CH_4) give rise to higher boiling point since more energy is required to separate the molecules apart.

---

36. The Valence Shell Electron Pair Repulsion theory (VSEPR) is used to predict the shapes of molecules.

Which shape is correctly predicted by VSEPR?

	number of bonded electron pairs around central atom	number of lone pairs around central atom	shape
A	2	2	non-linear
B	2	2	tetrahedral
C	3	1	trigonal planar
D	3	1	linear

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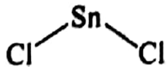
number of bonded electron pairs around central atom	number of lone pairs around central atom	shape
2	2	non-linear (bent, angular)
3	1	trigonal pyramidal

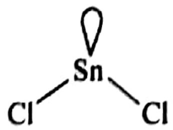
---

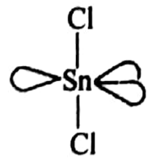
37. Which of the following structures represents the gaseous $SnCl_2$ molecule?

(represents an unshared lone pair of electrons.)

A Cl–Sn–Cl

B 

C 

D 

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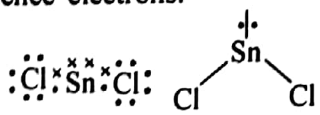
Sn has 4 valence electrons.



There are 3 regions of electron clouds around Sn. To minimise electronic repulsion, they are directed in a trigonal planar manner. Since this is a lone pair of electrons, $SnCl_2$ is bent (or angular, non-linear, V-shaped).

---

38. When heated, solid iodine readily forms iodine vapour.

What does this information suggest about the nature of the particles in these two physical states of iodine?

	solid	vapour
A	ionic	atomic
B	ionic	molecular
C	molecular	atomic
D	molecular	molecular

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Since the solid readily sublimes when heated, this shows that the forces of attraction between iodine particles are not strong. Hence, the solid should be simple molecular. As the sublimation process does not require a high temperature, the covalent bond in the molecule is not broken in the vapour state. Hence, iodine vapour is still molecular.

---

39. Which one of the following is **not** planar?

A boron trichloride

B methanal

C the phenoxide (phenate) ion

D propene

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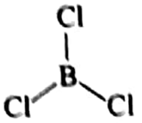
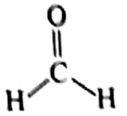
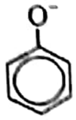
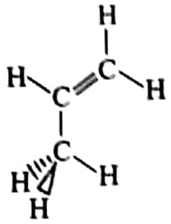
The shapes of the molecules are given as follows:

A:  (trigonal planar)

B:  (trigonal planar)

C: 

D: 

The methyl group in propene is tetrahedral, i.e. non-planar.

---

40. Why is the molecule of BCl_3 planar, whereas the molecule of PH_3 is pyramidal?

A The boron atom has no d orbitals available for bonding.

B The boron atom in BCl_3 has six electrons in its valency shell, whereas the phosphorus atom in PH_3 has eight.

C The repulsion between chlorine atoms is greater than that between hydrogen atoms.

D The covalent radius of phosphorus is greater than that of boron.

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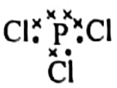

6 electrons   8 electrons

B is in Group III and P is in Group V. Bonding with 3 Cl atoms leaves B with a vacant P_z orbital (no lone pair) and P with a filled sp^3 orbital (lone pair). By using VSEPR, BCl_3 is trigonal planar and PCl_3 is trigonal pyramidal.

---

41. Which bonding type does not correspond to its description of physical properties?

	bonding type	physical properties
A	giant covalent	high melting point, conducts electricity when in solution but not when solid
B	simple covalent	low melting point, does not conduct electricity in any state
C	metallic	variety of melting point, conducts electricity when solid and when molten
D	ionic	high melting point, conducts electricity when in molten but not when solid

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Substances with a giant covalent structure do not readily dissolve in solvent. Even when it dissolves, they exist as giant molecules and hence not able to conduct electricity in solution.

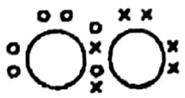
---

42. When barium metal burns in oxygen, the ionic compound barium peroxide, BaO_2, is formed.

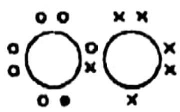
Which dot-and-cross diagram could represent the structure of the anion in BaO_2?

A

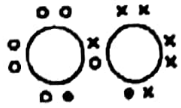
B



C



D



key: o electron from first oxygen atom; × electron from second oxygen atom; • electron from barium atom

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In BaO_2, the anion exists as O_2^{2-} where 2 electrons are transferred from Ba.

---

43. Which of the following statements about the properties associated with ionic and covalent bonds is correct?

A The only covalent compounds with high melting points are those in which hydrogen bonds occur.

B Any covalent compound that contains both oxygen and hydrogen in its molecule forms hydrogen bonds.

C Ionic bonds and covalent bonds cannot both occur in the same compound.

D Ionic compounds differ from metals in that ionic compounds do not conduct electricity in the solid state.

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In a solid ionic compound, the ions are localised and hence they cannot conduct electricity. In a metal, the delocalised electrons are responsible for its electrical conductivity.

A: Diamond, SiO_2 are giant covalent substances (without H-bonds) with high melting points.

B: CH_3CHO does not form H-bonds with another molecules of itself (the H atom needs to be covalently bonded to N, O, F).

C: $NH_4^+Cl^-$ has ionic bond and covalent bonds (N–H bond).

44. *Use of the Data Booklet is relevant to this question.*

Which particle contains a single unpaired electron?

A a molecule of H_2S

B one of the particles formed after the heterolytic fission of a chlorine molecule

C the ammonium ion in NH_4Cl

D the copper ion in CuO

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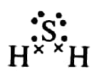
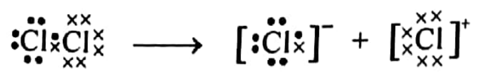
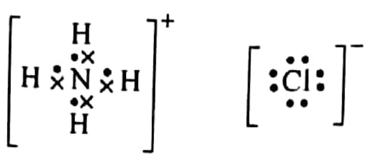
In CuO, the copper ion is Cu^{2+}. Its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$. There is a single unpaired electron in the 3d orbital.

A: 

B: 

C: 

45. Consider the following four compounds:

1 $(CH_3)_3CH$

2 $CH_3CH_2CH_2OH$

3 $CH_3CH_2CH_2SH$

4 $CH_3CH_2CH_2CH_3$

What is the order of increasing boiling point of the compounds (lowest first)?

A 1 4 3 2

B 2 3 4 1

C 3 2 4 1

D 4 1 2 3

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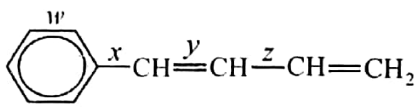
All the compounds exist as discrete molecules. The boiling point therefore depends on the strength of the intermolecular force of attraction. 1 and 4 are isomers. However, 1 is highly branched and hence has weaker VDW forces. 4 is therefore higher boiling than 1. VDW forces in 3 is stronger than that in 4 because 3 has a larger molecular size and more electrons per molecule. Hence, 3 has a higher boiling point than 4. 2 has the highest boiling point because it is capable of intermolecular hydrogen-bonding which is stronger than the VDW forces.

46. Four carbon–carbon bonds are labelled in the diagram.



Which bonds are made up of an sp^2–sp^2 overlap?

A w and y only

B w, x and y only

C w, x, y and z

D x, y and z only

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sp^2 C atoms are trigonal planar and there are 2 single bonds and 1 double bond at this C.

47. Which of the following statements best explains why the boiling point of butanone (79.6 °C) is higher than that of pentane (36.1 °C)?

[A_r: H, 1.0; C, 12; O, 16]

A The butanone molecule has a larger surface area than the pentane molecule.

B The covalent bonds in the butanone molecule are stronger than those in the pentane molecule.

C There are hydrogen bonds between butanone molecules, but not between pentane molecules.

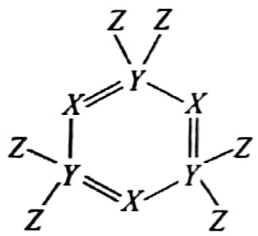
D There are dipole-dipole forces between butanone molecules, but only van der Waals' forces between pentane molecules.

★★

The M_r of butanone and pentane are both 72. Permanent dipole-permanent dipole interactions exist between butanone molecules due to the presence of the polar C=O bond. The hydrocarbon has only weak van der Waals' attractions operating between the molecules.

---

48. A stable molecule containing atoms of the elements *X*, *Y* and *Z* has the following structure.



Which elements could *X*, *Y* and *Z* be?

	X	*Y*	*Z*
A	N	P	Cl
B	O	S	Cl
C	B	C	H
D	P	Si	H

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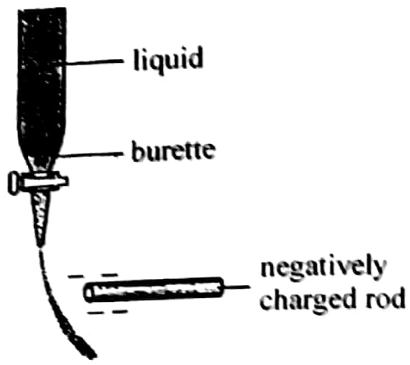
X uses 3 of its valence electrons for bonding and it is angular shaped, suggesting that there is either 1 or 2 lone pairs of electrons. Hence, *X* has either 5 or 7 valence electrons, i.e. *X* is either a Group V or Group VII element. *Y* is is likely to be a Group V element since the diagram shows that there are 5 valence electrons. However, *Y* cannot be N because N is unable to expand its octet configuration. The structure shows that *Y* has accomodated 10 electrons. Forming only a single bond, *Z* could be hydrogen or a Group VII element.

---

49. The diagram shows a liquid flowing from a burette and a charged rod being brought near the flow.



Which liquid would be deflected as shown?

A bromine

B cyclohexane

C hexachloroethane

D trichloromethane

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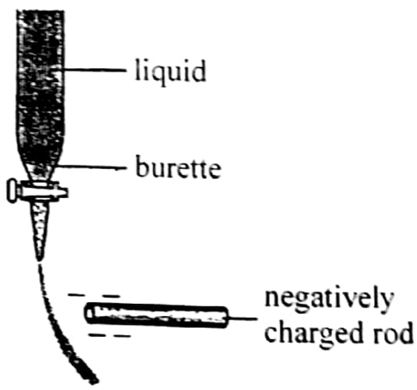
$CHCl_3$ is polar. In the presence of the negatively charged rod, the molecules aligned themselves such that the $\delta+$ end of the molecules faces the rod.

Consequently, the stream of liquid becomes attracted to the rod.

---

50. A slow stream of water from a tap can be deflected by an electrostatically charged plastic rod because water is a polar molecule.



Why is a water molecule polar?

A Molecules are bonded together by hydrogen bonds.

B The oxygen and hydrogen atoms have different electronegativities.

C The oxygen atom has two lone pairs of electrons.

D Water is able to dissociate into ions.

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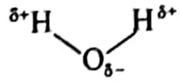
In a H_2O molecule, the H–O bonds are polar due to the difference in their electronegativities. Since the molecule is non-linear, the dipole moment of the 2 H–O bonds do not cancel each other vectorically. Hence H_2O is polar.



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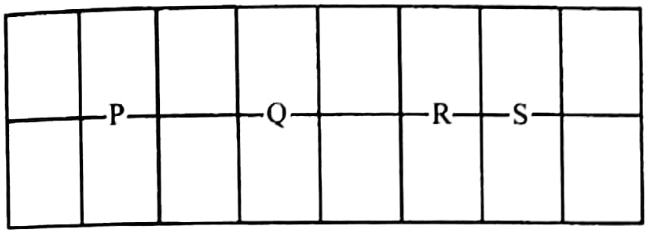
51. The grid represents two periods of the Periodic Table, for the elements 3 to 18.



An element from one group, P, Q R or S, reacts with an element from another of these groups to produce a compound with a giant covalent structure.

Which are the two groups?

A P and R B Q and R

C Q and S D R and S

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An example of a compound with a giant covalent structure is SiO_2 which is formed by silicon in Group IV and oxygen in Group VI. Since Q is in Group IV and R is in Group VI, the answer is (B). P is from Group II and forms ionic compounds instead of covalent compounds with Q, R or S. S is from Group VII and one S only forms one bond with Q or R. Hence, S cannot form covalent compounds with giant covalent structure.

---

52. Three substances, *R*, *S*, *T*, have physical properties as shown.

substance	mp/°C	bp/°C	electrical conductivity	
			of solid	of liquid
R	801	1413	poor	good
S	2852	3600	poor	good
T	3550	4827	good	not known

What could be the identities of *R*, *S* and *T*?

	R	*S*	*T*
A	NaF	KCl	Cu
B	NaBr	BaO	SiO_2
C	NaCl	MgO	C [graphite]
D	NaBr	CaO	C [diamond]

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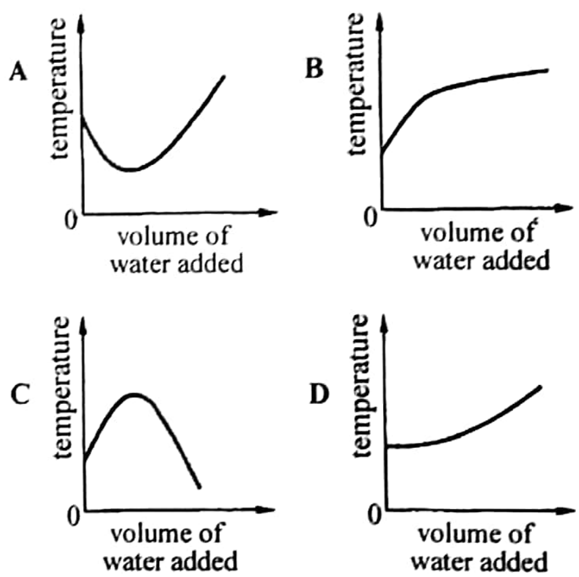
Both *R* and *S* are ionic compounds since they have high melting point and boiling point. They conduct electricity in liquid state (not in solid state). However, since *S* has a higher melting point and boiling point, *S* has a stronger ionic bond, i.e. (B), (C) and (D) (higher ionic charges and smaller ionic radii).

T conducts electricity, it cannot be SiO_2 or diamond.

---

53. When water is stirred with glucose, strong hydrogen bonds are initially formed between glucose molecules and water molecules, but as more water is added, these hydrogen bonds are broken.

Which graph best represents the observed temperature changes?



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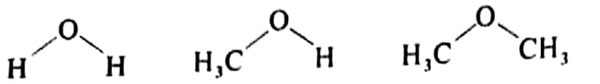
When hydrogen bonds are formed initially, heat is released (exothermic) and temperature rises. When more water is added, hydrogen bonds are broken and this requires energy (endothermic) and temperature drops.

---

54. Water, methanol and methoxymethane, CH_3OCH_3, have similarly shaped molecules.



What is the strongest intermolecular force in water, methanol and methoxymethane?

	H_2O	CH_3OH	CH_3OCH_3
A	hydrogen bonds	hydrogen bonds	permanent dipoles
B	hydrogen bonds	hydrogen bonds	induced dipoles
C	permanent dipoles	permanent dipoles	induced dipoles
D	hydrogen bonds	permanent dipoles	induced dipoles

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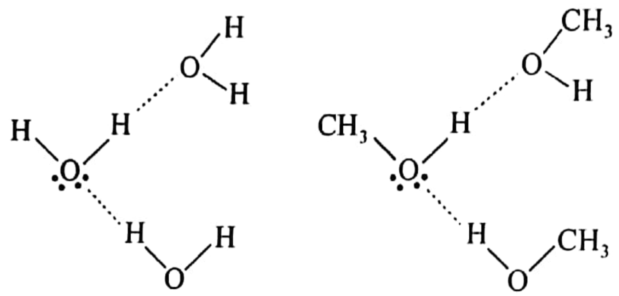
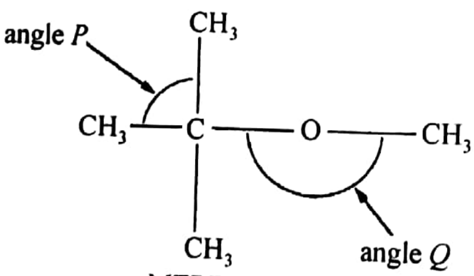
In both H_2O and CH_3OH, there exist O–H bonds in the molecules. Hence, intermolecular H-bonds are present.



In CH_3–O–CH_3, the molecule is polar (non-linear molecule) due to the polar C–O bonds. Hence, permanent dipoles interactions are present.

---

55. MTBE is a constiuent of petrol.



MTBE

What are the values of angle *P* and angle *Q* in a molecule of MTBE?

	angle *P*	angle *Q*
A	90°	105°
B	90°	180°
C	109°	105°
D	109°	180°

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Carbon is in Group IV and has 4 valence electrons. All the 4 electrons are used for bonding. Hence, the arrangement is tetrahedral with bond angles=109.5°.

Oxygen is in Group VI and has 6 valence electrons. However, only 2 electrons are used for bonding (2 σ bonds), leaving behind 2 lone pairs of electrons. The electronic arrangement around oxygen is also tetrahedral. The presence of the 2 lone pairs of electrons causes the 2 C–O bonds to be closer to each other since they exert greater repulsion. Hence, the bond angle is less than 109.5°.

---

56. Ethanol is much more stable in water than is ethyl ethanoate. Which one of the following statements correctly accounts for this?

A Ethanol is a polar molecule, but ethyl ethanoate is non-polar.

B Ethanol is a non-polar molecule, but ethyl ethanoate is polar.

C A hydrogen bond forms between the hydrogen of the –OH group in ethanol and the oxygen of a water molecule.

D A hydrogen bond forms between the hydrogen of the –OH group in ethanol and the hydrogen of a water molecule.

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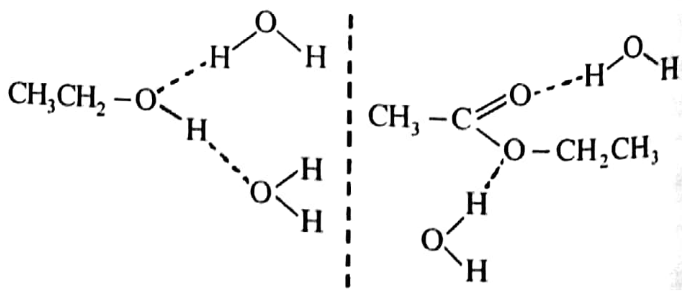
The H of H_2O is able to form H-bonds with the O of –OH and the O of $-\overset{\overset{\displaystyle O}{\|}}{C}-O-$ respectively. However, only the H of –OH is able to form H-bonds with the O of H_2O and ethyl ethanoate is unable to do so. In fact, the ester does not mix well with H_2O due to its long C chain.



57. Covalent bonds are formed by orbital overlap. The shape of unsaturated hydrocarbon molecules can be explained in terms of hybridisation of orbitals.

Which bond is **not** present in

$$HC \equiv CCH_2CH = CH_2?$$

A a π bond formed by 2p–2p overlap

B a σ bond formed by 1s–2sp overlap

C a σ bond formed by 2sp–2sp^2 overlap

D a σ bond formed by 2sp^2–2sp^3 overlap

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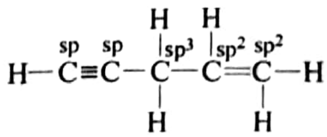


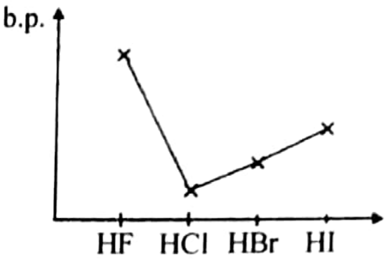
There is no sp–sp^2 overlap of orbitals to form a σ bond.

The σ bonds present are

Csp–H1s, Csp^3–H1s, Csp^2–H1s

Csp–Csp, Csp–Csp^3, Csp^3–Csp^2, Csp^2–Csp^2

58. The diagram shows the variation of the boiling points of the hydrogen halides.



What explains the higher boiling point of hydrogen fluoride?

A The bond energy of HF molecules is greater than in other hydrogen halides.

B The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule.

C The electronegativity of fluorine is much higher than for other elements in the group.

D There is hydrogen bonding between HF molecules.

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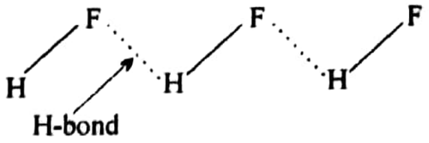
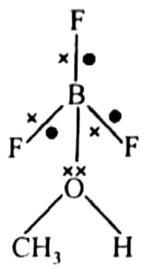
F is small and highly electronegative. In HF, H-bonds exist between HF molecules.



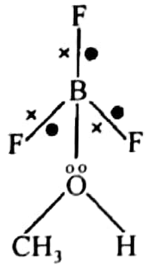
59. $BF_3.CH_3OH$ is a reagent used to form methyl esters from compounds containing acyl groups. In the diagrams, ×, • and o represent electrons from B, F and O, respectively.

Which tetrahedral structure illustrates the electron pairs around the boron atom?

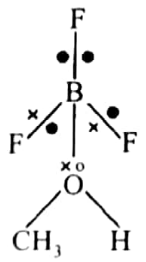
A



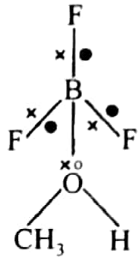
B



C



D



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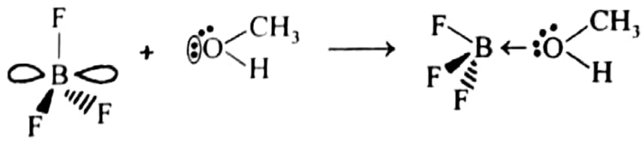
In a BF_3 molecule, there are 3 B–F covalent bonds arranged in a trigonal planar manner with a vacant orbital perpendicular to the plane. The oxygen of CH_3OH uses a lone pair of electrons to form a dative bond with B.



60. The boiling point of water (100 °C) is greater than that of HF (20 °C).

Which statement is a correct explanation of this?

A Each hydrogen bond formed between water molecules is stronger than that formed between HF molecules.

B There are more atoms in a water molecule than there are in an HF molecule, so van der Waals' forces are stronger in water.

C There are, on average, more hydrogen bonds between water molecules than there are between HF molecules.

D The water molecule has a greater permanent dipole than the HF molecule.

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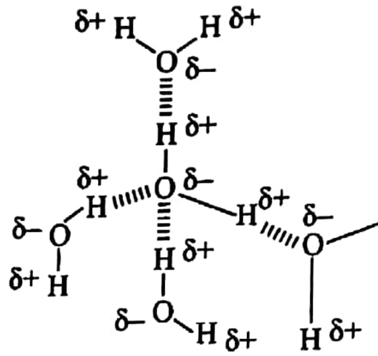
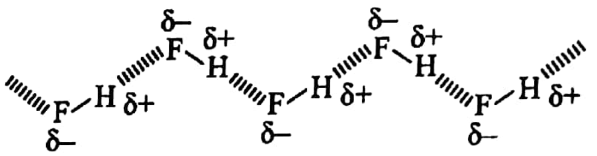
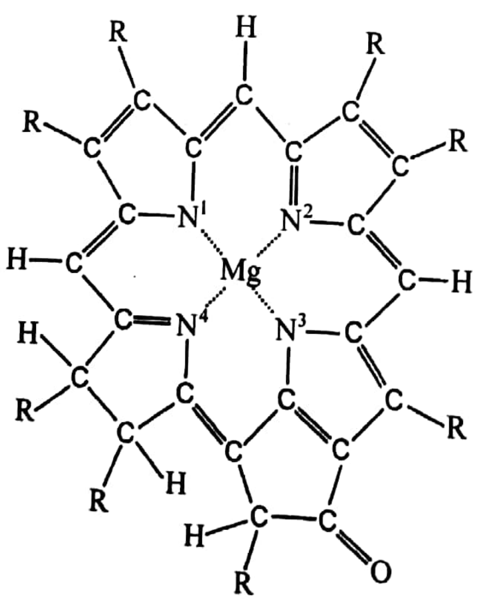
There are more extensive H-bonding between the H_2O molecules.





Each H_2O molecule can form 2 H bonds through the H atoms and 2 H-bonds through the 2 l.p. of O. In HF, there is only 1 H-bond through the H and 1 H-bond through a l.p. of F.

61. Plants appear green due to the presence of chlorophyll. There are several closely related chlorophylls and the diagram shows a simplified version of one. The various different side-groups are all shown as R.



Note that the four N atoms and the Mg ion are planar.

Which of the descriptions of the bonds between Mg and the numbered N atoms is most likely to be correct?

	N atoms numbered 1 and 3	2 and 4
A	co-ordinate	ionic
B	co-ordinate	π
C	ionic	co-ordinate
D	π	co-ordinate

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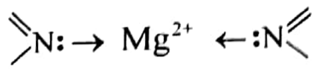
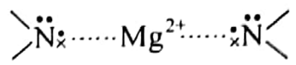
N-2 and N-4 each has a lone pair of electrons to form a co-ordinate (dative) bond with Mg^{2+}.



N-1 and N-3 each receives an electron from Mg (to form Mg^{2+}). Hence, the interaction is ionic.



Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** *to* **D** *should be selected on the basis of*

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

62. Which of the following molecules and ions have a regular trigonal planar shape?

1 $AlCl_3$

2 CH_3^+

3 PH_3

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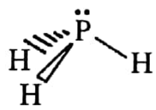
PH_3 is trigonal pyramidal.



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63. Which of the following are features of the structure of metallic copper?

1 ionic bonds

2 delocalised electrons

3 lattice of ions

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Being a metal, Cu has a lattice of the metal cations in a sea of delocalised electrons. The attraction between the cations and the electrons constitutes the metallic bonds.

---

64. Which particles have a single unpaired electron?

1 the copper ion in CuO

2 the methyl free radical

3 a molecule of NO

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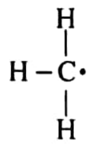
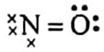
*1. Cu^{2+} : [Ar] $3d^9$

O^{2-} : $1s^2\ 2s^2\ 2p^6$

*2. 

*3. 

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65. Which of the following solids have giant lattices?

1 iodine

2 sodium

3 sodium iodide

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1. I_2 exists as diatomic molecules and hence does not have a giant lattice.

*2,*3. Both sodium (a metal) and sodium iodide (an ionic compound) have giant lattices.

---

66. In which of the following reactions is the bond angle in the product greater than that in the reactant?

1 $H_2O(\ell) + H^+(aq) \rightarrow H_3O^+(aq)$

2 $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

3 $CO_2(g) + OH^-(aq) \rightarrow HCO_3^-(aq)$

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*1. Bond angle of H_3O^+ is bigger since there is only 1 lone pair versus 2 lone pairs in H_2O.

2. C_2H_6: 109.5°; C_2H_4: 120°

3. HCO_3^-: 120°; CO_2: 180°

---

67. Which statements correctly describe the graphite lattice?

1 The lattice contains delocalised electrons.

2 Each carbon atom in the lattice has three closest neighbours.

3 The valency of each carbon atom in the lattice is 3.

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In each layer, each C atom uses 3 electrons to form σ bonds with 3 other C atoms (hence 2 and 3 are correct). This leaves behind a lone electron on each C atom and this forms a layer of delocalised electrons (1 is correct).

---

68. Which of the following systems contain delocalised electrons?

1 cyclohexene
2 graphite
3 sodium

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1. In cyclohexene, the electrons in the π-bond is localised between 2 carbon atoms.

*2. Within each layer, the lone electron of each sp^2 hydridised C atom overlaps with those of the adjacent C atoms, forming a delocalised cloud of π-electrons.

*3. Being a metal, Na consists of a lattice of Na^+ immersed in a sea of mobile electron cloud.

Note: It is due to the presence of delocalised electron cloud that makes graphite and Na conductors of electricity.

---

69. Which pairs of compounds contain one that is giant ionic and one that is simple molecular?

1 Al_2O_3 and Al_2Cl_6
2 SiO_2 and $SiCl_4$
3 P_4O_{10} and PCl_3

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*1. Al_2O_3 is ionic; Al_2Cl_6 is simple molecular.

2. SiO_2 is giant covalent; $SiCl_4$ is simple molecular.

3. P_4O_{10} and PCl_3 are simple molecular.

---

70. Silicon carbide has a similar structure to diamond.

Which of the following are advantages of using a silicon carbide ceramic compared with steel?

1 Silicon carbide has a higher melting point.
2 Silicon carbide is more resistant to oxidation.
3 Silicon carbide is less likely to deform under compression.

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Having a diamond structure with strong covalent bonds between Si and C atoms, SiC has a high melting point, is resistant to corrosion and is less likely to deform under compression. Its physical properties are similar to those of diamond.

---

71. In microwave ovens, the wave energy produced is absorbed by certain polar molecules.

Which of the following would absorb microwave energy?

1 C_2H_5OH
2 NaCl
3 SiO_2

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*1. C_2H_5OH is a polar molecule as it contains a polar O–H bond.

2. NaCl is ionic and does not exist as molecules.

3. SiO_2 is giant molecular.

---

72. Which of the following statements about the properties of graphite are correct?

1 Graphite can be used as a lubricant.
2 Graphite is a good conductor of electricity in the direction parallel to the planes containing hexagonal rings of carbon but a poor conductor perpendicular to these planes.
3 Carbon-to-carbon distances between the planes of hexagonal rings are greater than carbon-to-carbon distances within those planes.

Helping Concepts *Exam Favourite Rating* ★★

*1. Weak van der Waals' forces exist between each layer of C atoms. The layers can therefore slide over one another without shattering the lattice. This makes graphite a good lubricant.

*2. Within each layer, each C atom is sp^2 hybridised and it bonds with 3 other C atoms in a trigonal planar manner, forming hexagonal rings. Each C atom is left with a lone electron and these electrons form a mobile electron cloud which contributes to the electrical conductivity in the direction parallel to the planes. Electrons are unable to move from one plane to another and hence, graphite is unable to conduct electricity perpendicular to these planes.

*3. The van der Waals' forces between each plane is weaker than the covalent bonds within each layer.

---

73. Silicon tetrachloride, $SiCl_4$, is a liquid of low boiling point.

In the presence of water, it decomposes to form silicon(IV) oxide and hydrogen chloride.

What types of bonding occur in $SiCl_4(\ell)$?

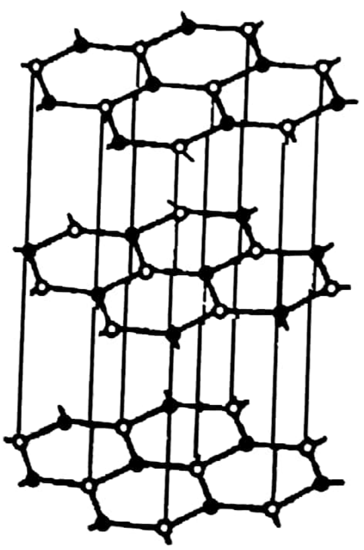
1 co-ordinate bonding
2 covalent bonding
3 van der Waals' forces

Helping Concepts *Exam Favourite Rating* ★★

There are strong Si–Cl bonds in the molecule and weak VDW forces between the molecules.

---

74. The diagram shows the structure of boron nitride which is similar to that of graphite.



Key:
• boron
o nitrogen

Which properties is this compound likely to have?

1 It is a lubricant.
2 It is transparent when pure.
3 It is very hard.

Helping Concepts *Exam Favourite Rating* ★★★

The properties of BN should be similar to that of graphite since they share similar structures. Hence, BN should be slippery, non-transparent and can be used as a lubricant.

---

75. Which of the following contain hydrogen bonds?

1 $NH_4Cl(s)$
2 $NH_3(\ell)$
3 $HNO_3(\ell)$

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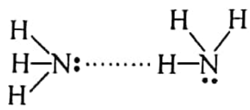
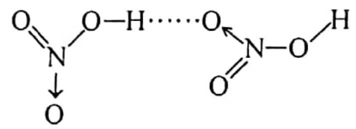
1. The N in NH_4^+ does not contain lone electron pair for hydrogen bonding.

*2.


*3.


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76. Which of the following are true statements about the structure of sodium chloride?

1 The Na^+ and Cl^- ions are both arranged in a face-centred cubic lattice.
2 The distance between the nuclei of adjacent ions is the sum of the two ionic radii.
3 Each Na^+ ion is surrounded by six Cl^- ions.

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The Na^+Cl^- lattice consists of two interlocking face-centred cubic lattices of Na^+ and Cl^-. Each Na^+ is surrounded octahedrally by six Cl^-, and vice versa. The interionic distance is given by the sum of the ionic radii of Na^+ and Cl^-.

---

77. In which sequences are the molecules quoted in order of increasing bond angle within the molecule?

Topic 3 Chemical Bonding

1 H_2O NH_3 CH_4
2 H_2O SF_6 BF_3
3 CH_4 CO_2 SF_6

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*1. All the 3 molecules have 4 region of electron clouds and hence they are directed tetrahedrally. However, there are 2 lone pair, 1 lone pair and no lone pair of electrons in H_2O, NH_3 and CH_4 respectively. As l.p.–l.p. > l.p.–b.p. > b.p.–b.p. repulsion, H_2O would have the smallest bond angle while CH_4 has the largest bond angle.

2. H_2O (~109.5°, V-shaped), SF_6 (90°, octahedral), BF_3 (120°, trigonal planar).

3. CH_4 (109.5°, tetrahedral), CO_2 (180°, linear), SF_6 (90°, tetrahedral).

2 It fumes in moist air due to the formation of hydrogen chloride.
3 In the vapour phase it has a covalent molecular structure.

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1. When $AlCl_3$ dissolves in benzene, it exists as Al_2Cl_6 molecules. The solution obtained does not conduct electricity since there is no mobile ion.

*2. $AlCl_3$ undergoes hydrolysis with the moisture in the air to give HCl fumes.

$$AlCl_3(s) + H_2O(\ell) \rightleftharpoons Al(OH)Cl_2(s) + HCl(g)$$

*3. In the vapour phase, $AlCl_3$ exists as simple Al_2Cl_6 molecules at temperatures below 183 °C. Above this temperature, the dimer begins to dissociate to give $AlCl_3$ monomeric molecules.

78. Which statements concerning the lattice structures of graphite and diamond are correct?

1 The C–C–C bond angle between nearest neighbours is smaller in diamond than in graphite.
2 The shortest carbon–carbon bond occurs in diamond.
3 All covalent bonds in diamond are of the same strength but those in graphite are not.

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*1. In diamond, each C atom is tetrahedrally bonded to 4 other C atoms. Bond angle = 109.5°. In graphite, each C atom is bonded to 3 other C atoms in a trigonal planar manner. Bond angle = 120°.

2. In diamond, each C–C is a normal σ bond. In graphite, there is a sea of delocalised electrons along each plane. There is partial double bond character in the C–C bonds. Hence, the C–C bond length is shorter in graphite.

3. The C–C bonds in graphite have the same bond length.

79. Which are correct descriptions of the properties of anhydrous aluminium chloride?

1 It dissolves in benzene to give a solution which conducts electricity.

80. The Group II metals have higher melting points than the Group I metals.

Which factors could contribute towards the higher melting points?

1 There are smaller interatomic distances in the metallic lattice of the Group II metals.
2 Two valency electrons are available from each Group II metal atom for bonding the atom into the metallic lattice.
3 Group II metals have the higher first ionisation energies.

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Metallic bonding is present in both Group I and Group II metals. The strength of the metallic bond depends on the number of electrons per atom available for delocalisation and the interatomic distance between the atoms. The more the electrons available and shorter the interatomic distance, the stronger the metallic bond.

*1. Atoms of Group II are smaller than those of Group I in the same period. Atomic size decreases across a period.

*2. Atoms of Group II metals have 2 valence electrons available for bonding whereas those of Group I have only 1.

3. This statement is correct but does not explain the phenonmenon.

81. Glucose can be regarded as a simple molecular solid of formula

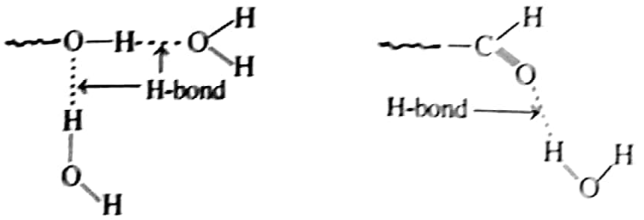
$HOCH_2CH(OH)CH(OH)CH(OH)CH(OH)CHO$.

It is readily soluble in water because water molecules form hydrogen bonds to

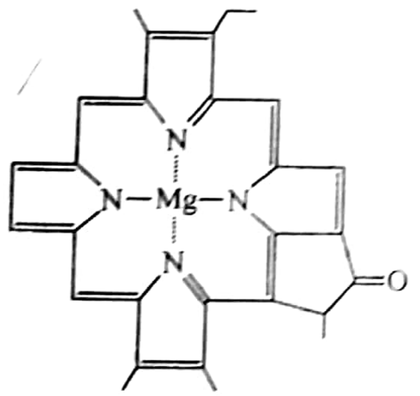
1 the carbon atoms of the glucose molecules.
2 the oxygen atom of the >C=O group of the glucose molecules.
3 the –OH groups of the glucose molecules.

Helping Concepts *Exam Favourite Rating* ★★★

Hydrogen bonds can be formed either between the O of H_2O and the H of the –OH of glucose, or between the H of H_2O and the electronegative O of glucose.



82. A simplified structure of a molecule of chlorophyll is shown.



The magnesium atom is situated in the centre of a planar arrangement of nitrogen atoms.

What does this structure suggest about the nature of the bonding around the magnesium atom?

1 dative covalency
2 σ bonding
3 sp^3 hybridisation

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*1,*2. Dative covalent bonds are formed between Mg and two of the N atoms (shown by ...... line). The other two N atoms form σ bonds with Mg atom (shown by —— line).

3. Since the structure is planar around Mg, the N atoms are sp^2 hybridised.

83. After an oil spillage at sea, a liquid hydrocarbon layer floats on the surface of the water.

Which of the following statements helps to explain why liquid hydrocarbons both float on, and are less dense than, water?

1 There are only van der Waals' interactions between hydrocarbon molecules.
2 Hydrogen bonding between the molecules in liquid water causes them to pack close together.
3 Hydrocarbon molecules are not solvated by water.

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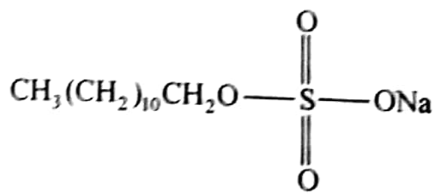
A liquid that floats on H_2O is less dense than H_2O. The converse, however, is not necessarily true. A liquid that is less dense than H_2O may not necessarily float on H_2O. Instead, it may mix with H_2O.

*1. The van der Waals' interactions are different from the H-bonding in H_2O. Therefore, the 2 liquid do not mix. Furthermore, VDW forces are weak and therefore, the hydrocarbon molecules are further apart. It has a *lower density*.

*2. The statement implies that H_2O is more dense. Since the 2 types of interactions are different, the 2 liquids do not mix.

*3. The statement explains why the 2 liquids do not mix.

84. Long-chain alkanes are converted on an industrial scale into alkylsufates for use as detergents, e.g. sodium lauryl sulfate.



sodium lauryl sulfate

What deductions about the properties of this substances can be made from this structure?

1 Part of the structure is polar and is water-attracting.
2 The alkyl chain is soluble in oil droplets.
3 All the C–C–C bond angles are tetrahedral.

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*1. The $R-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-$ end is polar.

*2. The alkyl chain is hydrophobic and hence is soluble in oil droplets.

*3. The C–C–C bond angles are tetrahedral since it is saturated (i.e. no C=C double bonds or C≡C triple bonds).

---

85. Carbon forms double bonds with each of the Group VI elements oxygen, sulfur and selenium. In each case, the double bond is polar.

In the molecules carbon dioxide (CO_2), carbonyl sulfide (COS) and carbonyl selenide (COSe), the polarities of these double bonds do not necessarily cancel.

	overall polarity of molecule
CO_2	0
COS	0.71
COSe	0.73

Which factors could account for these observations?

1 The C=S bond is more polar than the C=Se bond.
2 The C=O bond is more polar than the C=S bond.
3 The C=Se bond is more polar than the C=O bond.

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The Group VI elements are generally more electronegative than Group IV elements.

The order of polarity of the double bonds is C=O > C=S > C=Se since the order of electronegativity is O > S > Se.

---

86. Which of the following properties of a aluminium chloride are related to the lack of an octet of electrons in the aluminium atom in this compound?

1 its tendency to dimerise
2 its covalent character
3 its acidity in aqueous solution

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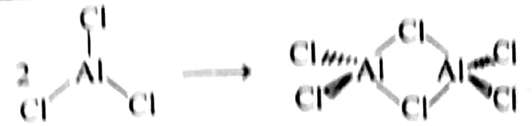
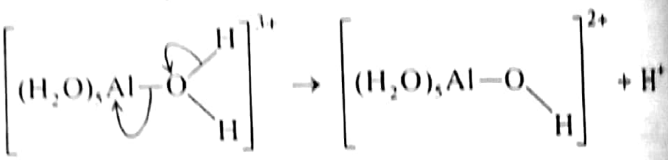
*1. 

$AlCl_3$ dimerises readily to give Al_2Cl_6 so that Al, which has a sextet configuration, gains stability by acquiring an octet configuration.

2,3. Its covalent character and acidity in aqueous solution are due to its high polarising power, i.e. high charge (+3) and small size. The ionic bond, if formed, is greatly polarised and covalency results. Its acidity is due to the successive elimination of protons from the H_2O ligands.



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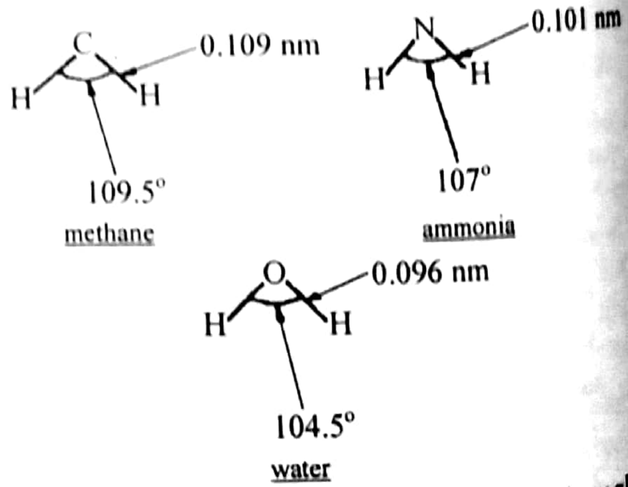
87. The bond lengths and bond angles in the molecules of methane, ammonia and water may be represented as follows.



What causes this trend in the bond angles shown?

1 increasing repulsion between hydrogen atoms as the bond length decreases
2 the number of non-bonding electron pairs in the molecule
3 a non-bonding electron pair having a greater repulsive force than a bonding electron pair

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1. If it were true, then one would expect an increase in bond angle instead.

*2,*3. According to VSEPR, the repulsion between electron pairs decreases in the order:

lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

H_2O with the greatest number of lone electron pairs have the smallest bond angle.

TOPIC 4

The Gaseous State

Key content that you will be examined on:

1. Ideal gas behaviour and deviations from it
2. $pV = nRT$ and its use in determining a value for M_r.

The Gaseous State

Topic 4

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. When compared at the same pressure and temperature, which one of the following properties has the same value for H_2, and for D_2? [$D = {}^2_1H$]

   A density

   B average molecular speed

   C relative molecular mass

   D average molecular kinetic energy

Helping Concepts *Exam Favourite Rating* ★★★

Average molecular kinetic energy is only dependent on the temperature.

$$K.E. = \frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT$$

---

2. Which of the following elements in its crystalline form will have the lowest enthalpy change of vaporisation?

   A argon **B** chlorine

   C phosphorus **D** silicon

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The lowest enthalpy change of vaporisation is given by one with the weakest intermolecular forces, in this case, van der Waals' forces. This, in turn, depends on the number of electrons per molecule (or molecular size) of the species ($Ar < Cl_2 < P_4 < S_8$; Si is macromolecular).

---

3. Which statement applies to both ideal and real gases?

   A Collisions between molecules are elastic.

   B Molecules are in constant random motion.

   C Molecules attract each other.

   D Molecules have zero size.

Helping Concepts *Exam Favourite Rating* ★★★

The differences between an ideal gas and a real gas are such that in an ideal gas,

A: collisions are elastic without loss of energy.

C: there are no inter-particle attraction.

D: the gas particles have zero volume.

---

4. A given mass of ideal gas occupies a volume V and exerts a pressure p at 27 °C.

   At which temperature will the same mass of the ideal gas occupy the same volume V and exert a pressure $2p$?

   A 54 °C **B** 54 K

   C 600 °C **D** 600 K

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$p \propto T$ $\quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$ $\quad \boxed{600\ K}$

Using $\frac{p_1}{T_1} = \frac{p_2}{T_2}$,

$$\frac{p}{273+27} = \frac{2p}{T_2} \qquad \frac{P}{300} = \frac{2P}{T}$$

$$T_2 = 600\ \text{K}$$

---

5. When granulated zinc reacts with dilute sulfuric acid, hydrogen gas is given off.

   How does the volume of the hydrogen evolved, when a sample of zinc reacts with an excess of acid, depend on temperature and pressure?

   A It increases with increase in temperature and is independent of pressure.

   B It increases with decrease in temperature and is independent of pressure.

   C It increases with increase in temperature and increases with increase in pressure.

D It increases with increase in temperature and decreases with increase in pressure.

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Using $pV = nRT$, it can be easily seen that V increases as T increases; while V decreases as p increases.

---

6. Under what conditions of temperature and pressure will a real gas behave most like an ideal gas?

	temperature	pressure
A	low	low
B	low	high
C	standard	standard
D	high	low

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At a high temperature, the gas particles are moving at very high speeds. The interactions between gas particles become negligible.

At a low pressure, the gas particles are, on the average, very far apart. The interactions between gas particles become negligible. Furthermore, the volume of the gas particles compared to the volume of the container also becomes negligible.

---

7. Which gas is likely to deviate most from ideal gas behaviour?

A HCl B He

C CH_4 D N_2

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There is no intermolecular forces of attraction between molecules of a ideal gas. The intermolecular forces between HCl molecules are permanent dipole-permanent dipole interactions and they are stronger than the van der Waals' forces in (B), (C) and (D). Hence, HCl deviates most from ideal gas behaviour.

---

8. Measured values of the pressure, volume and temperature of a known mass of a gaseous compound are to be substituted into the equation

$$pV = nRT$$

in order to calculate the relative molecular mass, M_r, of the compound.

Which conditions of pressure and temperature would give the most accurate value of M_r?

	pressure	temperature
A	high	high
B	high	low
C	low	high
D	low	low

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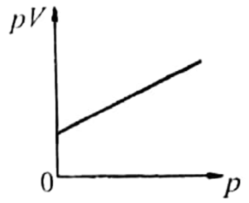
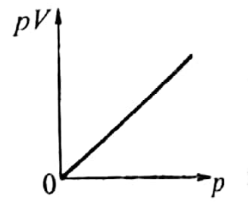
This is an ideal gas equation. To find the most accurate value of M_r, measurements should be taken at conditions that approach ideal behaviour, i.e. high temperature and low pressure.

---

9. Which curve shows the correct graph of pV against p for a fixed mass of an ideal gas at constant temperature?

A


B


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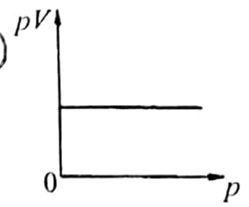
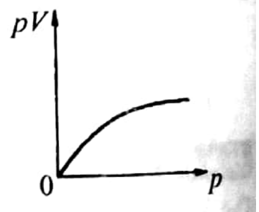


D


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Using ideal gas equation, $pV = nRT$, for a fixed mass of gas (n = constant) at constant temperature, pV = constant.

Therefore, no matter how p varies, pV remains constant. In fact as p increases, V decreases in such a way that pV remains constant.

---

10. *Use of the Data Booklet is relevant to this question.*

Which expression gives the pressure exerted by 1.6×10^{-3} mol of N_2 in a container of volume $3.0\ dm^3$ at 273 °C?

273
273
546K

$1.6 \times 10^{-3} \times 273 \times 2$

44.4/3

A $\dfrac{1.6\times10^{-3}\times8.31\times273}{3.0\times10^{-6}}$ Pa

B $\dfrac{1.6\times10^{-3}\times8.31\times(273+273)}{3.0\times10^{-6}}$ Pa

C $\dfrac{1.6\times10^{-3}\times8.31\times273}{3.0\times10^{-3}}$ Pa

D $\dfrac{1.6\times10^{-3}\times8.31\times(273+273)}{3.0\times10^{-3}}$ Pa

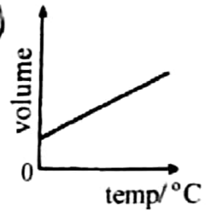
Helping Concepts *Exam Favourite Rating* ★★★

$pV = nRT$

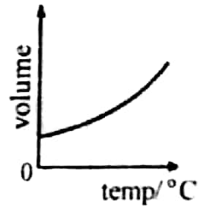
$$p=\frac{nRT}{V}$$

$$=\frac{(1.6\times10^{-3}\ \text{mol})\times8.31\ \text{J K}^{-1}\text{mol}^{-1}\times(273+273)\ \text{K}}{(3.0\times10^{-3})\ \text{m}^3}$$

C



D



Helping Concepts *Exam Favourite Rating* ★★★

For an ideal gas,

$$pV = nRT$$
$$= nR(273+t)$$

where t is the temperature in °C.

At a constant pressure, p is a constant and so are n and R.

Hence, $V \propto (273+t)$ so that a plot of V against t is a straight line that does not pass through the origin.

---

11. Which of the following exerts the highest pressure?

A 1 mol of N_2 at 0 °C in 11.2 dm^3

B 1 mol of N_2 at 27 °C in 22.4 dm^3

C 1 mol of H_2O at 27 °C in 1 dm^3

D 1 mol of C_4H_{10} at its normal boiling point

Helping Concepts *Exam Favourite Rating* ★★★

Ideal gas equation, $pV = nRT$.

A: $p=\dfrac{1\times8.31\times273}{11.2/1000}=2.02\times10^5$ Pa

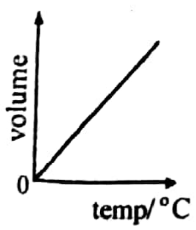
B: $p=\dfrac{1\times8.31\times(273+27)}{22.4/1000}=1.11\times10^5$ Pa

C,D: Both are liquids at the given conditions. Also for (D), the saturated vapour pressure at its normal boiling point is 1.01×10^5 Pa, i.e. 1 atm.

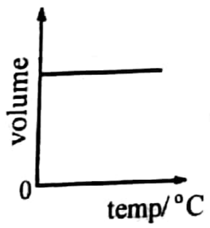
---

12. Which graph is correct for a given mass of an ideal gas at constant pressure?

A



B



13. The density of ice is 1.00 g cm^{-3}.

What is the volume of steam produced when 1 cm^3 of ice is heated to 323 °C (596 K) at a pressure of one atmosphere (101 kPa)?

[1 mole of a gas occupies 24.0 dm^3 at 25 °C (298 K) and one atmosphere.]

A 0.267 dm^3 B 1.33 dm^3

C 2.67 dm^3 D 48.0 dm^3

Helping Concepts *Exam Favourite Rating* ★★★

Mass of 1 cm^3 of H_2O = 1 g

Amount of $H_2O = \dfrac{1\ \text{g}}{18\ \text{g mol}^{-1}} = \dfrac{1}{18}$ mol

Volume of steam at 298 K $= (\frac{1}{18}\ \text{mol})(24\ \text{dm}^3\ \text{mol}^{-1})$
$= 1.33\ \text{dm}^3$

Volume of steam at 323 K $= 1.33\times\frac{596}{298}$
$= 2.67\ \text{dm}^3$

---

14. A small spacecraft of capacity 10 m^3 is connected to another of capacity 30 m^3. Before connection, the pressure inside the smaller craft is 50 kPa and that inside the larger is 100 kPa.

If all measurements are made at the same temperature, what is the pressure in the combined arrangement after connection?

A 75 kPa
B 87.5 kPa
C 100 kPa
D 125 kPa

Helping Concepts *Exam Favourite Rating* ★★

$n_1 = \frac{p_1V_1}{RT}$ where $p_1 = 50$ kPa, $V_1 = 10$ m^3.

$n_2 = \frac{p_2V_2}{RT}$ where $p_2 = 100$ kPa, $V_2 = 30$ m^3.

$$\frac{p_T V_T}{RT} = n_T = n_1 + n_2 = \frac{1}{RT}(p_1V_1 + p_2V_2)$$

$$\Rightarrow p_T V_T = p_1V_1 + p_2V_2 \quad (\text{but } V_T = V_1 + V_2)$$

$$\Rightarrow p_T = \frac{p_1V_1 + p_2V_2}{V_1 + V_2}$$

$$= \frac{(50\times10^3)\times10 + (100\times10^3)\times30}{10+30}$$

$$= 87.5\times10^3 \text{ Pa (or 87.5 kPa)}$$

15. A sample of m g of an organic compound is vaporised in a gas syringe and occupies V cm^3 at T K and p atm.

What is the relative molecular mass of the compound, M_r?

A $M_r = \frac{m\times22400\times T}{p\times V\times273}$

B $M_r = \frac{m\times22400\times(T+273)}{p\times V\times273}$

C $M_r = \frac{m\times22400\times273\times p}{V\times T}$

D $M_r = \frac{m\times22400\times273\times p}{V\times(T+273)}$

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For an ideal gas, $pV = nRT$

$$pV = \frac{m}{M_r}RT$$

$$M_r = \frac{mRT}{pV}$$

where p in Pa and V in m^3.

$$\therefore M_r = \frac{mRT}{(p\times10^5)(V\times10^{-6})} = \frac{10(mRT)}{pV}$$

For $n = 1$,

$$(10^5)(22.4\times10^{-3}) = R\times273$$

$$R = \frac{2240}{273}$$

$$\therefore M_r = \frac{m\times22400\times T}{p\times V\times273}$$

16. In a syringe experiment, 0.10 g of a gas is found to occupy 83.1 cm^3, measured at standard pressure (1.0×10^5 Pa) and 27 °C.

What is the relative molecular mass of the gas?

A $\frac{0.10\times8.31\times27}{1.0\times10^5\times83.1}$

B $\frac{0.10\times8.31\times300}{1.0\times10^5\times83.1}$

C $\frac{0.10\times8.31\times27}{1.0\times10^5\times83.1\times10^{-6}}$

D $\frac{0.10\times8.31\times300}{1.0\times10^5\times83.1\times10^{-6}}$

Helping Concepts *Exam Favourite Rating* ★★★

$$pV = nRT$$

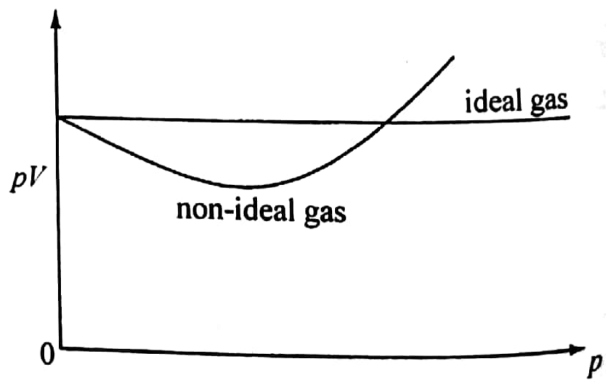
For 0.10 g of the gas,

$$n = \frac{0.10}{M_r}$$

$$M_r = \frac{0.10}{n} = \frac{0.10\times R\times T}{pV} = \frac{0.10\times8.31\times300}{1.0\times10^5\times83.1\times10^{-6}}$$

where $p = 1.0\times10^5$ Pa;
$V = 83.1$ cm^3 $= 83.1\times10^{-6}$ m^3;
$T = 27$ °C $= 300$ K.

17. The value of pV is plotted against p for two gases, an ideal gas and a non-ideal gas, where p is the pressure and V is the volume of the gas.



Which gas shows the greatest deviation from ideality?

A ammonia
B ethene
C methane
D nitrogen

Helping Concepts *Exam Favourite Rating* ★★

An ideal gas assumes no intermolecular interaction among the gas particles. Hence, NH_3, which has the strongest intermolecular H-bonding, shows the greatest deviation. The other 3 gases have weaker VDW forces.

---

18. A 2 g sample of hydrogen at temperature T and of volume V exerts a pressure p. Deuterium, ^2_1H, is an isotope of hydrogen.

    Which of the following would also exert a pressure p at the same temperature T?

    A 2 g of deuterium of volume V

    B 4 g of deuterium of volume $\frac{V}{2}$

    C a mixture of 1 g of hydrogen and 2 g of deuterium of total volume V

    D a mixture of 2 g of hydrogen and 1 g of deuterium of total volume $2V$

Helping Concepts *Exam Favourite Rating* ★★★

$$2\text{ g of } H_2 \equiv 1 \text{ mol of } H_2$$

In C,

$$1\text{ g of } H_2 \equiv \tfrac{1}{2} \text{ mol of } H_2$$
$$2\text{ g of } D_2 \equiv \tfrac{1}{2} \text{ mol of } D_2$$

A total of 1 mole of gas exert the same pressure of p given the same volume V and temperature T.

A: $\frac{1}{2}p$

B: $2p$

D: $\frac{5}{8}p$

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

19. What assumptions are made in the kinetic theory about an ideal gas?

1. There are no forces of attraction between molecules.
2. The molecules are in a state of continual, random motion.
3. The size of the molecules is negligible.

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All the three are assumptions made in the kinetic theory about an ideal gas.

20. Which of the following equations apply to an ideal gas?

(p = pressure, V = volume, m = mass, M = molar mass, ρ = density, c = concentration, R = gas constant, T = temperature)

1. $p = \dfrac{\rho RT}{M}$
2. $pV = MRT$
3. $pV = \dfrac{cRT}{M}$

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$$pV = nRT$$

*1. $pV = \dfrac{m}{M}RT \Rightarrow p = \dfrac{m}{V}\cdot\dfrac{RT}{M} = \dfrac{\rho RT}{M}$

2. $pV = \dfrac{m}{M}RT$ (not MRT!)

3. For a gas,

$$\rho = c\ (\text{g m}^{-3})$$

$$\therefore p = \frac{cRT}{M} \quad \left(\text{not } pV = \frac{cRT}{M}!\right)$$

21. Reasons why a real gas deviates from ideal behaviour include that the molecules in a real gas

1. have different speeds.
2. have a definite size.
3. are subject to intermolecular forces.

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Two of the assumptions made in the kinetic theory of an ideal gas include

1. gas particles have negligible sizes; and
2. gas particles move independently for one another.

Deviation of a real gas from ideality implies that the assumptions are not valid.

For any gas, real or ideal, the gas particles do not move at a uniform speed. There is always a spread of molecular speed as seen in the Boltzmann distribution.

22. Which statements correctly represent the behaviour of an ideal gas?

(p = pressure, V_m = molar gas volume, M = molar mass, c = concentration, d = density and T = temperature)

1. $pV_m \propto T$
2. $pM \propto dT$
3. $p \propto cT$

Helping Concepts *Exam Favourite Rating* ★★

*1. $pV = nRT \Rightarrow p\dfrac{V}{n} = RT \Rightarrow pV_m = RT$
$\Rightarrow pV_m \propto T$

*2. $pV = nRT \Rightarrow pV = \dfrac{m}{M}RT \Rightarrow pM = \dfrac{m}{V}RT$
$\Rightarrow pM = dRT \Rightarrow pM \propto dT$

*3. $pV = nRT \Rightarrow p = \dfrac{n}{V}RT \Rightarrow p = cRT$
$\Rightarrow p \propto cT$

23. The Gas laws can be summarised in the ideal gas equation

$$pV = nRT$$

where each symbol has its usual meaning.

Which of the following statements are correct?

1 One mole of any ideal gas occupies the same volume under the same conditions of temperature and pressure.

2 The density of an ideal gas at constant pressure is inversely proportional to the temperature.

3 The volume of a given mass of an ideal gas is doubled if its temperature is raised from 25 °C to 50 °C at constant pressure.

Helping Concepts *Exam Favourite Rating* ★★★

*1. The ideal gas equation is valid for any (ideal) gas. Hence, for any ideal gas, if $n = 1$ mole and T and p are constant, V would also be constant.

*2. $pV = nRT = \frac{m}{M}RT$

$$d = \frac{m}{V} = \frac{pM}{RT} \Rightarrow d \propto \frac{1}{T} \text{ (if } p = \text{constant)}$$

3. The unit for T is K. From 25 °C to 50 °C, the change in T is **not** doubled (298 K to 323 K). Hence, the volume is **not** doubled.

---

24. **P** and **Q** are ideal gases that do not react together. The mass of 1 mol of **P** is four times that of **Q**. It follows from kinetic theory that, at standard temperature and pressure,

1 the average kinetic energy of a molecule of **P** is equal to that of a molecule of **Q**.

2 the mass of 1 dm^3 of **P** is four times that of 1 dm^3 of **Q**.

3 on mixing 1 dm^3 of **P** with 1 dm^3 of **Q**, the partial pressure of each gas in the mixture will be 50 kPa (0.5 atm).

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*1. Average kinetic energy is dependent on temperature only.

$$\text{Average K.E.} = \frac{3}{2}kT$$

where k = Boltzmann constant.

*2. Under identical conditions (constant T and p), different gases with the same volume have the same amount of gas molecules ($pV = nRT \Rightarrow V \propto n$).

*3. A total volume of 2 dm^3 is obtained on mixing 1 dm^3 of each gas so that a standard pressure of 1 atm is maintained. Hence, the partial pressure of each gas is 0.5 atm.

---

25. When a sample of a gas is compressed at constant temperature from 15 atm to 60 atm, its volume changes from 76.0 cm^3 to 20.5 cm^3. Which of the following statements are possible explanations of this behaviour?

1 The gas behaves non-ideally.

2 The gas dimerises.

3 Gas is adsorbed onto the vessel walls.

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For an ideal gas at constant temperature,

$$\frac{pV}{n} = \text{constant.}$$

*1. When the pressure changes from 15 to 60 atm, the new volume should be $\frac{15 \times 76.0}{60} = 19.0 \text{ cm}^3$. The difference in value could be due to the non-ideal behaviour of the gas, so much so that the equation $pV = nRT$ becomes only an approximation.

2. Using $\frac{p_1V_1}{n_1} = \frac{p_2V_2}{n_2}$,

$$n_2 = \frac{p_2V_2}{p_1V_1} \times n_1 = \frac{60 \times 20.5}{15 \times 76.0} \times n_1 = 1.08n_1$$

In the final stage, there should be an increase in the number of gas molecules. Dimerisation gives rise to a decrease in the number of gas molecules.

3. Gas adsorbing onto the vessel walls reduces the number of gas molecules.

---

26. Consider one mole of ideal gas at a given pressure.

Which processes will increase the number of molecules which have an energy greater than a particular value?

1 increasing the temperature

2 introducing more of the same gas into the same volume at the same temperature

3 compressing the gas at constant temperature

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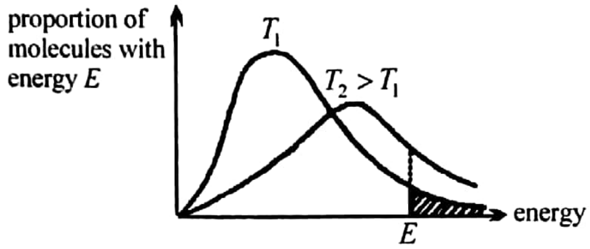
*1. Increasing temperature increases the average kinetic energy of the molecules. There will be an increase in the number of molecules which have an energy greater than a particular value.

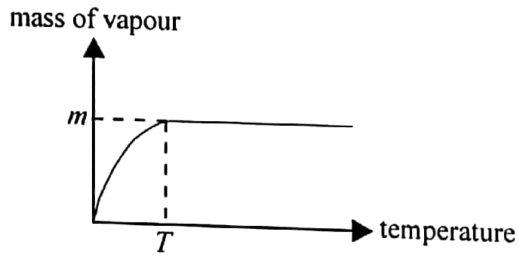


*2. Introducing more of the same gas into the same volume at the same temperature basically increases the total number of molecules with the same energy distribution. However, it should be noted that the **fraction** of molecules with a particular energy remains the same.

3. Compressing the gas at **constant temperature** has no effect on the energy distribution of the gas molecules.

---

27. A quantity of solid Y was placed in a previously evacuated vessel and the apparatus was then held at a series of different temperatures. At each temperature, the mass of Y in the vapour state was calculated from pressure measurements. The results are shown below.



What can be deduced from the diagram?

1 The mass of Y used in the experiment was m.

2 The pressure of the vapour was constant for all temperatures above temperature T.

3 Liquid appeared at temperature T.

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*1. At temperature T and above, all the solid Y has vaporised. This gives a constant mass of Y at temperature $\geq T$. Hence, the mass registered is the mass of Y used.

2. As T increases, p also increases.

3. At T, all the Y exists as vapour.

TOPIC 5

Chemical Energetics

Key content that you will be examined on:

1. Enthalpy changes: ΔH, of formation; combustion; hydration; solution; neutralisation; atomisation; bond energy; lattice energy; electron affinity
2. Hess' law, including Born-Haber cycles
3. Entropy and Free Energy

Chemical Energetics

Topic 5

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which class of reaction always has an endothermic enthalpy change?

A atomisation B combustion

C formation D solution

Helping Concepts *Exam Favourite Rating* ★★

Atomisation involves the breaking of the attractive forces between the particles to form gaseous atoms without any bond formation. Hence, it is always an endothermic process.

2. Which equation represents the change corresponding to the enthalpy change of atomisation of iodine?

A $\frac{1}{2}I_2(s) \rightarrow I(g)$

B $I_2(s) \rightarrow 2I(g)$

C $I_2(\ell) \rightarrow 2I(g)$

D $I_2(g) \rightarrow 2I(g)$

Helping Concepts *Exam Favourite Rating* ★★★

The enthalpy change of atomisation of iodine is the formation of 1 mole of gaseous iodine atoms from the element at standard state, i.e. $I_2(s)$.

3. Which one of the following equations does the enthalpy change represent the lattice energy of sodium chloride?

A $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$

B $Na(g) + Cl(g) \rightarrow NaCl(s)$

C $Na^+(g) + Cl^-(g) \rightarrow NaCl(g)$

D $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

Helping Concepts *Exam Favourite Rating* ★★★

Lattice energy is the energy given out when gaseous ions combine to form 1 mole of solid ionic crystal lattice.

4. Which of the following processes is endothermic?

EXO

A the condensation of steam

B the electrolysis of water

C the freezing of water EXO

D $Ca(s) + 2H_2O(\ell) \rightarrow Ca(OH)_2(aq) + H_2(g)$

Helping Concepts *Exam Favourite Rating* ★★★

$$2H_2O(\ell) \rightarrow 2H_2(g) + O_2(g)$$

In the electrolysis of water, energy is supplied in the form of electricity.

5. Which one of the following is involved in determining the enthalpy change in a chemical reaction?

A the number of stages involved in the chemical reaction

B the activation energy of the reaction

C the initial and final states of the reacting system

D the intermediates in the overall chemical reaction

Helping Concepts *Exam Favourite Rating* ★

If the initial and final states of the reacting system are defined, the enthalpy change of the chemical reaction is not affected by the path taken - Hess' law.

6. Which one of the following equations correctly defines the enthalpy change of formation of carbon monoxide?

A $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

B $C(s) + O(g) \rightarrow CO(g)$

C $C(s) + CO_2(g) \rightarrow 2CO(g)$

D $C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

Helping Concepts *Exam Favourite Rating* ★★★

The enthalpy change of formation of CO is the enthalpy change when 1 mole of gaseous CO is formed from its constituent elements, i.e. C and O_2, at their standard states.

---

7. Which of the following is the lattice energy likely to have the greatest numerical value (i.e. the greatest magnitude, disregarding sign)?

A lithium fluoride

B lithium iodide

C rubidium chloride

D sodium chloride

Helping Concepts *Exam Favourite Rating* ★★

The most exothermic lattice energy is given by one with the highest ionic charges and smallest ionic sizes.

$$|\text{L.E.}| \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$$

$$r_{Li^+} < r_{Na^+} < r_{Rb^+}$$

$$r_{F^-} < r_{Cl^-} < r_{I^-}$$

---

8. Which value would be required to estimate the lattice energy for the hypothetical ionic compound MgH?

A the electron affinity of hydrogen

B the first ionisation energy of hydrogen

C the magnesium-hydrogen bond energy

D the standard enthalpy change of formation of MgH_2

Helping Concepts *Exam Favourite Rating* ★★

MgH exists as Mg^+H^-. Hence, the first electron affinity of H is required for calculation.

$H(g) + e^- \rightarrow H^-(g) \quad \Delta H = 1\text{st electron affinity}$

---

9. The lattice energies (enthalpies) of rubidium fluoride (RbF) and caesium chloride (CsCl) are –760 kJ mol^{-1} and –650 kJ mol^{-1} respectively. What is the lattice energy of caesium fluoride (CsF) likely to be? (Atomic numbers: Rb, 37; Cs, 55)

A –620 kJ mol^{-1}

B –720 kJ mol^{-1}

C –800 kJ mol^{-1}

D –900 kJ mol^{-1}

RbF = –760
CsCl = –650
CsF = x

Helping Concepts *Exam Favourite Rating* ★★

$$|\text{L.E.}| \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$$

For ions with similar charges (Cs^+, Rb^+; Cl^-, F^-), L.E. depends only on the ionic sizes. Since $r_{Rb^+} < r_{Cs^+}$ and $r_{F^-} < r_{Cl^-}$, the interionic distance in CsF is between that of RbF and CsCl. Therefore, its L.E. should be intermediate.

---

10. Which of the following reactions can the bond energy of the C–F bond be determined by using only the standard enthalpy change of the reaction?

A $CF_4(g) \rightarrow C(g) + 4F(g)$

B $CF_4(g) \rightarrow CF_2(g) + F_2(g)$

C $CF_4(s) \rightarrow CF_4(g)$

D $2F_2(g) + C(s) \rightarrow CF_4(g)$

Helping Concepts *Exam Favourite Rating* ★★

The standard enthalpy change of the reaction in option A is the energy absorbed to break 4 moles of C–F bonds in 1 mole of CF_4 molecules to obtain 1 mole of C atoms and 4 moles of F atoms. Hence, the bond energy of C–F bond (kJ/mol) will be given by the standard enthalpy change for the reaction divided by 4.

---

11. The heat liberated in the neutralisation given below is –114 kJ.

$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(\ell)$

By using this information, what is the most likely value for the heat liberated in the following neutralisation?

$Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$

A −57 kJ   B −76 kJ

C −114 kJ   D −171 kJ

Helping Concepts *Exam Favourite Rating* ★★

The quoted value of −114 kJ corresponds to the formation of 2 moles of H_2O. Hence, the enthalpy change for the second neutralisation is also −114 kJ since the equation also shows the formation of 2 moles of H_2O in the neutralisation.

---

12. The value of the enthalpy change for the process represented by the equation

$$Na(s) \rightarrow Na^+(g) + e^-$$

is equal to

A the first ionisation energy of sodium.

B the enthalpy change of vaporisation of sodium.

C the sum of the first ionisation energy and the electron affinity of sodium.

D the sum of the enthalpy change of atomisation and the first ionisation energy of sodium.

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$Na(s) \rightarrow Na(g)$ $\Delta H_{atomisation}$

$Na(g) \rightarrow Na^+(g) + e^-$ $\Delta H_{1st\ I.E.}$

---

13. Why does the exothermic reaction

C (diamond) $\rightarrow$ C (graphite) $\Delta H = -3$ kJ mol^{-1}

not occur spontaneously?

A A tetrahedral configuration is always more stable than a planar one.

B Diamond has only strong covalent bonds whereas graphite has both covalent bonds and van der Waals' forces.

C Graphite has delocalised electrons.

D The change from diamond to graphite has a high activation energy.

Helping Concepts *Exam Favourite Rating* ★★★

Although ΔH is negative and the reaction is thermodynamically favourable, it is kinetically not feasible, i.e. the activation energy is very high and the reaction is very slow. A lot of energy is required to break the C–C covalent bonds and restructure the lattice (from tetrahedra to layered structure).

---

14. When water freezes, 6.0 kJ mol^{-1} of heat enthalpy is evolved.

What is the entropy change when 54 g of water freezes at 0 °C?

A −66 J K^{-1} B −22 J K^{-1}

C 22 J K^{-1} D 66 J K^{-1}

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During freezing (at equilibrium),

$$\Delta G^o = 0 \text{ kJ mol}^{-1}$$

$\Delta G^o = \Delta H^o - T\Delta S^o$

$0 = (-6.0\times10^3 \text{ J mol}^{-1}) - 273\Delta S^o$

$\Delta S^o = -22 \text{ J K}^{-1}\text{ mol}^{-1}$

$n_{H_2O} = \frac{54}{18} = 3$ mol

$\therefore$ For 54 g of water,

$$\Delta S^o = -3\times 22 = -66 \text{ J K}^{-1}$$

---

15. Which statement about the standard enthalpy change of formation of carbon dioxide is correct?

A It is equal to the standard enthalpy change of combustion of carbon.

B It is equal to twice the bond energy of the C=O bond.

C It is the energy released when one mole of carbon dioxide is formed from carbon at the temperature of combustion of the carbon.

D It is the same for carbon dioxide produced from graphite and from diamond.

Helping Concepts *Exam Favourite Rating* ★★★

The chemical equation for standard enthalpy change of formation of CO_2 is given below.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

This is also the equation for the standard enthalpy change of combustion of C.

---

16. Which of the following ions is the enthalpy change of hydration likely to be the most exothermic?

	ionic radius/nm	charge on ion
A	0.065	+2
B	0.095	+1
C	0.135	+2
D	0.169	+1

Helping Concepts *Exam Favourite Rating* ★★★

The most exothermic enthalpy change of hydration is given by one which has the highest charge density, i.e. the highest charge (positive or negative) and the smallest ionic size.

$$\left|\Delta H_{\text{hydration}}\right| \propto \left|\frac{q}{r}\right|$$

---

17. Which statement helps to explain why calcium and chlorine form $CaCl_2$ rather than CaCl?

A Less energy is required to remove one electron from the calcium atom than to remove two electrons.

B More energy is released in forming chloride ions from chlorine molecules in the formation of $CaCl_2(s)$ than in the formation of CaCl(s).

C The lattice energy of CaCl(s) is less exothermic than that of $CaCl_2(s)$.

D When CaCl(s) is formed from its elements, more energy is released than when $CaCl_2(s)$ is formed from its elements.

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In the Born-Haber cycle, one of the steps involves the lattice energy. For CaCl, Ca exists in Ca^+ and it has a smaller charge and bigger size than Ca^{2+} in $CaCl_2$.

$$\left|\text{L.E.}\right| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

From the relationship, it can be easily seen that the lattice energy for CaCl would be less exothermic. This makes the formation of CaCl(s) less favourable.

---

18. The radius and charge of each of six ions are shown in the table.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius/nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids *JX*, *LY* and *MZ* are of the same lattice type.

What is the correct order of their lattice energies placing the one with the highest numerical value first?

A $JX > LY > MZ$

B $JX > MZ > LY$

C $LY > MZ > JX$

D $MZ > JX > LY$

Helping Concepts *Exam Favourite Rating* ★★

The highest lattice energy is given by one with the highest ionic charges and smallest ionic sizes.

$$\left|\text{L.E.}\right| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

---

19. Iodine trichloride, ICl_3, is made by reacting iodine with chlorine.

$I_2(s) + Cl_2(g) \rightarrow 2ICl(s) \quad \Delta H^\circ = +14\text{ kJ mol}^{-1}$

$ICl(s) + Cl_2(g) \rightarrow ICl_3(s) \quad \Delta H^\circ = -88\text{ kJ mol}^{-1}$

By using the data above, what is the enthalpy change of the formation for solid iodine trichloride?

ICl_3 -14KJ/mol

A -60 kJ mol^{-1}

B -74 kJ mol^{-1}

C -81 kJ mol^{-1}

D -162 kJ mol^{-1}

$2ICl \rightarrow I_2 + Cl_2 + 14\text{KJ}$

$\cancel{ICl} + Cl_2 \rightarrow ICl_3$

Helping Concepts *Exam Favourite Rating* ★★★

Consider $ICl(s) + Cl_2(g) \rightarrow ICl_3(s) \quad \Delta H_r^\circ$.

Then $\Delta H_r^\circ = \Delta H_f^\circ(ICl_3) - \Delta H_f^\circ(ICl)$

$-88 = \Delta H_f^\circ(ICl_3) - \frac{1}{2}(+14)$

$\Delta H_f^\circ(ICl_3) = -81\text{ kJ mol}^{-1}$

---

20. The standard enthalpy changes of formation of iron(II) oxide, FeO(s), and aluminium oxide, $Al_2O_3(s)$, are -266 kJ mol^{-1} and -1676 kJ mol^{-1} respectively.

What is the enthalpy change under standard conditions for the following reaction?

$$3FeO(s) + 2Al(s) \rightarrow 3Fe(s) + Al_2O_3(s)$$

A $+878$ kJ mol^{-1}

B -878 kJ mol^{-1}

C -1942 kJ mol^{-1}

D -2474 kJ mol^{-1}

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$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$
$$= \Delta H_f^\circ(Al_2O_3) - 3\Delta H_f^\circ(FeO)$$
$$= -1676 - 3(-266)$$
$$= -878 \text{ kJ mol}^{-1}$$

---

21. When steam condenses, 44 kJ mol^{-1} of heat enthalpy is evolved.

What is the entropy change when 54 g of steam condenses at 100 °C?

A -354 J K^{-1} mol^{-1}

B -118 J K^{-1} mol^{-1}

C 118 J K^{-1} mol^{-1}

D 354 J K^{-1} mol^{-1}

Helping Concepts *Exam Favourite Rating* ★★

When steam condenses at equilibrium, $\Delta G^\circ = 0$.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$0 = -44 \text{ kJ mol}^{-1} - (273+100)\Delta S^\circ$$
$$\Delta S^\circ = -0.118 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$n_{H_2O} = \frac{54}{18} = 3 \text{ mol}$$

$\therefore$ Entropy change $= -3 \times 0.118$
$$= -0.354 \text{ kJ K}^{-1} \text{ mol}^{-1}$$
$$= -354 \text{ J K}^{-1} \text{ mol}^{-1}$$

---

22. The enthalpy changes for two reactions are given by the equations below.

$$2Fe(s) + 1\tfrac{1}{2}O_2(g) \rightarrow Fe_2O_3(s) \quad \Delta H^\circ = -822 \text{ kJ mol}^{-1}$$
$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H^\circ = -110 \text{ kJ mol}^{-1}$$

What is the enthalpy change for the following reaction?

$$3C(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + 3CO(g)$$

$Fe_2O_3 \longrightarrow 2Fe + 1\frac{1}{2}O_2$

A $+712$ kJ mol^{-1}

B $+492$ kJ mol^{-1}

C -492 kJ mol^{-1}

D -712 kJ mol^{-1}

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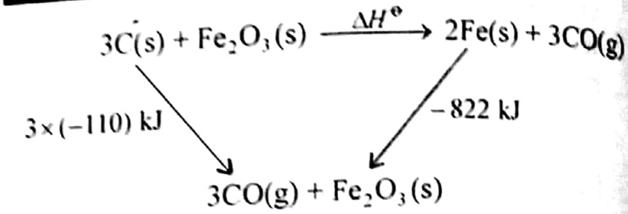

$$\Delta H^\circ = 3 \times (-110) - (-822)$$
$$= +492 \text{ kJ mol}^{-1}$$

---

23. The enthalpy changes of formation of gaseous ethene and gaseous ethane are 52 kJ mol^{-1} and -85 kJ mol^{-1} at 298 K.

What is the enthalpy change of reaction at 298 K for the following process?

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

A -137 kJ mol^{-1}

B -33 kJ mol^{-1}

C 33 kJ mol^{-1}

D 137 kJ mol^{-1}

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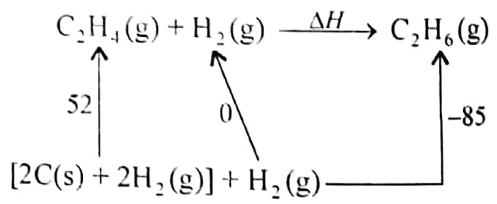

$$\therefore \Delta H = -52 + (-85) = -137 \text{ kJ mol}^{-1}$$

---

24. Phosphine reacts with hydrogen iodide to form phosphonium iodide in the reaction shown.

$$PH_3(g) + HI(g) \rightarrow PH_4^+I^-(s) \quad \Delta H^\circ = -101.8 \text{ kJ mol}^{-1}$$

Given that ΔH_f° for $PH_3(g) = +5.4$ kJ mol^{-1}, and ΔH_f° for $HI(g) = +26.5$ kJ mol^{-1}, what is the standard enthalpy change of formation of phosphonium iodide?

+822

A -133.7 kJ mol^{-1}
B -69.9 kJ mol^{-1}
C $+69.9$ kJ mol^{-1}
D $+133.7$ kJ mol^{-1}

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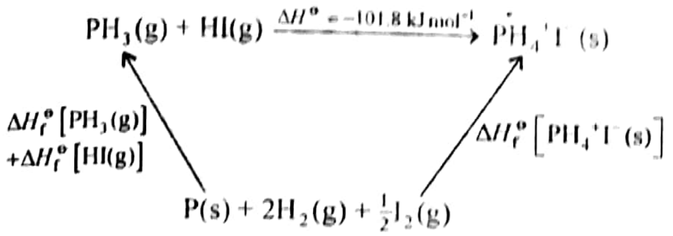

$$\Delta H_f^\circ[PH_4^+I^-(s)] = \Delta H_f^\circ[PH_3(g)] + \Delta H_f^\circ[HI(g)] + \Delta H^\circ$$
$$= +5.4 + 26.5 - 101.8$$
$$= -69.9 \text{ kJ mol}^{-1}$$

---

25. Given the following enthalpy changes

$I_2(g) + 3Cl_2(g) \rightarrow 2ICl_3(s)$ $\Delta H^\circ = -214$ kJ mol^{-1}
$I_2(s) \rightarrow I_2(g)$ $\Delta H^\circ = +38$ kJ mol^{-1}

What is the standard enthalpy change of formation of iodine trichloride, ICl_3?

A $+176$ kJ mol^{-1}
B $+138$ kJ mol^{-1}
C -88 kJ mol^{-1}
D -138 kJ mol^{-1}

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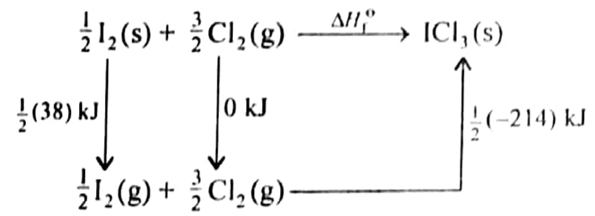

$$\therefore \Delta H_f^\circ = \tfrac{1}{2}(38) + \tfrac{1}{2}(-214) = -88 \text{ kJ mol}^{-1}$$

---

26. Some enthalpy changes of combustion are given below.

	ΔH_c / kJ mol^{-1}
$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	-283
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$	-286
$CH_3OH(\ell) + 1\frac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$	-715

What is the enthalpy change of the following reaction?

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(\ell)$$

A -146 kJ mol^{-1}
B -140 kJ mol^{-1}
C $+140$ kJ mol^{-1}
D $+146$ kJ mol^{-1}

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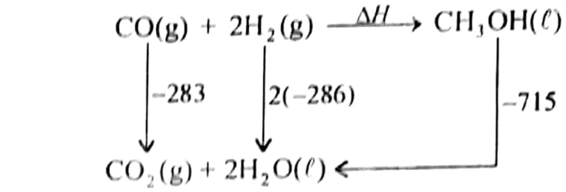

$$\therefore \Delta H = (-283) + 2(-286) - (-715)$$
$$= -140 \text{ kJ mol}^{-1}$$

---

27. The enthalpy change of reaction between calcium and water can be measured in the laboratory.

$$Ca(s) + 2H_2O(\ell) \rightarrow Ca(OH)_2(s) + H_2(g)$$

What information, other than that obtained in this experiment, is needed to calculate a value for the enthalpy change of formation of $Ca(OH)_2(s)$?

A enthalpy change of atomisation of calcium
B enthalpy change of combustion of hydrogen
C first and second ionisation energies of calcium
D lattice energy of calcium hydroxide

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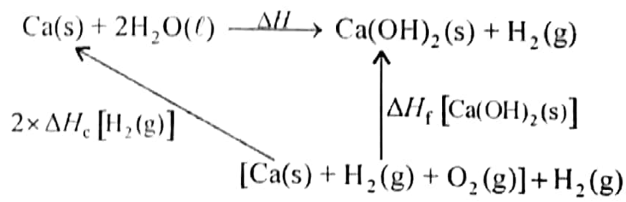

$$\therefore \Delta H = \Delta H_f[Ca(OH)_2(s)] - 2\times\Delta H_c[H_2(g)]$$

---

28. Gaseous phosphorus pentachloride can be decomposed into gaseous phosphorus trichloride and chlorine by heating. The table below gives the bond energies.

bond	bond energy/kJ mol^{-1}
P – Cl (in bond chlorides)	330
Cl – Cl	240

What is the enthalpy change in the decomposition of PCl_5 to PCl_3 and Cl_2?

A –420 kJ mol^{-1}

B –90 kJ mol^{-1}

C +90 kJ mol^{-1}

D +420 kJ mol^{-1}

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$$PCl_5 \rightarrow PCl_3 + Cl_2$$

In the process, 2 P–Cl bonds are broken and 1 Cl–Cl bond is formed.

$$\therefore \Delta H = 2BE(P-Cl) - BE(Cl-Cl)$$
$$= 2(330) - 240$$
$$= +420 \text{ kJ mol}^{-1}$$

29. The standard enthalpy change of combustion of but-1-ene, $C_4H_8(g)$, is x kJ mol^{-1}.

The standard enthalpy change of the reaction $2C_2H_4(g) \rightarrow C_4H_8(g)$ is y kJ mol^{-1}.

What is the standard enthalpy change of combustion of ethene, $C_2H_4(g)$?

A $\frac{x}{2} + y$ kJ mol^{-1}

B $x + \frac{y}{2}$ kJ mol^{-1}

C $\frac{x+y}{2}$ kJ mol^{-1}

D $\frac{x-y}{2}$ kJ mol^{-1}

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$$C_2H_4(g) + 3O_2(g) \xrightarrow{\Delta H_c^\circ} 2CO_2(g) + 2H_2O(\ell)$$
$$\downarrow \tfrac{1}{2}y \qquad\qquad \nearrow \tfrac{1}{2}x$$
$$\tfrac{1}{2}C_4H_8(g) + 3O_2(g)$$

$$\Delta H_c^\circ = \tfrac{1}{2}(x+y)$$

30. In oil refineries, an important process is the recovery of any sulfur from petroleum. Sulfur compounds are converted into the gas hydrogen sulfide, H_2S, by using a catalyst. The H_2S is then oxidised by using a controlled amount of air to give steam, $H_2O(g)$, and sulfur, $S(s)$.

The enthalpy change of formation of $H_2S(g)$ is –20.5 kJ mol^{-1} and that of $H_2O(g)$ is –243.0 kJ mol^{-1}.

What is the enthalpy change of reaction per mole of H_2S?

A –202.5 kJ mol^{-1}

B –222.5 kJ mol^{-1}

C –263.5 kJ mol^{-1}

D –445.0 kJ mol^{-1}

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$$H_2S(g) + \tfrac{1}{2}O_2(g) \xrightarrow{\Delta H^\circ_{rxn}} H_2O(g) + S(s)$$
$$\Delta H_f^\circ[H_2S(g)] \uparrow \qquad\qquad \nearrow \Delta H_f^\circ[H_2O(g)]$$
$$S(s) + H_2(g) + \tfrac{1}{2}O_2(g)$$

$$\therefore \Delta H_{rxn} = -\Delta H_f^\circ[H_2S(g)] + \Delta H_f^\circ[H_2O(g)]$$
$$= -(-20.5) + (-243.0)$$
$$= -222.5 \text{ kJ mol}^{-1}$$

31. Gallstones can form in the gall bladder and are very painful. The inorganic part of gallstones is calcium ethanedioate which is insoluble in water. The corresponding magnesium ethanedioate is soluble in water.

Which factor accounts for the difference in solubility between calcium ethanedioate and magnesium ethanedioate?

A Calcium ethanedioate has a higher solubility product than magnesium ethanedioate.

B Calcium ethanedioate has a numerically higher lattice energy than magnesium ethanedioate.

C Calcium ions have a lower enthalpy change of hydration than magnesium ions.

D Calcium is more electropositive than magnesium.

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$$M^{2+}C_2O_4^{2-}(s) \xrightarrow{\Delta H_{soln}} M^{2+}(aq) + C_2O_4^{2-}(aq)$$

L.E. $\qquad \Delta H_{hydration}$

$$M^{2+}(g) + C_2O_4^{2-}(g)$$

$\Delta H_{soln} = \Delta H_{hyd} - \text{L.E.}$

$r_{Ca^{2+}} > r_{Mg^{2+}}$

The hydration energy of Ca^{2+} is less exothermic than that of Mg^{2+}. This makes ΔH_{soln} of CaC_2O_4 less exothermic and hence less soluble.

---

32. One suggestion for the reduction of greenhouse gas emissions from coal-fired power stations is to separate the CO_2 from the flue gases and pump it into the sea bed, where it will dissolve in water under pressure.

$$CO_2(g) + nH_2O(\ell) \rightleftharpoons CO_2(aq)$$

During this process, hydrogen bonds are formed between CO_2 and H_2O molecules.

What will be the signs of ΔH and ΔS for this equilibrium for the forward reaction?

	ΔH	ΔS
A	–	–
B	–	+
C	+	–
D	+	+

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Since bonds are formed, heat is evolved and $\Delta H < 0$. As a result of the bonding, the movement of H_2O and CO_2 become more restricted and there is greater order. Hence, $\Delta S < 0$.

---

33. Some $\Delta H_f^\ominus$ values are given below.

compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
$H_2O(\ell)$	–286
$CO_2(g)$	–394
$C_6H_{12}O_6(s)$	–1273

The overall reaction in photosynthesis can be represented by the floowing equation.

$$6CO_2(g) + 6H_2O(\ell) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

Which row correctly describes the signs of ΔH and ΔS for this reaction?

	ΔH	ΔS
A	–	–
B	–	+
C	+	–
D	+	+

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$$\Delta H_r^\ominus = \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants})$$
$$= (-1273) - [6(-394) + 6(-286)$$
$$= +2807 \text{ kJ mol}^{-1}$$

There are equimolar of gaseous reactants (CO_2) and products (O_2). However, there is a change from the less orderly liquid (H_2O) to the more orderly solid ($C_6H_{12}O_6$). Hence, $\Delta S < 0$.

---

34. In an experiment to measure the enthalpy change of neutralisation of hydrogen acid, 20 cm^3 of solution containing 0.04 mol of HCl is placed in a plastic cup of negligible heat capacity.

A 20 cm^3 sample of aqueous sodium hydroxide containing 0.04 mol of NaOH, at the same initial temperature, is added and the temperature rises by 15 K.

If the heat capacity per unit volume of the final solution is 4.2 J K^{-1} cm^{-3}, what is the enthalpy change of neutralisation of hydrochloric acid?

A $\dfrac{20 \times 4.2 \times 15}{0.04}$ J mol^{-1}

B $40 \times 4.2 \times 15 \times 0.08$ J mol^{-1}

C $\dfrac{40 \times 4.2 \times 15}{0.04}$ J mol^{-1}

D $\dfrac{20 \times 4.2 \times 15}{0.08}$ J mol^{-1}

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Heat evolved, $q = Vc\Delta T$

$$= (20 + 20) \times 4.2 \times 15$$
$$= 40 \times 4.2 \times 15$$

$$\therefore \Delta H_{\text{neutralisation}} = -\frac{q}{\text{no. of mol of NaOH or HCl}}$$

$$= -\frac{40 \times 4.2 \times 15}{0.04} \text{ J mol}^{-1}$$

---

35. At temperatures below 13 °C, shiny, ductile metallic tin, known as 'white tin', changes slowly into a grey powder which is brittle.

Data for each form of tin are given in the table.

	ΔH_f° / kJ mol^{-1}	S° / J K^{-1} mol^{-1}
white	0	51.4
grey	−2.09	44.1

What is the expression for ΔG°, in J mol^{-1}, for the formation of grey tin from white tin at 12 °C?

A $\Delta G^\circ = -2.09 - 285(-7.3)$

B $\Delta G^\circ = -2.09 - 12(+7.3)$

C $\Delta G^\circ = -2090 - 12(+7.3)$

D $\Delta G^\circ = -2090 - 285(-7.3)$

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$$\Delta G^\circ = \Delta G^\circ(\text{grey}) - \Delta G^\circ(\text{white})$$
$$= [-2.09 \times 10^3 - (273+12)(44.1)] - [0 - (273+12)(51.4)]$$
$$= -2090 - 285(-7.3)$$

Note: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

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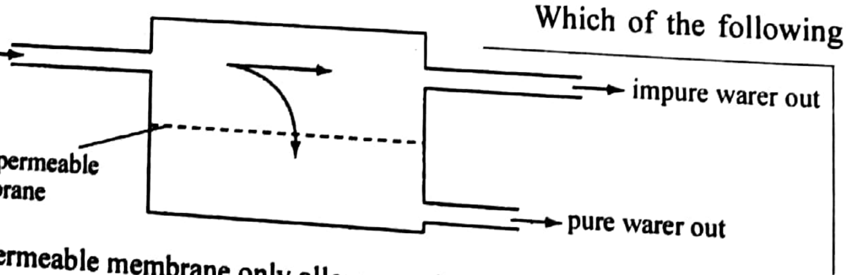
36. Reverse osmosis is a method of obtaining pure water from seawater or polluted water. The process works by applying a constant pressure to a sample of impure water next to a semi-permeable membrane.



The semi-permeable membrane only allows small molecules such as water through, but keeps back all other molecules and ions.

The enthalpy change of dilution of NaCl(aq), i.e. ΔH for the process

$$NaCl(aq, conc) + nH_2O \rightarrow NaCl(aq, dil)$$

is very small, and can be considered as being zero. What are the correct signs of ΔS and ΔG for the reverse osmosis process?

	ΔS	ΔG
A	−	−
B	−	+
C	+	−
D	+	+

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During reverse osmosis, the NaCl solution becomes more concentrated as H_2O leaves the solution as pure H_2O via the membrane. There would be greater order in the NaCl solution. Hence, $\Delta S < 0$.

Since $\Delta G = \Delta H - T\Delta S$
$= -T\Delta S$ if $\Delta H \approx 0$,
$\Delta G > 0$.

The reverse osmosis process is not spontaneous.

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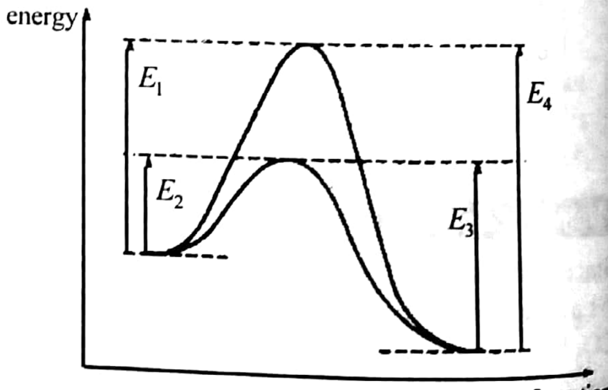
37. The energy diagram represents the reaction occurring with and without a catalyst.



Which of the following statements is correct?

A E_4 is the activation energy for the reverse catalysed reaction.

B The forward reaction, with catalyst, is endothermic.

C The enthalpy change of reaction is $(E_2 - E_3)$.

D The enthalpy change of reaction is reduced by using a catalyst.

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A: E_1 and E_4 are the activation energies for the forward and reverse uncatalysed reaction respectively. E_2 and E_3 are the activation energies for the forward and reverse catalysed reaction respectively.

B: Since the product is at a lower energy state, heat is given out during the reaction and the reaction is exothermic.

C: $\Delta H = E_2 - E_3 = E_1 - E_4$

D: The use of a catalyst does not affect ΔH since the initial and final energy states are not affected.

Topic 8 Chemical Energetics

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

38. Which reactions represent standard enthalpy changes at 298 K?

1. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
2. $C(g) + 6H(g) \rightarrow C_2H_6(g)$
3. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

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*1. All $NH_3(g)$, $HCl(g)$ and $NH_4Cl(s)$ are in their standard states.

2. Carbon should be in the solid state.

3. H_2O should be in the liquid state.

39. Which of the following reactions does the value of ΔH° represent **both** a standard enthalpy change of combustion **and** a standard enthalpy change of formation?

1. $C(s) + O_2(g) \rightarrow CO_2(g)$
2. $2C(s) + O_2(g) \rightarrow 2CO(g)$
3. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

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(2) does not represent ΔH of combustion of C because combustion of C should give CO_2 and not CO.

(3) does not represent ΔH of formation of CO_2 because for formation, the reactants must be elements and not compounds (CO).

40. Which statements are correct for the neutralisation of a strong acid by a strong alkali in aqueous solution at 25 °C?

1. It is an endothermic process.
2. It can be represented as
$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(\ell)$$
3. The enthalpy change per mole of H_2O formed is independent of the acid or alkali used.

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1. $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell) \quad \Delta H^\circ < 0$
The reaction is exothermic.

*2,*3. The enthalpy change per mole of H_2O is independent of the acid and alkali used as long as they are strong acids and alkalis.

41. Which of the following are always endothermic processes?

1. the hydration of a gaseous cation
2. the dissociation into atoms of a diatomic molecule
3. the sublimation of a solid

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1. Hydration is always an exothermic process because ion-solvent bonds are formed without breaking any other bonds.

*2. Energy is taken in to break the covalent bonds in a molecule to give atoms.

*3. Sublimation is a process whereby a solid transform into a gas without changing into a liquid. Energy is taken in to separate the molecules apart, i.e. intermolecular forces are broken.

42. The following equations each represent a step in the Born-Haber cycle for the enthalpy change of formation of sodium chloride.

Which changes have a negative ΔH value?

1. $Cl(g) + e^- \rightarrow Cl^-(g)$
2. $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$
3. $Na(s) \rightarrow Na(g)$

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*1. The first electron affinity of Cl is exothermic. Cl has a strong tendency to take in 1 electron so as to achieve a stable octet structure.

2,3. These reactions are endothermic. The energy change corresponds to enthalpy change of atomisation. Energy is taken in to break the Cl–Cl bonds or the metallic bonds in Na.

---

43. Which of the following classes of reaction always have an endothermic (positive) enthalpy change?

1 atomisation

2 neutralisation

3 solution

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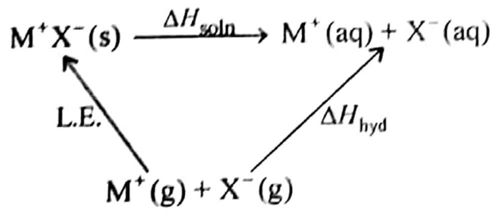
*1. During atomisation, energy is required to break the bonds between the atoms. Hence it is always endothermic.

2. Neutralisation is an exothermic process.

3. Enthalpy change of solution may be exothermic or endothermic, depending on the lattice energy and hydration.

E.g.



$\Delta H_{soln} = -L.E. + \Delta H_{hyd}$

---

44. Magnesium oxide and sodium fluoride are isoelectronic (have the same number of electrons).

Which of the following are reasons why the value of the lattice energy of magnesium oxide is four to five times that of sodium fluoride.

1 the higher enthalpy change of hydration of the doubly charged cations

2 the higher electrostatic attraction between the doubly charged ions

3 the shorter internuclear distance between the doubly charged ions

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1. Enthalpy change of hydration does not affect L.E.

*2. $$|L.E| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

Doubly charged ions experience greater electrostatic attraction than do singly charged ions.

*3. Mg^{2+} and O^{2-} are smaller than Na^+ and F^- respectively. Hence, $(r_+ + r_-)$ is also smaller and therefore, |L.E.| is higher.

---

45. Which of the enthalpy changes of the following reactions can only be obtained by application of the Hess' law?

1 The hydration of anhydrous copper sulfate to form crystals of $CuSO_4.5H_2O$.

2 The formation of methane from its elements.

3 The combustion of glucose, $C_6H_{12}O_6$.

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*1. $CuSO_4(s) + 5H_2O(\ell) \rightarrow CuSO_4.5H_2O(s)$

The reaction cannot be properly carried out. Some $CuSO_4$ may dissolve while some may not be completely hydrated.

*2. $C(s) + 2H_2(g) \rightarrow CH_4(g)$

The reaction does not take place.

3. $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(\ell)$

The enthalpy change of combustion can be measured without the application of Hess' law, by burning a fixed mass of glucose and measuring the heat evolved.

---

46. Which factors contribute to the lattice energy of calcium chloride being numerically greater than that of potassium bromide?

1 The radius of the chloride ion is smaller than that of the bromide ion.

2 The charge on the calcium ion is greater than that on the potassium ion.

3 Chlorine is more highly electronegative than bromine.

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$$|L.E.| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

*1. $r_{Cl^-} < r_{Br^-}$

*2 $q_{Ca^{2+}}\ (=2+) > q_{K^+}\ (=1+)$

3. The statement is true but it does not explain why $CaCl_2$ has a numerically larger lattice energy than KBr.

---

47. Calcium reacts with water to form calcium hydroxide and hydrogen.

$$Ca(s) + 2H_2O(\ell) \rightarrow Ca(OH)_2(s) + H_2(g)$$

The standard enthalpy change for this reaction can be measured in the laboratory.

What further information is needed in order to calculate the standard enthalpy change of formation of calcium hydroxide, ΔH_f° ?

1 ΔH_f° for $H_2O(\ell)$

2 ΔH_f° for $H_2(g)$

3 first and second ionisation energies of Ca

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$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{pdt}) - \sum \Delta H_f^\circ(\text{rxt})$$
$$= \Delta H_f^\circ[Ca(OH)_2(s)] - 2(\Delta H_f^\circ[H_2O(\ell)])$$

---

48. The values of two lattice energies are given below.

NaF, –915 kJ mol^{-1};

MgO, –3933 kJ mol^{-1}.

Which of the following correct statements help to explain the difference between these two values?

1 In each of these compounds, the ions are isoelectronic (have the same number of electrons).

2 The attraction between doubly charged ions is about four times that between singly charged ions.

3 The interionic distance in NaF is 0.102 nm and that in MgO is 0.074 nm.

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$$|L.E.| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

1. The statement is true but it does not help to explain the observation.

*2. When both charges, q_+ and q_- are doubled, lattice energy increases by 4 times.

*3. The smaller interionic distance in MgO, i.e. smaller $(r_+ + r_-)$ causes the ionic bonds to be stronger. Hence, higher lattice energy is expected.

---

49. Solutes dissolve in solvents to form solutions. If a semi-permeable membrane, that allows solvent molecules to pass through it, is placed between a pure solvent and a solution containing a solute in that solvent, pure solvent only will go through the membrane into the solution. This process is called osmosis.

In which processes will ΔS be positive?

1 dissolving the solute in a solvent

2 the evaporation of the solvent from the solution

3 the passage of the solvent through a semi-permeable membrane during osmosis

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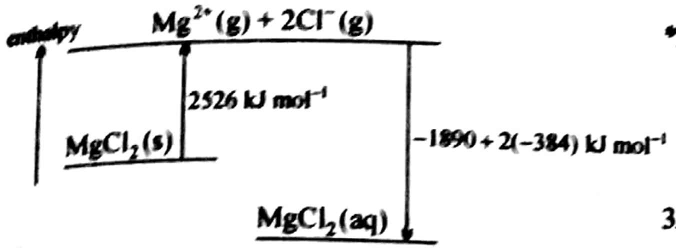
*1. When a solute dissolves in a solvent, the solute particles are more widely dispersed and they move randomly, compared to the solid structure. Hence, ΔS is positive.

*2. When a solvent evaporates, the solvent particles move even more randomly and rapidly compared to in the liquid state. Hence, ΔS is positive.

*3. The solution becomes diluted as more solvent enters the solution via osmosis. The situation is similar to 1.

---

50. The enthalpy level diagram shown represents the dissolving of anhydrous magnesium chloride in a large volume of water.



Which statements about the process are correct?

1 The lattice energy of magnesium chloride is -2526 kJ mol^{-1}.

2 The enthalpy change of hydration of the chloride ion is -384 kJ mol^{-1}.

3 The enthalpy change of solution of anhydrous magnesium chloride is -132 kJ mol^{-1}.

Helping Concepts | *Exam Favourite Rating* ★★★

*1. $Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s)$

*2. $\Delta H_{hyd} = \Delta H_{hyd}(Mg^{2+}) + 2 \times \Delta H_{hyd}(Cl^-)$

$= (-1890) + 2(-384)$

$\therefore \Delta H_{hyd}(Cl^-) = -384$ kJ mol^{-1}

*3. $\Delta H_{soln} = \Delta H_{hyd} - \text{L.E.}$

$= [-1890 + 2(-384)] - (-2526)$

$= -132$ kJ mol^{-1}

---

51. The conversion of graphite into diamond is an endothermic reaction ($\Delta H = +3$ kJ mol^{-1}).

$$C\text{ (graphite)} \rightarrow C\text{ (diamond)}$$

Which statements are correct?

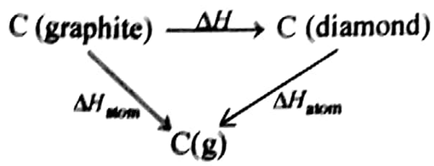
1 The enthalpy change of atomisation of diamond is smaller than that of graphite.

2 The bond energy of the C–C bonds in graphite is greater than that in diamond.

3 The enthalpy change of combustion of diamond is greater than that of graphite.

Helping Concepts | *Exam Favourite Rating* ★★

*1.



$\Delta H = \Delta H_{atom}(\text{graphite}) - \Delta H_{atom}(\text{diamond})$

Since $\Delta H > 0$,

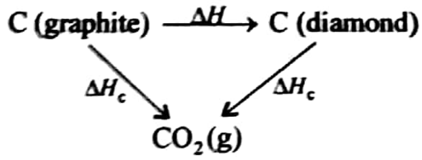
$\Delta H_{atom}(\text{graphite}) > \Delta H_{atom}(\text{diamond})$

*2. $\Delta H = BE(C-C)_{graphite} - BE(C-C)_{diamond}$

Since $\Delta H > 0$,

$BE(C-C)_{graphite} > BE(C-C)_{diamond}$

3.



$\Delta H = \Delta H_c(\text{graphite}) - \Delta H_c(\text{diamond})$

Since $\Delta H > 0$,

$\Delta H_c(\text{graphite}) > \Delta H_c(\text{diamond})$

Note: Diamond has a more exothermic ΔH_c than graphite.

TOPIC 6

Electrochemistry

Key content that you will be examined on:

1. Redox processes: electron transfer and changes in oxidation number (oxidation state)
2. Electrode potentials
   (i) Standard electrode (redox) potentials, $E^{\ominus}$; the redox series
   (ii) Standard cell potentials, $E^{\ominus}_{cell}$, and their uses
   (iii) Batteries and fuel cells
3. Electrolysis
   (i) Factors affecting the amount of substance liberated during electrolysis
   (ii) The Faraday constant; the Avogadro constant; their relationship
   (iii) Industrial uses of electrolysis

Electrochemistry

Topic 6

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which treatment is frequently used to protect aluminium articles from subsequent corrosion?

   A making the aluminium the anode during electrolysis

   B dipping the aluminium in hot aqueous sodium hydroxide

   C dipping the aluminium in molten cryolite

   D coating the aluminium with a less reactive metal

Helping Concepts *Exam Favourite Rating* ★

Al is anodised to increase the protective layer of Al_2O_3. At the anode, O_2 is released and it oxidises the Al anode to Al_2O_3, thereby increases its thickness.

---

2. An aqueous solution contains 1 mol of $S_2O_3^{2-}$ ions and this reduces 4 mol of Cl_2 molecules. What is the sulfur-containing product of this reaction?

A S	**B** SO_2
C SO_3^{2-}	**D** SO_4^{2-}

Helping Concepts *Exam Favourite Rating* ★★

$$4Cl_2 + 8e^- \rightarrow 8Cl^-$$

4 moles of Cl_2 gain 8 moles of electrons. Therefore, 1 mole of $S_2O_3^{2-}$ have to loss 8 moles of electrons and each S atom has to lose 4 electrons (since there are 2 S atoms per $S_2O_3^{2-}$ ion). Hence, the oxidation state of S increases of +4 units, i.e. the final oxidation state is +6.

---

3. A current is passed through two cells connected in series. The first cell contains XSO_4(aq) while the second cell contains Y_2SO_4(aq). The relative atomic masses of X and Y are in the ratio 1 : 2.

   What is the ratio

   mass of X liberated : mass of Y liberated?

A 1 : 1	**B** 1 : 2
C 1 : 4	**D** 2 : 1

Helping Concepts *Exam Favourite Rating* ★★

Molar ratio of X to Y liberated = 1 : 2

∴ Mass of X liberated : Mass of Y liberated

$= n_1 \times (M_r)_1 : n_2 \times (M_r)_2$

$= n_1 \times 1 : n_2 \times 2$

$= (1 \times 1) : (2 \times 2)$

$= 1 : 4$

---

4. When 5 mol of electrons are passed through a molten aluminium salt, what is the maximum mass of aluminium formed at the cathode?

   [A_r: Al, 27]

A 5.4 g	**B** 16.2 g
C 27 g	**D** 45 g

Helping Concepts *Exam Favourite Rating* ★★★

$$Al^{3+} + 3e^- \rightarrow Al$$

Amount of Al produced $= \frac{5}{3}$ mol

Mass of Al produced $= \frac{5}{3} \times 27 = 45$ g

Ur

5. In which one of the following reactions does hydrogen behave as an oxidising agent.

   A $C_2H_4 + H_2 \rightarrow C_2H_6$

   B $C_2H_5CHO + H_2 \rightarrow C_2H_5CH_2OH$

   C $N_2 + 3H_2 \rightarrow 2NH_3$

   D $2Na + H_2 \rightarrow 2NaH$

Helping Concepts *Exam Favourite Rating* ★★★

An oxidising agent decreases its oxidation state since it is being reduced. In (D), H changes its oxidation state from 0 to −1. In this case, H_2 oxidises the highly reactive Na by gaining an electron from a Na atom to form H^-.

$$Na \rightarrow Na^+ + e^-$$

$$\frac{1}{2}H_2 + e^- \rightarrow H^-$$

---

6. Two electrode potentials are given.

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad E^\ominus = +0.77\ V$$

$$Br_2 + 2e^- \rightleftharpoons 2Br^- \quad E^\ominus = +1.07\ V$$

Which species is the strongest reducing agent?

A Fe^{3+} B Fe^{2+}
C Br_2 D Br^-

Helping Concepts *Exam Favourite Rating* ★★★

$$O + ne^- \rightleftharpoons R \quad E^\ominus$$

O is a strong oxidising agent if $E^\ominus$ is highly positive.
R is a strong reducing agent if $E^\ominus$ is highly negative.

---

7. An ion is discharged at the cathode during the electrolysis of a molten salt containing the ion.

What could describe this ion?

	proton number	electronic configuration
A	11	2,8
B	16	2,8,8
C	17	2,8,8
D	18	2,8,8

Helping Concepts *Exam Favourite Rating* ★★★

A cation migrates to the negative cathode and is reduced to form the element.

$$Na^+ + e^- \rightarrow Na$$

A: Na^+
B: S^{2-}
C: Cl^-
D: Ar

---

8. A cheap carbon monoxide detector for a gas heater consists of a patch containing palladium chloride crystals. When carbon monoxide is present, the crystals turn from orange to black as the following reaction takes place.

$$CO(g) + \underset{\text{orange}}{PdCl_2(s)} + H_2O(\ell) \rightarrow CO_2(g) + \underset{\text{black}}{Pd(s)} + 2HCl(aq)$$

Which is the element whose oxidation number decreases in this reaction?

A carbon B chloride
C hydrogen D palladium

Helping Concepts *Exam Favourite Rating* ★★★

The oxidation state of Pd decreases from +2 in $PdCl_2$ to 0 in Pd.

---

9. During electrolysis under suitable conditions, 0.015 mol of chromium is deposited on the cathode when 0.090 mol of electrons is passed through a chromium-containing electrolyte.

Which of the following substances could have been the electrolyte?

A $CrCl_3$ B CrF_4
C CrF_5 D $Na_2Cr_2O_7$

Helping Concepts *Exam Favourite Rating* ★★

$$Cr^{n+} + ne^- \longrightarrow Cr$$

To deposit 0.015 mol of Cr, 0.015n mol of electrons are required.

$$\therefore\ 0.015n = 0.090$$

$$n = 6$$

Therefore, Cr has an oxidation state of +6 in the compound. The oxidation of Cr in the options are (A) +3; (B) +4; (C) +5; (D) +6.

---

10. *Use of the Data Booklet is relevant to this question.*

In many areas, tap water becomes slightly acidic due to dissolved carbon dioxide.

By considering the relevant $E^\ominus$ values, which of the following metals will **not** be dissolved by tap water containing carbon dioxide?

A chromium B copper
C iron D lead

Helping Concepts *Exam Favourite Rating* ★★★

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad E^\circ = 0.00\ V$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\circ = +0.34\ V$$

Overall reaction:

$$Cu(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$$

$E^\circ_{cell} = 0 - (+0.34) = -0.34\ V < 0$

Reaction is energetically not feasible under standard conditions.

---

11. A student electrolyses concentrated aqueous sodium chloride using carbon electrodes. She ensures that the solution is continually stirred.

What happens as the electrolysis proceeds?

A H_2 is produced at the anode.

B HCl is formed.

C NaClO is formed.

D The NaCl gets more concentrated.

Helping Concepts *Exam Favourite Rating* ★★

Electrolysing concentrated NaCl produces H_2 at the cathode and Cl_2 at the anode (alongside with little O_2). The electrolyte becomes alkaline as a result of the accumulation of OH^-.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

In the cold, Cl_2 will dissolve and react with OH^- to undergo disproportionation. ClO^- and Cl^- are formed.

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$$

---

12. Some data relating to magnesium and its compounds are as follows.

standard electrode potential of magnesium = −2.38 V
melting point of magnesium oxide = 2850 °C
melting point of magnesium chloride = 714 °C

What is the most suitable method for extracting magnesium metal from its ores?

A electrolysis of aqueous magnesium chloride

B electrolysis of molten magnesium chloride

C electrolysis of molten magnesium oxide

D reduction of magnesium oxide with carbon

Helping Concepts *Exam Favourite Rating* ★★★

The very negative E° value of Mg shows that Mg^{2+} is very difficult to be reduced to Mg. Therefore, normal chemical reduction is not suitable. A feasible way would be the electrolysis of molten Mg^{2+}, in this case, $MgCl_2$ ($MgCl_2$ has a lower melting point than MgO).

---

13. *Use of the Data Booklet is relevant to this question.*

Which reactant is likely to be reduced by Sn^{2+}(aq) ions?

A Fe^{3+}(aq)	**B** H^+(aq)
C Pb^{2+}(aq)	**D** V^{3+}(aq)

Helping Concepts *Exam Favourite Rating* ★★★

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$

$E^\circ_{cell} = +0.77 - (+0.15) = +0.62\ V > 0$

Hence, the reaction is energetically feasible.

To have a positive E_{cell}, E° of the substance reduced must be greater than the E° of the substance oxidised. The E° for Sn^{4+}/Sn^{2+} is +0.15 V. Hence, to be reduced by Sn^{2+}, the cation must have E° greater than +0.15 V. E° of Fe^{3+}, H^+, Pb^{2+} and V^{3+} are +0.77 V, 0 V, −0.13 V and −0.26 V respectively. Hence, from the options, only Fe^{3+} is reduced by Sn^{2+}.

---

14. When ammonia is converted into nitric acid on a commercial scale, the following reactions can occur.

In which reaction does the greatest change in oxidation number of the nitrogen occur?

reaction	
A	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
B	$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$
C	$2NO + O_2 \rightarrow 2NO_2$
D	$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$

Helping Concepts *Exam Favourite Rating* ★★★

A: NH_3 : −3; NO: +2; ΔO.S. = +5

B: NO_2 : +4; HNO_3: +5; ΔO.S. = +1

C: NO : +2; NO_2: +4; ΔO.S. = +2

D: NH_3 : −3; NO: +2; N_2 : 0; ΔO.S. = +3, −2

15. Four standard electrode potentials are listed below.

(iii)	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34 V
(iv)	$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22 V
(ii)	$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$	0.00 V
(i)	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76 V

Which cell potential could be obtained by combining two of these standard electrodes?

A +0.42 V B +0.54 V
C +0.56 V D +0.98 V

Helping Concepts *Exam Favourite Rating* ★★★

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \quad E^\circ = +0.22\ V$$
$$Zn^{2+}(s) + 2e^- \rightarrow Zn(s) \quad E^\circ = -0.76\ V$$

$E^\circ_{cell} = +0.22 - (-0.76) = +0.98\ V$

Overall reaction:

$$2AgCl(s) + Zn(s) \rightarrow 2Ag(s) + 2Cl^-(aq) + Zn^{2+}(aq)$$

16. *Use of the Data Booklet is relevant to this question.*
Gold medals awarded in the Olympic Games have a silver core and a pure gold coating of mass 6.0 g.

For what period of time must the core of the medal be immersed in a solution of 0.10 mol dm^{-3} gold(III) chloride in order to achieve an electroplated coating weighing 6.0 g using a current of 0.10 A?

A 2.9×10^3 s B 8.8×10^3 s
C 2.9×10^4 s D 8.8×10^4 s

Helping Concepts *Exam Favourite Rating* ★★★

$$Au^{3+} + 3e^- \rightarrow Au$$

A_r of Au = 197

$$n_{Au} = \frac{6.0}{197}\ \text{mol}$$

$$n_{e^-} = 3 \times n_{Au} = \frac{18}{197}\ \text{mol}$$

$$Q = n_{e^-} \times F = \frac{18}{197} \times 96500\ C$$

Using $Q = It$,

$$\frac{18}{197} \times 96500 = 0.10 \times t$$
$$t = 88\,000\ s$$

17. The e.m.f. of a simple cell was found to be 1.2 V under standard conditions. The following standard electrode potentials are given.

[The letters are not the usual symbols for the elements concerned.]

Red	P^+/P	−1.8 V	(i)
~~Oxd~~ Red	Q^{2+}/Q	+0.3 V	(iv)
Red	R^+/R	−0.9 V	(ii)
Red	S^{2+}/S	−0.3 V	(iii)

What were the two electrodes of the cell?

A P and Q
B P and S
C Q and R
D Q and S

Helping Concepts *Exam Favourite Rating* ★★★

The reaction involved is

$$Q^{2+} + 2R \rightarrow Q + 2R^+$$

$E^\circ_{cell} = 0.3 - (-0.9) = 1.2\ V$

18. $KMnO_4(aq)$ is added with shaking to a sample of acidified $Fe^{2+}(aq)$ in a conical flask until the $KMnO_4$ is in large excess.

What colour changes are seen in the conical flask.

A The pale green solution turns darker green, and finally purple.
B The pale green solution turns pink, and finally purple.
C The purple solution fades to pink, and finally colourless.
D The purple solution fades to pink, and finally yellow.

Helping Concepts *Exam Favourite Rating* ★★

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Fe^{2+} (pale green) is oxidised to Fe^{3+} (yellow). As the reaction proceeds and is eventually completely oxidised, there will be excess MnO_4^- in the solution which will appear pink at first (small quantity of excess MnO_4^-) and finally purple.

19. *Use of the Data Booklet is relevant to this question.*
In acidic solution, MnO_4^- ions oxidise Cl^- ions to Cl_2. The value of E° for the reaction is +0.16 V. Which statement or equation is correct?

A The oxidation number of chlorine changes from −1 to +2.

B The oxidation number of manganese changes from +7 to +4.

C $2MnO_4^- + 8H^+ + 6Cl^- \rightarrow 2MnO_2 + 4H_2O + 3Cl_2$

D $2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$

Helping Concepts | *Exam Favourite Rating* ★★★

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad E^\circ = +1.52\text{ V}$

$Cl_2 + 2e^- \rightarrow 2Cl^- \quad E^\circ = +1.36\text{ V}$

Overall reaction:

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$$

$E^\circ = +1.52 - 1.36 = +0.16\text{ V}$

---

20. The standard electrode potentials of $Ag^+(aq)|Ag(s)$ and $Zn^{2+}(aq)|Zn(s)$ are +0.80 V and −0.76 V respectively.

Which of the following conclusions can be drawn from these data?

A Silver displaces zinc from a solution containing zinc ions.

B Silver is an oxidising agent.

C Zinc has a greater tendency than silver to form positively charged ions.

D Zinc ions can act as a reducing agent.

Helping Concepts | *Exam Favourite Rating* ★★★

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E^\circ = +0.80\text{ V}$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\circ = -0.76\text{ V}$$

Overall reaction:

$$2Ag^+(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$$

$E^\circ_{cell} = +0.80 - (-0.76) = +1.56\text{ V}$

From the E° value, it can be seen that Ag^+ has a greater tendency to be reduced than is Zn^{2+}. In other word, Zn has a greater tendency to form Zn^{2+} than is Ag to Ag^+.

---

21. A current of 8 A is passed for 100 min through molten aluminium oxide using inert electrodes.

What will be the approximate volume of gas liberated, measured at s.t.p.?

A 2.8 dm^3 **B** 5.6 dm^3

C 8.4 dm^3 **D** 11.2 dm^3

Helping Concepts | *Exam Favourite Rating* ★★★

$$2O^{2-}(l) \rightarrow O_2(g) + 4e^-$$

Quantity of electricity used $= I \times t$
$= 8 \times 6000$ sec
$= 48000$ C

Amount of electrons passed $= \dfrac{48000\text{ C}}{96000\text{ C mol}^{-1}}$
$= 0.5$ mol

Amount of O_2 evolved $= \dfrac{0.5}{4}$
$= 0.125$ mol

Volume of O_2 evolved $= 0.125 \times 22.4$
$= 2.8\text{ dm}^3$

---

22. The standard redox potential for the half-cell reaction $Fe^{3+} + e^- = Fe^{2+}$ is +0.77 V.

Which cell would be used to determine this standard value?

A Fe electrode in 1 mol dm^{-3} Fe^{3+} against Fe electrode in 1 mol dm^{-3} Fe^{2+}.

B Pt electrode in 1 mol dm^{-3} Fe^{3+} against Pt electrode in 1 mol dm^{-3} Fe^{2+}.

C Fe electrode in a solution containing 1 mol dm^{-3} Fe^{3+} and 1 mol dm^{-3} Fe^{2+} against a standard hydrogen electrode.

D Pt electrode in a solution containing 1 mol dm^{-3} Fe^{3+} and 1 mol dm^{-3} Fe^{2+} against a standard hydrogen electrode.

Helping Concepts | *Exam Favourite Rating* ★★★

To measure the standard redox potential, a standard half-cell must be connected to a standard hydrogen electrode. In the standard half-cell, all the chemicals must be present (at 1 mol dm^{-3}), i.e. Fe^{3+} and Fe^{2+}. Since there is no conducting electrode, an inert electrode such as Pt has to be used.

---

23. *Use of the Data Booklet is relevant to this question.*

Pseudohalogens are compounds that are similar in some of their properties to halogens. For example, thiocyanogen and the thiocyanate ion can be interconverted by the following redox equilibrium.

$$\underset{\text{thiocyanogen}}{(SCN)_2(aq)} + 2e^- \rightleftharpoons \underset{\text{thiocyanate}}{2SCN^-(aq)} \quad E^\ominus = x\ V$$

Aqueous chlorine and aqueous bromine both oxidise the thiocyanate ion to thiocyanogen, but aqueous iodine does not.

What could be the value of x?

A −1.27 **B** −0.77

C +0.77 **D** +1.27

Helping Concepts *Exam Favourite Rating* ★★★

The $E^\ominus$ should be that between those of Br_2/Br^- and I_2/I^-.

$$E^\ominus_{Br_2/Br^-} = +1.07\ V$$

$$E^\ominus_{I_2/I^-} = +0.54\ V$$

24. *Use of the Data Booklet is relevant to this question.*

If iron is heated separately with chlorine, bromine and iodine, what are the likely products?

	chlorine	bromine	iodine
A	$FeCl_2$	$FeBr_2$	FeI_2
B	$FeCl_3$	$FeBr_2$	FeI_2
C	$FeCl_3$	$FeBr_3$	FeI_2
D	$FeCl_3$	$FeBr_3$	FeI_2

Helping Concepts *Exam Favourite Rating* ★★★

$$Fe + \tfrac{3}{2}Cl_2 \rightarrow FeCl_3$$

$$E^\ominus_{cell} = 1.36 - (-0.04) = +1.40\ V > 0$$

$$Fe + \tfrac{3}{2}Br_2 \rightarrow FeBr_3$$

$$E^\ominus_{cell} = 1.07 - (-0.04) = +1.11\ V > 0$$

$$Fe + I_2 \rightarrow FeI_2$$

$$E^\ominus_{cell} = 0.54 - (-0.44) = +0.98\ V > 0$$

Fe^{3+} can oxidise I^- to give I_2:

$$Fe^{3+} + I^- \rightarrow Fe^{2+} + \tfrac{1}{2}I_2$$

$$E^\ominus_{cell} = 0.77 - 0.54 = +0.23\ V > 0$$

25.

Half equation	$E^\ominus$ / V
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$2H^+(aq) + O_2(g) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77

What will be observed when a few drops of acidified aqueous hydrogen peroxide are added to an excess of aqueous potassium iodide?

A The solution turns brown and effervescence occurs.

B The solution turns brown without effervescence.

C The solution does not change colour and effervescence occurs.

D The solution turns purple and effervescence occurs.

Helping Concepts *Exam Favourite Rating* ★★★

Overall reaction:

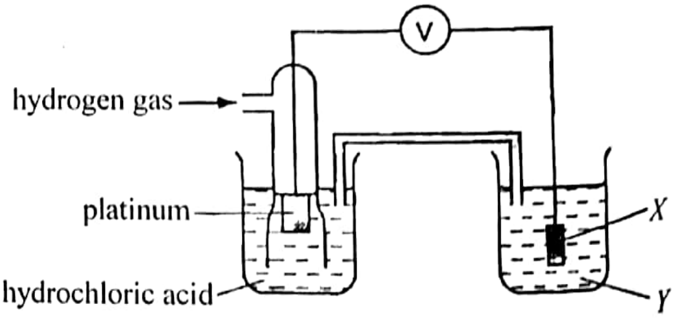
$$2I^-(aq) + H_2O_2(aq) + 2H^+ \rightarrow 2H_2O(l) + I_2(aq)$$

$$E^\ominus_{cell} = +1.77 - 0.54 = 1.23\ V$$

The solution turns brown as a result of the formation of I_2. However, there is no effervescence since no O_2 gas is evolved.

26. The diagram shows the apparatus needed to measure $E^\ominus$ for the reaction below.

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$$



What are the identities of X and Y?

	X	Y
A	Fe	$Fe^{3+}(aq)$
B	Fe	$Fe^{2+}(aq) + Fe^{3+}(aq)$
C	Pt	$Fe^{3+}(aq)$
D	Pt	$Fe^{2+}(aq) + Fe^{3+}(aq)$

Helping Concepts *Exam Favourite Rating* ★★★

In the Fe^{3+}/Fe^{2+} half cell, an inert electrode (e.g. Pt or C) is required.

---

27. Sodium thiosulfate is used in the textile industry to remove an excess of chlorine from bleaching processes by reducing it to chloride ions.

$$S_2O_3^{2-} + 4Cl_2 + 5H_2O \rightarrow 2HSO_4^- + 8H^+ + 8Cl^-$$

In this reaction, how many moles of electrons are supplied per mole of thiosulfate?

A 1	**B** 2
C 4	**D** 8

Helping Concepts *Exam Favourite Rating* ★★★

Balancing the half equation $S_2O_3^{2-}/HSO_4^-$:

$$S_2O_3^{2-} + 5H_2O \rightarrow 2HSO_4^- + 8H^+ + 8e^-$$

Step 1: Balance S

$$S_2O_3^{2-} \rightarrow \underline{2}HSO_4^-$$

Step 2: Balance O by adding H_2O

$$S_2O_3^{2-} + \underline{5}H_2O \rightarrow 2HSO_4^-$$

Step 3: Balance H by adding H^+

$$S_2O_3^{2-} + 5H_2O \rightarrow 2HSO_4^- + \underline{8}H^+$$

Step 4: Balance charge by adding electrons

$$S_2O_3^{2-} + 5H_2O \rightarrow 2HSO_4^- + 8H^+ + 8e^-$$

---

28. When a large current was passed through acidified aqueous copper(II) sulfate, there was simultaneous liberation, at the cathode, of x mol of copper and y dm^3 of hydrogen (measured at s.t.p.).

How many moles of electrons passed through the solution?

A $x+\dfrac{y}{22.4}$	**B** $x+\dfrac{y}{11.2}$
C $x+\dfrac{y}{5.6}$	**D** $2x+\dfrac{y}{11.2}$

Helping Concepts *Exam Favourite Rating* ★★

Both Cu and H_2 are liberated at the cathode.

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$2H^+ + 2e^- \rightarrow H_2$$

(i) 1 mole of Cu requires 2 moles of electrons. Therefore, x moles of Cu requires $2x$ moles of electrons.

(ii) 22.4 dm^3 (1 mole) of H_2 requires 2 moles of electrons.

Hence, y dm^3 of H_2 requires $\frac{2y}{22.4} = \frac{y}{11.2}$ moles of electrons.

∴ Total number of moles of electrons required

$$= 2x + \frac{y}{11.2}$$

---

29. *Use of the Data Booklet is relevant to this question.*

When aqueous hydrogen peroxide, H_2O_2, is mixed with acidified potassium dichromate(VI), there is a colour change from orange to green. When aqueous hydrogen peroxide is added to acidified potassium iodide solution, there is a colour change from colourless to brown.

The oxidation number of oxygen in H_2O_2 is -1.

What are the oxidation numbers of oxygen after the reactions with potassium dichromate(VI) and potassium iodide?

	after reaction with potassium dichromate(VI)	after reaction with potassium iodide
A	-2	-2
B	-2	0
C	0	-2
D	0	0

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H_2O_2 is oxidised by $K_2Cr_2O_7$. Hence, the oxidation number of O increases (from -1 to 0). The oxidation number of Cr decreases from +6 to +3. H_2O_2 oxidises KI to I_2. The oxidation number of O decreases (from -1 to -2). The oxidation number of I increases from -1 to 0.

---

30. The dissociation constant, K_w, for the ionisation of water, $H_2O \rightleftharpoons H^+ + OH^-$, at different temperatures is given below.

temperature/°C	K_w / mol^2 dm^{-6}
0	1.15×10^{-15}
25	1.00×10^{-14}
50	5.50×10^{-14}

What can be deduced from this information?

A Only at 25 °C are $[H^+]$ and $[OH^-]$ equal.

B The equilibrium lies furthest to the right at 0 °C.

C The forward reaction is exothermic.

D The pH of water decreases as temperature increases.

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$$H_2O \rightleftharpoons H^+ + OH^-$$

A: H_2O is neutral at all temperatures where $[H^+]=[OH^-]$.

B,C: Given that at 0 °C, K_w is the smallest, it shows that the equilibrium lies more to the left at 0 °C but more to the right at 50 °C. This also shows that a higher temperature favours dissociation. Hence, the forward reaction is endothermic.

D: At a higher temperature, K_w is higher. This means that $[H^+]=[OH^-]=K_w^{\frac{1}{2}}$ is also higher. Hence, this translates to a lower pH where $pH=-lg[H^+]$.

However, water is still neutral at a higher temperature even though pH is lower than 7 because $[H^+]=[OH^-]$.

Amount of NaCl used $=\dfrac{58.5\times10^3}{23+35.5}=1000$ mol

Therefore,

mass of $Cl_2=\frac{1}{2}\times1000\times71=35500$ g $=35.5$ kg

mass of $H_2=\frac{1}{2}\times1000\times2=1000$ g $=1$ kg

mass of $NaOH=1000\times40=40000$ g $=40$ kg

31. *Use of the Data Booklet is relevant to this question.*

In the commercial electrolysis of brine, the products are chlorine, hydrogen and sodium hydroxide.

What is the maximum yield of each of these products when 58.5 kg of sodium chloride are electrolysed as brine?

	yield of chlorine/kg	yield of hydrogen/kg	yield of sodium hydroxide/kg
A	35.5	1	40
B	35.5	2	40
C	71	1	40
D	71	1	80

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Overall reaction:

$$2NaCl(aq)+2H_2O(\ell)\rightarrow 2NaOH(aq)+H_2(g)+Cl_2(g)$$

32. A current is produced in the following cell.

Pt | Y^{2+}(aq), Y^{3+}(aq) || XO_4^-(aq), X^{2+}(aq), H^+(aq) | Pt

electrode	$E^\ominus$ (298 K)/V
Pt | Y^{3+}(aq), Y^{2+}(aq)	−0.77
Pt | XO_4^-(aq), X^{2+}(aq)	+1.52

When a current is flowing, which one of the following species is oxidised?

A XO_4^-(aq) **B** X^{2+}(aq)

C Y^{3+}(aq) **D** Y^{2+}(aq)

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When a current is produced, it shows that the cell is functioning as a voltaic cell, i.e. $E^\ominus_{cell}>0$.

$\therefore E^\ominus_{cell}=+1.52-(+0.77)$
$=+0.75\text{ V}>0$

In other word,

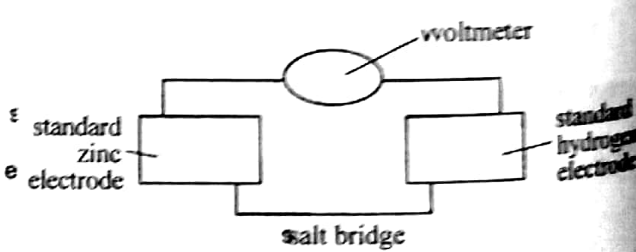
$XO_4^- + 8H^+ + 5e^- \rightarrow X^{2+} + 4H_2O$ (reduction)

$Y^{2+} \rightarrow Y^{3+} + e^-$ (oxidation)

Hence, Y^{2+} is oxidised.

33. *Use of the Data Booklet is relevant to this question.*

The diagram represents an experiment to confirm the value of $E^\ominus$ (Zn^{2+}(aq)/Zn(s)), the standard electrode potential of zinc.



The e.m.f. of the cell was found to be 0.78 V rather than the expected 0.76 V.

Two students, X and Y, suggested possible explanations.

X: $[Zn^{2+}(aq)]$ was greater than 1.00 mol dm^{-3}

Y: $[H^{+}(aq)]$ was greater than 1.00 mol dm^{-3}

Which of their suggestions could be correct?

A both X and Y

B X only

C Y only

D neither X nor Y

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$$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad E^\circ = -0.76\ V$$

$$H^+ + e^- \rightleftharpoons \frac{1}{2}H_2 \qquad E^\circ = 0\ V$$

$$E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{Zn^{2+}/Zn}$$

If $E_{cell} = 0.78$ V,

either $E_{H^+/H_2} > 0$ or/and $E_{Zn^{2+}/Zn} < -0.76$ V.

X: $E_{Zn^{2+}/Zn} > -0.76$ V

Y: $E_{H^+/H_2} > 0$ V

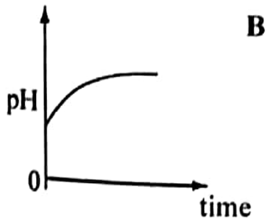
---

34. Sulfur dioxide gas is converted into sulfate ions when it is bubbled into aqueous manganate(VII) ions.

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(\ell)$$

$$SO_2(g) + 2H_2O(\ell) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

Which graph shows how the pH changes as sulfur dioxide is bubbled at a constant rate into a well-stirred solution of manganate(VII) ions until its colour just fades?

A


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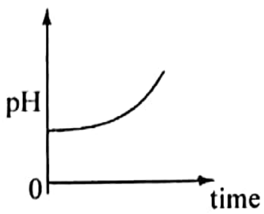

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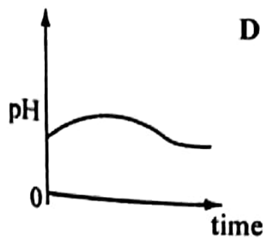
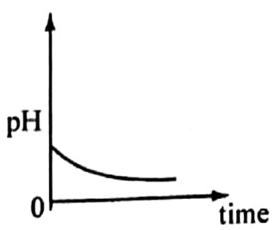


D


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Overall reaction:

$$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

As the reaction proceeds, H^+ is produced. Hence, the pH drops continuously until the end of reaction.

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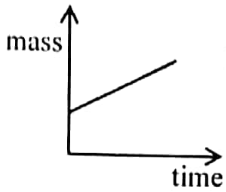
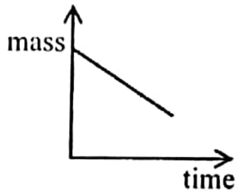
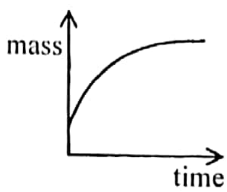
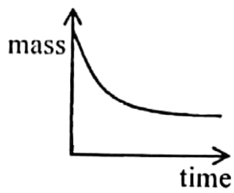
35. Electrolysis of aqueous copper(II) sulfate was carried out using copper electrodes and a steady current.

Which graph shows the change in mass of the cathode with time?

A


B


C


D


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At the cathode, Cu^{2+} migrates there and is reduced to form Cu.

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Hence, the mass of the cathode increases with time.

No. of coulumbs that flows through the electrolyte = current × time

No. of coubumbs that produces 1 mol of Cu atoms
= Faraday constant (F) × charge on the ions
= $2F$

No. of moles of Cu atoms produced

$$= \frac{\text{current} \times \text{time}}{2F}$$

Mass of Cu atoms produced
= no. of moles × molar mass

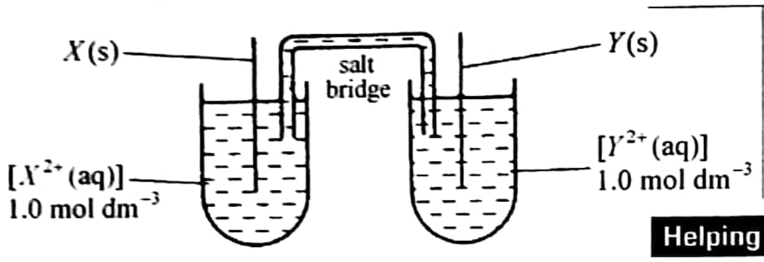
$$= \left(\frac{\text{current} \times \text{time}}{2F} \times 64\right)\ g$$

Since the current is a constant, the mass of copper increases linearly with time.

Standard red. pot.

36. The standard electrode potentials for the metals X and Y are given below.

$$X^{2+}(aq)/X(s) \qquad E^{\ominus} = +0.30\text{ V}$$
$$Y^{2+}(aq)/Y(s) \qquad E^{\ominus} = -0.40\text{ V}$$



The cell shown in the diagram is set up.

Which of the following is a correct description of this cell?

	electrode at which positive ions enter the solution	e.m.f./V
A	X	0.70
B	X	0.75
C	Y	0.10
D	Y	0.70

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$$X^{2+} + 2e^- \rightleftharpoons X \qquad E^{\ominus} = +0.30\text{ V}$$
$$Y^{2+} + 2e^- \rightleftharpoons Y \qquad E^{\ominus} = -0.40\text{ V}$$

Overall reaction:

$$X^{2+}(aq) + Y(s) \rightarrow X(s) + Y^{2+}(aq)$$

$E^{\ominus}_{cell} = +0.30 - (-0.40) = 0.70\text{ V}$

The electrode at which positive ions enter the solution (anode; oxidation) is therefore Y.

37. An acidified solution contains $CaCl_2$, $FeCl_2$ and $MnCl_2$, each of concentration 0.10 mol dm^{-3}. Carbon dioxide is blown through the solution until it is saturated with carbon dioxide at 25 °C. The concentration of CO_3^{2-}(aq) in the solution reaches 1×10^{-9} mol dm^{-3}.

The value of the solubility product of each of the carbonates at 25 °C is given below.

$CaCO_3$	3.8×10^{-9} mol^2 dm^{-6}
$FeCO_3$	3.2×10^{-11} mol^2 dm^{-6}
$MnCO_3$	2.5×10^{-13} mol^2 dm^{-6}

Which statement describes what happens in the solution?

A $CaCO_3$ and $FeCO_3$ only are precipitated.
B $CaCO_3$ only is precipitated.
C $FeCO_3$ and $MnCO_3$ only are precipitated.
D $MnCO_3$ only is precipitated.

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For precipitation to take place, ionic product > K_{sp}.

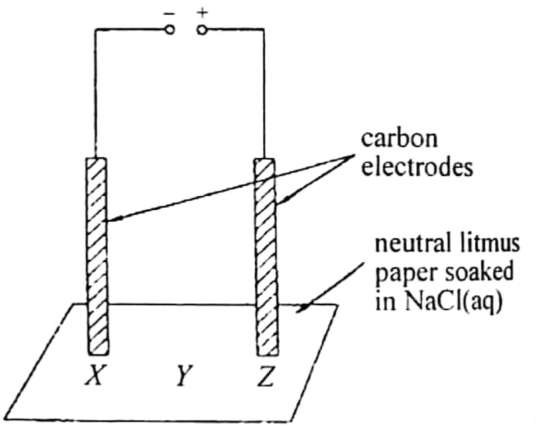
$$MCO_3(s) \rightleftharpoons M^{2+}(aq) + CO_3^{2-}(aq)$$

For the 3 compounds,

$$\text{ionic product} = 0.10 \times 1 \times 10^{-9}$$
$$= 10^{-10}\ (\text{mol dm}^{-3})^2$$

Hence, $FeCO_3$ and $MnCO_3$ are precipitated.

38. A direct current is passed through the apparatus shown in the diagram below.



After a few minutes, what colours would be observed on the paper at the three points, X, Y and Z.

	X	Y	Z
A	red	purple	blue
B	red	white	blue
C	blue	purple	red
D	blue	purple	white

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H^+, Na^+ migrate to X and OH^-, Cl^- migrate to Z. At equilibrium, Y should be neutral, i.e. purple. Discharge of H^+ at X leaves an excess of OH^-, i.e. blue.

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

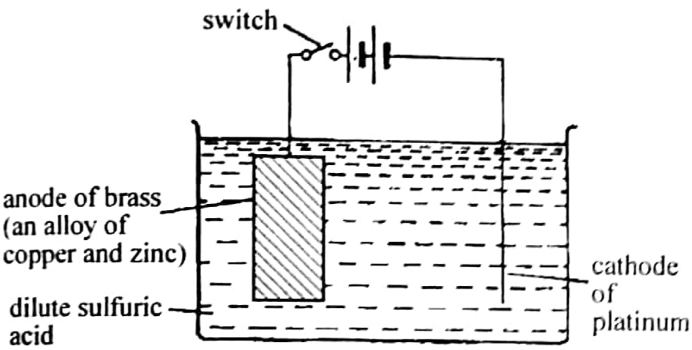
OH^- or Cl^- may be discharged at Z, depending on their concentrations. If Cl^- is discharged, Cl_2 evolved will bleach the litmus, i.e. white.

$$Cl^- \rightarrow \tfrac{1}{2}Cl_2 + e^-$$

If OH^- is discharged, oxygen evolved may also bleach the litmus, i.e. white.

$$2OH^- \rightarrow H_2O + [O] + 2e^-$$

39. The circuit shown in the diagram was set up.



Which electrode reactions will occur on closing the switch?

	anode reaction	*cathode reaction*
A	copper dissolves preferentially	hydrogen is evolved
B	zinc and copper both dissolve	copper is precipitated
C	zinc and copper both dissolve	hydrogen is evolved
D	zinc dissolves preferentially	hydrogen is evolved

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$$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad E^\ominus = -0.76\ V$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\ominus = +0.34\ V$$

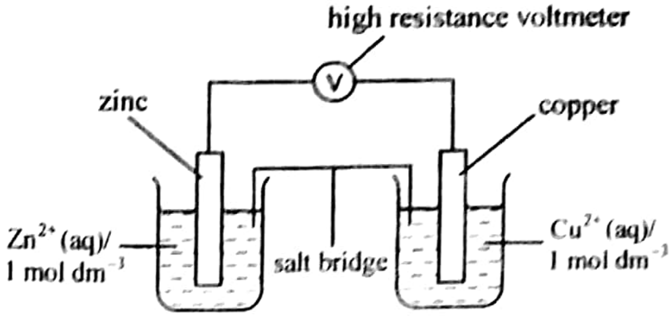
At the anode, Zn is oxidised since Zn^{2+}/Zn has a more negative reduction potential (i.e. the backward reaction has a greater tendency to take place). Hence, Zn dissolves.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

At the cathode, H^+, being the only cation, is discharged to give H_2 gas.

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

40. A student set up the cell shown.



The following values for the cell potential were determined as a change was continuously made.

reading number	cell potential/V
1	1.100
2	1.090
3	1.081
4	1.074
5	1.064

What continuous change in the copper half-cell could produce these results?

A add a reagent to the solution that complexes with $Cu^{2+}(aq)$

B increase the concentration of $Cu^{2+}(aq)$

C increase the surface area of copper immersed in the solution

D increase the surface area of the salt bridge immersed in the solution

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$$E^\ominus_{cell} = E^\ominus_{Cu^{2+}/Cu} - E^\ominus_{Zn^{2+}/Zn}$$

When $E^\ominus_{Cu^{2+}/Cu}$ decreases or $E^\ominus_{Zn^{2+}/Zn}$ increases, $E^\ominus_{cell}$ drops. This can be done by either increasing $[Zn^{2+}]$ or decreasing $[Cu^{2+}]$.

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\ominus_{Cu^{2+}/Cu} = +0.34\ V$$

$$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad E^\ominus_{Zn^{2+}/Zn} = -0.76\ V$$

When a complexing agent is added to Cu^{2+}, it forms a complex with Cu^{2+} and hence decreases $[Cu^{2+}]$.

41. Two separate electrolyses were performed as follows, under the same conditions of temperature and pressure.

1 When molten copper(II) chloride was electrolysed for five minutes, 100 cm^3 of chlorine were collected from the anode.

2 When aqueous sulfuric acid was electrolysed for five minutes, 200 cm^3 of oxygen were collected from the anode.

If the current used in electrolysis 1 was I, what was the current used in electrolysis 2?

A $0.5I$ **B** I

C $2I$ **D** $4I$

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1. $$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$$

$$n_{e^-} = 2 \times n_{Cl_2} = \frac{2V_{Cl_2}}{V_m}$$

$$I_1 t = Q = n_{e^-} \times F$$

$$I_1 = \frac{2V_{Cl_2} \times F}{V_m \times t}$$

2. $$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

$$n_{e^-} = 4 \times n_{O_2} = \frac{4V_{O_2}}{V_m}$$

$$I_2 t = Q = n_{e^-} \times F$$

$$I_2 = \frac{4V_{O_2} \times F}{V_m t}$$

Since $V_{O_2} = 2 \times V_{Cl_2}$,

$$I_2 = \frac{8V_{Cl_2} \times F}{V_m \times t} = 4I_1$$

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

42. What are the conditions usually quoted for the standard electrode potential of hydrogen to be 0.00 V?

1 The concentration of $H^+(aq)$ is 1 mol dm^{-3}.

2 The temperature is 0 °C. V. Imp

3 The atmospheric pressure is exactly 1 atm.

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The conditions are

$$[H^+] = 1 \text{ mol dm}^{-3};$$
$$T = 25\ °C \text{ or } 298\text{ K};$$
$$p_{H_2} = 1 \text{ atm (not atmospheric pressure).}$$

---

43. Which conditions are necessary when an electrode potential is measured using a standard hydrogen electrode as the reference electrode?

1 the use of hydrogen gas at 101 kPa (1 atm)

2 measurement of the e.m.f. when the current delivered by the cell is effectively zero

3 a pH of 1.0 for the solution at the hydrogen electrode

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The conditions are

$$p_{H_2} = 101 \text{ kPa or 1 atm};$$
$$[H^+] = 1 \text{ mol dm}^{-3} \text{ or pH} = 0;$$
$$T = 298 \text{ K or } 25\ °C.$$

The e.m.f. measured should be when the current = 0.

When there is a current flow, the system suffers a drop in potential due to internal resistance.

---

44. Sodium reacts with ammonia to give hydrogen and sodamide which is ionic.

0 −3 +1 −3 +1 0

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$

Which changes in oxidation number of the three elements involved occur?

1 −3 to −2

2 0 to +1

3 +1 to 0

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Na: 0 to +1

H: +1 to 0 (in H_2)

N: no change

---

45. An aqueous copper(II) salt is electrolysed between copper electrodes, using a constant current. What affects the mass of copper deposited on the cathode?

1 the time taken

2 the concentration of the solution

3 the nature of the anion present

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$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
$$Q = It$$

The amount of electronic charges used depends on the time taken for the current to flow. The longer the time, the greater the electronic charges and hence the greater the amount of Cu deposited.

The concentration of the solution and the nature of the anion present have no effect on the mass of Cu deposited.

---

46. The standard potential for the electrode reaction represented by the equation

$$Pb^{4+}(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq)$$

is +1.69 V. What may be deduced from this information alone?

1 Lead(IV) compounds can act as oxidising agents.

2 Lead is more stable in the +2 than in the +4 oxidation state.

3 $Pb(SO_4)_2$ will not exist.

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*1,*2. From the positive value of E°, it may be inferred that Pb^{4+} is readily reduced to Pb^{2+}. Hence, Pb^{4+} can act as an oxidising agent and it is less stable than Pb^{2+}.

3. The stability of $Pb(SO_4)_2$ cannot be deduced from the given information.

---

47. Which of the following statements are true for a standard cell set up using the half-cells below?

$Ni^{2+}(aq)/Ni(s)$ $\quad E^\circ = -0.25$ V

$Sn^{2+}(aq)/Sn(s)$ $\quad E^\circ = -0.14$ V

1 Electrons flow in the external circuit from Ni to Sn.

2 The concentration of $Sn^{2+}(aq)$ will decrease.

3 Oxidation occurs at the Ni terminal.

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Overall reaction:

$$Ni(s) + Sn^{2+}(aq) \rightarrow Ni^{2+}(aq) + Sn(s)$$

$$E^\circ_{cell} = -0.14 - (-0.25) = +0.11 \text{ V}$$

*1,*3. Ni is oxidised to Ni^{2+} ($Ni \rightarrow Ni^{2+} + 2e^-$) and the electrons released flow from Ni to Sn through the external circuit.

*2. As more and more Sn^{2+} are reduced, its concentration decreases.

---

48. The equation for a reaction is shown below.

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

Which of the following statements about this reaction are correct?

1 Hydrogen peroxide is oxidised to oxygen.

2 Hydrogen ions are oxidised to water.

3 The oxidation number of manganese changes by 6.

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$$2\underset{+7}{Mn}O_4^- + 5H_2\underset{-1}{O_2} + 6H^+ \rightarrow 2\underset{+2}{Mn}^{2+} + 8H_2\underset{-2}{O} + 5\underset{0}{O_2}$$

The oxidation state of Mn decreases by 5 (from +7 to +2), i.e. Mn is reduced. Henceforth, O is oxidised and its oxidation state should increase, i.e. from −1 to 0; and H_2O_2 is oxidised to O_2. H is not involved in the redox since its oxidation state **does not change.**

---

49. Which statements about the reaction given are correct?

$$IO_3^-(aq) + 2I^-(aq) + 6H^+(aq) + 6Cl^-(aq) \rightarrow 3ICl_2^-(aq) + 3H_2O(\ell)$$

1 The oxidation number of the iodine in the iodate ion, $IO_3^-(aq)$, changes from +5 to +1.

2 The oxidation number of the iodine in the iodide ion, $I^-(aq)$, changes from −1 to +2.

3 The oxidation number of chlorine changes from −1 to −2.

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*1,2. In the reaction, IO_3^- (O.S. = +5) is reduced by I^- (O.S. = −1) to ICl_2^- (O.S. = +1). I^- is oxidised to the same product, ICl_2^-.

3. Cl^- is not oxidised or reduced.

---

50. A 1 mol dm^{-3} aqueous copper(II) salt is electrolysed between copper electrodes, using a constant current for 60 s.

What affects the mass of copper deposited on the cathode?

1 decreasing the time taken

2 increasing the concentration of the solution

3 the nature of the anion present

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$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$m_{Cu} = n_{Cu} \times M_{Cu}$$
$$= 2 \times n_e \times M_{Cu}$$
$$= 2 \times \frac{Q}{F} \times M_{Cu}$$
$$= 2 \times \frac{It}{F} \times M_{Cu}$$

[M_{Cu} = molar mass of Cu; Q = quantity of electricity; $F = 96500$ C mol^{-1}]

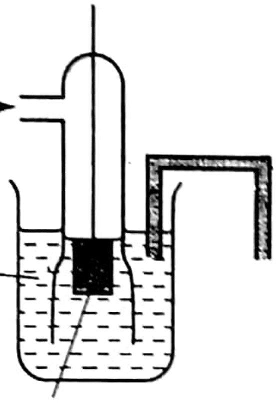
Hence, the mass of Cu deposited will depend on the current (I), time duration of electrolysis (t).

3. There is no information to suggest that Au is a d-block element (although it is!).

---

51. In the diagram of the standard hydrogen electrode below, which labels are **not** correct?

1 H_2(g) at 101 kPa and 273 K



2 1.0 mol dm^{-3} H_2SO_4

3 platinum foil coated with finely divided platinum

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*1. T is 298 K.

*2. $[H^+] = 1$ mol dm^{-3}

Hence, $[H_2SO_4]$ should be 0.5 mol dm^{-3}.

---

52. The discharge at the cathode of 1.00 mol of gold ions from an aqueous solution of a gold salt requires 2.90×10^5 C of electricity.

Which of the following conclusions can be drawn from these observations?

1 The gold ions are positively charged.

2 The magnitude of the charge on the gold ions is three times the electronic charge.

3 Gold is a d-block (transition) element.

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*1. Cations migrate to cathode and are reduced.

$$Au^{n+} + ne^- \rightarrow Au$$

*2. 1 mol of electrons carries 96500 C of charge. In 2.90×10^5 C of electricity, there are $\frac{2.90 \times 10^5}{96500} = 3$ mol of electrons. Since 1 mol of gold ions take in 3 mol of electrons, the magnitude of the charge is 3 times that of the electronic charge.

i.e. $Au^{3+} + 3e^- \rightarrow Au$

---

53. *Use of the Data Booklet is relevant to this question.*

When 193 C of electricity are passed through a molten compound of a metal, 1.00×10^{-3} mol of atoms of the metal is deposited at the cathode.

What could the metal be?

1 copper

2 lead

3 silver

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Amount of electrons passed $= \frac{193}{9.65 \times 10^4}$

$= 2 \times 10^{-3}$ mol

$$M^{n+} + ne^- \rightarrow M$$

1×10^{-3} mol of M^{n+} require 2×10^{-3} mol of electrons.

Therefore, 1 mol of M^{n+} require 2 mol of electrons.

Hence, $n = 2$.

∴ The metal could be Cu(Cu^{2+}) and Pb(Pb^{2+}), but not Ag(Ag^+).

---

54. Pain is often felt when a piece of aluminium foil touches a dental amalgam filling in a tooth because an electric current momentarily flows. The amalgam contains tin. The standard electrode potentials are as follows.

Al^{3+}(aq)/Al(s)	$E^\circ = -1.66$ V
Sn^{2+}(aq)/amalgam	$E^\circ = -0.13$ V

Which of the following are features of the cell obtained?

1 The aluminium foil acts as the negative electrode.

2 Sn^{2+} ions are momentarily discharged into the saliva in the mouth.

3 The e.m.f. of the cell is +1.79 V.

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Overall reaction:

$$2Al(s) + 3Sn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Sn\ (amalgam)$$

$$E^\circ_{cell} = -0.13 - (-1.66) = +1.53\ V$$

*1. Al is oxidised, liberating electrons.

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$$

Hence, Al acts as the negative electrode (anode).

2,3. Sn^{2+} are discharged into the amalgam and $E^\circ_{cell} = +1.53$ V.

---

55. In a fuel cell in which ethanol comes into contact with fresh air on the surface of a catalyst, the reactions taking place at the two electrodes are as follows.

electrode 1:

$$CH_3CH_2OH(\ell) + H_2O(\ell) \rightleftharpoons CH_3CO_2H(\ell) + 4H^+(aq) + 4e^-$$

electrode 2:

$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(\ell)$$

Which statement is correct?

1 The electrode potential of electrode 1 becomes more negative as the concentration of ethanol increases.

2 Hydrogen is reduced at electrode 2.

3 Oxygen is reduced at both electrodes.

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The overall reaction is the oxidation of ethanol to form CH_3CO_2H.

*1. The electrode potential of electrode 1 measures that of the reverse reaction (reduction). When $[C_2H_5OH]$ increases, oxidation of C_2H_5OH becomes more readily, but the reduction of CH_3CO_2H becomes more difficult. Hence, the electrode potential decreases.

2. At electrode 2, hydrogen is not involved in redox reaction.

3. At both electrodes, oxygen is not involved in redox reaction.

---

56. *Use of the Data Booklet is relevant to this question.*

The cell shown below is set up under standard conditions.

$$Cr(s) \mid Cr^{3+}(aq) \mid Fe^{2+}(aq) \mid Fe(s)$$

Which statements are true for this cell?

1 The e.m.f. of the cell is 0.30 V.

2 If the electrodes are connected by a piece of wire, iron will be deposited.

3 If the electrodes are connected by a piece of wire, electrodes will flow through the wire from chromium to iron.

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$$Cr^{3+} + 3e^- \rightleftharpoons Cr \qquad E^\ominus = -0.74 \text{ V}$$

$$Fe^{2+} + 2e^- \rightleftharpoons Fe \qquad E^\ominus = -0.44 \text{ V}$$

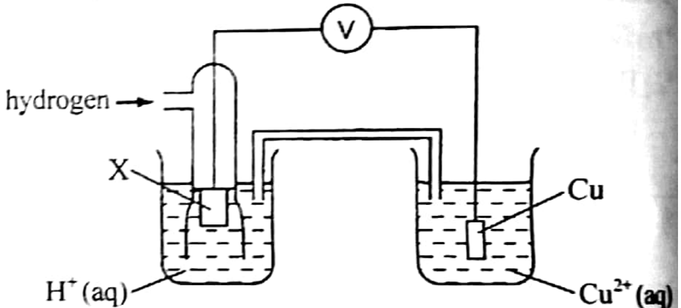
*1. $E^\ominus_{cell} = -0.44 - (-0.74) = +0.30$ V

*2. At the cathode, $Fe^{2+} + 2e^- \rightarrow Fe$. Hence, Fe will be deposited.

*3. At the Cr anode, Cr loses electrons. Hence, electrons flow from Cr to Fe is the external circuit.

---

57. The diagram shows apparatus that can be used to measure the standard electrode potential of copper, $E^\ominus$.



Which factors are essential for an accurate $E^\ominus$ to be measured?

1 The hydrogen should be dry.

2 The $Cu^{2+}(aq)$ should be at a concentration of 1.0 mol dm^{-3}.

3 The electrode X should be made of platinum.

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For a standard hydrogen electrode,

electrode = Pt;
$p_{H_2} = 1$ atm;
$[H^+] = 1$ mol dm^{-3};
$T = 25$ °C.

For the Cu^{2+}/Cu half cell,

electrode = Cu;
$[Cu^{2+}] = 1$ mol dm^{-3};
$T = 25$ °C;

1. H_2 will be moist since there is aqueous H^+ in the system.

---

58. 1.0 mol dm^{-3} aqueous solutions of three elements in Group VII of the Periodic Table have standard electrode potentials as follows.

$$X_2(aq) + 2e^- \rightleftharpoons 2X^-(aq) \quad +1.36\text{ V}$$
$$Y_2(aq) + 2e^- \rightleftharpoons 2Y^-(aq) \quad +1.07\text{ V}$$
$$Z_2(aq) + 2e^- \rightleftharpoons 2Z^-(aq) \quad +0.54\text{ V}$$

Which statements are correct?

1 There is an increase in oxidising power in the sequence X_2, Y_2, Z_2.

2 There is an increase in reducing power in the sequence X^-, Y^-, Z^-.

3 The reaction
$2Z^-(aq)+Y_2(aq) \rightarrow Z_2(aq)+2Y^-(aq)$ occurs.

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1,*2. The higher the $E^\ominus$, the greater the tendency for the forward reaction to take place. Hence, X_2 has the greatest tendency to undergo reduction. It is the strongest O.A.
Conversely, Z^- has the highest tendency to undergo oxidation (backward reaction) and Z^- is the strongest R.A.

*3. $E^\ominus_{cell} = +1.07 - 0.54$
$= +0.53\text{ V} > 0$
The reaction is energetically feasible.

---

59. Some standard redox potentials are given below.

$$\tfrac{1}{2}Br_2 + e^- \rightleftharpoons Br^- \quad +1.07\text{ V}$$
$$\tfrac{1}{2}Cr_2O_7^{2-} + 7H^+ + 3e^- \rightleftharpoons Cr^{3+} + \tfrac{7}{2}H_2O \quad +1.33\text{ V}$$
$$\tfrac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^- \quad +1.36\text{ V}$$
$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \quad +1.52\text{ V}$$

Which of the following statements are correct under standard conditions?

1 Bromine will oxidise chloride ions to chlorine.

2 Manganate(VII) ions in acid solution will oxidise chloride ions to chlorine.

3 Manganate(VII) ions in acid solution will oxidise chromium(III) ions to dichromate(VI) ions.

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1. $Br_2 + 2Cl^- \rightarrow 2Br^- + Cl_2$
$E^\ominus_{cell} = +1.07 - 1.36 = -0.29\text{ V} < 0$

*2. $2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$
$E^\ominus_{cell} = +1.52 - 1.36 = +0.16\text{ V} > 0$

*3. $6MnO_4^- + 10Cr^{3+} + 11H_2O$
$\rightarrow 6Mn^{2+} + 5Cr_2O_7^{2-} + 22H^+$
$E^\ominus_{cell} = +1.52 - 1.33 = +0.19\text{ V} > 0$

---

60. A titration is carried out between 0.05 mol dm^{-3} potassium manganate(VII) in alkaline solution and 0.05 mol dm^{-3} potassium methanoate. The following reaction occurs.

$$2KMnO_4 + 3KOH + HCO_2K$$
$$\rightarrow 2K_2MnO_4 + K_2CO_3 + 2H_2O$$

Which of the following statements are correct about this reaction?

1 The potassium methanoate acts as a reducing agent.

2 The volume of aqueous potassium methanoate solution required is half that of the aqueous potassium manganate(VII).

3 The oxidation number of the manganese is increased by one unit.

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$$2KMnO_4 + 3KOH + \underset{+2}{HCO_2K}$$
$$\rightarrow \underset{+6}{2K_2MnO_4} + \underset{+4}{K_2CO_3} + 2H_2O$$

*1. The oxidation state of C increases from +2 to +4. Therefore, HCO_2K acts as a reducing agent.
Alternatively, a half equation may be constructed to see that HCO_2^- is a reducing agent.
$$HCO_2^- + 3OH^- \rightarrow CO_3^{2-} + 2H_2O + 2e^-$$

*2. Let V be the volume of $KMnO_4$ used.
Amount of $KMnO_4$ = concentration × volume
$= 0.05\text{ mol dm}^{-3} \times V\text{ dm}^3$
$= 0.05V$ mol

Amount of $HCO_2K = (\tfrac{1}{2} \times 0.05V)$ mol

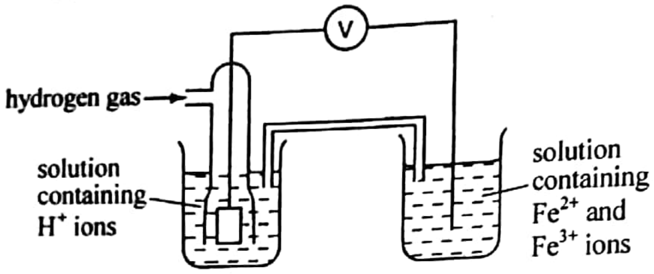
Volume of $HCO_2K = \dfrac{\text{amount}}{\text{concentration}}$
$= \dfrac{(\tfrac{1}{2} \times 0.05V)\text{ mol}}{0.05\text{ mol dm}^{-3}}$
$= \tfrac{1}{2}V\text{ dm}^3$

3. The oxidation state of Mn is decreased (Not increased) by 1 unit, i.e. from +7 to +6.

---

61. *Use of the Data Booklet is relevant to this question.*

The diagram shows a cell set up under standard conditions.



Which statements are correct?

1 $E^{\ominus}_{cell} = 0.77$ V

2 The left hand electrode is the negative electrode.

3 The right hand solution contains 0.5 mol dm^{-3} Fe^{2+} ions and 0.33 mol dm^{-3} Fe^{3+} ions.

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*1. $E^{\ominus}(Fe^{3+}/Fe^{2+}) = +0.77$ V

Hence, $E^{\ominus}_{cell} = +0.77 - 0 = +0.77$ V.

*2 The half reactions taking place are

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

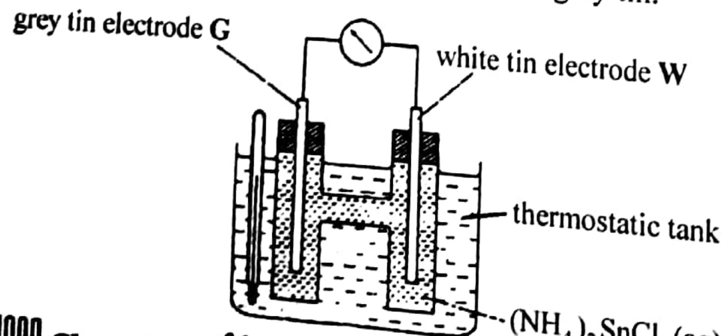
$$\tfrac{1}{2}H_2 \rightarrow H^+ + e^-$$

The left electrode is the anode and is the negative electrode (where electrons flow from it to the other electrode in the external circuit).

3. The concentrations for both ions should be 1 mol dm^{-3}.

---

62. The diagram shows an apparatus to find the transition temperature (18 °C) at which white and grey tin are in equilibrium. Below 18 °C, white tin dissolves from **W** and is deposited on **G** as grey tin.



Which of the following statements are correct?

1 The stable form of tin at 25 °C is grey.

2 Below 18 °C, electrons flow through the external circuit from **W** to **G**.

3 At 18 °C, no current flows.

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$$\underset{\text{white}}{Sn} \underset{>18\,°C}{\overset{<18\,°C}{\rightleftharpoons}} \underset{\text{grey}}{Sn}$$

1. Since below the transition temperature (18 °C), white Sn dissolves, it is less stable. Hence, above 18 °C, grey Sn will be less stable.

*2. Below 18 °C, white Sn dissolves.

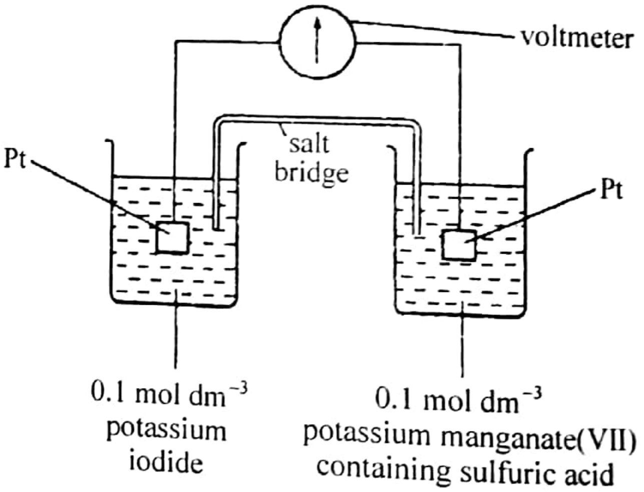
$$\underset{\text{white}}{Sn} \rightarrow Sn^{2+} + 2e^-$$

Therefore, electrons flow from **W** to **G** in the external circuit.

*3. At 18 °C, both are in thermodynamic equilibrium. Hence, there is no current flow.

---

63. A cell involving aqueous potassium iodide and acidified potassium manganate(VII) is shown.



electrode	$E^{\ominus}$ / V
Pt | $\tfrac{1}{2}I_2$(aq), I^-(aq)	+0.54
Pt | MnO_4^-(aq), Mn^{2+}(aq)	+1.52

Which observations about this arrangement are correct?

1 The $E^{\ominus}$ for this cell is 2.06 V.

2 The potassium iodide solution turns brown.

3 The purple colour of the potassium manganate(VII) solution becomes less intense.

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$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \quad E^\ominus = +1.52\ V$

$I_2 + 2e^- \rightleftharpoons 2I^- \quad E^\ominus = +0.54\ V$

Overall reaction:

$2MnO_4^- + 16H^+ + 10I^- \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$

1. $E^\ominus_{cell} = +1.52 - (+0.54) = +0.98\ V$

*2. As the reaction proceeds, I_2 is formed. Hence, a brown colour is observed.

*3. As MnO_4^- is consumed, the purple colour intensity decreases.

TOPIC 7

Equilibria

Key content that you will be examined on:

1. Chemical equilibria: reversible reactions; dynamic equilibrium
   - (i) Factors affecting chemical equilibria
   - (ii) Equilibrium constants
   - (iii) The Haber process
2. Ionic equilibria
   - (i) Brønsted-Lowry theory of acids and bases
   - (ii) Acid dissociation constants, K_a and the use of pK_a
   - (iii) Base dissociation constants, K_b and the use of pK_b
   - (iv) The ionic product of water, K_w
   - (v) pH: choice of pH indicators
   - (vi) Buffer solutions
   - (vii) Solubility product; the common ion effect

Topic 7

Equilibria

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which expression represents the solubility product of lead(II) chloride?

A $[Pb^{2+}][Cl^-]^2$ B $[Pb^{2+}][2Cl^-]$

C $[Pb^{2+}][2Cl^-]^2$ D $\frac{[Pb^{2+}][Cl^-]^2}{[PbCl_2]}$

Helping Concepts *Exam Favourite Rating* ★★★

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_{sp} = [Pb^{2+}(aq)][Cl^-(aq)]^2$$

---

2. For which equilibrium does K_c have no units?

A $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

B $CH_3OH(\ell) + CH_3CO_2H(\ell) \rightleftharpoons CH_3CO_2CH_3(\ell) + H_2O(\ell)$

C $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$

D $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Helping Concepts *Exam Favourite Rating* ★★★

$$K_c = \frac{[CH_3CO_2CH_3][H_2O]}{[CH_3OH][CH_3CO_2H]}$$

This reaction is **not** carried out in aqueous solution. Hence, H_2O is not in large excess and the $[H_2O]$ term cannot be ignored. The units for options (A), (C) and (D) are mol dm^{-3}, (mol dm^{-3})$^{-4}$ and mol dm^{-3} respectively.

---

3. Which system does the equilibrium constant, K_c, have units of (concentration)$^{-1}$?

A $H_2 + I_2 \rightleftharpoons 2HI$

B $H_2O + CH_3CO_2C_2H_5 \rightleftharpoons C_2H_5OH + CH_3CO_2H$

C $2NO_2 \rightleftharpoons N_2O_4$

D $CH_4 + H_2O \rightleftharpoons CO + 3H_2$

Helping Concepts *Exam Favourite Rating* ★★★

$$K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

(A) and (B) have no units while (D) has units of (concentration)^2.

---

4. The pH human blood is constant at about 7.40.

Which ion or molecule present in the human body will remove contaminating $H^+(aq)$ ions from the blood to keep the pH constant?

A CO_3^{2-} B HCO_3^-

C H_2CO_3 D PO_4^{3-}

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In blood,

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

HCO_3^- reacts with excess H^+ and hence maintain a constant pH in blood.

---

5. When the system $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is in equilibrium at 444 °C, at 1 atm pressure, the value of the equilibrium constant, K_p, is 50.

What is the value of K_p at a pressure of 2 atm at the same temperature?

A 25 B 50

C 100 D 200

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K_p is affected only by a change in temperature and remains constant if temperature is kept constant.

6. A 1 dm^3 solution was made by mixing 0.0040 mol of HCl(aq) and 0.0025 mol of NaOH(aq).

What was the pH of the resulting solution?

A 2.19
B 2.40
C 2.60
D 2.82

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$$NaOH + HCl \rightarrow NaCl + H_2O$$

At the end of the reaction, there is an excess of 0.0015 mol HCl.

Hence, $[H^+] = \frac{0.0015}{1} = 1.5 \times 10^{-3}$ mol dm^{-3}

$\therefore$ pH $= -\lg[H^+] = 2.82$

---

7. 10 cm^3 of a 0.01 mol dm^{-3} solution of nitric acid is diluted with 90 cm^3 of water.

What is the pH of the resulting solution?

A 1
B 2
C 3
D 4

Helping Concepts *Exam Favourite Rating* ★★★

$$HNO_3 \rightarrow H^+ + NO_3^-$$

$n_{H^+} = \frac{10}{1000} \times 0.01 = 10^{-4}$ mol

$[H^+] = \frac{10^{-4}}{\frac{100}{1000}} = 10^{-3}$ mol dm^{-3}

pH $= -\lg(10^{-3}) = 3$

---

8. Hydrogen and iodine vapour exist in equilibrium with hydrogen iodide at a constant temperature in a gas syringe.

$$H_2 + I_2 \rightleftharpoons 2HI$$

Which of the following will increase when the pressure is increased at constant temperature? [Assume that the mixture shows ideal behaviour.]

A the energy of activation
B the enthalpy change
C the partial pressure of hydrogen iodide
D the rate constant for the forward reaction

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When the pressure is increased at constant temperature, the partial pressures of H_2, I_2 and HI increase, and vice versa. (A), (B) and (D) are not affected.

---

9. Which one of the following statements is correct about a reaction for which the equilibrium constant is independent of temperature?

A The activation energies for both forward and reverse reactions are zero.
B The enthalpy change is zero.
C Its rate constants do not vary with temperature.
D There are equal numbers of moles of reactants and products.

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When the enthalpy change is zero, changing temperature will not shift the equilibrium. Hence, the equilibrium constant remains unaffected.

---

10. Why is ethanoic acid a stronger acid in liquid ammonia than in aqueous solution?

A Ammonia is a stronger base than water.
B Ammonium ethanoate is completely ionised in aqueous solution.
C Ammonium ethanoate is strongly acidic in aqueous solution.
D Liquid ammonia is a more polar solvent than water.

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NH_3 is a stronger base than water. It has a graeter tendency to deprotonate CH_3CO_2H. Hence, more CH_3CO_2H will ionise and therefore, it is a stronger acid in liquid NH_3.

---

11. Which one of the following acid solutions can be used to give an effective buffer solution at a pH < 7 by partial neutralisation with aqueous NaOH?

A 0.01 mol dm^{-3} CH_3CO_2H
B 0.1 mol dm^{-3} HI

C 0.01 mol dm^{-3} HCl

D 0.0001 mol dm^{-3} H_2S

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A buffer with pH < 7 contains a mixture of a weak acid and its salt. Thus, a weak acid is required. An excess of the acid converts NaOH to its salt. Together with the excess acid, a buffer would result. However, the concentrations of the acid and the salt must not be too small so as to maintain a sufficiently large reservoir of both the species (effective buffer). This rules out (D). Furthermore, H_2S is more volatile than CH_3CO_2H to be used.

---

12. The pH of a 1.0 mol dm^{-3} solution of a weak monobasic acid is 4. What is the dissociation constant of the weak acid?

A 1.0×10^{-2} mol dm^{-3} pH=pK$_B$+

B 1.0×10^{-4} mol dm^{-3}

C 1.0×10^{-7} mol dm^{-3}

D 1.0×10^{-8} mol dm^{-3}

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	HA	$\rightleftharpoons$	H^+	+ A^-
initial conc/mol dm^{-3}	1		0	0
conc at eqm/mol dm^{-3}	$1-a$		a	a

$$K_a = \frac{a^2}{1-a} \approx a^2 \text{ (for small } a,\ 1-a \approx 1)$$
$$= (10^{-4})^2$$
$$= 1.0 \times 10^{-8} \text{ mol dm}^{-3}$$

---

13. Which one of the following is a correct statement about the effect of a catalyst.

A It increases the rate constant for the forward reaction but not that of the back reaction.

B It increases the yield of product in an equilibrium.

C It increases the speed of the reactant particles and therefore the rate of molecular collision.

D It provides an alternative route for a reaction.

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A catalyst provides an alternative route for a reaction to take place with a lower activation energy so that the speed of the reaction is increased.

A: It increases both the forward and backward rate constants to the same extent.

B: The yield is not affected.

C: The average molecular speed is not affected. It is only affected by a change in temperature.

---

14. A gas X dissociates on heating to set up the equilibrium below.

$$X(g) \rightleftharpoons Y(g) + Z(g)$$

A quantity of X was heated at constant pressure p at a certain temperature. The equilibrium partial pressure of X was found to be $\frac{1}{7}p$. What is the equilibrium constant K_p, at this temperaure?

A $\frac{6}{7}p$ B $\frac{9}{7}p$

C $\frac{36}{7}p$ D $6p$

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Let x be the partial pressure of y at equilibrium. Therefore, the partial pressure of z at equilibrium is also x since from the stoichiometry of the equation, equal amounts of y and z ere formed.

Hence, total presure, $p = \frac{1}{7}p + x + x$

$$x = \frac{3}{7}p$$

$$\therefore K_p = \frac{p_Y \cdot p_Z}{p_X} = \frac{(\frac{3}{7}p)(\frac{3}{7}p)}{\frac{1}{7}p} = \frac{9}{7}p$$

---

15. When $SOCl_2$ is added to $Ba(OH)_2$, a vigorous reaction occurs and the temperature falls from 25 °C to 0 °C.

What are the correct signs of ΔG and ΔS in this reaction?

	ΔG	ΔS
A	−	−
B	−	+
C	+	−
D	+	+

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Since the reaction is spontaneous, $\Delta G < 0$.
Given that T decreases, $\Delta H > 0$ (i.e. endothermic)

$$\Delta G = \Delta H - T\Delta S$$

Since $\Delta G < 0$ and $\Delta H > 0$, ΔS must be positive.

---

16. When vanadium(II) compounds are dissolved in water, the following equilibrium is established.

$$V^{2+} + H_2O \rightleftharpoons V^{3+} + \tfrac{1}{2}H_2 + OH^-$$

What would alter the composition of the equilibrium mixture in favour of the V^{2+} ions?

A adding an acid
B adding a reagent that selectively precipitates V^{3+} ions
C allowing the hydrogen to escape as it forms
D making the solution more alkaline

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Making the solution alkaline would increase $[OH^-]$. By Le Chatelier's principle, the equilibrium would shift to the left. Hence, $[V^{2+}]$ increases.

---

17. In the mixture of NO and CO_2 (initially containing 4 mol of NO and 0.9 mol of CO_2) reaction occurs according to the equation below.

$$NO(g) + CO_2(g) \rightleftharpoons NO_2(g) + CO(g)$$

At equilibrium, 0.1 mol of CO_2 was present. What is the equilibrium constant, K_c, at the temperature of this experiment?

A 0.2   **B** 0.5
C 1.6   **D** 2.0

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	$NO(g)$	$+CO_2(g)$	$\rightleftharpoons NO_2(g)$	$+CO(g)$
Initial amt/mol	4	0.9	0	0
Eqm amt/mol	3.2	0.1	0.8	0.8

$$K_c = \frac{[NO_2(g)][CO(g)]}{[NO(g)][CO_2(g)]} = \frac{(\frac{0.8}{V})(\frac{0.8}{V})}{(\frac{3.2}{V})(\frac{0.1}{V})} = 2.0$$

---

18. Soft drinks often have sodium citrate added to them to act as a buffer.

Which statement about buffer solutions is correct?

A The pH of a buffer solution changes slightly when very large amounts of acid or base are added.
B The pH of a buffer solution increases very slightly when small amounts of acid are added.
C The pH of a buffer solution increases very slightly when small amounts of base are added.
D The pH of a buffer solution remains unchanged when small amounts of acid or base are added.

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A buffer solution has the ability to resist pH changes when a little acid or alkali is added to it.

In this case, the buffer contains citrate (A^-) and citric acid (HA). When a little acid is added, A^- reacts with H^+ and remove the acidity. When a little alkali is added, HA reacts with OH^- and remove the alkalinity.

---

19. An equilibrium can be represented by the following equation.

$$P(aq) + Q(aq) \rightleftharpoons 2R(aq) + S(aq)$$

In a certain mixture, the equilibrium concentration of Q is 10 mol dm^{-3}.

What will be the new equilibrium concentration of Q if 5 mol of pure Q is dissolved in the mixture?

A 15 mol dm^{-3}
B between 10 mol dm^{-3} and 15 mol dm^{-3}
C 10 mol dm^{-3}
D between 5 mol dm^{-3} and 10 mol dm^{-3}

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When 5 moles of pure Q is added, the concentration of Q increases, i.e. more than 10 mol dm^{-3}. However, by Le Chatelier's principle, the equilibrium will shift to the right so as to reduce the change that is imposed onto the system. In doing so, the concentration of Q will be reduced, i.e. less than 15 mol dm^{-3}.

20. The dissociation of dinitrogen tetraoxide into nitrogen dioxide is represented by the equation below.

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H^{\circ} = +57.2 \text{ kJ mol}^{-1}$

If the temperature of an equilibrium mixture of the gases is increased at constant pressure, the volume of the mixture will

A increase, but only because of a shift of equilibrium towards the right.

B increase, both because of a shift of equilibrium towards the right and also because of thermal expansion.

C stay the same, because any thermal expansion could be exactly counteracted by a shift of equilibrium towards the left.

D decrease, because a shift of equilibrium towards the left would more than counteract any thermal expansion.

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Since the forward reaction is endothermic, an increase in temperature shifts the equilibrium to the right according to Le Chatelier's principle, by absorbing the excess heat. In this case, more gas particles are produced and there is an increase in volume. Furthermore, heating will also cause the gases to expand.

---

22. Stomach juices have a pH of 1.0.

Aspirin is a monobasic (monoprotic) acid represented by HA ($K_a = 1 \times 10^{-4}$ mol dm^{-3}) which dissociates into ions H^+ and A^-.

What are the relative concentration of H^+, A^- and HA when aspirin from a tablet enters the stomach?

A $[HA] > [H^+] = [A^-]$

B $[H^+] = [A^-] > [HA]$

C $[H^+] > [A^-] > [HA]$

D $[H^+] > [HA] > [A^-]$

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$$HA \rightleftharpoons H^+ + A^- \qquad K_a = 10^{-4} \text{ mol dm}^{-3}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

At pH = 1,

$$[H^+] = 10^{-1} \text{ mol dm}^{-3}$$

Hence, $\dfrac{[A^-]}{[HA]} = \dfrac{K_a}{[H^+]} = 10^{-3} \Rightarrow [HA] = 10^3 \times [A^-]$

i.e. $[HA] > [A^-]$

The presence of stomach juice with a pH = 1.0 suppresses the dissociation of aspirin, so much so that $[H^+] > [A^-]$. (i.e. $[H^+] \neq [A^-]$)

---

21. The following equilibrium exists in a mixture of concentrated nitric acid and concentrated sulfuric acid.

$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$

Which statement about this equilibrium is correct?

A Addition of H_2O will reduce the NO_2^+ concentration.

B HNO_3 and NO_2^+ are a conjugate acid-base pair.

C The nitric acid acts as an oxidising agent.

D The sulfuric acid acts as a dehydrating agent.

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The equilibrium is set up using concentrated acids. Adding H_2O dilutes the system and reduces the tendency to form NO_2^+. Equilibrium shifts to the left and hence $[NO_2^+]$ decreases.

---

23. Which one of the following affects the value of the solubility product, K_{sp}, of silver sulfide when it is precipitated by passing hydrogen sulfide into aqueous silver nitrate?

$2AgNO_3(aq) + H_2S(g) \rightarrow Ag_2S(s) + 2HNO_3(aq)$

A an increase in temperature

B the addition of aqueous sodium sulfate

C the addition of aqueous silver nitrate

D the presence of an excess of acid

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$$Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$$

$K_{sp} = [Ag^+]^2[S^{2-}]$

K_{sp} is a thermodynamic property and is similar to equilibrium constant. Its value is only affected by a change in temperature.

---

24. Which statement explains the observation that magnesium hydroxide dissolves in aqueous ammonium chloride, but not in aqueous sodium chloride?

A The ionic radius of the NH_4^+ ion is similar to that of Mg^{2+} but not that of Na^+.

B NH_4Cl dissociates less fully than NaCl.

C The ions Na^+ and Mg^{2+} are isoelectronic (have the same number of electrons).

D The ion NH_4^+ acts as an acid.

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NH_4^+ readily hydrolyses in H_2O to form H_3O^+.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

H_3O^+ or simply H^+, reacts with OH^- and causes the reaction below to shift to the right.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

Hence, $Mg(OH)_2$ dissolves.

25. At a total pressure of 1.0 atm, dinitrogen tetraoxide is 50% dissociated at a temperature of 60 °C, according to the following equation.

$$N_2O_4 \rightleftharpoons 2NO_2$$

What is the value of the equilibrium constant, K_p, for this reaction at 60 °C?

A $\frac{1}{3}$ atm

B $\frac{2}{3}$ atm

C $\frac{4}{3}$ atm

D 2 atm

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	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial	p_i		0
Eqm.	$\frac{1}{2}p_i$		p_i

$\frac{1}{2}p_i + p_i = 1$ atm

$p_i = \frac{2}{3}$ atm

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{(\frac{2}{3})^2}{\frac{2}{6}} = \frac{4}{3} \text{ atm}$$

26. Nitrogen dioxide decomposes on heating according to the following equation.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

When 4 mol of nitrogen dioxide were put into a $1\ dm^3$ container and heated, the equilibrium mixture contained 0.8 mol of oxygen.

What is the numerical value of the equilibrium constant K_c, at the temperature of the experiment?

A $\frac{0.8 \times 0.8}{2.4}$

B $\frac{0.8^2 \times 0.8}{4^2}$

C $\frac{1.6 \times 0.8}{2.4^2}$

D $\frac{1.6^2 \times 0.8}{2.4^2}$

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	$2NO_2(g)$	$\rightleftharpoons$	$2NO(g)$	$+ O_2(g)$
Initial amt/mol	4		0	0
Eqm amt/mol	2.4		1.6	0.8

$$K_c = \frac{[NO(g)]^2[O_2(g)]}{[NO_2(g)]^2} = \frac{(\frac{1.6}{1})^2(\frac{0.8}{1})}{(\frac{2.4}{1})^2}$$

$$= \frac{1.6^2 \times 0.8}{2.4^2} \ (mol\ dm^{-3})$$

27. An acetate 'hot pack' is a useful source of instant low-grade heat, used to increase the blood's circulation and relieve the pain of bruises and sprains. The heat is produced when the following reaction occurs.

$$CH_3CO_2Na(aq) + 3H_2O(\ell) \rightarrow CH_3CO_2Na.3H_2O(s)$$

What data is required to calculate the value for the enthalpy change for this reaction?

A $\Delta H_f^\ominus$ for $CH_3CO_2Na(aq)$, $H_2O(\ell)$ and $CH_3CO_2Na.3H_2O(s)$

B $\Delta H_f^\ominus$ for $CH_3CO_2Na(s)$, $H_2O(\ell)$ and $CH_3CO_2Na.3H_2O(s)$

C lattice energies of $CH_3CO_2Na(s)$ and $CH_3CO_2Na.3H_2O(s)$

D $\Delta H^\ominus_{solution}$ for $CH_3CO_2Na(s)$

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$$\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

28. For the equilibrium

$$2NH_3(\ell) \rightleftharpoons NH_4^+(\ell) + NH_2^-(\ell)$$

the ionic product of liquid ammonia is 1.00×10^{-22} $mol^2\ dm^{-6}$. What is the concentration of positive ions in liquid ammonia?

A 5.00×10^{-23} mol dm^{-3}

B 1.00×10^{-22} mol dm^{-3}

C 5.00×10^{-12} mol dm^{-3}

D 1.00×10^{-11} mol dm^{-3}

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$$2NH_3(\ell) \rightleftharpoons NH_4^+(\ell) + NH_2^-(\ell)$$

The equilibrium is very similar to that for H_2O.

$$K_{NH_3} = [NH_4^+(\ell)][NH_2^-(\ell)]$$
$$= 1.00\times10^{-22}\ mol^2\ dm^{-6}$$

Since $[NH_4^+(\ell)] = [NH_2^-(\ell)]$,

$$[NH_4^+(\ell)] = (1.00\times10^{-22})^{\frac{1}{2}}$$
$$= 1.00\times10^{-11}\ mol\ dm^{-3}$$

29. Which one of the statements about the forward and reverse reactions, $P+Q \rightleftharpoons R+S$, is correct when the system is at equilibrium?

A The ratio of the rates of the forward reaction to that of the reverse reaction equals the equilibrium constant.

B The rates of both the forward and the reverse reactions are equal to zero.

C The rates of the forward and reverse reactions are equal.

D The rate constant for the forward reaction equals the rate constant for the reverse reaction.

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At equilibrium (dynamic equilibrium), P and Q are continuously reacting to give R and S, and vice versa ($\therefore$ (B) is wrong). The forward and reverse rates are thus equal. The equilibrium constant, K_c, is expressed as

$$K_c = \frac{\text{forward rate constant}}{\text{reverse rate constant}} = \frac{[R][S]}{[P][Q]}.$$

However, $K_c \neq \frac{\text{forward rate}}{\text{reverse rate}}$ and forward rate constant $\neq$ reverse rate constant unless $K_c = 1$ ($\therefore$ (D) is wrong).

30. The pK_b value for aqueous ammonia at 25 °C is 4.8.

What is the correct pK_a value for the ammonium ion at this temperature? (K_b denotes the base dissociation constant and K_a denotes the acid dissociation constant.)

A −4.8 B 2.2

C 4.8 D 9.2

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$$K_w = K_a \times K_b \Rightarrow K_a = \frac{K_w}{K_b}$$

where K_w denotes the ionic product of water.

$$\Rightarrow pK_a = -\log K_a$$
$$= -\log\frac{K_w}{K_b}$$
$$= -\log K_w - pK_b$$
$$= 14 - 4.8$$
$$= 9.2$$

31. A nitrogen-hydrogen mixture, initially in the mole ratio of 1 : 3, reached equilibrium with ammonia when 50% of the nitrogen had reacted. The total final pressure was p.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

What was the partial pressure of ammonia in the equilibrium mixture?

A $\frac{p}{8}$ B $\frac{p}{6}$

C $\frac{p}{4}$ D $\frac{p}{3}$

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	$3H_2$	+ N_2	$\rightleftharpoons$ $2NH_3$
initial pressure	$3x$	x	0
pressure at eqm	$\frac{3}{2}x$	$\frac{1}{2}x$	x

$$\frac{3}{2}x + \frac{1}{2}x + x = p \Rightarrow x = \frac{p}{3}$$

32. Two equilibria are shown below.

reaction I: $2X_2(g) + Y_2(g) \rightleftharpoons 2X_2Y(g)$

reaction II: $X_2Y(g) \rightleftharpoons X_2(g) + \frac{1}{2}Y_2(g)$

The numerical value of K_c for reaction I is 2. Under the same conditions, what is the numerical value of K_c for reaction II?

A $\frac{1}{\sqrt{2}}$ B $\frac{1}{2}$

C $\frac{1}{4}$ D -1

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For reaction I,

$$K_c = \frac{[X_2Y]^2}{[X_2]^2[Y_2]} = 2\ \text{dm}^3\ \text{mol}^{-1}$$

For reaction II:

$$K_c = \frac{[X_2][Y_2]^{\frac{1}{2}}}{[X_2Y]} = \frac{1}{\left(\frac{[X_2Y]^2}{[X_2]^2[Y_2]}\right)^{1/2}} = \frac{1}{\sqrt{2}}\ \text{mol}^{\frac{1}{2}}\ \text{dm}^{-\frac{3}{2}}$$

---

33. Which substance, in 1 mol dm^{-3} aqueous solution, would have the same hydrogen ion concentration as 1 mol dm^{-3} of hydrochloric acid?

A ethanoic acid

B nitric acid

C sodium hydroxide

D sulfuric acid

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$$HCl \rightarrow H^+ + Cl^-$$

HNO_3 is a strong acid and it dissociates completely.

$$HNO_3 \rightarrow H^+ + NO_3^-$$

A: $$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$$

CH_3CO_2H is a weak acid and the dissociation is incomplete. Hence, $[H^+] < 1$ mol dm^{-3}.

B: NaOH is an alkali.

D: H_2SO_4 is dibasic and $[H^+] = 2$ mol dm^{-3}.

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

---

34. The value of the ionic product of water, KK_w,aries with temperature.

temperature/°C	K_w / mol^2 dm^{-6}
25	1.0×10^{-14}
62	1.0×10^{-13}

What can be deduced from this information?

A The ionic dissociation of water is an endothermic process.

B The ionic dissociation of water increases by a factor of 5 between 25 °C and 62 °C.

C The association of water molecules by hydrogen bonding increases as temperature rises.

D Water is not a neutral liquid at 62 °C.

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$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+][OH^-]$$

As temperature increases, KK_w icreases. This shows that the equilibrium position shifts to the right as there are now more H^+ and OH^-. By Le Chatelier's principle, the forward reaction is thus endothermic.

---

35. The gas-phase reaction of carbon monoxide with hydrogen forming methanol is an example of an equilibrium. The reaction was investigated by mixing 2.0 mol of H_2(g) with 1.0 mol of CO(g) and allowing equilibrium to be established.

	$2H_2(g)$ +	$CO(g)$ $\rightleftharpoons$	$CH_3OH(g)$
initial moles	2.0	1.0	0

At equilibrium, x mol of H_2 had reacted with CO.

What are the amounts, in moles, of each of the components of the equilibrium mixture?

	H_2(g)	CO(g)	CH_3OH(g)
A	$2.0-\frac{1}{2}x$	$1.0-x$	$\frac{1}{2}x$
B	$2.0-\frac{1}{2}x$	$1.0-2x$	x
C	$2.0-x$	$1.0-\frac{1}{2}x$	$\frac{1}{2}x$
D	$2.0-x$	$1.0-x$	$\frac{1}{2}x$

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	$2H_2$ +	CO $\rightleftharpoons$	CH_3OH
initial/mol	2	1	0
change/mol	$-x$	$-\frac{1}{2}x$	$\frac{1}{2}x$
eqm/mol	$2-x$	$1-\frac{1}{2}x$	$\frac{1}{2}x$

---

36. Methanol is manufactured industrially by the catalytic reaction shown.

$CO(g) + 2H_2(g) \rightarrow CH_3OH(g) \quad \Delta H = -92\ kJ\ mol^{-1}$

The operating conditions are:

250 °C; a pressure between 50 atm and 100 atm; a copper-based catalyst.

Which factor influences the choice of these conditions?

A The catalyst increases the equilibrium yield of methanol.

B At lower pressures, the rate of formation of methanol increases.

C At lower temperatures, the equilibrium yield of methanol increases.

D At lower temperatures, the rate of formation of methanol increases.

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Option A is incorrect since the catalyst only affects the rate of the reaction but has no influence on the equilibrium yield as it affects the backward and forward reaction to the same extent.

Option B is incorrect since lower pressure decreases the rate of collision and hence, the rate of formation of methanol should decrease.

Option C is *correct* since the forward reaction is exothermic and would be favoured by a lower temperature thus increasing equilibrium yield.

Option D is incorrect since lower temperature decreases the number of molecules having energy greater than or equal to the activation energy and so the number of successful collisions and hence, the rate of formation of methanol should decrease.

37. When 0.20 mol of hydrogen gas and 0.15 mol of iodine gas are heated at 723 K until equilibrium is established, the equilibrium mixture is found to contain 0.26 mol of hydrogen iodide.

The equation for the reaction is as follows.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

What is the correct expression for the equilibrium constant K_c?

A $\dfrac{2\times0.26}{0.20\times0.15}$ **B** $\dfrac{(2\times0.26)^2}{0.20\times0.15}$

C $\dfrac{(0.26)^2}{0.07\times0.02}$ **D** $\dfrac{(0.26)^2}{0.13\times0.13}$

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	H_2	+	I_2	$\rightleftharpoons$	2HI
initial amt/mol	0.2		0.15		0
eqm amt/mol	0.2−0.13 = 0.07		0.15−0.13 = 0.02		0.26

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(\frac{0.26}{V})^2}{(\frac{0.07}{V})(\frac{0.02}{V})} = \frac{(0.26)^2}{0.07\times0.02}$$

38. *Use of the Data Booklet is relevant to this question.*

Water dissociates as shown.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At 25 °C, the equilibrium value of $[H^+]$ is 10^{-7} mol dm^{-3}; $[H_2O] = \frac{1000}{18}$ mol dm^{-3}.

What is the order of increasing numerical value of pH, pK_a and pK_w for this equilibrium at this temperature? [p$K_w = -\log K_w$]

	smallest		largest
A	pH	pK_a	pK_w
B	pH	pK_w	pK_a
C	pK_a	pK_w	pH
D	pK_w	pK_a	pH

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$pH = -\lg(10^{-7}) = 7$

$pK_w = -\lg(10^{-14}) = 14$

$$K_a = \frac{[H^+][OH^-]}{[H_2O]} \Rightarrow [H_2O]K_a = [H^+][OH^-] = K_w$$

$$\text{Hence, } K_a = \frac{K_w}{[H_2O]}$$

$$-\lg K_a = -\lg K_w + \lg[H_2O]$$

$$pK_a = pK_w + \lg\frac{1000}{18}$$

$$= 14 + 1.74$$

$$= 15.74$$

39. Public swimming pools are often chlorinated to kill bacteria. As an alternative to chlorination, silver ions can be used in a concentration of not more than 10^{-6} mol dm^{-3} and not less than 10^{-7} mol dm^{-3} of silver ions.

Which of the following compounds would, in saturated solution, provide the necessary concentration of silver ion?

	compound	solubility product
A	AgBr	5×10^{-13} mol² dm⁻⁶
B	AgCl	2×10^{-10} mol² dm⁻⁶
C	$AgIO_3$	2×10^{-8} mol² dm⁻⁶
D	Ag_2CO_3	5×10^{-12} mol³ dm⁻⁹

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$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

$K_{sp} = [Ag^+][Br^-] = 5\times10^{-13}$ mol² dm⁻⁶

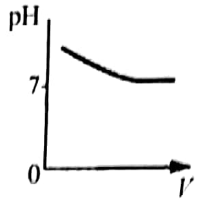
But $[Ag^+] = [Br^-]$,

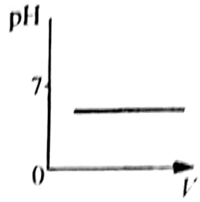
$\therefore [Ag^+] = (5\times10^{-13})^{\frac{1}{2}} = 7.1\times10^{-7}$ mol dm⁻³

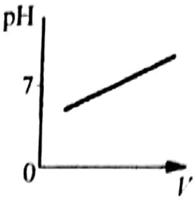
---

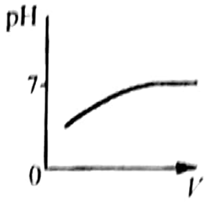
40. A sample of 1 mol of ethanoic acid is diluted at constant temperature to a volume V.

Which diagram shows how the pH of the acid varies with V?

A 

B 

C 

D 

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As the acid is diluted, the pH gradually increases because $[H^+]$ decreases. Eventually, the pH will gradually level off at pH = 7 at infinite dilution where $[H^+]$ approaches 10^{-7} mol dm⁻³ (it cannot go lower than this value!). This is because as the acid becomes very diluted, the self ionisation of H_2O cannot be neglected anymore.

$$H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$$

$[H^+]$ from H_2O is 10^{-7} mol dm⁻³.

---

41. The gas-phase reaction of carbon monoxide with hydrogen forming methanol is an example of an equilibrium. The reaction was investigated by mixing 2.0 mol of $H_2(g)$ with 1.0 mol of $CO(g)$ in a 0.5 dm³ flask and allowing equilibrium to be established.

	$2H_2(g)$ +	$CO(g)$ ⇌	$CH_3OH(g)$
initial moles	2.0	1.0	0

At equilibrium, x mol of H_2 had reacted with CO. What is the equilibrium concentration of CO?

A $(1.0 - \frac{1}{2}x)$ mol dm⁻³

B $\dfrac{(1.0 - \frac{1}{2}x)}{0.5}$ mol dm⁻³

C $\dfrac{(1.0 - x)}{0.5}$ mol dm⁻³

D $\dfrac{(1.0 - 2x)}{0.5}$ mol dm⁻³

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	$2H_2$ +	CO ⇌	CH_3OH
n_i	2.0	1.0	0
Δn	$-x$	$-0.5x$	$0.5x$
n_{eqm}	$2.0 - x$	$1.0 - 0.5x$	$0.5x$

$[CO] = \dfrac{1.0 - 0.5x}{0.5}$ mol dm⁻³

---

42. A sample of 1 mol of N_2O_4 was placed in an empty 1 dm³ container and allowed to reach equilibrium according to the following equation.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At equilibrium, x mol of the N_2O_4 had dissociated. What is the value of the equilibrium constant, K_c, at the temperature of the experiment?

A $\dfrac{2x^2}{(1-x)^2}$ B $\dfrac{2x^2}{1-x}$

C $\dfrac{4x}{1-x}$ D $\dfrac{4x^2}{1-x}$

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	$N_2O_4(g)$ ⇌	$2NO_2(g)$
Initial amt/mol	1	0
Amt at eqm/mol	$1-x$	$2x$

$$K_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]} = \frac{(\frac{2x}{1})^2}{(\frac{1-x}{1})} = \frac{4x^2}{1-x} \text{ (mol dm}^{-3}\text{)}$$

---

43. An acidified solution containing 0.10 mol dm^{-3} of zinc sulfate and 0.10 mol dm^{-3} of copper(II) sulfate is saturated with hydrogen sulfide at 15 °C. The concentration of S^{2-}(aq) in the solution is then 10^{-35} mol dm^{-3}.

The solubility product of zinc sulfide at 15 °C is 10^{-24} mol^2 dm^{-6} and that of copper(II) sulfide is 10^{-40} mol^2 dm^{-6}.

Which statement describes what happens in the solution?

A No precipitate is formed.

B Copper(II) sulfide only is precipitated.

C Copper(II) sulfide is precipitated followed by zinc sulfide.

D Zinc sulfide is precipitated followed by copper(II) sulfide.

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$$M^{2+}S^{2-}(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq)$$

$K_{sp} = [M^{2+}]_{eqm}[S^{2-}]_{eqm}$

$[Zn^{2+}][S^{2-}] = 0.1 \times 10^{-35}$
$= 10^{-36} \text{ (mol dm}^{-3})^2 < K_{sp}$

Hence, ZnS will not be precipitated.

$[Cu^{2+}][S^{2-}] = 0.1 \times 10^{-35}$
$= 10^{-36} \text{ (mol dm}^{-3})^2 > K_{sp}$

Hence, $CuSO_4$ is precipitated.

---

44. Each of the following equilibria is subjected to two changes carried out separately:

(i) the pressure is reduced at constant temperature;

(ii) the temperature is increased at constant pressure.

For which equilibrium will both of these changes result in an increase in the proportion of products?

A $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; $\Delta H = +53$ kJ mol^{-1}

B $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$; $\Delta H = -950$ kJ mol^{-1}

C $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H = -92$ kJ mol^{-1}

D $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $\Delta H = +57$ kJ mol^{-1}

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According to Le Chatelier's principle, reducing pressure at constant temperature causes equilibria B and D to shift to the right since there are more gas particles on the right. This helps to rebuild the pressure. However, increasing temperature at constant pressure causes equilibrium D to shift to the right since the forward reaction is endothermic.

---

45. Known amounts of hydrogen and iodine are allowed to come to equilibrium at 500 °C in a vessel of known volume.

$$H_2 + I_2 \rightleftharpoons 2HI$$

From which experimental method can K_c be found?

A measuring the total pressure in the vessel

B slow cooling to 20 °C, breaking open the vessel under aqueous potassium iodide, and titrating the iodine present with aqueous sodium thiosulfate

C rapid cooling to 20 °C, breaking open the vessel under aqueous potassium iodide, and titrating the iodine present with aqueous sodium thiosulfate

D withdrawal of a measured sample of the equilibrium mixture, followed by complete decomposition of the hydrogen iodide present, and then titrating the total amount of iodine with aqueous sodium thiosulfate

Helping Concepts *Exam Favourite Rating* ★

By rapidly cooling to 20 °C, the rate of reaction is decreased drastically so that the amount of H_2, I_2 and HI remained the same as the amount present at equilibrium at 500 °C. By titrating the iodine present with sodium thiosulfate, the concentration of iodine may be found and the concentrations of hydrogen and hydrogen iodide can then be calculated.

Hence K_c can be computed.

Option A is incorrect since the total pressure of the system remains constant as the number of gaseous molecules on both sides of the equation are the same.

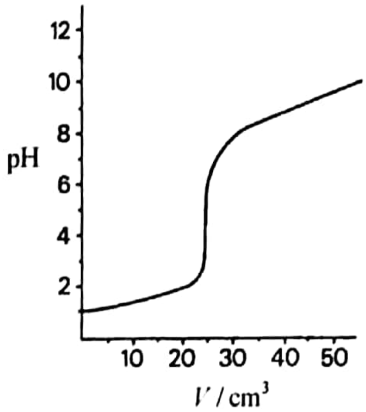
Option B is incorrect since slowly cooling the system to 20 °C would cause equilibrium to be re-established so that amount of the substances will not be similar to that at 500 °C.

Option D is incorrect since decomposition of hydrogen iodide to iodine does not allow the amount of hydrogen iodide originally present at equilibrium to be determined.

---

46. In an acid-base titration, a 0.10 mol dm^{-3} solution of a base is added to 25 cm^3 of a 0.10 mol dm^{-3} solution of an acid.

The pH value of the solution is plotted against the volume, V, of base added as shown in the diagram.



This diagram could represent a titration between

A CH_3CO_2H(aq) and NH_3(aq).

B CH_3CO_2H(aq) and KOH(aq).

C HCl(aq) and KOH(aq).

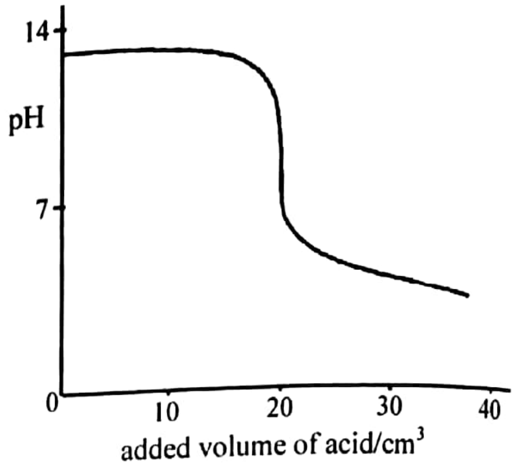
D HCl(aq) and NH_3(aq).

Helping Concepts *Exam Favourite Rating* ★★★

The graph starts with a pH of 1, indicating that the acid is a strong acid. Since there is only 1 equivalence point, the acid should be monobasic. The equivalence point is at about pH = 5, showing that the base is a weak base. hence, the answer is (D) because HCl is a strong monobasic acid while NH_3, is a weak base.

---

47. The graph shows the change in pH when 0.10 mol dm^{-3} acid is gradually added to 10 cm^3 of 0.10 mol dm^{-3} alkali.



Which of the following substances could have given these results?

	alkali	acid
A	$Ba(OH)_2$	CH_3CO_2H
B	$Ba(OH)_2$	H_3PO_4
C	$Ca(OH)_2$	H_2SO_4
D	NaOH	H_2SO_4

Helping Concepts *Exam Favourite Rating* ★★

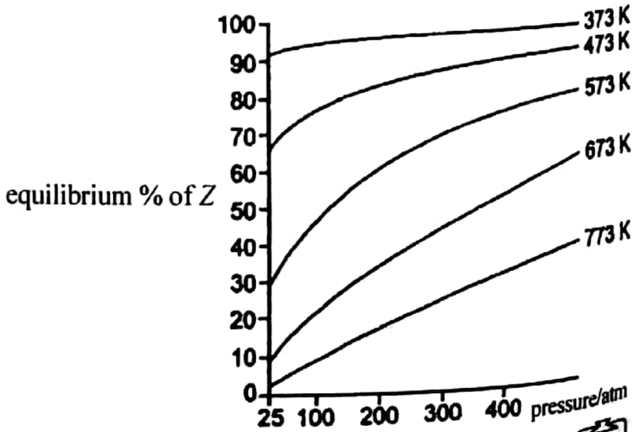
The pH at the equivalence point is greater than 7 showing that the reaction is between a strong base and a weak acid. The salt of the weak acid hydrolyses in water to give a pH greater than 7.

---

48. In an industrial process, two gases X and Y react together to form a single gaseous product Z.

$$X(g) + Y(g) \rightleftharpoons Z(g)$$

The percentage yield of product Z varies according to the pressure and the temperature as shown in the graphs.



Which statement about this equilibrium reaction is correct?

A Decreasing the temperature decreases the value of the equilibrium constant.

B Decreasing the temperature increases the rate of this reaction.

C Increasing the pressure increases the value of the equilibrium constant.

D The reaction is exothermic in the forward direction.

Helping Concepts *Exam Favourite Rating* ★★

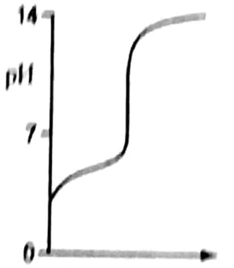
As temperature increases, the yield of Z decreases. This shows that the equilibrium shifts to the left.

49. Pyruvic acid is a weak acid that is an important intermediate in many biochemical processes.

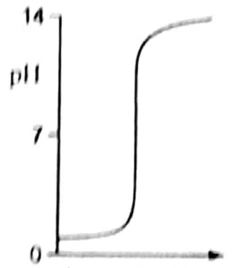
CH_3COCO_2H
pyruvic acid

Which graph best represents the change in pH that occurs when a sample of pyruvic acid is titrated with NaOH(aq)?

A

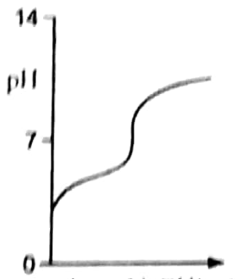


B



C

D



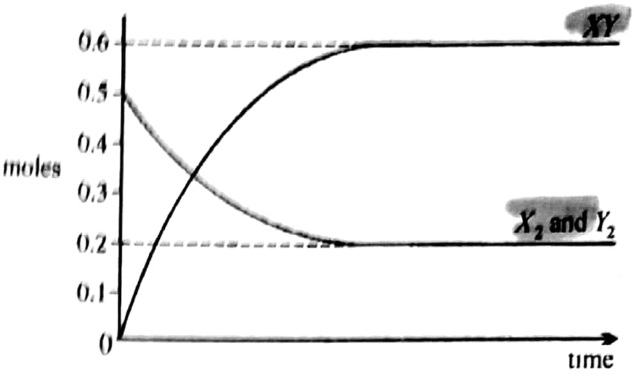
Helping Concepts *Exam Favourite Rating* ★★

The acid is a weak monoprotic organic acid. Hence, the titration curve fits that of a weak acid–strong base titration. It starts at a relatively high acidic pH (weak acid) and ends at a very high pH (strong base).

50. Two diatomic gases, X_2 and Y_2, react as follows.

$$X_2(g) + Y_2(g) \rightleftharpoons 2XY(g)$$

A mixture containing 0.5 moles each of X_2 and Y_2 is heated in a closed container and the reaction allowed to reach equilibrium. The graph shows how the number of moles of each gas varies with time.



Which is the value of the equilibrium constant K_c for this reaction?

A 1.5 **B** 3

C 9 **D** 18

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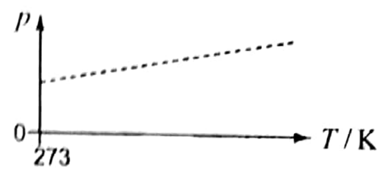
$$K_c = \frac{[XY]^2}{[X_2][Y_2]} = \frac{(\frac{n_{XY}}{V})^2}{(\frac{n_X}{V})(\frac{n_Y}{V})} = \frac{n_{XY}^2}{n_X \cdot n_Y} = \frac{0.6^2}{0.2\times0.2} = 9$$

51. The graph shows the pressure-temperature (p-T) relationship of a 1 mol sample of helium in an enclosed volume.

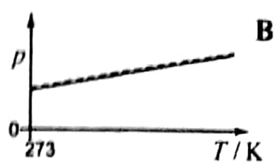


Similar pressure-temperature measurements were made for a 1 mol sample of a gas which dissociates.

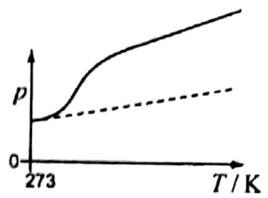
$$X_2(g) \rightleftharpoons 2X(g); \quad \Delta H \text{ positive}$$

Which graph best represents the p-T relationship of the gas?

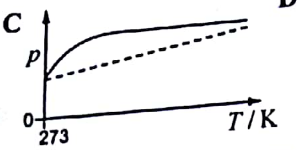
A



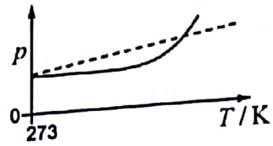
B



C



D



Helping Concepts *Exam Favourite Rating* ★★

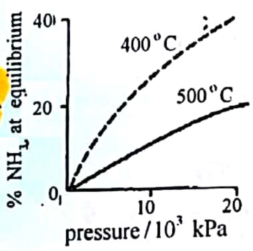
Since $\Delta H > 0$, as temperature increases, there will be greater dissociation. The pressure becomes greater than expected. At extreme high temperature, when dissociation is near to complete, the pressure would be double than expected (since n is double).

---

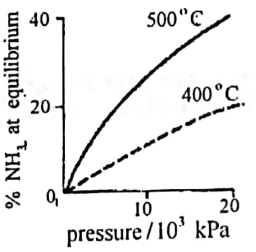
52. The percentage of ammonia obtainable, if equilibrium were to be established during the Haber process, is plotted against the operating pressure for two temperatures, 400 °C and 500 °C.

Which of the following correctly represnts the two graphs?

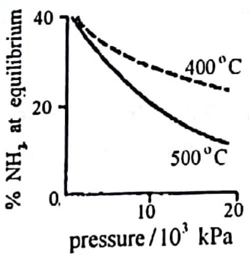
A



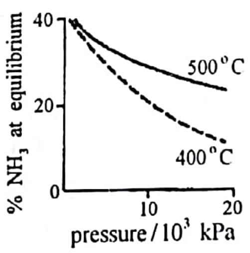
B



C



D



Helping Concepts *Exam Favourite Rating* ★★★

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

(The forward reaction is exothermic.)

By LCP, higher pressure and lower temperature favour the forward reaction, i.e. higher percentage of NH_3. This is because when the equilibrium shifts to the right, less gas particles are produced and this tends to lower the pressure; and heat is produced and this tends to raise the temperature.

Note: The graphs should start from zero since there is no NH_3 in the beginning.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

53. Which of the following could act as buffer solutions?

1 $NaHCO_3$ and Na_2CO_3

2 CH_3CO_2H and NaCl

3 HNO_3 and $NaNO_3$

Helping Concepts *Exam Favourite Rating* ★★★

A buffer solution usually comprises a weak acid and its salt, or a weak alkali and its salt.

*1. $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

weak acid: HCO_3^-

salt (or conjugate base): CO_3^{2-}

2. acid: CH_3CO_2H

salt: absent

3. weak acid: absent

salt: absent

54. A reversible reaction is catalysed.

Which of the following statements about this system are correct?

1 The catalyst alters the mechanism of the reaction. True for a catalyst

2 The catalyst reduces the energy of activation (the energy barrier) for both the forward and the backward reaction.

3 The catalyst alters the composition of the equilibrium mixture.

Helping Concepts *Exam Favourite Rating* ★★

A catalyst speeds up both the forward and backward reactions to the same extent by providing an alternative path with lower activation energies. The equilibrium is thus not affected, i.e. composition unaltered except that the equilibrium is attained faster.

55. The reaction shown is reversible.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g); \ \Delta H = +61.7 \text{ kJ mol}^{-1}$$

When, at the same temperature, the pressure is increased, which of the following decrease?

1 the proportion of $NO_2(g)$ present at equilibrium

2 the value of the equilibrium constant K_p

3 the activation energies of both forward and reverse reactions.

Helping Concepts *Exam Favourite Rating* ★★★

*1. When p increases, the equilibrium shifts to the left according to Le Chatelier's principle to produce less gaseous particles so as to reduce the pressure. Hence, the proportion of NO_2 at equilibrium decreases.

2. K_p is only affected by a change in temperature.

3. E_a is not affected by a change in p.

56. For the gas phase reaction

$$2X + Y \rightleftharpoons 2Z \qquad \Delta H = -x \text{ kJ mol}^{-1}$$

the yield of Z at equilibrium could be increased by

1 increasing the pressure.

2 increasing the temperature.

3 using a catalyst.

Helping Concepts *Exam Favourite Rating* ★★★

*1. There is a reduction in volume in the forward reaction. By Le Chatelier's principle, increasing pressure will shift the equilibrium to the right, i.e. higher yield of Z, so as to produce less number of particles in order to reduce the pressure.

2. If $x > 0$, then $\Delta H < 0$. Increasing temperature shifts the equilibrium to the left so as to absorb the excess heat since the backward reaction is endothermic. Hence, less Z is produced.

3. Using a catalyst merely speeds up the rate at which the equilibrium is attained, without affecting the equilibrium constant nor shifting the equilibrium.

57. Which of the following in aqueous solution do not considerably change in pH when relatively small volumes of strong acid or strong alkali are added?

1 a mixture of sodium carbonate and sodium hydrogencarbonate

2 a mixture of sodium ethanoate and ethanoic acid

3 a mixture of sodium sulfate and sodium chloride

Helping Concepts *Exam Favourite Rating* ★★★

A buffer solution does not considerably change pH when a relatively small volumes of strong acid or strong alkali are added. It usually contains a mixture of a weak acid and its conjugate base, or a weak base and its conjugate acid.

*1. $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

*2. $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

3. A mixture of Na_2SO_4 and NaCl has no buffering capacity.

58. Poly(tetrafluoroethene) is a polymer used as a coating in non-stick kitchen utensils and for replacement bone joints. One of the stages in the manufacture of the polymer is

$$2CHClF_2(g) \rightleftharpoons C_2F_4(g) + 2HCl(g); \quad \Delta H = +128 \text{ kJ mol}^{-1}$$

Which of the following conditions will shift this equilibrium to the right?

1 high temperature

2 high pressure

3 using a catalyst

Helping Concepts *Exam Favourite Rating* ★★★

*1. By Le Chatelier's principle, a higher temperature favours the forward reaction since heat is absorbed when forming the products.

2. By Le Chatelier's principle, a higher pressure favours the backward reaction since there are less number of gaseous particles on the left side of the equilibrium.

3. A catalyst merely alters the rate of the reaction. It does not affect the position of the equilibrium.

59. What can be deduced from the following information?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \ \Delta H = -98 \text{ kJ mol}^{-1}$$

1 Increasing the pressure increases the equilibrium yield of $SO_3(g)$.

2 The maximum mass of sulfur trioxide that can be made from 64 g of sulfur dioxide is 80 g.

3 Increasing the temperature decreases the rate of the forward reaction.

Helping Concepts *Exam Favourite Rating* ★★★

*1. By Le Chatelier's principle, increasing pressure causes the equilibrium to shift to the right. This reduces the number of gas particles in the system and hence, helps to reduce the pressure.

*2. M_r of $SO_2 = 32 + (2\times16) = 64$

M_r of $SO_3 = 32 + (3\times16) = 80$

From the equation, 2 moles of SO_2 produce a maximum of 2 moles of SO_3 or 1 mole of SO_2 produces a maximum of 1 mole of SO_3. Hence, from 64 g of SO_2, a maximum of 80 g of SO_3 may be obtained.

3. Increasing temperature should increase the rate of forward reaction (also the backward reaction).

60. In water, the following equation exists.

$$H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq); \quad \Delta H^\circ = +57 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K}.$$

The ionic product of water is defined by the expression

$$[H^+][OH^-] = 1.0\times10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 298 \text{ K}.$$

What can be deduced from these data?

1 When water is heated, the concentration of $H^+(aq)$ increases.

2 When water is heated, the concentration of $OH^-(aq)$ increases.

3 The pH of pure water at temperatures greater than 25 °C is greater than 7.

Helping Concepts *Exam Favourite Rating* ★★★

*1,*2. Since the forward reaction is endothermic, heating H_2O causes the equilibrium to shift to the right according to Le Chatelier's principle by absorbing the excess heat. Hence, both $[H^+]$ and $[OH^-]$ increase.

3. Since $[H^+]$ increases, $pH = -\log[H^+]$ decreases, i.e. $pH < 7$.

---

61. Two students separately have available equal volumes of 0.1 mol dm^{-3} silver nitrate, sodium ethanoate and potassium bromide.

The first student, on mixing the sodium ethanoate and silver nitrate, obtains a white precipitate. On adding potassium bromide to this mixture, the precipitate turns cream.

The second student adds the silver nitrate to the potassium bromide and obtains a cream precipitate. On adding the sodium ethanoate to this mixture, there is no further change.

Which statements about these observations are correct?

1 Silver ethanoate is insoluble.

2 Silver bromide is less soluble than silver ethanoate.

3 Ethanoate can oxidise bromide.

Helping Concepts *Exam Favourite Rating* ★

*1,*2. Silver ethanoate and silver bromide are both insoluble in water and the latter has a lower K_{sp}. When CH_3COOAg ppt. is formed, adding Br^- causes ppt. of the less soluble AgBr (cream).

In the second experiment, when AgBr ppt. is formed, nothing happens when CH_3COO^- is added.

---

62. Which of the following statements are true about the Haber process for the manufacture of ammonia?

1 At higher temperatures, the yield goes down but the rate of production of ammonia is faster.

2 At higher pressures, the yield goes down but the rate of production of ammonia is faster.

3 In the presence of a catalyst, the yield goes down but the rate of production of ammonia is faster.

Helping Concepts *Exam Favourite Rating* ★★

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H < 0$$

*1. At higher temperatures, the reaction rate always increases. Since the forward reaction is exothermic, higher temperature hinders the forward reaction according to Le Chatelier's principle, i.e. lower yield.

2. At higher pressures, the reaction rate increases (pressure increase is equivalent to concentration increase). By Le Chatelier's principle, the equilibrium shifts to the right to produce less gas particles and hence reduces the pressure. Therefore, yield increases since more NH_3 is produced.

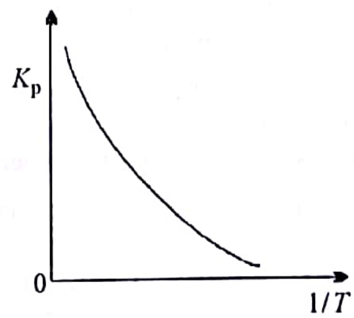
3. Using a suitable catalyst increases the rate of production of NH_3 without affecting production yield.

---

63. The equilibrium constant, K_p for the reaction

$$X(g) + Y(g) \rightleftharpoons Z(g)$$

is found to vary with temperature T as shown in the diagram below.



Which of the following conclusions can be drawn from this information?

1 The reaction is exothermic in the forward direction.

2 The equilibrium mixture contains a high proportion of Z at higher pressures.

3 The equilibrium mixture contains a high proportion of Z at higher temperatures.

Helping Concepts Exam Favourite Rating ★★

1,*3. As T increases, $1/T$ decreases. The graph shows that at higher T (lower $1/T$), K_p is higher, i.e. more Z. Therefore, the forward reaction is endothermic (not exothermic) where the equilibrium shifts to the right by absorbing excess heat according to Le Chatelier's principle.

*2. From the equation, there is a reduction in volume in the forward reaction. By Le Chatelier's principle, the equilibrium will shift to the right, i.e. more Z at higher pressures so as to reduce the pressure by producing less gas particles.

---

64. One explanation of the explosion at the Chernobyl nuclear power plant in 1986 is that the graphite reactor overheated and reacted with the cooling water according to the following equation.

$$C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g);\ \Delta H = +131\ \text{kJ mol}^{-1}$$

Which are possible reasons why the forward reaction is more likely to occur at high temperature?

1. Hydrogen and carbon monoxide do not react at high temperature.
2. At lower temperature, the position of equilibrium lies too far to the left.
3. The energy of activation is high.

Helping Concepts Exam Favourite Rating ★★★

1. Since the reaction shown is reversible, both reactions (forward and backward) take place at both low and high temperatures.

*2. Since the forward reaction is endothermic, the equilibrium lies mainly to the left at a low temperature according to Le Chatelier's principle.

*3. The forward reaction is likely to have a very high activation energy so much so that the rate of the reaction is very slow. The reaction becomes apparent only at a high temperature.

---

65. The use of chlorine as a disinfectant in swimming pools is now widely banned and the weak acid trichloroisocyanuric acid is used instead.

trichloroisocyanuric acid + OH^-
$\rightleftharpoons$ ClO^- + cyanuric acid

The ClO^- ion is the effective disinfectant.

Why is it necessary to keep the pH of the water at 7.5?

1. The concentration of H^+ is too low for the following reaction to occur.

   $$2H^+(aq) + ClO^-(aq) + Cl^-(aq) \rightarrow H_2O(\ell) + Cl_2(g)$$

2. The concentration of the ClO^- ion depends on the pH.
3. At a pH of 7.5, the concentration of the ClO^- ion is at a maximum.

Helping Concepts Exam Favourite Rating ★★

*1. The slightly alkaline pH is necessary to keep $[H^+]$ low so that the reaction between H^+, ClO^- and Cl^- as shown would not occur.

*2,3. From the equation,

trichloroisocyanuric acid + OH^-
$\rightleftharpoons$ ClO^- + cyanuric acid,

an increase in pH increases $[OH^-]$ which will shift the equilibrium to the right to increase $[ClO^-]$. Hence, $[ClO^-]$ is pH dependent and increases with pH.

TOPIC

8

Reaction Kinetics

Key content that you will be examined on:

1. Simple rate equations; orders of reaction; rate constants
2. Concept of activation energy
3. Effect of concentration, temperature, and catalysts on reaction rate
4. Homogeneous and heterogeneous catalysis
5. Enzymes as biological catalysts

Topic 8

Reaction Kinetics

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. The rate equation for reaction is given by:

$$\text{rate} = k[A][B]$$

If concentration units are mol dm^{-3}, what are the possible units of the rate constant, k?

A mol dm^{-3} s^{-1} mol dm^{-3} s^{-}

B mol^{-1} dm^{3} s^{-1} mol dm^{-3} x mol dm^{-3}

C mol^{-2} dm^{3} s^{-1} mol^{-} dm^{3} s^{-}

D mol^{-1} s^{-1}

Helping Concepts *Exam Favourite Rating* ★★★

The unit for rate is always mol dm^{-3} s^{-1}.

Therefore, mol dm^{-3} s^{-1} = k (mol dm^{-3})(mol dm^{-3})

k = mol^{-1} dm^{3} s^{-1}

---

2. If the reaction P + Q → R + S is described as being of *zero order* with respect to **P**, it means that why not this?

A P is catalyst in this reaction.

B no P molecules possess sufficient energy to react.

C the concentration of P does not change during the reaction.

D the rate of reaction is independent of the concentration of P.

Helping Concepts *Exam Favourite Rating* ★★

Zero order with respect to a reactant means that the rate is independent of the concentration of the reactant, i.e. a change in concentration of P has no effect on the rate of the reaction.

---

3. If the rate of decay of a radioactive isotope decreases from 200 counts per minute to 25 counts per minute after 24 hours, what is its half-life?

A 2 hours   B 4 hours

C 6 hours   D 8 hours

Helping Concepts *Exam Favourite Rating* ★★★

$$200 \xrightarrow{t_{1/2}} 100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25$$

$\therefore 3 \times t_{1/2} = 24$

$t_{1/2} = 8$ hours

Alternatively, let x be the half-life.

$$200 \times (\frac{1}{2})^{\frac{24}{x}} = 25 \Rightarrow (\frac{1}{2})^{\frac{24}{x}} = \frac{1}{8}$$

$$\Rightarrow \frac{24}{x} \ln\frac{1}{2} = \ln\frac{1}{8} \Rightarrow x = 8 \text{ hours}$$

---

4. The rate equation for the reaction

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

is: rate = $k[S_2O_8^{2-}(aq)][I^-(aq)]$, where k is the rate constant.

Which of the following conclusions can be drawn from this information?

confusion point

A The value of k depends on the concentrations of $S_2O_8^{2-}$ and I^- ions.

B The reaction goes to completion.

C The reaction is first order with respect to $S_2O_8^{2-}$ ion.

D The reaction is second order with respect to I^- ion.

Helping Concepts *Exam Favourite Rating* ★★

Since the power of $[S_2O_8^{2-}(aq)]$ in the rate equation is 1, the reaction is thus first order with respect to $S_2O_8^{2-}$ ion.

---

5. Which statement about the effect of a catalyst on a reversible reaction is correct?

1/3 × 8 (1 half hours life) 200 $\xrightarrow{(i)}$ 100 $\xrightarrow{(ii)}$ 50 $\xrightarrow{(iii)}$ 25

A It increases the equilibrium constant for the forward reaction.

B It increases the yield of product in an equilibrium.

C It increases the rate constant for both the forward reaction and the reverse reaction.

D It increases the rate constant for the forward reaction but not that of the reverse reaction.

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A catalyst increases the rate of a reaction by increasing the rate constant, regardless of whether it is a forward or a backward reaction ($\therefore$(D) is wrong). However, it does not affect the equilibrium constant (only affected by temperature) nor the yield of product.

6. A radioactive element has two isotopes, **G** and **H**, with half-lives of 5 min and 15 min respectively. An experiment starts with 4 times as many atoms of **G** as of **H**.

Radioactive decay is a first-order reaction.

How long will it be before the number of atoms of **G** left equals the number of atoms of **H** left?

A 5 min　　B 10 min

C 15 min　　D 20 min

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Let the number of atoms in **G** and **H** be $4x$ and x respectively.

G: $4x \xrightarrow{5\text{ min}} 2x \xrightarrow{5\text{ min}} x \xrightarrow{5\text{ min}} \frac{1}{2}x$

H: $x \xrightarrow{15\text{ min}} \frac{1}{2}x$

7. The decomposition of hydrogen peroxide in aqueous solution is a first order process.

If 10% of the hydrogen peroxide in a solution of concentration 0.1 mol dm^{-3} decomposes in 5 minutes at a certain temperature, what percentage of the hydrogen peroxide in a solution of concentration 0.2 mol dm^{-3} would decompose in 5 minutes at the same temperature?

A 5%　　B 10%

C 19%　　D 20%

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$t_{1/2}$ is a constant for a first order kinetic reaction regardless of the initial concentration of their reactants. Hence, the time taken for 10% of H_2O_2 to decompose is the same for different concentrations of H_2O_2.

8. The hydrolysis of $(CH_3)_3CBr$ (represented by RBr) by hydroxide ion proceeds in two steps.

$$RBr \rightarrow R^+ + Br^- \quad \text{(slow)}$$
$$R^+ + OH^- \rightarrow ROH \quad \text{(fast)}$$

Which one of the following rate equations is consistent with this scheme?

A rate $= k[RBr]^2$

B rate $= k[RBr][OH^-]$

C rate $= k[R^+][OH^-]$

D rate $= k[RBr]$

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The slow step of this hydrolysis of RBr is called the rate determining step. The overall rate of reaction depends on the rate of this slow rate determining step. Hence, the rate equation follows that of the rate determining step.

9. An experiment is set up to measure the rate of hydrolysis of methyl ethanoate.

$$CH_3CO_2CH_3 + H_2O \rightarrow CH_3CO_2H + CH_3OH$$

The hydrolysis is found to be slow in neutral aqueous solution but it proceeds at a measurable rate when the solution is acidified with hydrochloric acid.

What is the function of the hydrochloric acid in the reaction mixture?

A to increase the reaction rate by catalytic action

B to ensure that the reaction reaches equilibrium

C to maintain a constant pH during the reaction

D to suppress ionisation of the ethanoic acid formed

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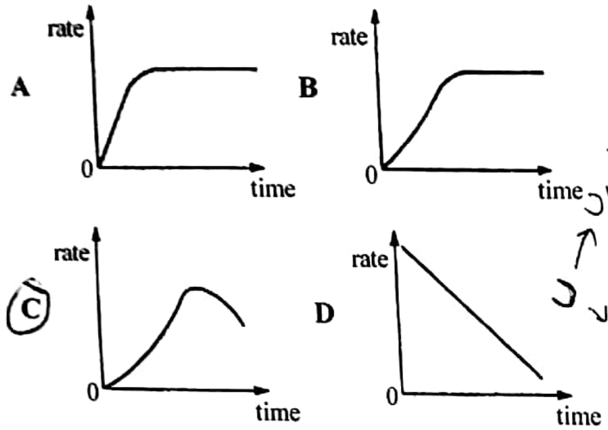
HCl increases the rate of hydrolysis and is not consumed at the end of the reaction. Therefore, it is acting as a catalyst.

When $[CH_3COCH_3]$ is large, it becomes almost constant and the reaction becomes pseudo zeroth order with respect to CH_3COCH_3. Any change in rate will not be due to CH_3COCH_3.

---

10. Which one of the following curves would be obtained if the rate of reaction was plotted against time for an auto-catalytic reaction (i.e. reaction in which one of the products catalyses the reaction)?



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In the beginning, as the reactants react, the product formed catalyses the reaction. Therefore, the reaction rate increases. A point is reached whereby the reaction rate decreases due to the excessive depletion of the reactants (as oppose to the catalytic effect of the product).

---

11. The acid-catalysed iodination of propanone may be investigated by reacting dilute aqueous iodine with solutions containing known concentrations of propanone and acid. The rate can be followed using a colorimeter.

Why is a large excess of propanone used?

A to buffer the acid concentration

B to give a convenient rate of reaction

C to keep the rate of reaction constant

D to keep the propanone concentration effectively constant

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$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + H^+ + I^-$$

$$R = k[CH_3COCH_3]^x[I_2]^y[H^+]^z$$

12. Lead is the final product formed by a series of changes in which the rate-determining step is the radioactive decay of uranium-238. This radioactive decay is a first-order reaction with a half-life of 4.5×10^9 years.

How long would it take for a rock sample, originally lead-free, to contain a molar proportion of uranium to lead of 1 : 3?

A 1.5×10^9 years

B 2.25×10^9 years

C 9.0×10^9 years

D 13.5×10^9 years

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$$U:\ x \xrightarrow{t_{\frac{1}{2}}} \frac{1}{2}x \xrightarrow{t_{\frac{1}{2}}} \frac{1}{4}x$$

$$Pb:\ 0 \qquad \frac{1}{2}x \qquad \frac{3}{4}x$$

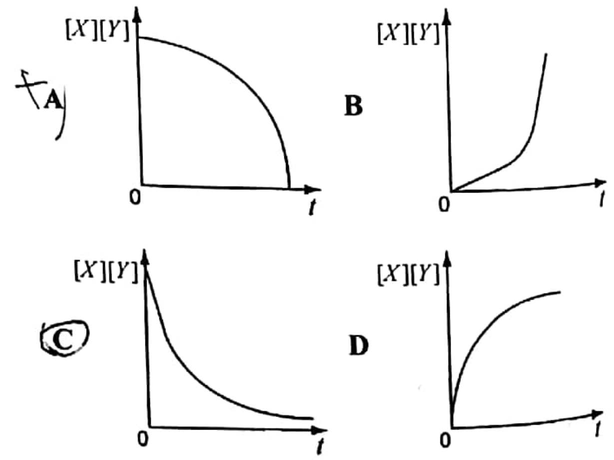
Hence, the time taken is $2t_{\frac{1}{2}}$.

---

13. The product $[X][Y]$ of the concentrations of X and Y is plotted against time, t, for the following second-order reaction.

$$X + Y \rightarrow Z$$

Which graph would be obtained?



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The concentrations of X and Y decrease with time (graphs B and D are wrong). In the initial stage, a steeper gradient is expected because as time passes, $[X]$ and $[Y]$ decrease and the rate of reaction declines. The gradient becomes less steep as time passes.

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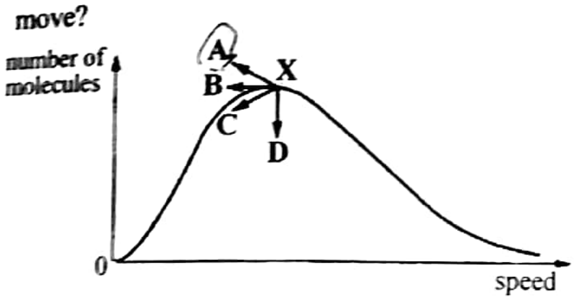
14. The diagram shows the Boltzmann distribution of the speeds of the molecules of a gas. Point **X** represents the most probable speed.

If the gas is cooled, in which direction does **X** move?



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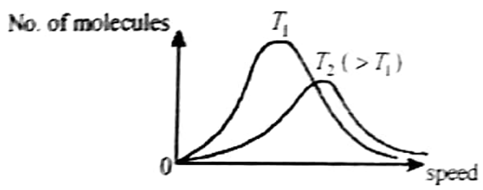
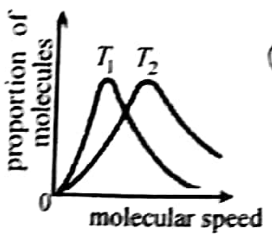
At a lower temperature, the curve shifts to the left and peaks at a higher value.

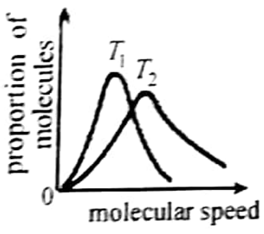


15. Which of the following diagrams correctly represents the Boltzmann distribution of molecular speeds at two temperatures T_1 and T_2, where $T_2 > T_1$?

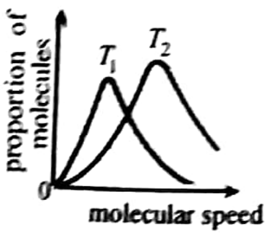
A



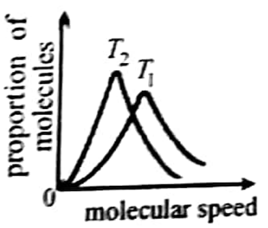
B



C



D



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At T_2 ($> T_1$), the maximum should be lower and shift to higher molecular speed so that the total area under the curve is maintained.

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16. It is often said that the rate of a typical reaction is roughly doubled by raising the temperature by 10 °C.

What explains this observation?

A Raising the temperature by 10 °C doubles the average energy of each molecule.

B Raising the temperature by 10 °C doubles the average velocity of the molecules.

C Raising the temperature by 10 °C doubles the number of molecular collisions in a given time.

D Raising the temperature by 10 °C doubles the number of molecules having more than a certain minimum energy.

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By Collision theory, particles react when they possess energy higher than the minimum energy required, i.e. activation energy, E_a. As temperature increases, the particles have higher average kinetic energy. Raising the temperature by 10 °C causes the rate to be doubled could only mean that the number of particles with energy $> E_a$ is doubled.

17. Propanone reacts with iodine in the presence of an acid.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

The mechanism involves the following steps.

include this in rate eq.

$$CH_3COCH_3 \xrightarrow{H^+} CH_3C(OH)=CH_2 \quad \text{(slow)}$$

$$CH_3C(OH)=CH_2 + I_2 \longrightarrow CH_3CI(OH)CH_2I \quad \text{(fast)}$$

$$CH_3CI(OH)CH_2I \longrightarrow CH_3COCH_2I + HI \quad \text{(fast)}$$

Which conclusion cannot be drawn from this information?

To check whether a specie is catalyst or not, see if it is genereated at end of rxn, if no generated include it in rate eq.

A Iodine is not involved in the rate-determing step.

B The acid acts as a catalyst.

C The overall order of the reaction is 3.

D The rate of the reaction is not affected by a change in the iodine concentrations.

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The rate equation is derived from the slow step (rate determining step), i.e. $R = k[CH_3COCH_3][H^+]$. Hence, the reaction is a second-order (not third) reaction.

18. The rate of the decomposition of the diazonium cation,

$$C_6H_5N_2^+ + H_2O \rightarrow C_6H_5OH + H^+ + N_2$$

can be followed by measuring the time taken for the same volume of nitrogen to be produced from a range of diazonium cation concentrations.

To find the order of the reaction with respect to the diazonium cation, which would be the most suitable graph to plot using the data?

A $[C_6H_5N_2^+]$ against time

B $[C_6H_5N_2^+]$ against 1/time

C volume N_2 against time

D volume N_2 against 1/time

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When different $[C_6H_5N_2^+]$ is used, the rate of reaction may vary. A more dilute solution would take a longer time to produce the same volume of N_2, if it is non-zero order w.r.t. $C_6H_5N_2^+$.

For a short t, $\frac{1}{t}$ gives a good estimate of the rate of reaction. Hence, by plotting $[C_6H_5N_2^+]$ vs $\frac{1}{t}$, the order of reaction w.r.t. $C_6H_5N_2^+$ can be deduced.

19. Lead is the final product formed by a series of changes in which the rate-determining stage is the radioactive decay of uranium-238. This radioactive decay is a first-order reaction with a half-life of 4.5×10^9 years.

What would be the age of a rock sample, originally lead-free, in which the molar proportion of uranium to lead is now 1 : 3?

A 1.5×10^9 years

B 2.25×10^9 years

C 4.5×10^9 years

D 9.0×10^9 years

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Molar ratio of U : Pb = 1 : 3

$$= \frac{1}{1+3} : \frac{3}{1+3}$$

$$= \frac{1}{4} : \frac{3}{4}$$

∴ Amount of U left is $\frac{1}{4}$ of the original.

$$1 \xrightarrow{t_{1/2}} \frac{1}{2} \xrightarrow{t_{1/2}} \frac{1}{4}$$

Therefore, the age of the rock sample is $2 \times t_{1/2}$, i.e. 9.0×10^9 years.

20. The reaction of acidified, aqueous potassium iodide with aqueous hydrogen peroxide

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

is thought to involve the following steps:

$$H_2O_2 + I^- \rightarrow H_2O + OI^- \quad \text{(slow)}$$

$$OI^- + H^+ \rightarrow HOI \quad \text{(fast)}$$

$$HOI + H^+ + I^- \rightarrow I_2 + H_2O \quad \text{(fast)}$$

Which one of the following conclusions **cannot** be drawn from this information?

A The iodide ion is oxidised by the hydrogen peroxide.

B The acid acts as a catalyst.

C The reaction is first order with respect to the iodide ion.

D The rate determining step is

$$H_2O_2 + I^- \rightarrow H_2O + OI^-.$$

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H^+ is consumed during the reaction (steps 2 and 3) and is not re-generated at the end. Hence, it cannot be a catalyst. To see weather a reactant is catalyst or not, see if it is regenerated in end or not?

21. The rate of the reaction $RBr + OH^- \rightarrow ROH + Br^-$ is given by the rate equation, rate $= k[RBr]$.

Which reaction mechanism is consistent with this rate equation?

A $RBr + OH^- \xrightarrow{slow} RBrOH^-$
$RBrOH^- \xrightarrow{fast} ROH + Br^-$

B $RBr \xrightarrow{fast} R^+ + Br^-$
$R^+ + OH^- \xrightarrow{slow} ROH$

C $RBr \xrightarrow{slow} R^+ + Br^-$
$R^+ + OH^- \xrightarrow{fast} ROH$

D $RBr + OH^- \xrightarrow{fast} RBrOH^-$
$RBrOH^- \xrightarrow{slow} ROH + Br^-$

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Since the rate equation shows a first order kinetics w.r.t. RBr, the rate determining step should be one that consists of only one RBr molecule as the reactant in the elementary step.

---

22. The table gives data for the reaction between X and Y at constant temperature.

experiment	[X]/mol dm^{-3}	[Y]/mol dm^{-3}	initial rate /mol dm^{-3} s^{-1}
1	0.3	0.2	4.0×10^{-4}
2	0.6	0.4	1.6×10^{-3}
3	0.6	0.8	6.4×10^{-3}

2x 4x 4x

$\frac{6.4}{1.6}$ $\frac{.4}{4}$

What is the rate equation for the reaction?

A rate = $k[X][Y]^2$

B rate = $k[X]^2[Y]$

C rate = $k[X]^2$

D rate = $k[Y]^2$

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Comparing experiments 2 and 3, the rate becomes 4 times faster when [Y] is doubled. Hence, order of reaction with respect to Y is 2. Comparing experiments 1 and 2, the rate is increased 4 times which can be attributed to [Y] being doubled. The doubling of [X] has no effect on the rate so that order of reaction with respect to X is 0. Hence, rate = $k[Y]^2$.

---

23. In power stations where hydrocarbon fuels are burned in air, nitrogen dioxide, NO_2, is present in the exhaust gases. In modern power stations the NO_2 is removed from the exhaust gases.

A group of students was asked why it is important to remove NO_2 from the exhaust gases from power stations.

Which is the **most** important reason to remove NO_2?

A NO_2 catalyses the formation of acid rain from atmospheric carbon dioxide.

B NO_2 catalyses the formation of acid rain from atmospheric sulfur dioxide.

C NO_2 causes global warming due to the thinning of the ozone layer.

D NO_2 is a greenhouse gas which would causes global warming.

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NO_2 catalyses the conversion of SO_2 to SO_3 and results in acid rain.

$$NO_2 + SO_2 \rightarrow NO + SO_3$$

NO is then readily re-converted back to NO_2.

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2$$

---

24. The reaction of hydrogen peroxide with iodide ions in acidic solution can be monitored by an initial rate method.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(\ell) + I_2(aq)$$

The rate equation was found to be as follows.

$$\text{Rate} = k[H_2O_2]^1[H^+]^0[I^-]^1$$

What could be the mechanism of this reaction?

A $H_2O_2 + H^+ \rightarrow H_2O + OH^+$ (fast)
$OH^+ + 2I^- + H^+ \rightarrow H_2O + I_2$ (slow)

B $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)
$H^+ + IO^- \rightarrow HIO$ (fast)
$HIO + H^+ + I^- \rightarrow I_2 + H_2O$ (fast)

C $2H^+ + 2I^- \rightarrow 2HI$ (fast)
$2HI + H_2O_2 \rightarrow I_2 + 2H_2O$ (slow)

D $H_2O_2 + I^- + H^+ \rightarrow H_2O + HIO$ (fast)
$HIO + I^- \rightarrow I_2 + OH^-$ (slow)
$OH^- + H^+ \rightarrow H_2O$ (fast)

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Since the rate equation is first order w.r.t. H_2O_2 and I^-, the rate determining step should be bimolecular (overall 2nd order) and involve 1 H_2O_2 molecule and 1 I^- ion.

---

25. A reaction between P and Q produces a gas. This reaction is first order with respect to P and second order with respect to Q. Two experiments were carried out.

In the first experiment, at given concentrations of P and Q, 100 cm^3 of gas were produced in the first minute of the reaction.

In the second experiment, under the same external conditions, the initial concentration of P is doubled and that of Q is halved.

What volume of gas will be produced in the second experiment, in the first minute of the reaction?

A 25 cm^3 B 50 cm^3

C 100 cm^3 D 200 cm^3

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$$R = k[P][Q]^2$$

1st experiment,

$$R_1 = k \cdot a \cdot b^2$$

2nd experiment,

$$R_2 = k(2a)(\frac{1}{2}b)^2 = \frac{1}{2}kab^2 = \frac{1}{2}R_1$$

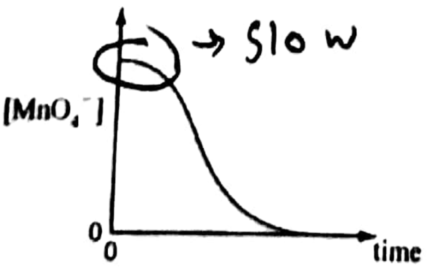
Hence, half the volume of gas will be collected.

---

26. The reaction of manganate(VII) ions with ethanedioate ions in acid solution may be represented by the following equation.

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq)$$
$$\rightarrow 2Mn^{2+}(aq) + 8H_2O(\ell) + 10CO_2(g)$$

The graph below shows concentration of manganate(VII) ions against time for this reaction.



What does the shape of the graph suggest about this reaction?

A it is exothermic.

B It is endothermic.

C It shows first order kinetics.

D It produces its own catalyst.

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In the beginning, the reaction is slow (slope is gentle). When Mn^{2+} is produced, it acts as a catalyst and catalyses the reaction (slope becomes steep). Towards the end of the reaction, the concentration of the reactants are low and the reaction becomes slow again.

---

27. The table shows experimental results obtained for the following reaction.

$$2XO + O_2 \rightarrow 2XO_2$$

partial pressure of XO (in arbitrary units)	100	100	50	50
partial pressure of O_2 (in arbitrary units)	100	25	100	-
relative rate	1.0	0.25	0.50	0.125

What is the missing value of the partial pressure of O_2 in the table?

A 12.5   B 25

C 40   D 50

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Let p_X represents the partial pressure of X.

When p_{O_2} is reduced to $\frac{1}{4}$ (2nd expt), the rate is also reduced to $\frac{1}{4}$. Hence, rate $\propto p_{O_2}$. When p_{XO} is reduced to $\frac{1}{2}$ (3rd expt), the rate is also reduced to $\frac{1}{2}$. Hence, rate $\propto p_{XO}$ and therefore, rate $\propto p_{O_2} \cdot p_{XO}$.

By comparing with the 1st experiment, the rate in the last experiment is reduced to $\frac{1}{8}$.

The given p_{XO} (50) reduces the rate to $\frac{1}{2}$. To further reduce the rate to $\frac{1}{8}$, p_{O_2} should be $(\frac{1}{4} \times 100) = 25$.

---

28. The hydrolysis of ethyl ethanoate in aqueous solution can be catalysed by hydrogen ions from sulfuric acid.

To determine the order of this reaction with respect to hydrogen ions, which method should be used?

A Measure the change in pH during the reaction.

B Measure the rate of the reaction several times, but with a different concentration of ethyl ethanoate each time.

C Measure the rate of the reaction several times, but with a different concentration of sulfuric acid each time.

D Remove samples at various time intervals and titrate against a standard solution of aqueous sodium hydroxide.

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To measure the effect on the rate by a parameter (in this case [H^+]), the reaction should be followed by varying that parameter ([H^+]) while keeping all other parameters (e.g. [ester], temperature, etc.) constant.

For (A) and (D), as the acid is a catalyst, [H^+] will remain constant and the pH and titre value will not change with time.

---

29. Photochromic glass, used for sunglasses, darkens when exposed to bright light and becomes more transparent again when the light is less bright. The depth of colour of the glass is related to the concentration of silver atoms.

The following reactions are involved.

reaction 1 $Ag^+ + Cl^- \rightleftharpoons Ag + Cl$

reaction 2 $Cu^+ + Cl \rightarrow Cu^{2+} + Cl^-$

reaction 3 $Cu^{2+} + Ag \rightarrow Cu^+ + Ag^+$

Which statement about these reactions is correct?

A Cu^+ and Cu^{2+} ions act as catalysts.

B Cu^+ ions act as an oxidising agent in reaction 2.

C Reaction 2 is the one in which light is absorbed.

D Ag^+ ions are oxidised in reaction 1.

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Since Cu^+ used up in reaction 2 but produced in reaction 3 and Cu^{2+} is produced in reaction 2 but used up in reaction 3, they are not chemically changed in the reaction. Also their presence speeds up the reaction since Cu^+ reduces Cl to Cl^- while Cu^{2+} oxidises Ag to Ag^+. Hence, they act as catalysts.

Statement B is incorrect since Cu^+ acts as a reducing agent and not an oxidising agent in reaction 2.

Statement C is incorrect since light is absorbed in reaction 1 rather than reaction 2.

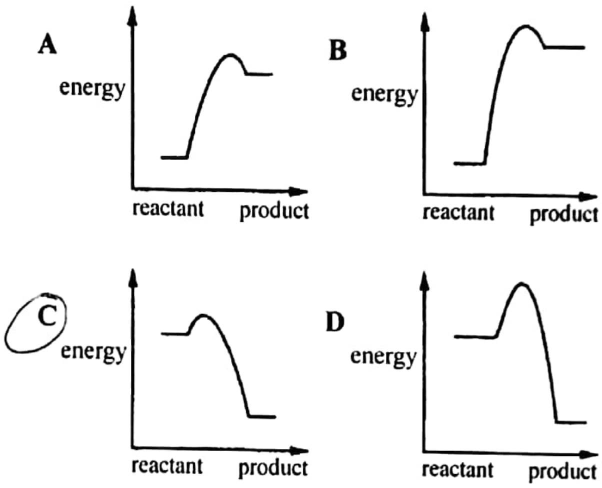
Statement D is incorrect since Ag^+ ions are reduced rather than oxidised in reaction 1.

---

30. Four reactions of the type shown are studied at the same temperature.

$$X(g) + Y(g) \rightarrow Z(g)$$

Which is the correct reaction pathway diagram for the reaction that would proceed most rapidly and with good yield?



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For a good yield, the product should be as stable as possible, i.e. low in energy. Hence, diagrams C and D. For a fast rate of reaction, the activation energy should be as low as possible. Reaction D is slower than reaction C.

---

31. The reaction between NO_2 and SO_2 is a key stage in the formation of acid rain.

$$NO_2(g) + SO_2(g) \rightarrow NO(g) + SO_3(g)$$

The initial rate of this reaction was measured for different concentrations of reactants and the following results obtained.

[NO_2]/ mol dm^{-3}	[SO_2]/ mol dm^{-3}	relative rate
0.005	0.005	1.00
0.006	0.006	1.44
0.008	0.006	1.92

Which row gives the correct orders of reaction with respect to the two reactants?

	order with respect to $[NO_2]$	order with respect to $[SO_2]$
A	1	0
B	1	1
C	2	0
D	2	1

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Comparing expt. 2 and 3, $[NO_2]$ increases to $\frac{0.008}{0.006} = \frac{4}{3}$ times. The rate increases to $\frac{1.92}{1.44} = \frac{4}{3}$ times. Hence, order w.r.t. $NO_2 = 1$.

Comparing expt. 1 and 2, $[NO_2]$ increases to $\frac{0.006}{0.005} = \frac{6}{5}$ times and $[SO_2]$ also increases to $\frac{6}{5}$ times. The rate of reaction increases to 1.44 times.

$\therefore (\frac{6}{5})^1(\frac{6}{5})^x = 1.44$ where x is the order w.r.t. SO_2.

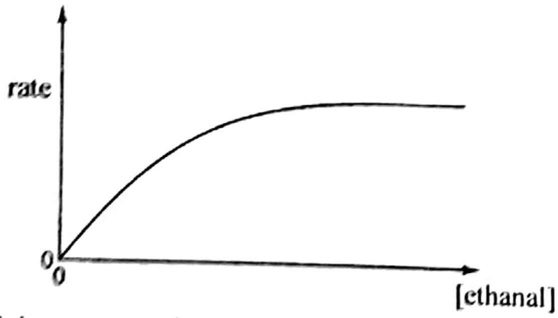
Hence, $x = 1$.

---

32. The enzyme *alcohol dehydrogenase* catalyses an important step in the production of ethanol by fermentation.

$$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$$

The graph shows how the rate of this enzyme-catalysed reaction varies with the concentration of ethanal.



Which statement best explains the reason for the flattening off of the curve?

A All the ethanal has been used up and the reaction has finished.

B As the ethanol product builds up the reaction slows down.

C At high ethanal concentrations all the active sites in the enzyme molecules are occupied by ethanal molecules.

D At high ethanal concentrations the ethanal inhibits the action of the enzyme.

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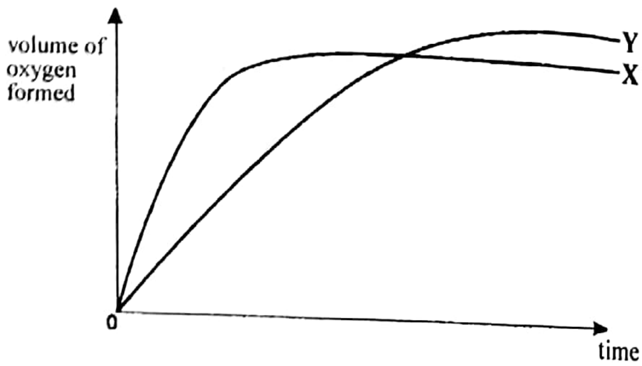
The catalysed reaction takes place when CH_3CHO is attached to the enzyme. As $[CH_3CHO]$ increases, more CH_3CHO molecules attach onto the enzyme and the reaction rate increases proportionally. However, when all the active sites have been occupied by CH_3CHO, further increase in $[CH_3CHO]$ will not help to further increase the rate of reaction.

---

33. In the following diagram, curve **X** was obtained by observing the decomposition of 100 cm^3 of 1.0 mol dm^{-3} hydrogen peroxide, catalysed by manganese(IV) oxide.



Which alteration to the original experimental conditions would produce curve **Y**?

A adding water

B adding some 0.1 mol dm^{-3} hydrogen peroxide

C using less manganese(IV) oxide

D lowering the temperature

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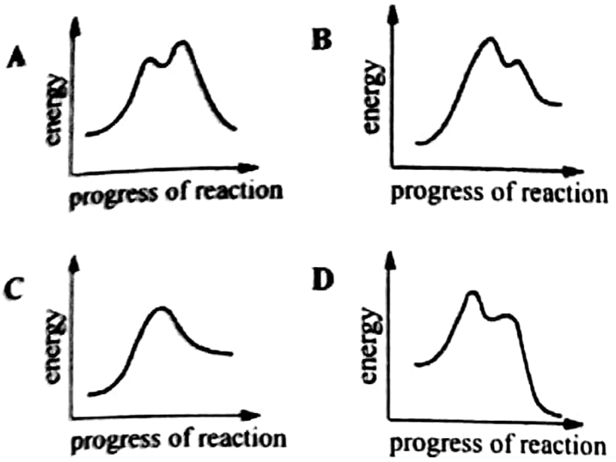
Adding some 0.1 mol dm^{-3} H_2O_2 dilutes the H_2O_2 solution and increases the total amount of H_2O_2 present. Hence, the rate of reaction becomes slower (more gentle slope) and the total volume of O_2 evolved is higher.

---

34. The nitration of benzene by concentrated nitric acid dissolved in concentrated sulfuric acid can be represented by the following equation.

$$C_6H_6 + NO_2^+ \rightleftharpoons C_6H_6NO_2^+ \rightarrow C_6H_5NO_2 + H^+$$

Which of the following reaction profiles correctly represents this mechanism?



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The energy profile should have 2 'humps' since the reaction takes place in 2 steps. The first step is the slow step and therefore, the activation energy of the first hump should also be higher. The reaction is exothermic. Hence, the products are at a lower energy than do the reactants.

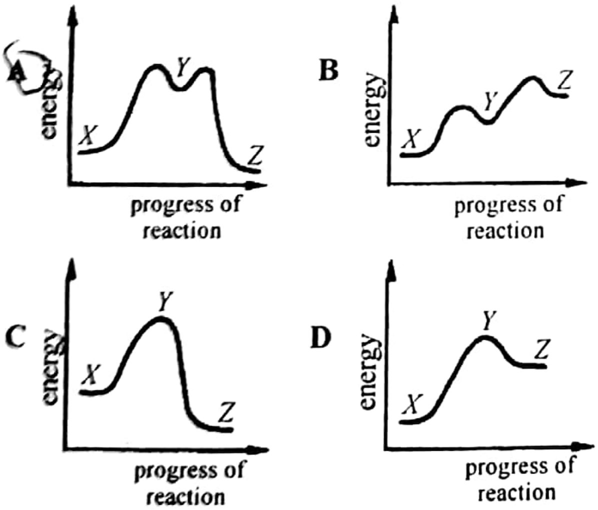
---

imp

35. In the conversion of compound X into compound Z, it was found that reaction proceeded by way of compound Y, which could be isolated. The steps involved were:

$$X \rightarrow Y; \quad \Delta H, \text{ positive}$$
$$Y \rightarrow Z; \quad \Delta H, \text{ negative}$$

Which reaction profile fits these data?



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Y is known as the intermediate and it should be at the 'valley' in the profile ($\therefore$ graphs C and D are wrong). Energy of Y should be higher than that of X (since ΔH is positive) and also higher than that of Z (since ΔH is negative).

---

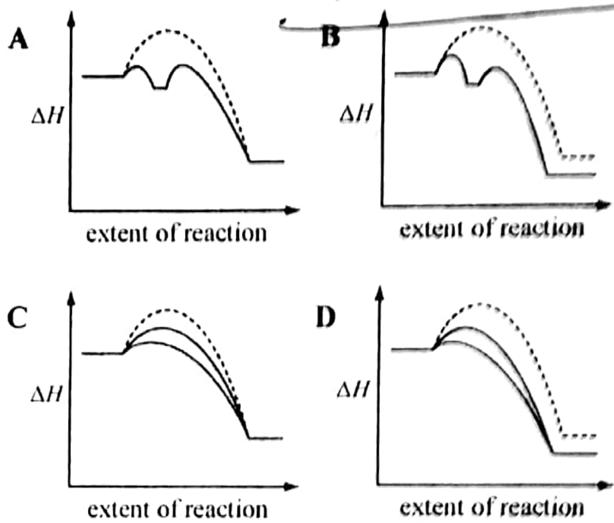
36. The uncatalysed reaction between SO_2 and O_2 is slow.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

The reaction is speeded up in the presence of the homogeneous catalyst NO, which participates as follows.

$$2NO + O_2 \rightarrow 2NO_2$$
$$2NO_2 + 2SO_2 \rightarrow 2NO + 2SO_3$$

Which reaction pathway diagram is most appropriate for describing the enthalpy changes occurring during the catalysed reaction? In each case the reaction pathway for the uncatalysed reaction is shown as a dashed line. 2 steps — 2 humps



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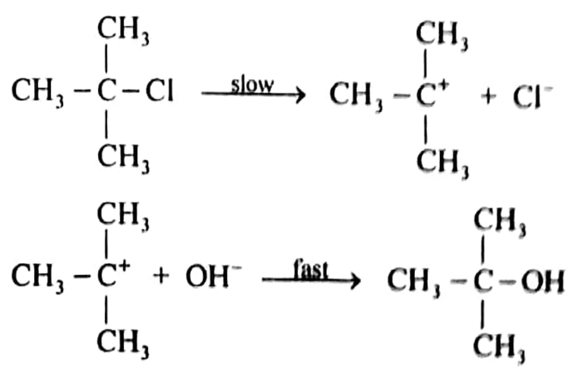
The energy levels of the reactants and products for uncatalysed reaction are not affected by the presence of a catalyst (i.e. B and D are wrong).

In the catalysed reaction, the mechanism goes through 2 steps. Hence, there should be 2 humps in the catalysed reaction, and the activation energy for the catalysed reaction is lower (lower hump).

---

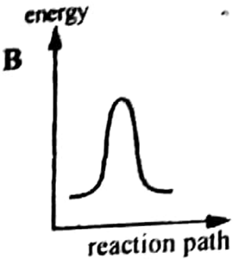
37. A possible mechanism of the hydrolysis of 2-chloro-2-methylpropane is shown.



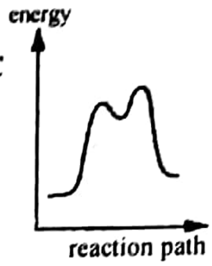
Which diagram represents the reaction profile for this mechanism?

A

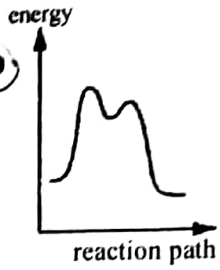
B



C



D



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The carbocation is an intermediate so that it would result in a minimum point in the energy profile. Hence, diagrams A and B are incorrect.

The first step is expected to have a higher activation energy since it requires bond breaking whereas that of the second step is expected to be lower since it involves reaction between oppositely charged particles. Both diagrams C and D show a higher activation energy in step 1. However, the alcohol formed is more stable than chloroalkane. Hence, diagram D is the answer.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

38. The rate equation for the reaction $I^- + CH_3Cl \rightarrow CH_3I + Cl^-$ is given below.

$$\text{rate} = k[I^-][CH_3Cl]$$

The reaction is therefore B

1 second order.

2 first order with respect to iodide ion.

3 speeded up by an excess of chloride ions.

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In the rate equation, the powers of $[I^-]$ and $[CH_3I]$ are 1. Therefore, the reaction is a second-order reaction but is first order with respect to I^- and CH_3I respectively. An excess of Cl^- will not change the forward rate.

Note: The concentration of Cl^- is not involved in the rate equation.

39. Which statements about the properties of a catalyst are correct? C

1 A catalyst increases the average kinetic energy of the reacting particles.

2 A catalyst increases the rate of the reverse reaction.

3 A catalyst has no effect on the enthalpy change ΔH° of the reaction.

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1. A catalyst does not affect the average kinetic energy of the particles. Temperature does.

*2. A catalyst increases the rate of both forward and backward reactions.

*3. The ΔH remains unchanged in the presence of a catalyst.

40. A theoretical reaction involves $P + Q \rightarrow$ product. The rate equation is rate $= k[P][Q]^x$ and the units of the rate constant, k, are $mol^y\ dm^z\ s^{-1}$.

Which sets of values of x, y and z fit the above information?

	x	y	z
1	0	−1	+3
2	1	−1	+3
3	2	−2	+6

C

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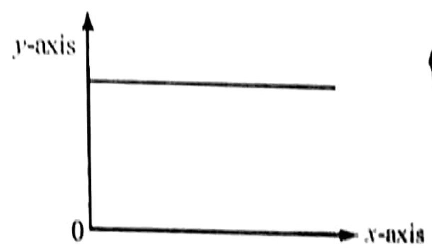
$$mol\ dm^{-3}\ s^{-1} = k(mol\ dm^{-3})(mol\ dm^{-3})^x$$
$$k = (mol\ dm^{-3})^{-x}\ s^{-1}$$
$$= mol^{-x}\ dm^{3x}\ s^{-1}$$

Hence, $y = -x$
$z = 3x$

41. The kinetics of the zero-order reaction $P \rightarrow Q$ were investigated under different conditions.

The table shows pairs of quantities that were plotted as graphs.

Which pairs gave the following graph?



B

	y-axis	x-axis
1	rate	time
2	rate constant	time
3	rate constant	temperature

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*1. For a zero-order reaction, the rate of reaction does not change with time.

*2,3. The rate constant, k, is a constant at constant temperature. It does not vary with time. However, when the temperature changes, k also changes (unless $\Delta H = 0$). 1M

2. The reaction does not indicate a reversible reaction.

3. Endothermic reactions can occur readily. E.g. the dissolution of NaCl in H_2O is endothermic and it takes place readily. On the other hand, some exothermic reactions may not readily occur. E.g. the conversion of diamond back to graphite.

---

42. The substitution reaction between $CH_4(g)$ and $Br_2(g)$ in the presence of ultraviolet light involves the following steps.

$$Br_2 \xrightarrow{\text{uv light}} 2Br\bullet$$
$$CH_4 + Br\bullet \rightarrow \bullet CH_3 + HBr$$
$$\bullet CH_3 + Br_2 \rightarrow CH_3Br + Br\bullet$$

Why is this called homogenous catalysis?

1 Bromine radicals are in the same physical state as bromine and methane.

2 Bromine and methane are in the same physical state.

3 The bromine molecule splits into two bromine radicals.

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Homogeneous means all the substances are in the same phase. In this case, CH_4 and Br_2 are in the gaseous phase. The catalyst $Br\bullet$ radical is also in the same gaseous phase. Hence, the reaction is known as homogeneous catalysis.

---

44. The rate of reaction between bromine and methanoic acid is first order with respect both to bromine and to methanoic acid.

$$Br_2(aq) + HCO_2H(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

Which of the following can be correctly deduced from this information?

1 Doubling the concentration of methanoic acid doubles the rate of evolution of gas.

2 Halving the concentration of both reactants simultaneously will halve the reaction rate.

3 The overall order of the reaction is 1.

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$$R = k[Br_2][HCO_2H]$$

*1. When $[HCO_2H]$ is doubled, R is doubled.

2. When both $[Br_2]$ and $[HCO_2]$ are halved, R decreases by 4 times. NP

3. The overall order is 2.

---

43. The conversion of graphite has only a small positive value of ΔH.

$$C\,(\text{graphite}) \rightarrow C\,(\text{diamond}); \quad \Delta H = +2.1 \text{ kJ mol}^{-1}$$

However, the production of synthetic diamonds is very difficult.

Which of the following statements help to explain this?

1 The activation energy of the reaction is large.

2 An equilibrium exists between diamond and graphite.

3 Only exothermic reactions can be made to occur readily.

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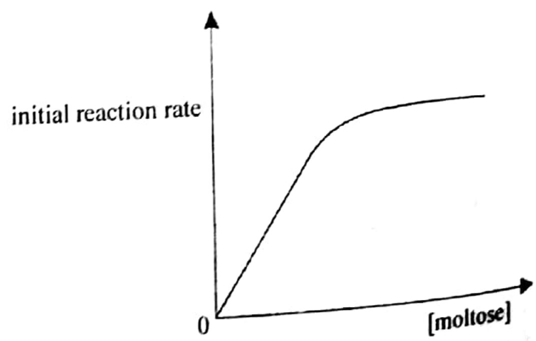
*1. The conversion of diamond from graphite involves breaking strong covalent bonds in graphite and restructing of the crystal lattice. A lot of energy is required to overcome this energy barrier.

45. The graph shows the results of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. The concentration of amylase was constant in all experiments.



Which of the following conclusion can be deduced from these results?

1 When [maltose] is low, the rate is first order with respect to [maltose].

2 When [maltose] is high, the rate is independent of [maltose].

3 When [maltose] is high, the rate is independent of [amylase].

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*1. When [maltose] is low, the graph is straight with a positive slope, indicating a direct dependence, i.e. first order with respect to [maltose].

*2. At high [maltose], the graph is horizontal, indicating that the rate does not vary with [maltose].

3. The graph does not show how the rate of the reaction varies with [amylase].

---

46. Which suggested mechanisms are consistent with the experimentally obtained rate equations?
D

rate equation	*suggested mechanism*
1 rate $= k_1[NO]^2[H_2]$	$2NO(g) + H_2(g) \xrightarrow{slow} N_2O(g) + H_2O(g)$ $N_2O(g) + H_2(g) \xrightarrow{fast} N_2(g) + H_2O(g)$
2 rate $= k_2[H_2][I_2]$	$H_2(g) \xrightarrow{slow} 2H(g)$ $2H(g) + I_2 \xrightarrow{fast} 2HI(g)$
3 rate $= k_3[HBr][O_2]$	$2HBr(g) + O_2(g) \xrightarrow{slow} 2HBrO(g)$ $HBrO(g) + HBr(g) \xrightarrow{fast} H_2O(g) + Br_2(g)$

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Only reactants in the rate determining step (rds) would appear in the rate equation and the order of the reaction w.r.t. a reactant would be the number of reactant particles involved in the rate determining step.

*1. 2 NO and 1 H_2 are involved in the rds so that rate $= k_1[NO]^2[H_2]$.

2. Only 1 H_2 is involved in the rds so that rate $= k_2[H_2]$.

3. 2 HBr and 1 O_2 are involved in the rds so that rate $= k_3[HBr]^2[O_2]$.

---

47. Methane is a greenhouse gas, but it is destroyed in the troposphere by the action of hydroxy radicals.
B

$$\bullet OH + CH_4 \rightarrow \bullet CH_3 + H_2O$$

A study of the rate of this reaction in a mixture, where the concentration of methane did not change, give the following results.

time after start of reaction/10^{-4} s	relative [•OH]
0.0	10.0
1.0	7.0
2.0	5.0
3.0	3.5
4.0	2.5
5.0	1.8

Which conclusions can be drawn about the kinetics of this reaction under these conditions?

1 The half-life is 2.0×10^{-4} s.

2 The reaction is first order with respect to [•OH].

3 The overall reaction is second order.

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*1,*2. From time $t = 0$ to 2×10^{-4} s and $t = 2 \times 10^{-4}$ s to 4×10^{-4} s, the relative [•OH] is halved from 10.0 to 5.0 and 5.0 to 2.5. The reaction is thus first order w.r.t. •OH and the half-life is 2×10^{-4} s.

3. Since $[CH_4]$ is constant, we are not able to deduce the order w.r.t. CH_4 from the data.

---

48. Hydrogen reacts with gaseous bromine to form hydrogen bromide,
B

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$

and with gaseous iodine to form hydrogen iodide.

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

For the first reaction, the rate equation is

$$\text{rate} = \frac{k_1[H_2][Br_2]^{1.5}}{[Br_2] + k_2[HBr]}$$

For the second reaction, the rate equation is

$$\text{rate} = k[H_2][I_2]$$

What can be deduced from this information only?

1 For the hydrogen/bromine reaction, the formation of HBr slows down the rate of the forward reaction.

2 Only the hydrogen/iodine reaction could be a single step reaction.

3 The mechanism of the hydrogen/bromine reaction involves free radicals.

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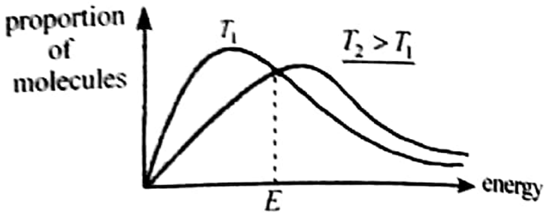
*1. The formation of HBr increases [HBr]. From the rate equation, rate decreases.

*2. The reaction could be single-step reaction since the stoichiometric ratio of the overall equation matches those in the rate equation. The reaction between H_2 and Br_2 is multi-step.

3. The information could not be inferred.

*2. The area under the curve represents the total number of molecules present in the system.

*3. From the curves, it can be clearly seen that the maximum of the curve is displaced to the right at a higher temperature.



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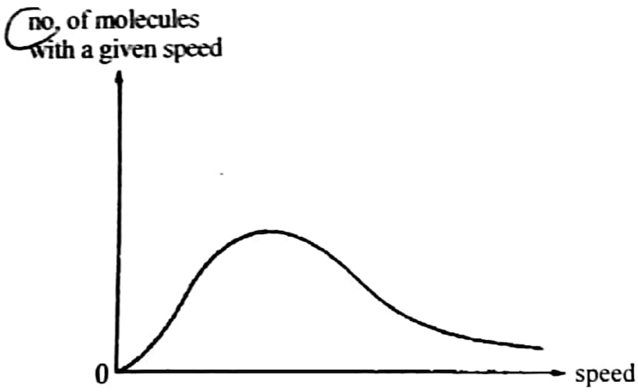
49 The graph shows the Boltzmann distribution of molecular speeds.



Which statements are correct?

1 Raising the temperature always decreases the number of molecules with a given speed.

2 The area under the curve is proportional to the number of molecules present.

3 Raising the temperature moves the maximum of the curve to the right.

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1. Raising the temperature decreases the number of molecules with lower speeds but increases the number of molecules with faster speeds.

50. The diagram represents the Boltzmann distribution of molecular energies at a given temperature.

As temperature increases, which of the following statements are correct?

1 The maximum of the curve is displaced to the right.

2 The proportion of molecules with energies above a given value increases.

3 At all energies, the proportion of molecules of a particular energy increases.

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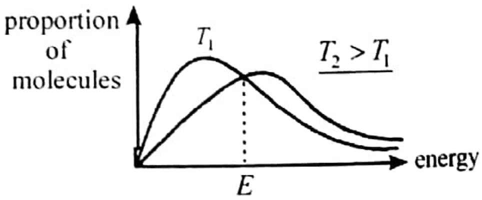


*1. From the curves, it can be clearly seen that the maximum of the curve is displaced to the right at a higher temperature.

*2. From the curves, the proportion of molecules with energies above E is higher at a higher temperature. For energies below E, there are more molecules at a lower temperature, thus showing that there are more molecules at a higher temperature with energies above that given value. On the whole, it may be argued that at a higher temperature, the average molecular energy increases and hence the statement is true.

3 At any particular energy less than E_a the number of molecules of that energy is lower at a higher temperature.

51. After the closure of a chemical plant in Switzerland, the reaction between 1-bromobutane and hydrogen sulfide ions (HS^-) was found to be taking place in the ground.

A

The following results were obtained.

initial concentration of 1-bromobutane /mol dm^{-3}	initial concentration of hydrogen sulfide ions /mol dm^{-3}	initial rate of reaction /mol dm^{-3} s^{-1}
0.1	0.1	1.5×10^{-5}
0.2	0.1	3.0×10^{-5}
0.3	0.1	4.5×10^{-5}
0.1	0.2	3.0×10^{-5}
0.1	0.3	4.5×10^{-5}

Which conclusions can be drawn about the reaction?

1 The reaction is first-order with respect to 1-bromobutane.

2 Both 1-bromobutane and hydrogen sulfide ions are involved in the rate-determining step.

3 The rate constant is $1.5\times10^{-3}mol^{-1}dm^{3}\ s^{-1}$.

Helping Concepts *Exam Favourite Rating* ★★★

*1. Comparing experiments 1 and 2, when the concentration of 1-bromobutane is doubled, the rate is also doubled. Hence, the reaction is first order w.r.t. 1-bromobutane.

*2. Comparing experiments 1 and 5, when the concentration of HS^- is tripled, the rate is also tripled. Hence, the reaction is first order w.r.t. HS^-.

Since the reaction is first order w.r.t. both 1-bromobutane and HS^-, both substances (1 unit each) are involved in the rate determining step.

*3.
$$R=k[\text{1-bromobutane}][HS^-]$$
Using experiment 1 (or any other set),
$$1.5\times10^{-5}=k(0.1)(0.1)$$
$$k=1.5\times10^{-3}\ (\text{mol dm}^{-3})^{-1}\,s^{-1}$$

52. Hydrogen peroxide reacts with acidified iodide ions, liberating iodine. In investigations of this reaction, the following results were obtained.

B

initial concentrations of reactants/mol dm^{-3}			initial rate of formation of iodine/mol dm^{-3} s^{-1}
$[H_2O_2]$	$[I^-]$	$[H^+]$	
0.010	0.010	0.10	2.0×10^{-6}
0.030	0.010	0.10	6.0×10^{-6}
0.030	0.020	0.10	1.2×10^{-5}
0.030	0.020	0.20	1.2×10^{-5}

Which statements follow from these results?

1 The rate equation for the reaction can be written: rate $=k[H_2O_2][I^-]$

2 The reaction is zero order with respect to acid.

3 The rate constant is $2\times10^{-1}\ mol^{-2}\ dm^{6}\ s^{-1}$.

Helping Concepts *Exam Favourite Rating* ★★★

*1,*2. Comparing experiments 1 and 2, when $[H_2O_2]$ is tripled, the initial rate is also tripled. The order of reaction w.r.t H_2O_2 is thus 1.

Comparing experiments 2 and 3, when $[I^-]$ is doubled, the initial rate is also doubled. The order of reaction w.r.t I^- is thus 1.

Comparing experiments 3 and 4, when $[H^+]$ is doubled, the initial rate remains the same. The order of reaction w.r.t H^+ is thus 0.

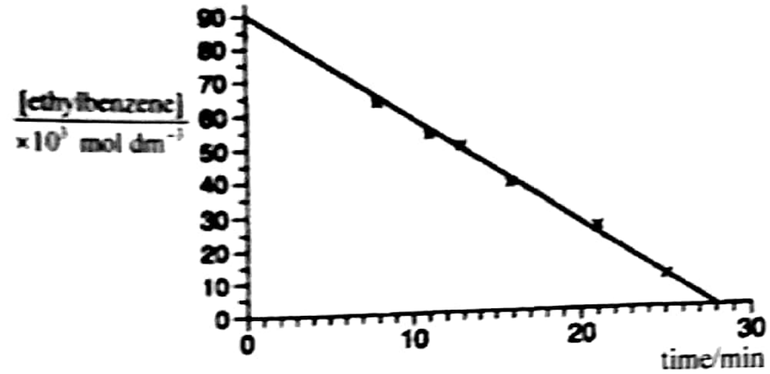
Hence, the rate of equation is
$$R=k[H_2O_2][I^-].$$

3. The unit for the rate constant, k, of a second-order reaction should be $mol^{-1}\ dm^{3}\ s^{-1}$.

Using any set of data, the value of k may be calculated by mere substitution.

E.g. using experiment 1,
$$2.0\times10^{-6}=k(0.01)(0.01)$$
$$k=2\times10^{-2}\ mol^{-1}\ dm^{3}\ s^{-1}$$

53. When ethylbenzene is nitrated by a solution of nitric acid in an inert solvent, the progress of the reaction can be followed by plotting the concentration of ethylbenzene against time. One such plot is given below.



What conclusions can be drawn from this result?

1 The reaction is zero order with respect to ethylbenzene.

2 The rate determining step involves only nitric acid.

3 For mixtures containing a fixed concentration of nitric acid, the slope of the line depends on the initial concentration of ethylbenzene.

If slope constant ✓ rex zero order -

Helping Concepts *Exam Favourite Rating* ★★

*1. Since the graph is linear,

i.e. $\frac{d[\text{ethylbenzene}]}{dt}$ = slope = constant,

the reaction is zero order w.r.t. ethylbenzene, the rate of decrease in [ethylbenzene] is constant.

*2. The reaction involves both ethylbenzene and nitric acid. Since from (1), the reaction rate is independent of [ethylbenzene]. Ethylbenzene cannot be involved in the rate determining step (rds). Hence, the rds must involve nitric acid.

3. The rate is independent of [ethylbenzene]. The slope does not depend on the initial [ethylbenzene].

TOPIC 9

The Periodic Table: Chemical Periodicity

Key content that you will be examined on:

1. Periodicity of physical properties of the elements: variation with proton number across the third period (sodium to argon) of:
   (i) atomic radius and ionic radius
   (ii) melting point
   (iii) electrical conductivity
   (iv) ionisation energy

2. Periodicity of chemical properties of the elements in the third period
   (i) Reaction of the elements with oxygen and chlorine
   (ii) Variation in oxidation number of the oxides (sodium to sulfur only) and of the chlorides (sodium to phosphorus only)
   (iii) Reactions of these oxides and chlorides with water
   (iv) Acid/base behaviour of these oxides and the corresponding hydroxides

Topic 9

The Periodic Table: Chemical Periodicity

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which of the following is the strongest reducing agent?

A Cl^- B Ar
C K^+ D Ca^{2+}

Helping Concepts *Exam Favourite Rating* ★★★

The strongest reducing agent is one whereby its valence electron is the easiest to be removed. Cl^- has the smallest nuclear charge and the greatest ionic size among the isoelectronic series: Cl^-, Ar, K^+ and Ca^{2+}; and the attraction for the valence electron is the weakest!

2. Which of the following oxides has a molecular structure as distinct from a giant structure?

A Na_2O B MgO
C Al_2O_3 D Cl_2O_7

Helping Concepts *Exam Favourite Rating* ★★★

Cl_2O_7 is simple molecular whereas Na_2O, MgO and Al_2O_3 are giant ionic.

3. Which species represented by the following formulae has the largest radius?

A P^{3-} B Cl^-
C Ar D K^+

Helping Concepts *Exam Favourite Rating* ★★★

The 4 ions are isoelectronic ($1s^2\,2s^2\,2p^6\,3s^2\,3p^6$). Since P^{3-} has the least number of protons, its attraction for the valence electrons is the weakest. Hence, the valence electrons are furthest away from the nucleus.

4. Which of the following elements has an oxide with a giant structure and a chloride which is readily hydrolysed?

A barium B carbon
C phosphorus D silicon

Helping Concepts *Exam Favourite Rating* ★★

SiO_2 is giant molecular and $SiCl_4$ is readily hydrolysed by H_2O.

$$SiCl_4(\ell) + 2H_2O(\ell) \rightarrow SiO_2(s) + 4H^+(aq) + 4Cl^-(aq)$$

5. Which compound is **not** a product of the reaction between an oxide of a third period element and water?

A NaOH B H_2SiO_3
C H_3PO_4 D H_2SO_4

Helping Concepts *Exam Favourite Rating* ★★★

SiO_2 does not dissolve or react with water.

A: $Na_2O + H_2O \rightarrow 2NaOH$
C: $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
D: $SO_3 + H_2O \rightarrow H_2SO_4$

6. In which of the following pairs is the radius of the second atom greater than that of the first atom?

A Na, Mg B Sr, Ca
C P, N D Cl, Br

Helping Concepts *Exam Favourite Rating* ★

Both Cl and Br are in Group VII and Br has more shells of electrons filled with greater screening effect. Hence, the attraction for valence electrons is weaker in Br and therefore, Br has a larger radius.

7. Which of the following oxides will produce the strongest acid when treated with water?

A Cl_2O
B Cl_2O_7
C P_2O_5
D SiO_2

Helping Concepts | Exam Favourite Rating ★★★

$Cl_2O_7(s) + H_2O(\ell) \rightarrow 2H^+(aq) + 2ClO_4^-(aq)$ - strong acid

SiO_2 is insoluble in water while the rest gives relatively weaker acids on dissolving in H_2O.

A: $Cl_2O(g) + H_2O(\ell) \rightarrow 2HOCl(aq)$

C: $P_2O_5(s) + 3H_2O(\ell) \rightarrow 2H_3PO_4(aq)$

8. The magnesium present in a magnesium/aluminium alloy could be obtained by dissolving the aluminium in

A dilute ammonia.
B dilute hydrochloric acid.
C dilute nitric acid.
D dilute sodium hydroxide.

Helping Concepts | Exam Favourite Rating ★★

Al is amphoteric and hence will dissolve in NaOH and Mg will remain in the elemental form.

$$Al(s) + OH^-(aq) + 3H_2O(\ell) \rightarrow [Al(OH)_4]^-(aq) + \tfrac{3}{2}H_2(g)$$

9. Which of the following oxides is **unlikely** to dissolve in aqueous sodium hydroxide?

A Al_2O_3
B MgO
C P_4O_{10}
D SiO_2

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MgO is basic and it does not dissolve in an alkali. (A) is amphoteric while (C) and (D) are acidic.

A: $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(\ell) \rightarrow 2[Al(OH)_4]^-(aq)$

$P_4O_{10}(s) + 12OH^-(aq) \rightarrow 4PO_4^{3-}(aq) + 6H_2O(\ell)$

$SiO_2(s) + 2OH^-(aq) \rightarrow SiO_3^{2-}(aq) + H_2O(\ell)$

10. Which of the following elements would be expected to form the largest ion with a noble gas electron configuration?

A aluminium
B chlorine
C phosphorus
D potassium

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The ions are Al^{3+}, Cl^-, P^{3-} and K^+.

The last 3 are isoelectronic. The one with the lowest nuclear charge (P) should have the largest ionic radius since the attraction for the valence electrons is the weakest. Al^{3+} is smaller because it has 1 shell of electrons less than the others.

11. For the elements in the third period of the Periodic Table, which property decreases consistently from sodium to chlorine?

A electrical conductivity
B ionisation energy
C melting point
D radius of the atom

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Across a period, the number of shell of electrons remain the same while the number of protons increases. Consequently, the attraction on the valence electrons become stronger and the atomic size decreases.

12. Coloured glass, as used in church windows, requires three oxides - one macromolecular, one ionic and one of a transition metal.

Which combination is likely to produce a coloured glass?

A Al_2O_3 MgO SnO
B P_4O_{10} CaO CuO
C SiO_2 CaO PbO
D SiO_2 PbO CoO

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SiO_2 is macromolecular, PbO is ionic; Co is a transition metal.

A,C: no transition metal

B: no macromolecular oxide

13. *X*, *Y* and *Z* are elements in the same short period of the Periodic Table. The oxide of *X* is amphoteric, the oxide of *Y* is basic and the oxide of *Z* is acidic.

What is the order of increasing atomic (proton) number for these elements?

A *XYZ* B *XZY*
C *YXZ* D *YZX*

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Z is a non-metal (since non-metallic oxides are acidic) and *Y* is a metal (since metallic oxides are basic). *X* is somewhere in between *Y* and *Z*.

14. An element of the third period (Na to S) is heated in chlorine. The product is purified and then added to water. The resulting solution is found to be neutral.

What is the element?

A sodium B aluminium
C silicon D phosphorus

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$$2Na + Cl_2 \rightarrow 2NaCl$$

Na readily reduces Cl_2 to form NaCl. Since NaCl is a salt that can be formed from a strong acid (HCl) and a strong base (NaOH), it is neutral in water.

15. Consider the sequence of oxides Na_2O, SiO_2, P_4O_{10}.
Which factor decreases from Na_2O to SiO_2 and also from SiO_2 to P_4O_{10}?

A covalent character
B melting point
C pH when mixed with water
D solubility in aqueous alkali

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Na_2O is a basic oxide and reacts with water to give NaOH so that its pH is higher than both SiO_2 and P_4O_{10}. Both SiO_2 and P_4O_{10} are acidic oxides but SiO_2 is insoluble while P_4O_{10} reacts with water to give H_3PO_4. Thus for P_4O_{10}, pH when mixed with water is lower than that of SiO_2.

16. Which of the following sets of solid elements, A, B, C or D, includes a giant metallic structure, a macromolecular structure and a simple molecular structure?

A Na Mg Al
B Mg Al Si
C C Si Sn
D Al Si S

Helping Concepts *Exam Favourite Rating* ★★★

Al has a giant metallic structure; Si has a giant molecular structure and S has a simple molecular structure.

17. Fruit juices and fizzy drinks such as lemonade are often sold in aluminium cans. What is the most important reason why aluminium is a suitable metal?

A Aluminium can be recycled.
B Aluminium has a very low density.
C Aluminium is the most abundant metal in the Earth's crust.
D Aluminium is resistant to corrosion by acids.

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The impermeable oxide layer makes Al corrosion consistant.

18. The chloride of element **J** does not react with water or dissolve in it. Which one of the following elements could **J** be?

A aluminium B carbon
C magnesium D phosphorus

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CCl_4 is an organic liquid and is immiscible with H_2O. Unlike the chlorides of the other congeners in Group IV, it is not hydrolysed by H_2O due to the absence of available vacant d-orbitals.

A: $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H^+(aq)$

C: $MgCl_2$ dissolves in water but undergoes slight hydrolysis.

D: $PCl_5(s) + 4H_2O(l)$
$\rightarrow H_3PO_4(aq) + 5H^+(aq) + 5Cl^-(aq)$

---

19. When either chlorine or hydrogen chloride is passed over a heated metal *M*, the same chloride is produced. An aqueous solution of this chloride is acidic. Which one of the following could be *M*?

A aluminium **B** barium
C copper **D** iron

Helping Concepts *Exam Favourite Rating* ★★★

$2Al + 6HCl \xrightarrow{\Delta} 2AlCl_3 + 3H_2$
$2Al + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3$

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$
$Al(H_2O)_6^{3+} \rightarrow [Al(H_2O)_5(OH)]^{2+} + H^+$
$Al(H_2O)_5(OH)^{2+} \rightarrow [Al(H_2O)_4(OH)_2]^+ + H^+$

---

20. The diagram shows part of the Periodic Table.

						H											He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

Which element in the diagram has the largest atomic radius?

A Br **B** K
C Kr **D** Sc

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Among the elements in the given Periodic Table, K has the highest number of shells of electrons (3) and the lowest number of protons.

---

21. An excess of cold water was added to 0.3 mol of a chloride of the third period of the Periodic Table at room temperature. 0.6 mol of HCl was formed. Which chloride was treated?

A $MgCl_2$ **B** $AlCl_3$
C PCl_5 **D** $SiCl_4$

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From the ratio, 1 mol of the chloride gives 2 mol of HCl.

A: $MgCl_2$ does not hydrolyse to give HCl.

B: $AlCl_3$ does not hydrolyse completely in H_2O. The maximum of HCl released is 3 mol per mol of $AlCl_3$.

C: $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

D: $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

---

22. The species Ar, K^+ and Ca^{2+} are isoelectronic (have the same number of electrons).

In what order do their radii increase?

	smallest →		largest
A	Ar	Ca^{2+}	K^+
B	Ar	K^+	Ca^{2+}
C	Ca^{2+}	Ar	K^+
D	Ca^{2+}	K^+	Ar

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Nuclear charge: $Ca^{2+} > K^+ > Ar$

The valence electrons are the most strongly bound in Ca^{2+} due to the highest nuclear charge and smallest ionic size.

---

23. Which statement concerning only the elements in the third period, sodium to argon, is correct?

A The element that has exactly four atoms in its molecule is sulfur.

B The element with the highest electrical conductivity is aluminium.

C The element with the highest melting point is aluminium.

D The element with the largest anion is chlorine.

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A: Sulfur has 8 atoms per molecule.

B: Al has 3 valence electrons per atom (Na has 1, Mg has 2). So it has the highest electrical conductivity.

C: Si has the highest melting point.

D: $P^{3-} > S^{2-} > Cl^-$

---

24. Which property of the first six elements of Period 3 (sodium to sulfur) continuously increases numerically?

A atomic radius

B first ionisation energy

C maximum oxidation number in oxide

D melting point

Helping Concepts | Exam Favourite Rating ★★

Maximum oxidation number in oxide increases continuously from sodium to sulfur (from +1 to +6) since the number of valence electrons increases.

Option A is incorrect since atomic radius decreases from Na to S as nuclear charge increases but shielding is approximately the same as electrons are added to the same shell.

Option B is incorrect since first I.E. of Al is lower than that of Mg and first I.E. of S is lower than that of P so that the increase is not continuous.

Option D is incorrect since melting point of P and S are lower than of Si.

---

25. The ions P^{3-}, S^{2-} and Cl^- have radii 0.212 nm, 0.184 nm and 0.181 nm respectively. Which one of the following correctly explains the decrease in radius in going from P^{3-} to Cl^-?

A increases in the total number of electrons and in the nuclear charge

B an increase in the total number of electrons with the nuclear charge remaining constant

C a constant total number of electrons and an increase in the nuclear charge

D a decrease in the total number of electrons with the nuclear charge remaining constant

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P^{3-}, S^{2-} and Cl^- are isoelectronic, i.e. they have the same electronic configuration $3s^2\ 3p^6$. The increase in nuclear charge gives rise to a decrease in ionic radius as the electrons are more firmly held.

---

26. Scrap metal often consists of a mixture of aluminium, iron, chromium and copper. After removing the iron magnetically, the aluminium is removed from the other metals by a physical rather than chemical method.

What property of aluminium enables it to be separated in this way?

A It has a low density.

B It has a low melting point.

C It is a poor conductor of electricity.

D It is non-magnetic.

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Both Cr and Cu are transition elements and they have higher melting points than Al which is in the main group. Al can be more easily melted and siphoned off where Cr and Cu remain as solids.

---

27. Phosphorus is an element in the third period, Na to Ar, of the Periodic Table.

What is true for phosphorus and none of the other elements in this period?

A Phosphorus has the highest melting point of the elements in this period.

B Phosphorus is the only element in this period which forms two acidic oxides.

C Phosphorus is the only element in this period with exactly four atoms in its molecule.

D Phosphorus is the only element in this period whose chlorides react with water to form acidic solutions.

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Phosphorus exists as P_4 molecules (the others are S_8, Cl_2).

B: S forms SO_2 and SO_3.

D: Chlorides of sulfur also hydrolyse in water to form acidic solutions.

---

28. An element Q has low proton number. It forms an amphoteric oxide and a chloride which, when anhydrous, is readily hydrolysed by water.

Which group in the Periodic Table might contain Q?

A II

B III

C IV

D V

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Q is likely to be Al.

Al_2O_3 is amphoteric and an aqueous solution of $AlCl_3$ is acidic due to hydrolysis.

$$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(OH)(H_2O)_5]^{2+} + H^+$$

A: Group II oxides are basic (not amphoteric).

C: Group IV oxides are amphoteric. However, with a low proton number, the element is likely to be carbon and neither CO and CO_2 is amphoteric.

D: Group V oxides are acidic.

---

29. Aluminium hydroxide has a decomposition temperature of 573 K. It is mixed with titanium dioxide to produce a paint which delays the spread of flames in the event of a fire.

Which statement explains why aluminium hydroxide is used in this way?

A It is acidic enough to absorb any ammonia produced in a fire.

B Water vapour is produced on decomposition.

C It reacts with acid produced on combustion.

D A large amount of energy is absorbed when aluminium hydroxide vaporises.

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At elevated temperature, H_2O is released and hence helps to put out fire.

$$Al(OH)_3(s) \rightarrow Al_2O_3(s) + H_2O(g)$$

---

30. The chloride of an element **R** is a liquid which has a boiling point of 76 °C and fumes in air.

After mixing 0.010 mol of the chloride with water, the resulting solution required 100 cm^3 of 0.30 mol dm^{-3} silver nitrate for complete precipitation of the chloride ion.

To which group of the Periodic Table does **R** belong?

A I

B II

C III

D IV

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$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

Amount of Ag^+ used = concentration × volume

$= 0.30 \text{ mol dm}^{-3} \times \frac{100}{1000} \text{ dm}^3$

$= 0.03$ mol

Amount of Cl^- present = 0.03 mol

Since 0.01 mol of the chloride contain 0.03 mol of Cl^-, its empirical formula is RCl_3. **R** is either in Group III or V.

---

31. A mixture of the oxides of two elements of the third period is dissolved in water. The solution is approximately neutral.

What could be the constituents of the mixture?

A Al_2O_3 and MgO

B Na_2O and MgO

C Na_2O and P_4O_{10}

D SO_3 and P_4O_{10}

Helping Concepts | Exam Favourite Rating ★★

Na_2O is basic and P_4O_{10} is acidic. When dissolved in water, they neutralise each other.

A: Al_2O_3 is insoluble. MgO dissolves slightly to give an alkaline pH.

B: Na_2O and MgO are both basic. pH value would be high.

D: SO_3 and P_4O_{10} are both acidic. pH value would be low.

---

32. *Use of the Data Booklet is relevant to this question.*

Copper and magnesium are metals that are widely used in alloys. Each metal forms many compounds containing a M^{2+} ion.

Which statement about the electron arrangements in these atoms and ions is correct?

A A Cu atom has fewer electrons than a Mg atom.

B Cu^{2+} and Mg^{2+} ions have similar outer electron configurations.

C A Cu^{2+} ion has one more occupied electron shell than a Mg atom.

D A Cu atom has two more occupied electron shells than a Mg^{2+} ion.

Helping Concepts *Exam Favourite Rating* ★★★

Cu : 2,8,18,1

Cu^{2+} : 2,8,17

Mg : 2,8,2

Mg^{2+} : 2,8

---

33. What is not a trend from left to right across the elements of the third period of the Periodic Table?

A The radii of the atoms decrease.

B The oxides of the elements change from basic to acidic.

C The melting points of the elements decrease steadily.

D The compounds of the elements change from ionic to covalent.

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A: The atomic radii decreases as the nuclear charge increases while shielding effect remains the same. The attraction for electrons increases and hence the atomic size decreases.

B: The elements change from metals to non-metals. Hence, the oxides change from being basic to amphoteric and then to acidic.

C: The metallic bond strength increases at first and melting point increases. When it becomes a non-metal, the melting point becomes very low.

D: As the elements change from metallic to non-metallic, the compounds of the elements change from ionic to covalent.

---

34. Element Z is in Period 3 of the Periodic Table. The following four statements describe the properties of element Z or its compounds.

Three statements are correct descriptions. One of the statements is not correct because it does not fit with the other three.

Which statement is not correct?

A Element Z is a solid at room temperature which conducts electricity.

B Element Z forms a chloride, ZCl_3, which reacts with more chlorine to give ZCl_5.

C The chloride ZCl_3 reacts with water to give an acidic solution.

D Adding NaOH(aq) to the solution resulting from the reaction of ZCl_3 with water produces a white precipitate which is soluble in an excess of NaOH(aq).

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A: Z is Group I, II or III.

B: Z is Group V.

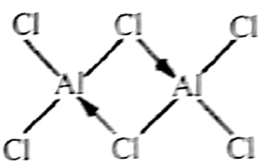
C: Z is Group III or V.

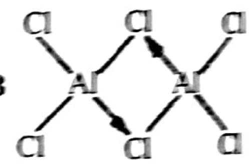
D: Z is group III (amphoteric).

---

35. Aluminium chloride sublimes at 178 °C.

Which structure best represents the species in the vapour at this temperature?

A 

B 

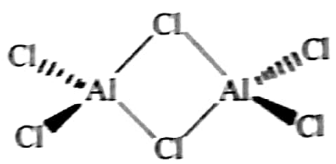
C Al• + 3Cl•

D $Al^{3+}(Cl^-)_3$

Helping Concepts *Exam Favourite Rating* ★★★

$$2AlCl_3(s) \xrightarrow{\text{heat}} Al_2Cl_6(g)\ (\text{dimer})$$

In the dimeric Al_2Cl_6, 2 units are linked together by dative bonds, electrons being donated by Cl to Al. Al_2Cl_6 is non-planar.



---

36. Element X is in Period 3 of the Periodic Table. The following four statements were made about the properties of element X or its compounds.

Three statements are correct descriptions and one is false.

Which statement does not fit with the other three?

A Adding NaOH(aq) to the solution resulting from the reaction of XCl_3 with water produces a white precipitate which is soluble in an excess of NaOH(aq).

B Element X forms a chloride XCl_3, which reacts with more chlorine to give XCl_5.

C Element X is a solid at room temperature.

D The oxide of X reacts with water to give an acidic solution.

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X is phosphorus (Group V).

B: $PCl_3 + Cl_2 \rightarrow PCl_5$

C: P_4 is a solid at room temperature.

D: $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

As non-metal oxides, both P_4O_6 and P_4O_{10} dissolve in water to form acids.

38. An acidic impurity is removed from the gaseous emissions of a coal-fired power station by passing them through an aqueous suspension of a mineral followed by oxidation.

Which of the following combinations satisfies these conditions?

	acidic impurity	mineral	oxidised product
A	NO_2	$MgCO_3$	$Mg(NO_2)_2$
B	P_4O_6	$Ca(OH)_2$	$Ca_3(PO_4)_2$
C	SiO_2	CaO	$CaSiO_3$
D	SO_2	$CaCO_3$	$CaSO_4$

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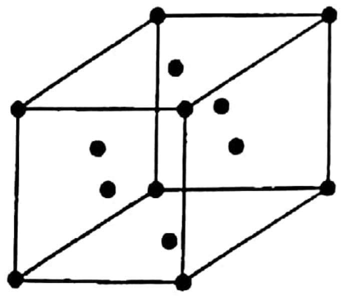
$$SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2$$

$$CaSO_3 \xrightarrow{\text{oxidation}} CaSO_4$$

In (A), the oxidised product should be $Mg(NO_3)_2$. In (C), oxidation does not take place.

37. Copper and iodine are both shiny crystalline solids. The crystal structures of copper and iodine are both face-centred cubic. The diagram shows the arrangement of the particles in this type of crystal lattice.



What are the particles present in each lattice?

	copper	iodine
A	atoms	anions
B	atoms	atoms
C	cations	atoms
D	cations	molecules

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Cu is metallic. The particles are copper ions in a sea of delocalised electrons.

I_2 is simple molecular. The particles are I_2 molecules with VDW forces between them.

39. *Use of the Data Booklet is relevant to this question.*

Natural water in reservoirs often contains very finely divided solid particles of between 1 and 100 nm in diameter which have negative charges on their surface.

One stage in purifying the water consists of adding salt solutions containing charge-density cations which neutralise the negative charges and cause the solid particles to join together and settle out.

Which compound, in aqueous solution, would be the most effective in precipitating finely divided solid particles?

A $MgCl_2$ **B** $AlCl_3$

C $FeCl_3$ **D** $SiCl_4$

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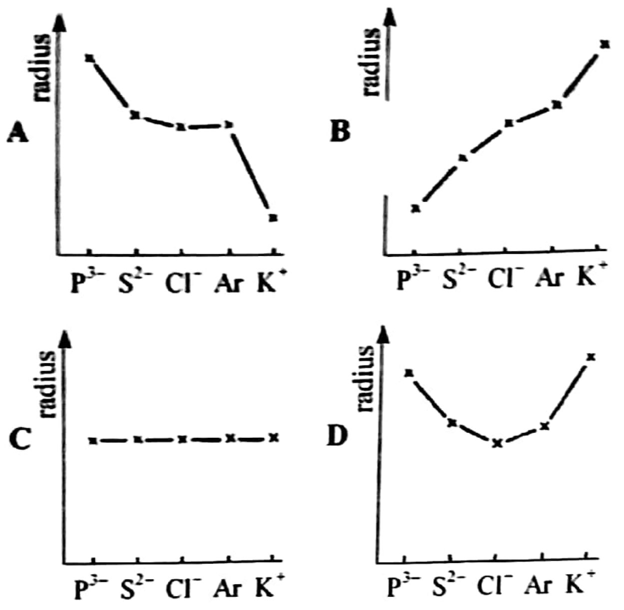
	$\frac{q}{r}$
Mg^{2+}	$\frac{2}{0.065}$
Al^{3+}	$\frac{3}{0.05}$
Fe^{3+}	$\frac{3}{0.064}$

Al^{3+} has the highest charge density.

$SiCl_4$ does not dissociate in water.

40. Which one of the graphs below correctly represents the relative radii of the species shown?



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The species given are isoelectronic. However, there is a progressive increase in the nuclear charge from P^{3-} to K^+. The attraction for the electrons becomes stronger and hence there is a decrease in their radii.

41. The sketch shows the atomic radii of five elements in order of increasing proton number.

In which part of the Periodic Table do these elements belong?

A Group II
B Group VII
C the period sodium to chlorine
D transition metals

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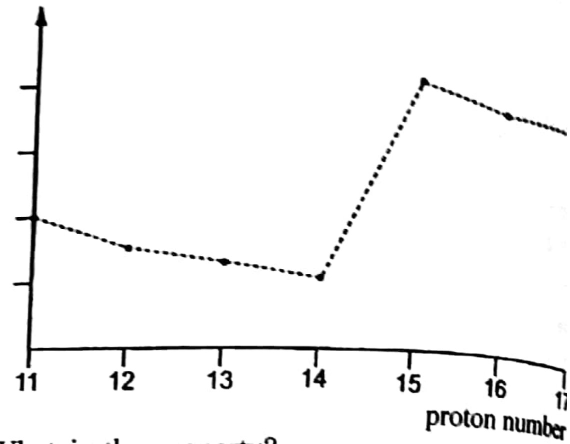
The atomic radius of transition elements do not vary significantly. Down a group (options A and B), atomic radius increases. Across a period (option C), atomic radius decreases steadily.

42. The graph shows how a property of the elements Na to Cl varies with proton number.



What is the property?

A electronegativity
B first ionisation energy
C ionic radius
D melting point

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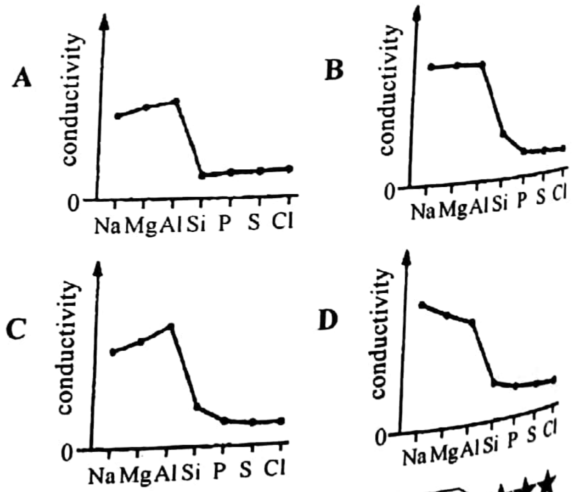
The species are Na^+, Mg^{2+}, Al^{3+}, Si^{4+} ($1s^2 2s^2 2p^6$) and P^{3-}, S^{2-}, Cl^- ($1s^2 2s^2 2p^6 3s^2 3p^6$). The first isoelectronic series (11 - 14) has a smaller ionic radii since the ions have 1 shell of electrons less. In both series, the ionic sizes decrease since nuclear charge increases while screening effect remains almost constant. The electrons become more tightly bound.

43. Which sketch shows the variation in electrical conductivity of the elements sodium to chlorine?



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From Na to Al, the number of valence electrons for delocalisation in the metal lattice increases. Hence, their electrical conductivity increases. As Si is a semi-conductor, its electrical conductivity is lower than that of the metals.

P_4, S_8 and Cl_2 exist as discreet molecules and hence do not conduct electricity.

---

44. The enthalpy change of fusion of a solid is defined as the amount of energy, in J or kJ, required to melt one mole of a solid at its melting point.

The table shows the enthalpy changes of fusion of four successive elements, *W* to *Z*, in the third period (sodium to argon) of the Periodic Table.

element	*W*	*X*	*Y*	*Z*
enthalpy change of fusion/kJ mol^{-1}	10.8	46.4	0.6	1.4

Which sequence of elements is represented by *W* to *Z*?

	W	*X*	*Y*	*Z*
A	Al	Si	P	S
B	Na	Mg	Al	Si
C	P	S	Cl	Ar
D	Si	P	S	Cl

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X (Si) has a much higher $\Delta H_f^{\ominus}$ than *W* (Al) due to the presence of the very strong network of strong covalent bonds between Si–Si.

Y (P_4) has a very low $\Delta H_f^{\ominus}$ as there are weak VDW forces between the P_4 molecules.

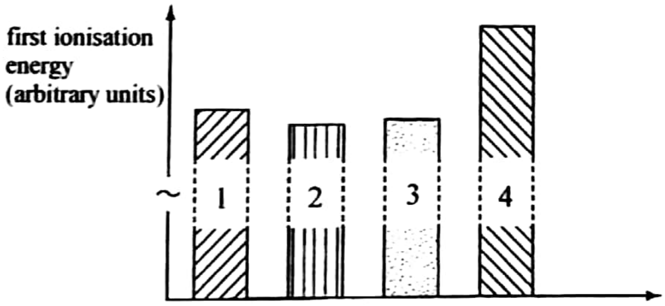
Z (S_8) has slightly higher $\Delta H_f^{\ominus}$ (but still low) than *Y* as it has a larger molecular size. Hence, it has slightly stronger VDW forces.

---

45. *Use of the Data Booklet is relevant to this question.*

The bar chart gives some information about the first ionisation energies of elements, numbered 1 to 4.

The elements are adjacent to each other in the Periodic Table with increasing proton number either across a period from left to right, or down a group.



What could these four elements be?

A B, C, N, O

B Co, Ni, Cu, Zn

C Mg, Ca, Sr, Ba

D Si, P, S, Cl

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The first I.E. fluctuates and do not show an increasing or decreasing trend. The elements are transition elements.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

46. Which of the following sets contain two covalent chlorides and two ionic chlorides?

1 NaCl $BaCl_2$ CCl_4 ICl

2 $BeCl_2$ $SiCl_4$ $PbCl_4$ SCl_2

3 $CaCl_2$ $SiCl_4$ PCl_3 SCl_2

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*1. NaCl and $BaCl_2$ are ionic and CCl_4 and ICl are covalent.

2. All are covalent.

3. $CaCl_2$ is ionic while the rest are covalent.

---

47. *Use of the Data Booklet is relevant to this question.*

Based on its position in the Periodic table, which properties will element X (atomic number 33) have?

1 It will form a chloride with formula XCl_5.

2 It will form an oxide with formula X_2O_3.

3 Its oxide will react with an alkali to form a salt.

Helping Concepts *Exam Favourite Rating* ★★

The element is As (Period 4, Group V). Just like P, it forms compounds in +3 and +5 oxidation states and its oxide is acidic.

---

48. In general, why do first ionisation energies decrease down a group of the Periodic Table?

1 The nuclear charge is increasing.

2 The electron to be ionised becomes progressively further from the nucleus.

3 There are progressively more electrons between the nucleus and the electron to be ionised.

Helping Concepts *Exam Favourite Rating* ★★★

$$M(g) \rightarrow M^+(g) + e^- \quad \Delta H = \text{Ist I.E.}$$

Lower first I.E. is experienced by one with larger atomic radius (down the group) and more screening electrons (down the group). When the valence electrons become further away from the nucleus, less energy would be required to remove the valence electrons.

---

49. Many ceramic materials based on silicon(IV) oxide have recently been developed.

Which properties apply to these materials?

1 They are heated during manufacture and form solids.

2 They are heat-resistant solids.

3 They are good conductors of electricity due to delocalised electrons.

Helping Concepts *Exam Favourite Rating* ★★

*1,*2. Silicon(IV) oxide and other materials are fired to give ceramics and are heat-resistant since SiO_2 has a high melting point.

3. SiO_2 does not have delocalised electrons and hence does not conduct electricity well.

---

50. Which of the following statements are correct for the sequence of compounds below considered from left to right?

NaF MgO AlN SiC

1 The electronegativity difference between the elements in each compound increases.

2 The formula-units of these compounds are isoelectronic (have the same number of electrons).

3 The bonding becomes increasingly covalent.

Helping Concepts *Exam Favourite Rating* ★★

1,*3. The difference in electronegativities decreases. Hence, the bonding becomes more and more covalent.

*2. All the compounds are isoelectronic.

---

51. The Group II metals have higher melting points than the Group I metals. Which of the following factors could contribute towards the higher melting points?

1 There are smaller interatomic distances in the metallic lattices of the Group II metals.

2 Two valency electrons are available from each Group II metals atom for bonding the atom into the metallic lattice.

3 Group II metals have the higher first ionisation energies

Helping Concepts | *Exam Favourite Rating* ★★

Smaller interatomic distances (1), and higher cationic charge and more valence electrons (2) contribute to stronger metallic bonds and hence higher melting points. Higher first I.E. (3) would lead to weaker metallic bond (but this is more than compensated by (1) and (2)).

---

52. In the Periodic Table, the electronegativity of the elements in

1 Period 3 increases from sodium to chlorine.

2 Group II increases from barium to beryllium.

3 Group VII increases from iodine to fluorine.

Helping Concepts | *Exam Favourite Rating* ★★★

Electronegativity, χ, is a measure of the ability of an atom to pull the electrons in a covalent bond.

*1. Across a period, atomic size decreases and number of protons increases. Hence, the ability to attract electron increases, i.e. χ increases.

*2,*3. Going up the group, atomic size decreases and screening effect decreases as a result of less filled shells of electrons. Hence, the attraction for electron increases, i.e. χ increases.

---

53. *Use of the Data Booklet is relevant to this question.*

Indium, $_{49}In$, is used in solar cells and transistors, and to coat high-speed bearings.

From its position in the Periodic Table, which properties will it be expected to possess?

1 In the vapour phase, the chloride has the formula In_2Cl_6.

2 Its oxide dissolves in aqueous acid.

3 Its ionic salts are highly coloured.

Helping Concepts | *Exam Favourite Rating* ★★

*1. In is in Group III and below Al. In the vapour phase, it will also form In_2Cl_6, just like Al_2Cl_6.

*2. In_2O_3 is also amphoteric, just like Al_2O_3.

3. In salts are white, just like Al salts. In is not a transition element.

---

54. What factors explain why a solution of aluminium chloride is acidic?

1 Chloride ions react with water to form hydrochloric acid.

2 Aluminium ions have a large charge/surface area ratio.

3 The H–O bonds are weaker in $[Al(H_2O)_6]^{3+}$ than in H_2O.

Helping Concepts | *Exam Favourite Rating* ★★

1. The Cl^- does not react with H_2O to form HCl. It is not hydrolysed.

*2,*3. Due to the high charge/surface ratio (or high charge density), Al^{3+} readily polarises the H–O in H_2O and weakens it. Therefore, hydrolysis takes place and H^+ is formed.

$$Al^{3+} \longleftarrow O\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H} \longrightarrow [Al(OH)]^{2+} + H^+$$

---

55. The following represents the electronic configuration of **both** a Group II cation and a Group VII anion.

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$$

The radius of the anion is approximately twice that of the cation.

Which reasons explain the difference in size?

1 The cation has a greater nuclear charge than the anion.

2 There is more electron shielding in the anion than in the cation.

3 On forming the anion from its atom, the extra electron repulsion makes the ion much larger.

Helping Concepts / Exam Favourite Rating ★★★

he 2 elements are $_{38}Sr$ and $_{35}Br$.

1. Sr has more protons than Br does. Hence, it attracts the electrons more tightly.
2. The shielding effect is the same since both ions are isoelectronic.
3. With additional electrons, there is greater electronic repulsion. The electron cloud expands to accomodate the extra electrons. However, this only explains that the anion is bigger than the atom.

---

56. Boron is a non-metallic element which is placed above aluminium in Group III of the Periodic Table. It forms a compound with nitrogen known as boron nitride which has a graphite structure.

Which of the following conclusions can be drawn from this information?

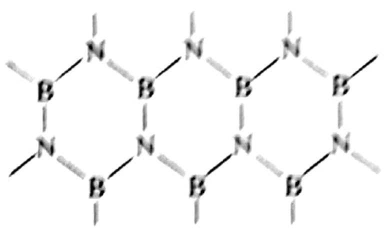
1 The empirical formula of boron nitride is BN.

2 The boron and nitrogen atoms are likely to be arranged alternately in a hexagonal pattern.

3 Boron nitride has a layer structure with van der Waals' forces between the layers.

Helping Concepts / Exam Favourite Rating ★★

In each layer, B and N are bonded to each other to form hexagonal rings and between each layer, there are van der Waals' forces.



The ratio of B : N is 1 : 1. Hence, its empirical formula is BN.

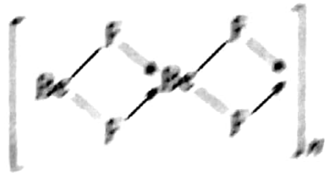
---

57. Beryllium is the first member of Group II and forms covalent compounds which are said to be electron deficient. In many ways, beryllium resembles aluminium.

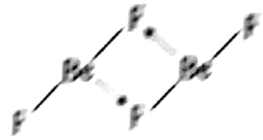
Which of the following are possible?

1 BeF_4^{2-}

2

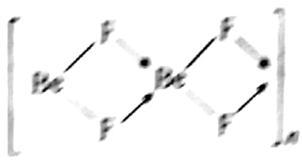


3



Helping Concepts / Exam Favourite Rating ★★★

*1,*2. Be is in Group II and BeF_2 can accept 2 lone pairs of electrons from either 2 F^- to form BeF_4^{2-} or from the 2 F atoms already bonded to another Be to form



3. The structure shown is incorrect since Be has no lone pairs of electrons to donate to F atoms.

TOPIC

10

Group II

Key content that you will be examined on:

1. Similarities and trends in the properties of the Group II metals magnesium to barium and their compounds

Topic 10

Group II

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which one of the following elements is likely to have an electronegativity similar to that of aluminium?

   A barium B beryllium
   C calcium D magnesium

Helping Concepts *Exam Favourite Rating* ★★

The size of Be is similar to that of Al. Hence, they have similar electronegativities. Be and Al are known to show diagonal relationship.

2. Which of the following elements is expected to show the greatest tendency to form some covalent compounds?

   A barium B calcium
   C magnesium D potassium

Helping Concepts *Exam Favourite Rating* ★★

Mg^{2+} is the smallest and hence has the highest charge density. It has the greatest polarising power and therefore shows the highest covalent character in its compounds.

3. Barium burns in oxygen to form barium oxide. What is the colour of the flame when this reaction occurs?

   A blue B green
   C lilac D orange

Helping Concepts *Exam Favourite Rating* ★

Ba burns in O_2 with an apple green flame.

4. What are the products of the thermal decomposition of magnesium nitrate?

   A magnesium nitride and oxygen
   B magnesium oxide and nitrogen
   C magnesium oxide, nitrogen and oxygen
   D magnesium oxide, nitrogen dioxide and oxygen

Helping Concepts *Exam Favourite Rating* ★★★

All Group II nitrates decompose to the corresponding oxide, NO_2 and O_2 on heating.

$$2Mg(NO_3)_2(s) \xrightarrow{\text{heat}} 2MgO(s) + 4NO_2(s) + O_2(g)$$

5. Which one of the following elements has the same oxidation number in all of its known compounds?

   A beryllium B bromine
   C chlorine D nitrogen

Helping Concepts *Exam Favourite Rating* ★★

Being a Group II element, Be forms invariably compounds of +2 oxidation states. This is because a Group II element has 2 valence electrons. It readily loses the valence electrons to form a stable noble gas electronic configuration.

6. Which of the following methods is the most suitable for the extraction of barium?

   A electrolysing aqueous barium chloride
   B electrolysing molten barium chloride
   C reducing barium oxide with aluminium
   D reducing barium oxide with carbon

Helping Concepts | Exam Favourite Rating ★★★

Ba is a reactive metal (more reactive than Mg and Ca). Normal reduction method using coke and electrolysis using an aqueous elecctrolyte are not feasible.

7. Which reaction will **not** take place readily under the conditions specified by the state symbols?
[Note: $H_2O(g)$ = steam]

A $Ba(s) + 2H_2O(\ell) \rightarrow Ba(OH)_2(aq) + H_2(g)$
B $CaO(s) + H_2O(\ell) \rightarrow Ca(OH)_2(s)$
C $Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$
D $Mg(s) + 2H_2O(\ell) \rightarrow Mg(OH)_2(aq) + H_2(g)$

Helping Concepts | Exam Favourite Rating ★

For the reaction to be taken, the system has to be heated to high temperature and steam is used (instead of liquid water). In addition, MgO will be formed, instead of $Mg(OH)_2$.

8. Which element is in Group II of the Periodic Table?

element	m.p./°C	density/ g cm^{-3}	electrical conductivity/ ohm^{-1} m^{-1}
A	98	0.97	2.4×10^7
B	113	2.07	5.0×10^{-16}
C	649	1.74	2.2×10^7
D	1744	11.3	6.0×10^7

Helping Concepts | Exam Favourite Rating ★★★

As a Group II element, its melting point, density and electrical conductivity must be relatively high. (A) has too low melting point and density while (D) has too high melting point and density.

9. Which pair of 0.1 mol dm^{-3} aqueous solutions is most likely to give a precipitate when added together?

A KBr and $MgSO_4$
B $NaNO_3$ and $CaCl_2$
C NH_3 and $BaCl_2$
D $MgSO_4$ and $SrCl_2$

Helping Concepts | Exam Favourite Rating ★★★

$SrSO_4$ is insoluble and is precipitated when solutions of $MgSO_4$ and $SrCl_2$ are mixed together.

10. Which of the following statements is true for strontium or its compounds?

A Strontium does not burn in air.
B Strontium does not react with steam.
C Strontium carbonate decomposes at a lower temperature than calcium carbonate.
D Strontium hydroxide is dehydrated to the oxide on being heated.

Helping Concepts | Exam Favourite Rating ★★

Just like the hydroxides of the other Group II metals, $Sr(OH)_2$ dehydrates upon heating.

$$Sr(OH)_2(s) \xrightarrow{\Delta} SrO(s) + H_2O(g)$$

11. Which property **decreases** on descending Group II (Mg to Ba)?

A the charge density of the cation
B the reactivity of the element with water
C the solubility of the oxide in water
D the thermal stability of the nitrate

Helping Concepts | Exam Favourite Rating ★★

A: Charge density of cation decreases because charge remains the same while cationic size increases as we go down Group II.

B: Reaction of Group II metal with H_2O is a redox reaction. Since reducing power of Group II metals increases down the group, reactivity increases.

C: Solubility of oxides of Group II metals increases down the group.

D: Thermal stability of Group II nitrates increases down the group. As charge density of M^{2+} decreases → polarising power decreases → ability to polarise the N–O bond in NO_3^- anion decreases → decomposition temperature of nitrates increases.

12. Which one of the following equations represents the reaction that occurs when calcium nitrate is heated strongly?

A $Ca(NO_3)_2 \rightarrow Ca(NO_2)_2 + O_2$

B $Ca(NO_3)_2 \rightarrow CaO + N_2O + 2O_2$

C $Ca(NO_3)_2 \rightarrow CaO_2 + 2NO_2$

D $2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$

Helping Concepts *Exam Favourite Rating* ★★★

Nitrates of Group II metals yield the metal oxide, NO_2 and O_2 on strong heating.

$$2M(NO_3)_2(s) \xrightarrow{\Delta} 2MO(s) + 4NO_2(g) + O_2(g)$$

13. Which one of the following statements is true?

A All nitrates of Group II metals are decomposed by heat to give the oxide NO_2.

B Aqueous sodium nitrate in acidic to litmus.

C Aqueous ammonium nitrate is alkaline to litmus.

D The alkali metal nitrites are insoluble in water.

Helping Concepts *Exam Favourite Rating* ★★★

$$2M(NO_3)_2(s) \xrightarrow{\Delta} 2MO(s) + 4NO_2(g) + O_2(g)$$

B: $NaNO_3$ is neutral.

C: NH_4NO_3 is acidic due to hydrolysis of NH_4^+.

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

14. When a mixture of white solids, F, is treated with an excess of dilute hydrochloric acid, a colourless gas is evolved and some, but not all, of the mixture dissolves.

Which mixture could be F?

A $Ba(NO_3)_2$ and $Ca(OH)_2$

B $BaSO_4$ and $CaCO_3$

C $CaCO_3$ and $MgSO_4$

D $Ca(OH)_2$ and $MgCO_3$

Helping Concepts *Exam Favourite Rating* ★★★

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The gas is CO_2. $BaSO_4$ remains insoluble in the solution.

15. What is observed when magnesium chloride is added to water?

	solubility in water	pH of resulting solution
A	dissolves	2
B	dissolves	6.5
C	insoluble	7
D	very slightly soluble	8

Helping Concepts *Exam Favourite Rating* ★★★

$MgCl_2$ dissolves readily in water and undergoes hydrolysis slightly. The resulting solution is slightly acidic.

$$Mg^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(OH)]^+(aq) + H^+(aq)$$

16. *Use of the Data Booklet is relevant to this question.*

What volume of oxygen, measured under room conditions, can be obtained from the complete thermal decomposition of 8.2 g of calcium nitrate ($M_r = 164$)?

A 150 cm^3 B 300 cm^3

C 600 cm^3 D 1200 cm^3

Helping Concepts *Exam Favourite Rating* ★★★

$$Ca(NO_3)_2 \rightarrow CaO + 2NO_2 + \tfrac{1}{2}O_2$$

$$n_{Ca(NO_3)_2} = \frac{8.2}{164} = 0.05 \text{ mol}$$

$$n_{O_2} = \frac{0.05}{2} = 0.025 \text{ mol}$$

$$V_{O_2} = 0.025 \times 24000 = 600 \text{ cm}^3$$

17. Lithium resembles magnesium in its chemical properties.

Which property of lithium compounds is unlikely to be correct?

A Lithium carbonate decomposes to give carbon dioxide on being heated.

B Lithium nitrate gives oxygen as the only gas on being heated.

C Lithium oxide in water produces a solution with pH greater than 7.

D Lithium sulfate is soluble in water.

Helping Concepts *Exam Favourite Rating* ★★★

Since $Mg(NO_3)_2$ gives O_2 and NO_2 when it decomposes, so does $LiNO_3$.

$$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

Note: Other Group I nitrates give O_2 and M_2O only.

---

18. Which factors help to explain the increase in thermal stability of the carbonates for Group II metals from magnesium to barium?

	charge density of cation	relative polarisation of carbonate and oxide ions
A	decreases	CO_3^{2-} less than O^{2-}
B	decreases	O^{2-} less than CO_3^{2-}
C	increases	CO_3^{2-} less than O^{2-}
D	increases	O^{2-} less than CO_3^{2-}

Helping Concepts *Exam Favourite Rating* ★★★

Down the group, cationic size increases while charge density decreases. Hence, the anion is polarised to a less extent and the decomposition of the anion becomes more difficult. Furthermore, O^{2-} is smaller than CO_3^{2-} and CO_3^{2-} is more easily polarised. Hence, O^{2-} is relatively more stable than CO_3^{2-}.

---

19. *Use of the Data Booklet is relevant to this question.*

Which is true for calcium or its compounds compared with the corresponding statements for magnesium?

A Calcium has a smaller atomic radius.

B Calcium oxide reacts less vigorously with water.

C Calcium reacts more vigorously with water.

D The sum of the first two ionisation energies of calcium is greater.

Helping Concepts *Exam Favourite Rating* ★★

Ca is below Mg in Group II. It has a larger radius due to an extra shell of electrons. It loses the valence electrons more easily than Mg since the attraction for the valence electrons is weaker. Hence, Ca is more reactive than Mg and it reacts more vigorously with water.

---

20. Which of the following conclusions can be drawn from the observation that $BaSO_4$ is precipitated immediately when solutions of barium chloride and sodium sulfate are mixed?

A $Ba(OH)_2$ is a very weak base.

B $BaSO_4$ forms a predominantly covalent molecule.

C $BaSO_4$ is strongly hydrated.

D Free $Ba^{2+}(aq)$ and $SO_4^{2-}(aq)$ ions probably exist in the initial solutions.

Helping Concepts *Exam Favourite Rating* ★★★

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Both $Ba^{2+}(aq)$ and $SO_4^{2-}(aq)$ must first exist in the initial solutions so that when they come together, the precipitate is formed when the ionic product $[Ba^{2+}(aq)][SO_4^{2-}(aq)]$ exceeds the solubility product.

---

21. Strontium lies between calcium and barium in Group II in the Periodic Table. Which of the following properties could be predicted for strontium?

A It forms a water-soluble carbonate which does not decompose on heating.

B It forms a sparingly soluble sulfate.

C It forms a nitrate which decomposes on heating to form strontium nitrite and oxygen.

D It is reduced by cold water, liberating hydrogen.

Helping Concepts *Exam Favourite Rating* ★★★

$CaSO_4$ is sparingly soluble while $BaSO_4$ is insoluble. Therefore, $SrSO_4$ is also sparingly soluble.

A: All the Group II carbonates are insoluble in water.

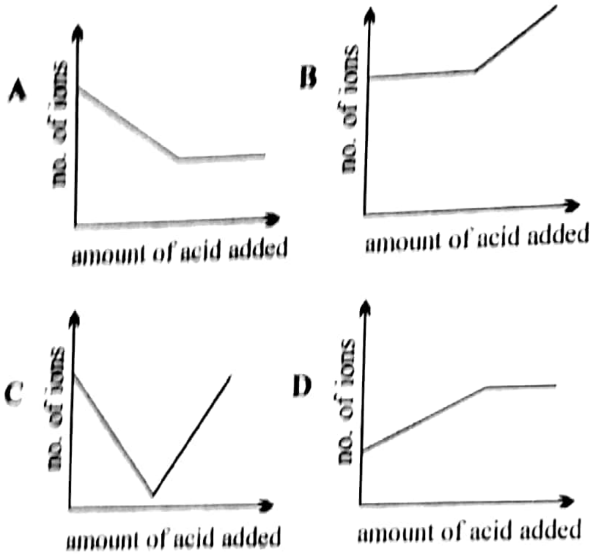
C: $M(NO_3)_2(s) \xrightarrow{\Delta} MO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

D: $M(s) + 2H_2O(l) \longrightarrow M^{2+}(aq) + 2OH^-(aq) + H_2(g)$

Note: (D) is wrong because Sr is oxidised (not reduced) by H_2O.

22. Dilute sulfuric acid was added to aqueous barium hydroxide until the acid was in excess.

Which graph shows the variation in the total number of ions in solution?



Helping Concepts | *Exam Favourite Rating* ★★

$[Ba^{2+}(aq) + 2OH^-(aq)] + [2H^+(aq) + SO_4^{2-}(aq)]$
$\rightarrow BaSO_4(s) + 2H_2O(l)$

$BaSO_4$ is insoluble in H_2O and H_2O does not ionise (negligible). Addition of H_2SO_4 therefore removes Ba^{2+} and OH^- from the solution. However, when all the $Ba(OH)_2$ have reacted, further addition of H_2SO_4 introduces H^+ and SO_4^{2-} ions.

23. Due to their similar ionic radii, the reactions of lithium and magnesium and their corresponding compounds are very similar.

Which statement concerning the reactions of lithium and its compounds is correct?

A Lithium carbonate decomposes on heating at a relatively low temperature, forming lithium oxide and carbon dioxide.

B Lithium nitrate decomposes on heating, forming lithium nitrite and oxygen.

C Lithium only burns slowly in oxygen.

D Lithium reacts violently with cold water, liberating hydrogen.

Helping Concepts | *Exam Favourite Rating* ★★

Compounds of Li behave similarly as the corresponding compounds of Mg.

$$MgCO_3 \rightarrow MgO + CO_2$$
$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

$MgCO_3$ decomposes at a relatively low temperature due to its high charge density. So does Li_2CO_3.

24. On the strong heating, $CaSO_4$ decomposes into CaO and SO_3.

The compound $CaCO_3$ decomposes at a lower temperature than $CaSO_4$.

Which factor best explains the greater thermal stability of $CaSO_4$?

A $CaCO_3$ has a higher lattice energy than $CaSO_4$.

B CO_2 is a smaller molecule than SO_3.

C CO_3^{2-} ions are more easily polarised than SO_4^{2-}.

D The charge density of CO_3^{2-} is greater than that of SO_4^{2-}.

Helping Concepts | *Exam Favourite Rating* ★★

The thermal decomposition is facilitated by the ease of polarisation of the anion by the cation. CO_3^{2-} is more easily polarised and hence $CaCO_3$ is more easily decomposed, i.e. it decomposes at a lower temperature.

25. One mole of each of the following compounds is strongly heated with a Bunsen flame and any gas produced is collected at room temperature and pressure.

From which compound is 24 dm^3 of gas likely to be collected?

[One mole of any gas occupies 24 dm^3 at room temperature and pressure.]

A $MgCl_2$ **B** $MgCO_3$

C $Mg(NO_3)_2$ **D** $Mg(OH)_2$

Helping Concepts | *Exam Favourite Rating* ★★★

24 dm^3 of gas is equivalent to 1 mole.

A: $MgCl_2$ does not decompose.

B $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

1 mole of $MgCO_3$ gives 1 mole of $CO_2(g)$.

C $Mg(NO_3)_2(s) \rightarrow MgO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

1 mole of $Mg(NO_3)_2$ gives a total of $2\frac{1}{2}$ moles of gases.

D $Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(\ell)$

H_2O is in the liquid state!

---

26. A researcher made up a 0.10 mol dm^{-3} solution of $Ba(OH)_2.8H_2O$ which he found in the laboratory cupboard and left the solution in an open beaker. A week later, he returned to the laboratory, used the solution for titration with 0.10 mol dm^{-3} HCl and was surprised to discover his titres were lower than expected.

What explains why the values were low?

A Some of the barium hydroxide had reacted with carbon dioxide in the air to form solid barium carbonate.

B Some water had evaporated from the barium hydroxide solution.

C The concentration of HCl was less than the stated 0.10 mol dm^{-3}.

D The crystals had less water of crystallisation than stated.

Helping Concepts | *Exam Favourite Rating* ★★★

$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(\ell)$

The formation of $BaCO_3$ is very similar to that of lime water ($Ca(OH)_2$) giving white precipitation. The alkalinity hence drops. When a sample of the solution is taken to titrate, the amount of HCl required would be lower.

---

27. Magnesium oxide is used in the making of the lining of blast furnaces. It is extracted from seawater as follows.

Aqueous calcium hydroxide is added to seawater.

$Ca(OH)_2(aq) + MgCl_2(aq) \rightarrow Mg(OH)_2(s) + CaCl_2(aq)$

The magnesium hydroxide is then filtered off and roasted.

Which of the following comparisons between calcium and magnesium explains why magnesium hydroxide forms?

A Magnesium is less electropositive than calcium.

B Magnesium is lower than calcium in the reactivity series.

C The enthalpy change of hydration for Mg^{2+} is less exothermic than for Ca^{2+}.

D The solubility product for $Mg(OH)_2$ is lower than that for $Ca(OH)_2$.

Helping Concepts | *Exam Favourite Rating* ★★★

$Mg(OH)_2$ has a lower solubility product than $Ca(OH)_2$ and is therefore less soluble than $Ca(OH)_2$. It is precipitated out.

Note: The solubilities of salts with different stoichiometries cannot be compared by using their solubility products directly.

---

28. Barium sulfate occurs naturally as barite, which is a solid ore. Magnesium sulfate, however, occurs mainly in solution.

Why is this?

A Barium ions are less readily hydrated than magnesium ions.

B Barium sulfate has a stronger crystalline lattice.

C Barium sulfate is more resistant to oxidation than magnesium sulfate.

D Magnesium sulfate is hydrolysed by naturally acidic solutions, but barium sulfate is not.

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(A) is *correct* since the energy required to break up the lattice of an ionic solid during dissolution is compensated by the energy given out when the ions are hydrated.

Ba^{2+} is bigger than Mg^{2+} so that its charge density is lower and hence, its hydration energy is less exothermic.

Since SO_4^{2-} is a large anion, difference in hydration energy is an important factor so that solubility of $BaSO_4$ is much less soluble than $MgSO_4$.

(B) is incorrect since $MgSO_4$ would have a stronger lattice as Mg^{2+} being smaller has the larger density and hence, stronger electrostatic attraction occurs between Mg^{2+} and SO_4^{2-} compared to that between Ba^{2+} and SO_4^{2-}.

(C) is incorrect since both $BaSO_4$ and $MgSO_4$ are resistant to oxidation.

(D) is incorrect even though $Mg(H_2O)_6^{2+}$ is likely to undergo more hydrolysis due to its greater charge density.

In naturally acidic solution, the amount of $Mg(H_2O)_6^{2+}$ hydrolysed is insignificant as the position of equilibrium in the following reaction would shift left:

$$Mg(H_2O)_6^{2+}(aq) + H_2O(\ell) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$$

29. The solubilities of the Group II metal sulfates decrease as the proton number of the metal increases.

What factor affects this trend?

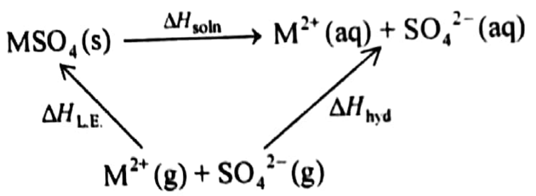
A the atomic radius of the metal atom

B the enthalpy change of formation of the sulfate

C the enthalpy change of hydration of the metal ion

D the first ionisation energy of the metal

Helping Concepts *Exam Favourite Rating* ★★★



$$\Delta H_{soln} = |\Delta H_{L.E.}| - |\Delta H_{hyd}|$$

SO_4^{2-} is large. A change of M^{2+} in size does not affect $\Delta H_{L.E.}$ significantly.

$$|\Delta H_{L.E.}| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

On the other hand, when M^{2+} increases in size down the group, ΔH_{soln} decreases significantly.

$$|\Delta H_{hyd}| \propto \left|\frac{q_+}{r_+}\right| + \left|\frac{q_-}{r_-}\right|$$

Thus, ΔH_{soln} becomes less exothermic down the group and the solubility decreases mainly due to the change in ΔH_{hyd}.

30. What changes occur in the magnitudes of

(i) the lattice energy,

(ii) the enthalpy change of hydration,

(iii) the solubility of the sulfate,

as Group II is descended?

	lattice energy	enthalpy change of hydration	solubility of sulfate
A	decrease	decrease	decrease
B	decrease	increase	decrease
C	increase	decrease	increase
D	increase	increase	decrease

Helping Concepts *Exam Favourite Rating* ★★★

$$|L.E.| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

$$|\Delta H_{hyd}| \propto \left|\frac{q_+}{r_+}\right| + \left|\frac{q_-}{r_-}\right|$$

Down the group, r_+ increases. Hence, both |L.E.| and $|\Delta H_{hyd}|$ decrease. The solubility of the sulfate decreases down the group.

$$\Delta H_{soln} = |L.E.| - |\Delta H_{hyd}|$$

Due to the large size of the anion (r_-), |L.E.| decreases marginally (as ($r_+ + r_-$) increases marginally). However, $\left|\frac{q_-}{r_-}\right|$ is small and hence the decrease in $\left|\frac{q_+}{r_+}\right|$ causes a significant decrease in $|\Delta H_{hyd}|$. Consequently, $|\Delta H_{soln}|$ decreases significantly and the solubility decreases.

31. Gallstones can form in the gall bladder and are very painful. The inorganic part of gallstones is calcium ethanedioate which is insoluble in water. The corresponding magnesium ethanedioate is soluble in water.

What factor accounts for the difference in solubility between calcium ethanedioate and magnesium ethanedioate?

A Calcium ethanedioate has a higher solubility product than magnesium ethanedioate.

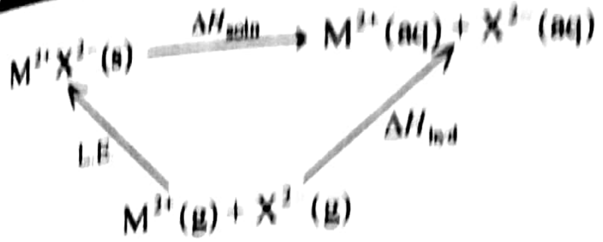
B Calcium ethanedioate has a numerically higher lattice energy than magnesium ethanedioate.

C Calcium ions have a lower enthalpy change of hydration than magnesium ions.

Topic 10 Group II

D Calcium is more electropositive than magnesium.

Helping Concepts | *Exam Favourite Rating* ★★★



$\Delta H_{soln} = \Delta H_{hyd} - L.E.$

Ca^{2+} is larger than Mg^{2+}. Hence, it has a lower charge density and attracts less H_2O molecules. Less energy is released compared to Mg^{2+} during hydration, i.e. $\Delta H_{hyd}(Ca^{2+})$ is less exothermic.

Consequently, $\Delta H_{soln}(CaX)$ is less exothermic and CaX is less soluble compared to MgX.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

32. Which statements about calcium oxide are correct?

1 It reacts with cold water.

2 It is a product when calcium nitrate is heated.

3 It can be reduced by heating with magnesium.

Helping Concepts *Exam Favourite Rating* ★★★

*1. $CaO(s) + H_2O(\ell) \rightarrow Ca(OH)_2(s)$

*2. $2Ca(NO_3)_2(s) \rightarrow 2CaO(s) + 4NO_2(g) + O_2(g)$

3. CaO is not reduced by Mg (Ca is more reactive than Mg).

---

33. Which of the following statements about the elements calcium, strontium and barium are correct?

1 Their oxides are amphoteric.

2 Aqueous solutions of their hydroxides have a pH greater than 7.

3 The elements react with cold water liberating hydrogen.

Helping Concepts *Exam Favourite Rating* ★★★

1,*2. Their oxides are basic.

$$M(OH)_2(s) \rightarrow M^{2+}(aq) + 2OH^-(aq)$$

*3. Group II elements are highly reactive metals and they readily reduce water to give H_2 gas.

$$M(s) + 2H_2O(\ell) \rightarrow M^{2+}(aq) + 2OH^-(aq) + H_2(g)$$

---

34. Which of the following statements about beryllium are true?

1 Beryllium compounds tend to be covalent rather than ionic.

2 Beryllium shows a fixed oxidation number of +2 in its compounds.

3 Beryllium reacts rapidly with cold water.

Helping Concepts *Exam Favourite Rating* ★★

*1. Due to its small size, Be^{2+} is highly polarising (similar to Al^{3+}) and hence tends to form covalent compounds.

*2. Being a main group element (Group II), it forms invariably compounds with +2 oxidation state.

3. Just like Al, a strong coating of BeO prevents Be from being attacked by cold water.

---

35. Which properties would be expected for the Group II element, strontium, or its compounds?

1 When heated in oxygen, strontium does not burn.

2 On being heated, strontium carbonate decomposes to give strontium oxide.

3 When strontium oxide is added to water, the solution is alkaline.

Helping Concepts *Exam Favourite Rating* ★★★

1. Sr is readily oxidised to form SrO by O_2. In fact, Sr reacts more readily than Mg and Ca.

*2. $SrCO_3 \xrightarrow{\text{heat}} SrO + CO_2$

*3. $SrO + H_2O \rightarrow Sr(OH)_2$

Just like $Ca(OH)_2$, $Sr(OH)_2$ solution is also alkaline.

---

36. In the reaction shown, M represents a Group II element.

$$MO_2 \rightarrow MO + \tfrac{1}{2}O_2$$

Which statements about this reaction are correct?

1 It is a redox reaction.

2 The anion in MO_2 contains 18 electrons.

3 The lattice energy of MO_2 is greater than the lattice energy of MO.

Helping Concepts | Exam Favourite Rating ★★★

*1. There is a change in oxidation state of O from −1 to −2 and 0. It is actually a disproportionation reaction.

*2. The compound is $M^{2+}O_2^{2-}$.
The number of electrons in O_2^{2-} is $2\times8+2=18$. Each O has 8 electrons and there is an extra 2 electrons in O_2^{2-} (over the number of protons).

3. $$\text{L.E.} \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

O^{2-} is smaller than O_2^{2-}. Hence MO has a more exothermic L.E. compared to MO_2.

37. Which of the following statements are true about the elements in Group II of the Periodic Table?

1 They are reducing agents.

2 The ionic radius increases down the group.

3 The electronegativity decreases down the group.

Helping Concepts | Exam Favourite Rating ★★★

*1. Group II elements are powerful reducing agents. They readily lose the only 2 valence electrons to form a stable octet electronic configuration. Furthermore, it can also be seen from the negative reduction potential of M^{2+}/M.

$$M^{2+} + 2e^- \rightleftharpoons M; \quad E^\circ < 0$$

*2. Going down the group, there are more shells of electrons. This gives greater screening effect. Although the nuclear charge increases, this is more than compensated by the additional shells of electrons and greater screening effect. Hence, the valence electrons become further away from the nucleus and the ionic (atomic) radius increases.

*3. With increasing atomic radius and screening effect down the group, the attraction for the valence electrons decreases. Hence, electronegativity decreases.

Note: Electronegativity is the measure on the pull of electrons of a covalent bond by the bonded atom.

38. Which statements about the elements calcium, strontium and barium are correct?

1 The ionic radius of the M^{2+} ion increases from calcium to barium.

2 The magnitude of the hydration energy of the M^{2+} ion increases from calcium to barium.

3 The energy required for the process $M(g) \rightarrow M^{2+}(g) + 2e^-$ increases from calcium to barium.

Helping Concepts | Exam Favourite Rating ★★★

*1. Down the group, there are additional shells of electrons. Hence, ionic size increases.

2. As ionic size increases, the charge density decreases and the ion can attract less H_2O molecules during hydration. Hence, $|\Delta H_{hyd}|$ decreases.

3. As atomic size increases down the group, the attraction for e^- decreases. Hence, I.E. decreases.

39. Which statements about the elements calcium, strontium and barium are correct?

1 The ionic radius of the M^{2+} ion increases from calcium to barium.

2 The magnitude of the hydration energy of the M^{2+} ion increases from calcium to barium.

3 The energy required for the process $M(g) \rightarrow M^{2+}(g) + 2e^-$ increases from calcium to barium.

Helping Concepts | Exam Favourite Rating ★★★

*1. Down the group, the atomic/ionic radius increases due to additional shells of electrons.

2. $$\text{H.E.} \propto \left|\frac{q}{r}\right|$$

Down the group, the H.E. becomes less exothermic due to increasing M^{2+} size.

3. Down the group, the valence electrons become further away from the nucleus. They become less tightly bound. Hence, I.E. decreases.

40. In hospitals, barium sulfate is used in taking X-ray photographs of the alimentary canal. It is mixed with food and eaten by the patient prior to the photographs being taken.

Why is the sulfate used rather than other compounds of barium?

1 Soluble barium compounds are poisonous.

2 Barium sulfate reacts with organic material in the body.

3 Barium sulfate forms sulfuric acid with the acid in the stomach.

Helping Concepts *Exam Favourite Rating* ★

The main reason for using the sulfate is that it is insoluble and therefore remains inert in our body. Otherwise, it would be a toxic chemical to be used.

---

41. Above-ground tests of nuclear explosions in the mid-20th century resulted in pollution by radioactive ^{90}Sr. It is an intense emitter of electrons that can damage body cells. Three properties of strontium are listed.

Which of these properties help to explain why this pollution caused particular concern?

1 Strontium sulfate has low solubility.

2 ^{90}Sr has a half-life of 29 years.

3 Strontium is immediately below calcium in Group II.

Helping Concepts *Exam Favourite Rating* ★

*2. The long half-life means that the emission of electrons will take place over a long period of time.

*3. Being immediately below Ca in Group II, Sr^{2+} has similar size as Ca^{2+}, and may replace Ca^{2+} in our body system when absorbed.

---

42. When coal is burnt, gaseous oxides of carbon and sulfur are formed which pollute the atmosphere. One method of preventing such pollution involves adding calcium carbonate to the burning coal. The temperature of the process causes the decomposition of the calcium carbonate into calcium oxide.

Which reactions will be important in helping to reduce atmosphere pollution?

1 Calcium oxide reacts with sulfur dioxide to form calcium sulfite.

2 Calcium oxide reacts with sulfur dioxide and more air to form calcium sulfate.

3 Calcium oxide reacts with carbon monoxide to form calcium carbonate.

Helping Concepts *Exam Favourite Rating* ★★

*1. $CaO + SO_2 \rightarrow CaSO_3$

*2. $CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$

3. CO is neutral and it does not react with basic CaO.

---

43. Which of the following statements concerning the Group II elements, magnesium, calcium and barium, are correct?

1 Their reactivity increases with increasing relative atomic mass.

2 The only oxidation number exhibited in their stable compounds is +2.

3 On strong heating their nitrates give off oxygen only.

Helping Concepts *Exam Favourite Rating* ★★★

*1. As the atomic size increases, the valence electrons become more loosely bound. The metal loses the valence electrons more easily and is more reactive.

*2. Being alkaline-earth metals, they show invariably compounds with oxidation state of +2.

3. $2M(NO_3)_2(s) \xrightarrow{\Delta} 2MO(s) + 4NO_2(g)\uparrow + O_2(g)\uparrow$

NO_2 gas is also evolved.

---

44. *Use of the Data Booklet is relevant to this question.*

Which properties would be expected from radium, $_{88}Ra$, or its compounds?

1 Radium carbonate decomposes only at a very high temperature.

2 Radium hydroxide is very insoluble.

3 Radium does not react with cold water.

Helping Concepts *Exam Favourite Rating* ★★

*1. Down Group II, the ease of decomposition of MCO_3 decreases. As the cationic size increases, the polarising power of the cation decreases. The CO_3^{2-} ion is polarised to a lesser extent and the C–O bond is weaken to a lesser extent. Hence, $RaCO_3$ decomposes at a very high temperature.

2. Down the group, the solubility of the hydroxide increases. E.g. $Mg(OH)_2$ is only slightly soluble while $Ca(OH)_2$ is sparingly soluble.

3. Ra reacts violently with water.

$$Ra + H_2O \rightarrow RaOH + \frac{1}{2}H_2$$

With a larger size, the valence electrons are less tightly bound. Ra readily loses the two valence electrons and is very reactive.

---

45. The solubilities in water of the sulfates of the Group II elements, MSO_4, decrease as the group is descended.

$$MSO_4(s) + aq \rightarrow M^{2+}(aq) + SO_4^{2-}(aq)$$

Which factors have to be considered in explaining this trend?

1 the hydration energy of M^{2+}(g)

2 the lattice energy of MSO_4(s)

3 the first two ionisation energies of element M

Helping Concepts *Exam Favourite Rating* ★★

$\Delta H_{soln} = -L.E. + \Delta H_{hyd}$

Down Group II, $r_{M^{2+}}$ increases.

*1. $$\left|\Delta H_{hyd}\right| \propto \frac{1}{r_{M^{2+}}}$$

ΔH_{hyd} becomes less exothermic down Group II. Hence, this makes ΔH_{soln} less exothermic down Group II.

2. $$|L.E.| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

L.E. becomes less exothermic down Group II. Hence, this makes ΔH_{soln} more exothermic down Group II.

(However, due to the large SO_4^{2-} anion size, the change in L.E. is not significant compared to ΔH_{hyd}.)

3. The I.E. do not affect ΔH_{soln}, L.E. and ΔH_{hyd}.

---

46. Which of the following factors helps to explain the differing solubility in water of magnesium sulfate compared with that of barium sulfate?

1 Barium sulfate has a numerically larger lattice energy than magnesium sulfate.

2 The enthalpy change of hydration of magnesium ions is more exothermic than that of barium ions.

3 The charge density of magnesium ions is greater than that of barium ions.

Helping Concepts *Exam Favourite Rating* ★★★

$$\begin{tikzcd}
MSO_4(s) \arrow[rr, "\Delta H_{soln}"] & & M^{2+}(aq) + SO_4^{2-}(aq) \\
& M^{2+}(g) + SO_4^{2-}(g) \arrow[ul, "L.E."] \arrow[ur, "\Delta H_{hyd}"'] &
\end{tikzcd}$$

$\Delta H_{soln} = |L.E.| - |\Delta H_{hyd}|$

1. $$|L.E.| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

Down the group, |L.E.| decreases since r_+ increases.

*2,*3. Since Mg^{2+} is smaller than Ba^{2+}, Mg^{2+} has a higher charge density and it is able to attract more H_2O molecules. It is more hydrated and its ΔH_{hyd} is more exothermic.

$$\left|\Delta H_{hyd}\right| \propto \left|\frac{q_+}{r_+}\right| + \left|\frac{q_-}{r_-}\right|$$

---

47. The solubilities of the sulfates of Group II metals (magnesium, calcium, strontium and barium) decrease down the group because

1 the cation size increases from Mg^{2+} to Ba^{2+}.

2 the hydration energy of the cations becomes less exothermic from Mg^{2+} to Ba^{2+}.

3 the sulfate ion is very much smaller than these cations.

Helping Concepts *Exam Favourite Rating* ★★★

$$\begin{tikzcd}
M^{2+}SO_4^{2-}(s) \arrow[rr, "\Delta H_{soln}"] & & M^{2+}(aq) + SO_4^{2-}(aq) \\
& M^{2+}(g) + SO_4^{2-}(g) \arrow[ul, "\Delta H_{L.E.}"] \arrow[ur, "\Delta H_{hyd}"'] &
\end{tikzcd}$$

$\Delta H_{soln} = -\Delta H_{L.E.} + \Delta H_{hyd}$

*1,*2. As the cationic size increases, ΔH_{hyd} becomes less negative. Therefore, ΔH_{soln} also becomes less exothermic, i.e. solubility decreases.

3. SO_4^{2-} ion is relatively large compared to the cations (this makes the variation in the $\Delta H_{L.E}$ less significant as compared to ΔH_{hyd}).

---

48. Anhydrous barium nitrate and anhydrous magnesium nitrate both decompose on heating, evolving nitrogen dioxide and oxygen and forming an oxide.

Which of the following statements concerning these decompositions are correct?

1 Nitrogen dioxide is evolved at a lower temperature from magnesium nitrate than from barium nitrate.

2 For both nitrates the volume of nitrogen dioxide evolved is four times greater than the volume of oxygen.

3 The numerical value of the lattice energy of magnesium nitrate is greater than that of barium nitrate.

Helping Concepts *Exam Favourite Rating* ★★★

*1. Mg^{2+} is smaller than Ba^{2+} and it is therefore more polarising. Hence, $Mg(NO_3)_2$ decomposes more readily at a lower temperature due to greater distortion of NO_3^- electron cloud by Mg^{2+}.

Note: The weakening of the N–O bond is greater in $Mg(NO_3)_2$.

*2. $M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

*3.
$$|L.E.| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$$

Mg^{2+} is smaller than Ba^{2+}. Hence, $Mg(NO_3)_2$ has a numerically larger lattice energy.

TOPIC 11

Group VII

Key content that you will be examined on:

1. The similarities and trends in the physical and chemical properties of chlorine, bromine and iodine
   - (i) Characteristic physical properties
   - (ii) The relative reactivity of the elements as oxidising agents
   - (iii) Some reactions of the halide ions
   - (iv) The reactions of chlorine with aqueous sodium hydroxide

Topic 11

Group VII

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which gaseous hydride most readily decomposes into its elements on contact with a hot glass rod?

   A ammonia

   B hydrogen chloride

   C hydrogen iodide

   D steam

Helping Concepts *Exam Favourite Rating* ★★★

H–I bond is the weakest and hence it is the easiest to decompose.

$$2HI \rightarrow H_2 + I_2$$

---

2. Which of the following compounds reacts with chlorine to give two products in which chlorine has different oxidation numbers?

   A ethene

   B potassium iodate(V)

   C potassium iodide

   D sodium hydroxide

Helping Concepts *Exam Favourite Rating* ★★★

Cl_2 undergoes disproportionation in an alkali.

$$\underset{0}{Cl_2}(g) + 2NaOH(aq)$$
$$\rightarrow Na\underset{-1}{Cl}(aq) + Na\underset{+1}{Cl}O(aq) + H_2O(\ell)$$

---

3. Concentrated sulfuric acid is added to separate solid samples of sodium chloride, sodium bromide or sodium iodide.

   With which sample(s) does sulfuric acid act as an oxidising agent?

   A sodium chloride only

   B sodium chloride and sodium bromide

   C sodium bromide and sodium iodide

   D sodium iodide only

Helping Concepts *Exam Favourite Rating* ★★

Both Br^- and I^- are strong enough reducing agents to reduce conc. H_2SO_4. Br_2 and I_2 are formed respectively.

---

4. Which of the following compounds is most likely to produce chlorine when concentrated hydrochloric acid is added to it?

   A Al_2O_3 **B** Fe_2O_3

   C CuO **D** PbO_2

Helping Concepts *Exam Favourite Rating* ★★★

PbO_2 acts as an oxidising agent and it oxidises concentrated HCl to Cl_2.

$$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O \quad E^\ominus = +1.47\,V$$
$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad E^\ominus = +1.36\,V$$

$$PbO_2(s) + 4H^+(aq) + 4Cl^-(aq)$$
$$\rightarrow PbCl_2(s) + Cl_2(g) + 2H_2O(\ell)$$

$$E^\ominus_{cell} = +1.47 - (+1.36) = +0.11\,V > 0$$

---

5. Which products are obtained when chlorine is bubbled into hot concentrated aqueous sodium hydroxide?

   A NaCl and NaClO

   B NaCl and $NaClO_3$

   C NaClO only

   D $NaClO_3$ only

Helping Concepts *Exam Favourite Rating* ★★★

Chlorine reacts with warm aqueous NaOH to give Cl^- and ClO_3^-.

$3Cl_2(g) + 6OH^-(aq)$
$\rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(\ell)$

Note that with cold aqueous KOH, Cl^- and ClO^- are formed.

$Cl_2(g) + 2OH^-(aq)$
$\rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(\ell)$

---

6. Which equation represents the reaction of chlorine with hot aqueous sodium hydroxide?

A $Cl_2 + 2NaOH \rightarrow NaClO + NaCl + H_2O$
B $2Cl_2 + 4NaOH \rightarrow NaClO_2 + 3NaCl + 2H_2O$
C $3Cl_2 + 6NaOH \rightarrow NaClO_3 + 5NaCl + 3H_2O$
D $4Cl_2 + 8NaOH \rightarrow NaClO_4 + 7NaCl + 4H_2O$

Helping Concepts *Exam Favourite Rating* ★★★

In hot NaOH, Cl_2 disproportionate to form Cl^- and ClO_3^-.

---

7. When chlorine reacts with hot aqueous sodium hydroxide, the reaction below occurs.

chlorine + sodium hydroxide
$\rightarrow$ water + sodium chloride + X

What is compound X?

A sodium chlorate(I)
B sodium chlorate(III)
C sodium chlorate(V)
D sodium chlorate(VII)

Helping Concepts *Exam Favourite Rating* ★

Cl_2 undergoes disproportionation with cold OH^- to give Cl^- and ClO^- but with hot OH^-, it gives Cl^- and ClO_3^- instead.

$$3Cl_2 + 6OH^- \xrightarrow{heat} 5Cl^- + ClO_3^- + 3H_2O$$

---

8. A weedkiller can be prepared by heating a bleach solution.

$$\underset{\text{bleach}}{3NaClO} \xrightarrow{heat} 2NaCl + \underset{\text{weedkiller}}{NaClO_3}$$

What are the oxidation states of chlorine in these three compounds?

A	−1	−1	+5
B	+1	−1	+5
C	+1	−1	+7
D	+2	+1	+7

Helping Concepts *Exam Favourite Rating* ★★★

The oxidation numbers of Cl in NaClO, NaCl and $NaClO_3$ are +1, −1 and +5 respectively.

---

9. Which anions containing chlorine are formed when chlorine is passed into cold aqueous potassium hydroxide?
What are the main ions in the filtrate?

A Cl^- and ClO^-
B Cl^- and ClO_3^-
C Cl^- and ClO_4^-
D ClO^- and ClO_3^-

Helping Concepts *Exam Favourite Rating* ★★★

Chlorine disproportionates in cold aqueous KOH to give Cl^- and ClO^-:

$Cl_2(g) + 2OH^-(aq)$
$\rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(\ell)$

---

10. What is the trend in boiling point and in electron affinity of the Group VII elements from chlorine to iodine?

	boiling point	*electron affinity*
A	increases	more negative
B	decreases	more negative
C	increases	less negative
D	decreases	less negative

Helping Concepts *Exam Favourite Rating* ★★

Molecular size of X_2 increases down the group. Hence, the strength of intermolecular VDW forces increases and boiling point increases down the group.

As the atomic size increases down the group, the attraction for electrons, or affinity for an additional electron also decreases. Hence, electron affinity becomes less negative.

11. Which one of the following compounds would give a mixture of white fumes and coloured fumes on warming with concentrated sulfuric acid?

A sodium bromide
B sodium chloride
C sodium ethanedioate
D sodium methanoate

Helping Concepts *Exam Favourite Rating* ★★★

$$Br^- + \underset{\text{conc.}}{H_2SO_4} \rightarrow HBr\uparrow + HSO_4^-$$

Being a more volatile acid than H_2SO_4, HBr is displaced out as white fumes. However, bromides are sufficiently strong reducing agents that can be oxidised by concentrated H_2SO_4 to give Br_2 (brown) and SO_2 (white fumes).

$$2Br^- + \underset{\text{conc.}}{H_2SO_4} + 2H^+ \rightarrow Br_2\uparrow + SO_2\uparrow + 2H_2O$$

12. When potassium chlorate(V), $KClO_3$, is heated at its melting point, it disproportionates to potassium chlorate(VII), $KClO_4$, and potassium chloride.

What is the maximum number of moles of potassium chlorate(VII) which could be produced from 0.1 mol of potassium chlorate(V)?

A 0.1　　B 0.08
C 0.075　　D 0.06

Helping Concepts *Exam Favourite Rating* ★★★

$$4KClO_3(s) \rightarrow 3KClO_4(s) + KCl(s)$$

Amount of $KClO_4$ produced $= \frac{3}{4}\times 0.1$
$= 0.075$ mol

13. An excess of aqueous silver nitrate is added to aqueous barium chloride, and the precipitate is removed by filtration.

What are the main ions in the filtrate?

A Ag^+ and NO_3^- only
B Ag^+, Ba^{2+} and NO_3^-
C Ba^{2+} and NO_3^- only
D Ba^{2+}, NO_3^- and Cl^-

Helping Concepts *Exam Favourite Rating* ★★★

$$2[Ag^+(aq) + NO_3^-(aq)] + [(Ba^{2+}(aq) + 2Cl^-(aq)]$$
$$\rightarrow 2AgCl(s) + 2NO_3^-(aq) + Ba^{2+}(aq)$$

The ions present are NO_3^-, Ba^{2+} and the excess Ag^+.

14. When a white solid X reacts with concentrated H_2SO_4, the products include pungent-smelling gases and a dark brown solution containing a yellow precipitate. When aqueous sodium thiosulfate is added, the precipitate remains but the dark brown colour disappears.

What is X?

A $AgNO_3$　　B $CaCO_3$
C NaBr　　D KI

Helping Concepts *Exam Favourite Rating* ★★

Solid potassium iodide first reacts with conc. H_2SO_4 to give HI and $KHSO_4$. HI is oxidised to iodine (brown solution). Conc. H_2SO_4 is itself reduced to sulfur (yellow solid) and pungent gases such as H_2S and SO_2 are evolved. With sodium thiosulfate, brown iodine is reduced to colourless iodide ions.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

15. Chlorine compounds show oxidation states ranging from –1 to +7.

What are the reagent(s) and conditions necessary for the oxidation of elemental chlorine into a compound containing chlorine in the +5 oxidation state?

A $AgNO_3$(aq) followed by NH_3(aq) at room temperature
B concentrated H_2SO_4 at room temperature
C cold dilute NaOH(aq)
D hot concentrated NaOH(aq)

Helping Concepts *Exam Favourite Rating* ★★

Cl_2 undergoes disproportionation to give Cl^- (O.S. = –1) and ClO_3^- (O.S. = +5) when heated with an alkali.

$$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$$

16. Which statement is most likely to be true for astatine which is below iodine in Group VII of the Periodic Table?

A Sodium astatide and hot concentrated sulfuric acid react to form astatine.

B Silver astatide reacts with dilute aqueous ammonia in excess to form a solution of a soluble complex.

C Astatine and aqueous potassium chloride react to form aqueous potassium astatide and chlorine.

D Potassium astatide and hot dilute sulfuric acid react to form only white fumes of hydrogen astatide.

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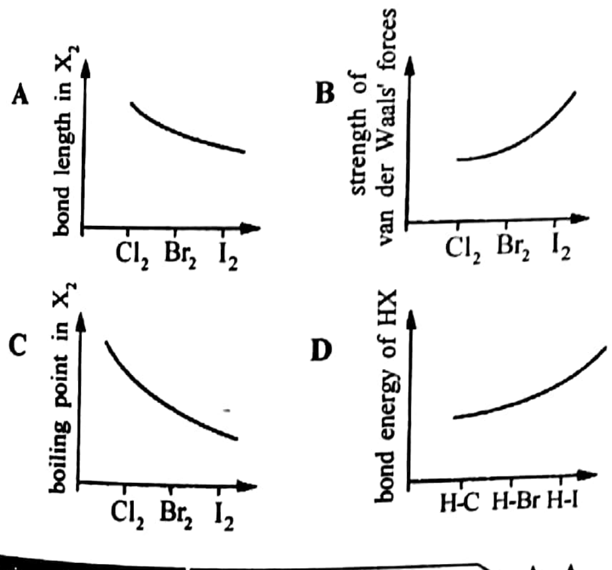
Down the group, reducing property of the halides increases as a result of the increasing size. Valence electrons become less tightly bound and the halides lose their electrons more readily. I^- is oxidised by hot concentrated H_2SO_4 to I_2. At^- being below I^-, is even more reducing than I^-. At^- will also be oxidised to At_2.

---

17. Which graph correctly describes a trend found in the halogen group?



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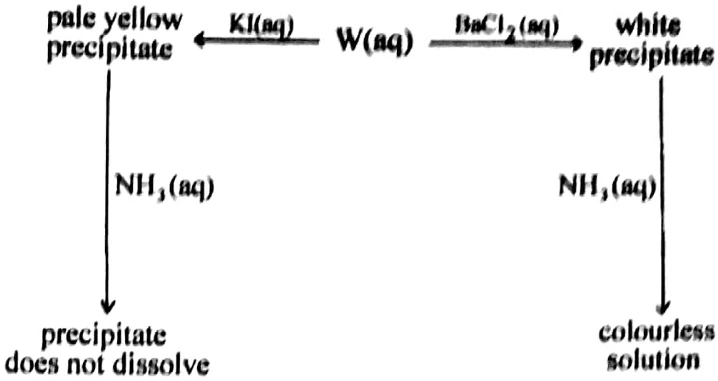
With increasing number of electrons in the molecule and hence increasing the molecular size, induced dipole-induced dipole (id-id) interaction (van der Waals' forces) increases.

---

18. A compound W reacts in the following ways.



What could compound W be?

A $AgNO_3$ B Ag_2SO_4

C $Pb(NO_3)_2$ D $PbSO_4$

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$$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$$

The yellow precipitate is AgI, which is insoluble in aqueous NH_3.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$
$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-$$

The white precipitate is AgCl, which dissolves readily in aqueous NH_3 to give a colourless solution containing diaaminesilver(I) complex (Tollens' reagent!).

---

19. An aqueous solution containing Br^- ions is treated with $AgNO_3$(aq), giving a precipitate **P**, which is then tested for its solubility in concentrated NH_3(aq).

What is the colour of **P** and its solubility in NH_3(aq)?

	colour of **P**	solubility in NH_3(aq)
A	white	insoluble
B	white	slightly soluble
C	cream	slightly soluble
D	yellow	insoluble

Helping Concepts *Exam Favourite Rating* ★★★

$$Ag^+(aq) + Br^-(aq) \rightleftharpoons \underset{\text{cream}}{AgBr(s)}$$
$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$$

Due to the extreme low solubility of AgBr, a very high concentration of NH_3 is needed to shift the second equilibrium to the right and reduce the concentration of Ag^+ to a sufficiently low value so that the first equilibrium may shift to the left. Hence, AgBr is only slightly soluble in concentrated NH_3.

20. Why is hydrogen iodide a stronger acid than hydrogen chloride?

A The molecule of hydrogen chloride is more polar than the molecule of hydrogen iodide.

B The enthalpy change of formation of hydrogen iodide is greater than that of hydrogen chloride.

C The enthalpy change of hydration of the iodide ion is greater than that of the chloride ion.

D The covalent bond in the hydrogen iodide molecule is weaker than that in the hydrogen chloride molecule.

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H–I bond is weaker than H–Cl bond so that HI can easily dissociate into H^+ and I^- in H_2O.

Covalent bond strength depends on the extent of overlap between orbitals. Iodine has a more diffuse p orbital than chlorine. Hence, the overlap of the p orbital with the 1s orbital of hydrogen is less effective. Therefore, H–I bond is weaker than H–Cl bond.

21. Tin(IV) iodide can be prepared by refluxing 0.04 mol of tin with 0.03 mol of iodine (I_2) dissolved in 50 cm^3 of tetrachloromethane (boiling point, 77 °C).

$$Sn + 2I_2 \rightarrow SnI_4$$

Orange crystals of the product are obtained by filtering the hot reaction mixture and then cooling the filtrate.

Which of the following would indicate that the reaction was complete?

A The boiling point of the mixture is 77 °C.

B No tin remains in the reaction flask.

C Crystals begin to be deposited from the boiling solvent.

D No more purple vapour is seen in the reaction vessel.

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From the amounts of Sn and I_2 given, it can be seen that I_2 is the limiting agent. Hence, when no more violet vapour of I_2 is observed, the reaction is completed.

22. The ash from burnt seaweed contains chlorides and iodides of some Group I and Group II elements. Some seaweed ash was treated with concentrated sulfuric acid and the resulting fumes passed first through a cold tube and then bubbled through aqueous silver nitrate.

What would be observed during the experiment?

	inside the cold tube	with aqueous silver nitrate
A	black deposit	white precipitate
B	black deposit	yellow precipitate
C	no deposit	white precipitate
D	no deposit	yellow precipitate

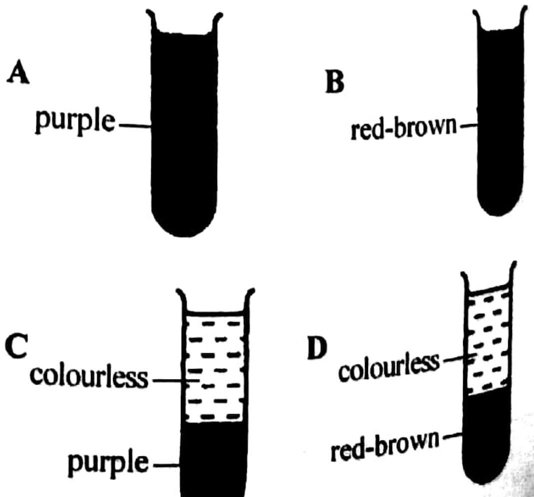
Helping Concepts *Exam Favourite Rating* ★★

I^- is oxidised to I_2 by conc. H_2SO_4. It is the black deposit in the cold tube.

Cl^- forms HCl with conc. H_2SO_4. It forms AgCl white ppt. with $AgNO_3$.

23. Aqueous chlorine is added to aqueous sodium bromide and the mixture is shaken with an equal volume of trichloroethane.

Which observation would be made?



Helping Concepts *Exam Favourite Rating* ★★★

Trichloroethane is immiscible with water and is denser. Two distinct layers of liquid should be observed, with the organic layer at the bottom.

$$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

Cl_2 oxidised Br^- to Br_2, itself being reduced to colourless Cl^-.

$$Br_2(aq) \rightleftharpoons Br_2(org)$$

The brown Br_2 liberated partitioned itself between the two layers of liquids, with most of it present in the organic layer, colouring it red-brown at the same time. Very little Br_2 is present in the aqueous layer. Thus, the aqueous layer appears colourless.

---

24. The solubility of the silver halides in aqueous ammonia decreases from AgCl to AgI.

What helps to explain this trend?

A As a more powerful ligand, NH_3 can displace Cl^- ions and Br^- ions, but not I^- ions.

B Cl^- ions and Br^- ions form complexes with $NH_3(aq)$, but I^- ions do not.

C The value of the solubility product of the silver halides decreases from AgCl to AgI.

D The covalent bonding between Ag and the halogen atom increases in strength from AgCl to AgI.

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$$AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq) \qquad K_{sp}$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \qquad K_{stab}$$

For the three halides, K_{stab} remains the same since X^- is not involved in the reaction. The minimum $[Ag^+]$ required to form the complex is the same. However, for a smaller K_{sp} (e.g. AgI), this minimum $[Ag^+]$ is still high enough such that $[Ag^+][I^-] > K_{sp}$.

Hence, AgI does not dissolve in aqueous NH_3. The solubility is thus governed by the K_{sp} of the respective AgX.

$$K_{sp}(AgCl) > K_{sp}(AgBr) > K_{sp}(AgI)$$

Hence, the solubility decreases from AgCl to AgI.

---

25. The table shows the results of experiments in which the halogens X_2, Y_2 and Z_2 were added to separate aqueous solutions containing X^-, Y^- and Z^- ions.

	$X^-(aq)$	$Y^-(aq)$	$Z^-(aq)$
X_2	no reaction	no reaction	no reaction
Y_2	X_2 formed	no reaction	Z_2 formed
Z_2	X_2 formed	no reaction	no reaction

Which set contains the ions X^-, Y^- and Z^- in order of their decreasing strength as a reducing agent?

	strongest →		weakest
A	X^-	Y^-	Z^-
B	X^-	Z^-	Y^-
C	Y^-	Z^-	X^-
D	Z^-	X^-	Y^-

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The first row (X_2) shows that X_2 is the weakest oxidising agent since it cannot oxidise Y^- and Z^-. The second row (Y_2) shows that Y_2 is more oxidising than X_2 and Z_2 since it can oxidise X^- and Z^-. The third row (Z_2) shows that Z_2 is less oxidising than Y_2 since it cannot oxidise Y^-; and it is more oxidising than X_2 since it oxidises X^- to X_2.

oxidising agent: $Y_2 > Z_2 > X_2$

reducing agent: $Y^- < Z^- < X^-$

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

26. Which changes can be regarded as oxidation of bromine?

1 $Br_2 \rightarrow BrO^-$

2 $Br_2 \rightarrow BrF$

3 $Br_2 \rightarrow BrI$

Helping Concepts *Exam Favourite Rating* ★★★

Oxidation is a process where there is an increase in oxidation state.

*1. $\underset{0}{Br_2} \rightarrow \underset{+1}{Br}O^-$

2. $\underset{0}{Br_2} \rightarrow \underset{-1}{Br}F$

In BrF, Br has a positive oxidation state because Br is less electronegative than F (F does not exist in positive oxidation state).

3. $\underset{0}{Br_2} \rightarrow \underset{-1}{Br}I$

In BrI, Br has a negative oxidation state because it is more electronegative than I.

27. Which quantities are greater for fluorine than chlorine?

1 standard electrode potential $E^\ominus$ for $X_2/2X^-$.

2 boiling point of the element X_2

3 ionic radius of the X^- ion

Helping Concepts *Exam Favourite Rating* ★★★

*1. $E^\ominus_{F_2/2F^-} = +2.87$ V

$E^\ominus_{Cl_2/2Cl^-} = +1.36$ V

2. Boiling point of Cl_2 is higher since Cl_2 has a larger molecular size (or more electrons per molecule) and hence, stronger VDW forces between the molecules.

3. Cl is in Period 3 while F is in Period 2. Cl^- has an extra shell of electrons and hence Cl^- is larger.

28. In which reactions does the oxidation state of chlorine change by one?

1 electrolysis of brine (anode reaction)

2 hydrogen + chlorine

3 sodium chloride + concentrated sulfuric acid

Helping Concepts *Exam Favourite Rating* ★★

*1. $Cl^- \rightarrow \frac{1}{2}Cl_2 + e$

O.S.: −1 to 0

*2. $H_2 + Cl_2 \rightarrow 2HCl$

O.S.: 0 to −1

3. $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

O.S.: −1 to −1

29. Which sodium salts form a precipitate when $AgNO_3(aq)$ followed by dilute $NH_3(aq)$ is added to its aqueous solution?

1 chloride

2 bromide

3 iodide

Helping Concepts *Exam Favourite Rating* ★★

1. AgCl is soluble in aqueous NH_3. Hence, no precipitate is observed after aqueous NH_3 is added, i.e. the precipitate dissolves.

*2. AgBr is sparingly soluble in aqueous NH_3. Some precipitate will remain after adding aqueous NH_3.

*3. AgI is insoluble in aqueous NH_3.

30. The element astatine, At, is below iodine in Group VII of the Periodic Table.

Which statements concerning At will be true?

1 It is a coloured solid at room temperature.

2 It is a more powerful oxidising agent than iodine

3 Its hydride is thermally stable.

Helping Concepts Exam Favourite Rating ★★

*1. Since the colour intensity increases down the group, At_2 is expected to be coloured. Furthermore, the melting point of the halogens increases down the group: F_2 and Cl_2 are gases. Br_2 is a liquid and I_2 is a solid. We expect At_2 also is a solid.

2. Oxidising power decreases down the group.

3. Thermal stability of HX decreases down the group.

---

31. For the sequence hydrogen chloride, hydrogen bromide and hydrogen iodide, there is an increase in

1 thermal stability.

2 bond length.

3 ease of oxidation.

Helping Concepts Exam Favourite Rating ★★★

1,*2. Due to the increasing size of the halogen, the H–X bond length becomes longer. The bond is weaker as a result of less effective overlap between the 1s-orbital of H and the more diffuse p-orbitals of X. The H–X bonds become more easily broken and hence, HX becomes more easily decomposed when heated.

$$2HX(g) \rightarrow H_2(g) + X_2(g)$$

*3. The reducing power of the halides increases down the group since the halides have more shells of electrons (greater screening effect) and larger sizes. The valence electrons are less tightly bound and can be more readily lost.

$$2HX \rightarrow 2H^+ + X_2 + 2e^-$$

The ease of oxidation can also be seen from the decreasing $E^\ominus$ value of X_2/X^-.

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \qquad E^\ominus = +1.36\text{ V}$$

$$Br_2 + 2e^- \rightleftharpoons 2Br^- \qquad E^\ominus = +1.07\text{ V}$$

$$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^\ominus = +0.54\text{ V}$$

---

32. When a hot glass rod is placed in a gas jar of hydrogen iodide, there is an immediate reaction as the hydrogen iodide decomposes.

Which statements about this reaction are correct?

1 Hydrogen iodide is purple coloured.

2 The hot rod provides the activation energy.

3 One of the products is a solid.

Helping Concepts Exam Favourite Rating ★★

1. HI is colourless.

*2. The heat supplies the energy to break the H–I bond.

$$2HI(g) \rightarrow H_2(g) + I_2(s)$$

*3. Solid iodine is formed.

---

33. The number of moles of chlorine that react with 1 mol of *X* is twice the number of moles of chlorine that react with 1 mole of *Y*.

Which of these pairs could be *X* and *Y*?

	X	*Y*
1	Mg(s)	Na(s)
2	H_2	KBr(aq)
3	cold NaOH(aq)	hot NaOH(aq)

Helping Concepts Exam Favourite Rating ★★★

*1. $Mg + Cl_2 \rightarrow MgCl_2$

$Na + \frac{1}{2}Cl_2 \rightarrow NaCl$

*2. $H_2 + Cl_2 \rightarrow 2HCl$

$KBr + \frac{1}{2}Cl_2 \rightarrow KCl + \frac{1}{2}Br_2$

3. $6NaOH + 3Cl_2 \rightarrow 3NaCl + 3NaClO + 3H_2O$

$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

---

34. *Use of the Data Booklet is relevant to this question.*

In the sequence HCl–HBr–HI, which statements are correct?

1 The enthalpy change of information becomes less exothermic.

2 The polarity of the hydrogen halide molecule increases.

3 The thermal stability of the hydrogen halide increases.

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	bond energy/kJ mol^{-1}
HCl	431
HBr	366
HI	299

*1. Progressively less heat is given out from HCl to HI due to the decrease in H–X bond strength.

2. Polarity decreases as electronegativity from Cl to I decreases.

3. Thermal stability decreases due to the decreases in H–X bond strength.

---

35. Which statements about the trends in the properties of the halogens are correct?

1 The electronegativity decreases on descending the group.

2 The volatility decreases on descending the group.

3 Their reactivity as oxidising agents decreases on descending the group.

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*1,*3. Down the group, the atoms become bigger and screening effect increases as there are more shells of electrons. Hence, the electrons become less tightly bound. Their ability to attract electrons (electronegativity) and their tendency to gain electrons (oxidising power) decrease.

*2. Down the group, the molecules (X_2) become larger and have more electrons per molecule. VDW forces become stronger and thus volatility decreases, i.e. melting point and boiling point increase.

---

36. Which of the following statements are correct for all three halogens, chlorine, bromine and iodine?

1 They all form hydrides which are strong acids in aqueous solution.

2 They all react with aqueous sodium hydroxide to form oxo-anions.

3 They all need to gain one electron to fill completely the p orbitals of their outer shells.

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Being members of Group VII, the 3 congeners show a great deal of similarity in the chemical properties:

*1. $HX + H_2O \rightarrow H_3O^+ + X^-$ (strong acids)

*2. $3X_2 + 6OH^- \rightarrow XO_3^- + 5X^- + 3H_2O$ (disproportionation)

*3. All have an $ns^2\ np^5$ configuration, requiring one more electron to completely fill the outer shell.

---

37. The number of moles of chlorine that react with 1 mol of *X* is twice the number of moles of chlorine that react with 1 mol of *Y*.

Which of these pairs could be *X* and *Y*?

	X	*Y*
1	Mg(s)	Na(s)
2	H_2(g)	KBr(aq)
3	cold NaOH(aq)	hot NaOH(aq)

Helping Concepts Exam Favourite Rating ★★

*1. $Mg + Cl_2 \rightarrow MgCl_2$

$Na + \frac{1}{2}Cl_2 \rightarrow NaCl$

*2. $H_2 + Cl_2 \rightarrow 2HCl$

$KBr + \frac{1}{2}Cl_2 \rightarrow KCl + \frac{1}{2}Br_2$

3. $2NaOH + Cl_2 \xrightarrow{\text{cold}} NaCl + NaClO + H_2O$

or $NaOH + \frac{1}{2}Cl_2 \xrightarrow{\text{cold}} \frac{1}{2}NaCl + \frac{1}{2}NaClO + \frac{1}{2}H_2O$

$6NaOH + 3Cl_2 \xrightarrow{\text{hot}} NaCl + 5NaClO_3 + 3H_2O$

or $NaOH + \frac{1}{2}Cl_2 \xrightarrow{\text{hot}} \frac{1}{6}NaCl + \frac{5}{6}NaClO_3 + \frac{1}{2}H_2O$

---

38. Which of the following statements are correct concerning redox properties?

1 A metal *M*, for which $E^\ominus$ for the half reaction $M^{n+} + ne^- = M$ is very negative, will be a good reducing agent.

2 The oxidising power of the halogens decreases from chlorine to iodine.

3 The reducing power of the hydrogen halides increases from hydrogen chloride to hydrogen iodide.

Helping Concepts *Exam Favourite Rating* ★★★

*1. A very negative E° value indicates that M^{n+} is very difficult to be reduced to M. On the other hand, M is very easily oxidised to M^{n+}. Hence, M would be a good reducing agent.

*2. From Cl_2 to I_2, the atomic size and screening effect increase. Therefore, the ability to attract an extra electron decreases and hence the oxidising power decreases.

*3. From (2), it follows that the reducing power of the halide increases from Cl^- to I^-.

---

39. Why is the addition of concentrated sulfuric acid to solid potassium iodide **unsuitable** for the preparation of hydrogen iodide?

1 Hydrogen iodide is not displaced by sulfuric acid.

2 Iodide ions are oxidised to iodine.

3 The product is contaminated by sulfur compounds.

Helping Concepts *Exam Favourite Rating* ★★

1. HI, being a volatile acid, is displaced by conc. H_2SO_4.

*2,*3. I^- is a sufficiently strong reducing agent and hence is oxidised by conc. H_2SO_4 to I_2. The reduction products of conc. H_2SO_4 include SO_2, S and H_2S.

$$2I^- + H_2SO_4 + 2H^+ \rightarrow I_2 + SO_2 + 2H_2O$$
$$6I^- + H_2SO_4 + 6H^+ \rightarrow 3I_2 + S + 4H_2O$$
$$8I^- + H_2SO_4 + 8H^+ \rightarrow 4I_2 + H_2S + 4H_2O$$

---

40. The concepts of bond energy, bond length and bond polarity are useful when comparing the behaviour of similar molecules, e.g. thermal stability.

For example, it could be said

"Compared with the HCl molecule, the bond _X_ of the HI molecules is _Y_."

Which pairs of words correctly complete the above sentence?

	X	Y
1	energy	greater
2	length	greater
3	polarity	less

Helping Concepts *Exam Favourite Rating* ★★

I is below Cl in the Periodic Table. It is thus bigger than Cl. Hence, the bond length of H–I bond is expected to be greater than that of H–Cl bond. H–I bond is weaker and its bond energy is thus smaller. Also I is less electronegative than Cl. Hence, H–I bond is less polar than H–Cl bond.

---

41. Which suggestions concerning the element astatine (proton number 85) are consistent with its position in Group VII?

1 The element is a solid at room temperature and pressure.

2 Hydrogen astatide is less stable to heat than hydrogen iodide.

3 Silver astatide is soluble in aqueous ammonia.

Helping Concepts *Exam Favourite Rating* ★★

*1. Down the group, molecular size (or number of electrons per molecule) increases. VDW forces become stronger and melting point and boiling point increase. Since I_2 is a solid, At_2 is also a solid.

*2. The bond strength of H–X decreases down the group. The bigger X atom has a more diffuse orbital and hence, poorer overlap with the hydrogen 1s orbital. Therefore, H–At is less stable to heat than H–I.

$$2HAt \rightarrow H_2 + At_2$$

3. The solubility of AgX in NH_3 increases down the group. AgCl is soluble; AgBr is sparingly soluble and AgI is insoluble. Hence, AgAt is also insoluble in NH_3.

TOPIC

12

An Introduction to the Chemistry of Transition Elements

Key content that you will be examined on:

1. General physical and characteristic chemical properties of the first set of transition elements, titanium to copper
2. Colour of complexes

An Introduction to the Chemistry of Transition Elements

Topic 12

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which of the following d-block elements can show the highest oxidation number in its compounds?

A chromium
B copper
C iron
D manganese

Helping Concepts Exam Favourite Rating ★★★

Mn can show the highest oxidation number of +7.

2. For which of the following transition metals does its ground-state atom have an unpaired electron in an s-orbital?

A chromium
B cobalt
C iron
D manganese

Helping Concepts Exam Favourite Rating ★★★

Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

3. *Use of the Data Booklet is relevant to this question.*

What is the electronic structure of the iron(II) ion?

A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$
C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$

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Fe: [Ar] $3d^6\ 4s^2$

Fe^{2+}: [Ar] $3d^6$

4. Which of the following ions is readily able to donate electrons?

A Al^{3+}
B Cu^{2+}
C Fe^{2+}
D Mg^{2+}

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$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$Fe^{2+}(3d^6)$ is able to lose another electron to give Fe^{3+}.

5. What is the electronic configuration of Cr^{3+}?

[Ar] represents $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

A [Ar] $3d^1\ 4s^2$
B [Ar] $3d^2\ 4s^2$
C [Ar] $3d^3\ 4s^0$
D [Ar] $3d^4\ 4s^0$

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$_{24}Cr$: [Ar] $3d^5\ 4s^1$

$_{24}Cr^{3+}$: [Ar] $3d^3$

When Cr loses 3 electrons, the 4s electron is lost first before the 3d electron.

6. Which species does **not** act as a ligand in the formation of complexes?

A CH_3NH_2
B Cl^-
C NH_4^+
D OH^-

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NH_4^+ does not have a lone pair of electrons for donation to a central atom/ion to form dative bond. It therefore cannot act as a ligand.

7. Iron has a proton (atomic) number of 26.

What is the electronic configuration of the iron cation which can form the complex ion $[Fe(CN)_6]^{4-}$?

$[[Ar] \equiv 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6]$

A $[Ar]\ 3d^3\ 4s^2$

B $[Ar]\ 3d^4\ 4s^2$

C $[Ar]\ 3d^5\ 4s^0$

D $[Ar]\ 3d^6\ 4s^0$

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$$x+6(-1)=-4 \Rightarrow x=+2$$

Therefore, Fe is in the +2 oxidation state.

Fe: $[Ar]\ 3d^6\ 4s^2$

Fe^{2+}: $[Ar]\ 3d^6\ 4s^0$

---

8. Titanium is manufactured from ilmenite which is a mixture of iron(II) titanate, $FeTiO_3$, and iron(III) titanate, $Fe_2(TiO_3)_3$. $2(3)+3Ti+(-18)$

What are the oxidation numbers of titanium in these two compounds? $6+3Ti-18$

A +2, +3   B +4, +2 $3Ti-12$

C +4, +3   D +4, +4 $Ti=$

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$FeTiO_4$: $(+2)+x+4(-2)=0 \Rightarrow x=+4$

$Fe_2(TiO_3)_3$: $2(+3)+3[y+3(-2)]=0 \Rightarrow y=+4$

---

9. Which atom has three unpaired electrons?

A Al   B Sc

C Cr   D Co

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element	Al	Sc	Cr	Co
electronic configuration	$[Ne]\ 3s^2\ 3p^1$	$[Ar]\ 3d^1\ 4s^2$	$[Ar]\ 3d^5\ 4s^1$	$[Ar]\ 3d^7\ 4s^2$
no. of unpaired electrons	1	1	6	3

---

10. *Use of the Data Booklet is relevant to this question.*

Which particle contains a single unpaired electron?

A a molecule of H_2S

B one of the particles formed after the heterolytic fission of a chlorine molecule

C the ammonium ion in NH_4Cl

D the copper ion in CuO

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In Cu^{2+}, the electronic configuration is $[Ar]\ 3d^9$.

---

11. Titanium has the electronic structure $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$.

Which of the following compounds is *unlikely* to exist?

A K_2TiO_4 ($+1\ +6\ -2$)   B K_3TiF_6 ($+3$?)

C $TiCl_3$ D TiO

Helping Concepts *Exam Favourite Rating* ★★★

Ti is able to utilise a maximum of 4 electrons ($3d^2\ 4s^2$) for bonding. Hence, the highest oxidation state it can show in compound formation is +4. In K_2TiO_4, Ti has an oxidation state of +6. Hence, it is unlikely to exist.

$$2(+1)+x+4(-2)=0$$
$$x=+6$$

---

12. Zn^{2+} has a full set of valence d electrons.

What is **not** a direct consequence of this property?

A Aqueous solution of its salts do not absorb visible light.

B Its complexes are colourless.

C Its complexes are octahedral.

D The metal exhibits only one oxidation state.

Helping Concepts *Exam Favourite Rating* ★★

Octahedral complexes are found in both completely and incompletely filled d-subshell central metal ions.

---

13. A constituent of wood preservative is manufactured by heating the ore chromite, $FeCr_2O_4$, with sodium carbonate in air.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Which species is oxidised and which species is reduced in this process?

	species oxidised	species reduced
A	chromium only	carbonate ion only
B	chromium only	carbonate ion and oxygen
C	chromium and iron	oxygen only
D	chromium and iron	carbonate ion and oxygen

Helping Concepts *Exam Favourite Rating* ★★

Chromium is oxidised from +3 (in $Cr_2O_4^{2-}$) to +6 (in CrO_4^{2-}) and iron is oxidised from +2 to +3. Oxygen (O_2) is reduced from 0 to −2.

---

14. *Use of the Data Booklet is relevant to this question.*

Sir Humphrey Davy showed that the corrosion of copper hulls of sea-going ships could be prevented by placing strips of 'sacrificial' metals on the hulls.

Which of these metals is least likely to dissolve when attached to the copper hull of a sea-going ship?

A iron B magnesium
C tin D zinc

Helping Concepts *Exam Favourite Rating* ★★

To function as a sacrificial metal for Cu, the metal must be more reactive than Cu. From the Data Booklet, it can be seen that Sn^{2+}/Sn has the least E° value, i.e. it is the least reactive among the 4 metals.

---

15. Metallic elements have different electrical conductivities.

What is the correct order of increasing electrical conductivity of each pair of these metals?

	Period 3	Period 4
A	Al < Mg	Cu < Ca
B	Al < Mg	Ca < Cu
C	Mg < Al	Cu < Ca
D	Mg < Al	Ca < Cu

Helping Concepts *Exam Favourite Rating* ★★★

Al has 3 valence electrons while Mg has only 2. Hence, Al is a better electrical conductor than Mg.

Cu is a transition element with 3d and 4s electrons. Hence, it is a better electrical conductor than Ca, which has only two 4s electrons.

---

16. Platinum(IV) chloride combines with ammonia to form compounds in which the co-ordination number of platinum is 6. A formula unit of one of the compounds contains a cation and only two chloride ions.

What is the formula of this compound?

A $Pt(NH_3)_6Cl_4$ B $Pt(NH_3)_5Cl_4$
C $Pt(NH_3)_4Cl_4$ D $Pt(NH_3)_3Cl_4$

Helping Concepts *Exam Favourite Rating* ★★

The compound with co-ordination number 6 may be looked upon as $[Pt(NH_3)_{6-x}Cl_x]^{2+}(Cl^-)_2$. Since Pt is in oxidation state IV, its chloride has a formula $PtCl_4$, i.e. 4Cl atoms. Hence $x = 2$.

---

17. Adding concentrated HCl(aq) to $CuSO_4$(aq) causes the colour of the solution to change from blue to green.

Which row best explains this observation?

	number of d-electrons around copper	energy gap between the d-orbitals
A	changes	changes
B	changes	remains the same
C	remains the same	changes
D	remains the same	remains the same

Helping Concepts *Exam Favourite Rating* ★

$$\underset{\text{blue}}{Cu^{2+}} + 4Cl^- \rightleftharpoons \underset{\text{yellow}}{CuCl_4^{2-}}$$

The green solution observed is due to a mixture of blue Cu^{2+} and yellow $CuCl_4^{2-}$. The reaction is a result of ligand exchange between H_2O and Cl^- and it is non-redox in nature. Hence, the number of d-electrons around Cu(II) remains the same, i.e. $3d^9$. However, as the energy gap between the d-orbitals changes (due to different ligands), the colour observed changes.

18. Titanium(IV) oxide is widely used in the paint industry as a white pigment. It is soluble in hot concentrated sulfuric acid according to the equation below.

$$TiO_2 + H_2SO_4 \rightarrow (TiO)^{2+} + SO_4^{2-} + H_2O$$

Which of the following describes the nature of this reaction?

A acid-base
B complex ion formation
C dehydration
D displacement

Helping Concepts *Exam Favourite Rating* ★★★

H_2SO_4 serves as an acid while TiO_2 functions as a base.

Salt ($TiO^{2+}SO_4^{2-}$) and H_2O are formed.

---

19. *Use of the Data Booklet is relevant to this question.*

Spatulas are often made from nickel.

Which aqueous solution should **not** be stirred with a nickel spatula because a reaction could occur?

A Co^{2+}(aq) **B** Cr^{3+}(aq)
C Fe^{3+}(aq) **D** Mn^{2+}(aq)

Helping Concepts *Exam Favourite Rating* ★★★

Nickel is oxidised by ions with $E^\ominus$ greater than $E^\ominus$ of Ni^{2+}/Ni (–0.25 V). $E^\ominus$ of Co^{2+}, Cr^{3+}, Fe^{3+} and Mn^{2+} are –0.28 V, –0.41 V, +0.77 V and –1.18 V respectively.

Hence, Ni reacts with Fe^{3+}.

$$2Fe^{3+} + Ni \rightarrow 2Fe^{2+} + Ni^{2+}$$

$E^\ominus_{cell} = +0.77 - (-0.25) = +1.02 \text{ V} > 0$

Hence, the reaction is energetically feasible.

---

20. *Use of the Data Booklet is relevant to this question.*

In the Aromas Red Sands aquifer, the drinking water source for part of California, there are high levels of soluble, toxic chromium(VI) compounds.

Which compound in the aquifer's sands is most likely to be responsible for the formation of the chromium(VI) compounds from the sparingly soluble chromium(III)-bearing rocks?

A Al_2O_3 **B** CuO
C Fe_2O_3 **D** ZnO

Helping Concepts *Exam Favourite Rating* ★★

The identified substance oxidises Cr(III) to Cr(VI). Among the 4 oxides, Fe_2O_3 is the most oxidising (Fe(II) → Fe(III)).

---

21. When copper(II) chloride is dissolved in water it gives a blue solution. When this solution is treated with an excess of concentrated hydrochloric acid it turns yellow.

What are the formulae of the copper species in the blue and yellow solutions?

	blue	yellow
A	$CuCl_2$	$[CuCl_4]^{2-}$
B	$CuCl_2(H_2O)_4$	$[CuCl_6]^{4-}$
C	$Cu(OH)_2$	$CuCl_2(H_2O)_4$
D	$[Cu(H_2O)_6]^{2+}$	$[CuCl_4]^{2-}$

Helping Concepts *Exam Favourite Rating* ★★★

$$Cu^{2+}(s) + 6H_2O \xrightarrow{aq.} [Cu(H_2O)_6]^{2+}$$
$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

---

22. When drops of NH_3(aq) are added to $Cu(NO_3)_2$(aq), a pale blue precipitate is formed. This precipitate dissolves when an excess of NH_3(aq) is added, forming a deep blue solution.

Which process does **not** occur in this sequence?

A dative bond formation
B formation of a complex ion
C precipitation of copper(II) hydroxide
D reduction of Cu^{2+} ions

Helping Concepts *Exam Favourite Rating* ★★★

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$$
$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

2nd equation: $Cu(OH)_2$ is formed as a precipitate.
3rd equation: Dative bonds are formed between Cu^{2+} and NH_3. A complex ion is formed.

23. *Use of the Data Booklet is relevant to this question.*
The salt $K_3Fe(CN)_6$ is prepared by oxidising $K_4Fe(CN)_6$.
Which reagent carries out this oxidation?

A $Ag(s)$ B $Cl_2(g)$
C $Cu^{2+}(aq)$ D $Fe^{2+}(aq)$

Helping Concepts *Exam Favourite Rating* ★★★

$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^\ominus = +0.36$ V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V

Overall: $Cl_2 + 2[Fe(CN)_6]^{4-} \rightarrow 2Cl^- + 2[Fe(CN)_6]^{3-}$

$E^\ominus_{cell} = +1.36 - 0.36 = +1.00 \text{ V} > 0$

The reaction is energetically feasible under standard conditions.

A: Ag is a reducing agent.

B: Cu^{2+}/Cu
$E^\ominus_{cell} = +0.34 - 0.36 = -0.02 \text{ V} < 0$
Cu^{2+}/Cu^{+}
$E^\ominus_{cell} = +0.15 - 0.36 = -0.21 \text{ V} < 0$

C: Fe^{2+}/Fe
$E^\ominus_{cell} = -0.44 - 0.36 = -0.80 \text{ V} < 0$

---

24. The data below refers to a particular element.

density	10.5 g cm^{-3}
first ionisation energy	730 kJ mol^{-1}
second ionisation energy	2070 kJ mol^{-1}
third ionisation energy	3360 kJ mol^{-1}
melting point	1235 K

Where in the Periodic Table is this element most likely to be found?

A Group I
B Group II
C Group VII
D the transition elements

Helping Concepts *Exam Favourite Rating* ★★

The high density and high melting point suggest that the element is a metal (hence not in Group VII) and is unlikely to be in Group I nor II as there is no sudden large difference between IE_1 and IE_2, and between IE_2 and IE_3 respectively.

---

25. The anti-cancer drug *cisplatin* has the formula $Pt(NH_3)_2Cl_2$. In the human body, one of the chloride ions of *cisplatin* is replaced by one water molecule.

$$Pt(NH_3)_2Cl_2 + H_2O \rightarrow [Pt(NH_3)_2(H_2O)Cl]^+ + Cl^-$$

What is the oxidation number of platinum in each of these substances?

	cisplatin	*in the aquacomplex*
A	+2	+1
B	+2	+2
C	+4	+3
D	+4	+4

Helping Concepts *Exam Favourite Rating* ★★★

In $Pt(NH_3)_2Cl_2$, NH_3 has zero charge.

$$\therefore x + 2(0) + 2(-1) = 0$$
$$x = +2$$

In $[Pt(NH_3)_2(H_2O)Cl]^+$,

$$y + 2(0) + 1(0) + (-1) = +1$$
$$y = +2$$

---

26. The table shows the possible oxidation states of five d-block elements in the Periodic Table. (The elements are represented by letters which are not their symbols.)

<u>element</u>	<u>possible oxidation numbers</u>						
P	–	–	3	–	–	–	–
Q	–	2	3	4	–	–	–
R	1	2	3	4	5	–	–
T	–	2	–	4	5	6	7

Which of the following ions is likely to exist?

A PO_2^{+} B QO_3^{-}
C RO_4^{2-} D TO_2^{2+}

Helping Concepts *Exam Favourite Rating* ★★

The oxidation state of T in TO_2^{2+} is +6.

$$x + 2(-2) = +2$$
$$x = +6$$

The oxidation states for the others are

A: $P = +5$
B: $Q = +5$
C: $R = +6$

27. The standard cell potentials for the redox equilibria of aqueous vanadium-containing ions and the colours of these ions are given below.

$$\underset{\text{yellow}}{VO_2^+} + 2H^+ + e^- \rightleftharpoons H_2O + \underset{\text{blue}}{VO^{2+}} \qquad E^\ominus = +1.00\ V$$

$$\underset{\text{blue}}{VO^{2+}} + 2H^+ + e^- \rightleftharpoons H_2O + \underset{\text{green}}{V^{3+}} \qquad E^\ominus = +0.34\ V$$

$$\underset{\text{green}}{V^{3+}} + e^- \rightleftharpoons \underset{\text{purple}}{V^{2+}} \qquad E^\ominus = -0.26\ V$$

What is likely to be the final colour when metallic tin is added to a solution containing VO^{2+}?

$$\underset{\text{colourless}}{Sn^{2+}} + 2e^- \rightleftharpoons Sn \qquad E^\ominus = -0.14\ V$$

A yellow
B blue
C green
D purple

Helping Concepts *Exam Favourite Rating* ★★★

$$2VO^{2+} + 4H^+ + Sn \rightarrow 2V^{3+} + 2H_2O + Sn^{2+}$$

$E^\ominus_{cell} = +0.48\ V$

$$2V^{3+} + Sn \rightarrow 2V^{2+} + Sn^{2+}$$

$E^\ominus_{cell} = -0.12\ V$

Hence, Sn can only reduce VO^{2+} to V^{3+} and the colour is green.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

28. The table contains data for three elements.
Which of the elements are transition metals?

element	m.p./°C	density/g cm^{-3}
1	1535	7.86
2	660	2.70
3	328	11.34

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A transition metal has a high melting point and a high density.

29. The element with the outer electronic structure $3d^5\ 4s^2$ will be expected to

1 form coloured ions.
2 form complex compounds.
3 have a low melting point.

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*1,*2. It is a transition element with partially filled 3d-subshell. Being a transition element, it forms coloured compounds and complex ions.

3. It has a high melting point since it is a transition metal with strong metallic bonds.

30. Which statements about the ammonia molecule and the ammonium ion are correct?

1 They are a conjugate acid/base pair.
2 They contain the same number of electrons.
3 They can both act as ligands in a complex ion.

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*1. $\underset{\text{base}}{NH_3} + H_2O \rightleftharpoons \underset{\text{conjugate acid}}{NH_4^+} + OH^-$

*2. In NH_3, there are 7(N) + 3 × 1(H) = 10 electrons.
In NH_4^+, there are also 10 electrons (but NH_4^+ has 1 proton more than NH_3).

3. In NH_4^+, there is no lone pair of electrons. It cannot function as a ligand.

31. Compounds containing CN^- are toxic, 50 mg of CN^- being fatal to humans.

Which of the following do **not** contain free CN^- ions?

1 NH_4CN
2 CH_3CN
3 $[Fe(CN)_6]^{4-}$

Helping Concepts | *Exam Favourite Rating* ★★★

1. $NH_4^+CN^-$ is ionic and it contains free CN^-.

*2. In CH_3CN, the nitrile group (CN) is covalently bonded to CH_3. Hence, there is no free CN^-.

*3. In $[Fe(CN)_6]^{4-}$, the CN^- ions act as ligands and are covalently bonded to Fe^{2+} through dative bonding. Hence, there is no free CN^-.

32. *Use of the Data Booklet is relevant to this question.*
Which transition metal atoms, in their ground states, have the same number of unpaired electrons as a sulfur atom in its ground state?

1 titanium
2 nickel
3 cobalt

Helping Concepts | *Exam Favourite Rating* ★★★

S: [Ne] $3s^2\ 2p^4$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

S has 2 unpaired electrons.

*1. Ti: [Ar] $3d^2\ 4s^2$ [↑][↑][ ][ ][ ] [↑↓]

Ti has 2 unpaired electrons.

*2. Ni: [Ar] $3d^8\ 4s^2$ [↑↓][↑↓][↑↓][↑][↑] [↑↓]

Ni has 2 unpaired electrons.

3. Co: [Ar] $3d^7\ 4s^2$ [↑↓][↑↓][↑][↑][↑] [↑↓]

Co has 3 unpaired electrons.

---

33. Which of the following pairs of reagents react together to produce a change in the oxidation numbers of the metal atoms?

1 aqueous potassium manganate(VII) and acidified aqueous iron(II) sulfate

2 aqueous ammonia and an aqueous suspension of silver chloride

3 aqueous ammonia and aqueous copper(II) sulfate

Helping Concepts *Exam Favourite Rating* ★★★

*1. $\underset{+7}{Mn}O_4^- + 5\underset{+2}{Fe}^{2+} + 8H^+ \rightarrow \underset{+2}{Mn}^{2+} + 5\underset{+3}{Fe}^{3+} + 4H_2O$

2. $\underset{+1}{Ag}Cl + 2NH_3 \rightarrow [\underset{+1}{Ag}(NH_3)_2]^+ + Cl^-$

3. $\underset{+2}{Cu}^{2+} + 4NH_3 \rightarrow [\underset{+2}{Cu}(NH_3)_4]^{2+}$

---

34. The hexa-aquairon(III) ion hydrolyses as shown.

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(\ell)$$
$$\rightleftharpoons [Fe(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

Which statements are correct?

1 The corresponding iron(II) ion, $[Fe(H_2O)_6]^{2+}$, is less likely to undergo hydrolysis.

2 The iron undergoes a change in oxidation state.

3 This hydrolysis is favoured by low pH values.

Helping Concepts *Exam Favourite Rating* ★★★

*1. Fe^{2+} has a lower charge density than Fe^{3+} and hence is less polarising. Thus, $[Fe(H_2O)_6]^{2+}$ is less likely to undergo hydrolysis.

2. Iron has an oxidation state of +3 in both $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5OH]^{2+}$.

3. $[H_3O^+]$ is higher at low pH values. By Le Chatelier's principle, the position of equilibrium shifts to the left so that the backward reaction instead of hydrolysis is favoured.

---

35. Which properties of transition elements are not shown by s-block elements such as calcium?

1 They have variable oxidation states.

2 Their ions can act as oxidising agents in aqueous solution.

3 Their ionic radii are less than their atomic radii.

Helping Concepts *Exam Favourite Rating* ★★

*1. Transition elements can use different number of electrons from both 3d and 4s orbitals (which are close in energy level) to form compounds. Hence, they show variable oxidation states. However, s-block elements form invariably +1 (Group I) or +2 (Group II) oxidation state in their compounds.

*2. Transition elements at a higher oxidation state can further gain electrons to form compounds of a lower oxidation state. Hence, they may function as an oxidising agent and undergo reduction. However, due to the fixed oxidation state of the ions of s-block elements, they do not accept electrons readily, unless they encounter (rarely) a very strong reducing agent to reduce the ions to the element.

3. Cations (both transition and s-block elements) are smaller than their respective atoms.

---

36. Scandium, Sc, is the first of the 3d block of elements in the Periodic Table.

Which properties of scandium are consistent with this fact?

1 Scandium has an ionic chloride.

2 Scandium readily forms oxidation states of +4 and +5.

3 Compounds containing the Sc^{3+} ion are always coloured.

Helping Concepts *Exam Favourite Rating* ★★

*1,2. As a d-block element, it readily forms Sc^{3+} ion.

3. Sc^{3+} has a $3d^0$ electronic configuration. Since the 3d subshell is not partially filled, Sc^{3+} does not show d-d transition. Hence, it is colourless.

37. In which of the following chemical reactions is the transition metal compound behaving as a catalyst?

1 the formation of ethanal from ethanol using acidified aqueous potassium dichromate(VI)

2 the formation of oxygen from hydrogen peroxide using iron(III) hydroxide

3 the chlorination of benzene using chlorine and iron(III) chloride

Helping Concepts *Exam Favourite Rating* ★★★

1. Cr is acting as an oxidising species whereby it is reduced from an oxidation state of +6 to +3.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

*2,*3. In both reactions, the oxidation state of Fe does not change at the end of the reactions.

$$2H_2O_2 \xrightarrow{Fe(OH)_3} 2H_2O + O_2\uparrow$$

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl\uparrow$$

38. *Use of the Data Booklet is relevant to this question.*

The exhaust systems of most new cars are fitted with catalytic converters that contain transition metals as catalysts to decrease the emission of atmospheric pollutants. Platinum and palladium are the two most common elements used. They come below nickel in the Periodic Table.

Which properties are nickel, palladium and platinum likely to have in common?

1 variable oxidation states

2 high melting points

3 similar atomic radii

Helping Concepts *Exam Favourite Rating* ★★

*1,*2. Being transition elements, they show variable oxidation states and have high melting points.

3. Since Pt and Pd are below Ni in the Periodic Table, they are expected to have larger atomic radii than Ni.

39. When hydrogen peroxide is added to acidified potassium dichromate(VI), the reaction that occurs is:

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 3O_2 + 7H_2O$$

Which of the following statements are correct for this reaction?

1 The hydrogen peroxide acts as a reducing agent.

2 The colour changes from orange to green.

3 The oxidation number of chromium does not change.

Helping Concepts *Exam Favourite Rating* ★★★

*1. H_2O_2 acts as a reducing agent and is oxidised to O_2:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

*2. $Cr_2O_7^{2-}$ (orange) is reduced to Cr^{3+} (green).

3. The oxidation state of Cr changes from +6 ($Cr_2O_7^{2-}$) to +3 (Cr^{3+}).

40. The conversion of CrO_4^{2-}(aq) into $Cr_2O_7^{2-}$(aq) is represented by the following equation.

$$\underset{\text{yellow}}{2CrO_4^{2-}}(aq) + 2H^+(aq) \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}}(aq) + H_2O(l)$$

Which statements are true of this reaction?

1 CrO_4^{2-}(aq) acts as a base.

2 Addition of OH^-(aq) alkali to $Cr_2O_7^{2-}$ causes a change of colour.

3 The conversion of CrO_4^{2-}(aq) into $Cr_2O_7^{2-}$(aq) involves a change of oxidation state.

Helping Concepts *Exam Favourite Rating* ★★★

*1. CrO_4^{2-} acts as a base in reacting with H^+ to give the 'salt', $Cr_2O_7^{2-}$ and H_2O.

*2. Adding OH^- removes H^+ in the system. According to Le Chatelier's principle, the depletion of H^+ causes the equilibrium to shift to the left, producing more yellow CrO_4^{2-}. Hence, the colour changes from orange to yellow.

3. The oxidation states of Cr in both CrO_4^{2-} and $Cr_2O_7^{2-}$ are +6.

TOPIC 13

Organic Chemistry: Introductory Topics

Key content that you will be examined on:

1. Molecular, structural and empirical formulae
2. Functional groups and the naming of organic compounds
3. Characteristic organic reactions
4. Shapes of organic molecules; σ and π bonds
5. Isomerism: *structural*; *geometrical*; *optical*

Organic Chemistry: Introductory Topics

Topic 13

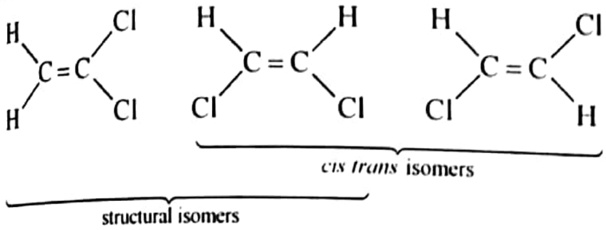
Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. What is the number of isomers of $C_2H_2Cl_2$ including *cis-trans* (geometrical) isomers?

A 1 B 2
C 3 D 4

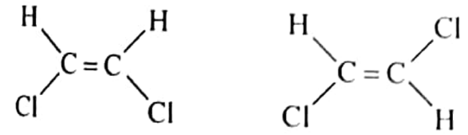
Helping Concepts *Exam Favourite Rating* ★★



2. Which formula could represent a compound which has *cis-trans* isomers?

A $C_2H_6O_2$ B $C_2H_2O_4$
C C_2H_3Cl D $C_2H_2Cl_2$

Helping Concepts *Exam Favourite Rating* ★★



cis *trans*

3. As the number of carbon atoms in the homologous series of alkane molecules **increases**, for which property of the alkanes does the numerical value **decrease**?

A density
B enthalpy change of vaporisation
C number of isomers
D vapour pressure

Helping Concepts *Exam Favourite Rating* ★★

As the number of carbon atoms increases, the molecules become bigger. VDW forces between the molecules become stronger and the molecules become more difficult to escape into the vapour phase. At equilibrium, there will be less amount of gaseous molecules. Hence, vapour pressure becomes lower.

4. How many esters are there with the molecular formula $C_4H_8O_2$?

A 2 B 3
C 4 D 5

Helping Concepts *Exam Favourite Rating* ★★

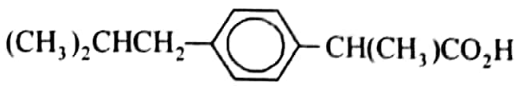
$CH_3-CH_2-\overset{\overset{\large O}{||}}{C}-O-CH_3$

$CH_3-\overset{\overset{\large O}{||}}{C}-O-CH_2-CH_3$

$H-\overset{\overset{\large O}{||}}{C}-O-CH_2CH_2CH_3$

$H-\overset{\overset{\large O}{||}}{C}-O-\underset{\underset{\large CH_3}{|}}{CH}-CH_3$

5. The compound *Ibuprofen* is an important anti-inflammatory drug used in the treatment of arthritis.



Ibuprofen

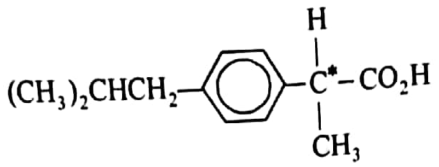
How many optical isomers does *Ibuprofen* have?

A 0 B 2

C 4 D 6

Helping Concepts *Exam Favourite Rating* ★★★

There is one chiral centre in the molecule.



where * : chiral centre

6. What is the smallest number of carbon atoms needed in a molecule containing only carbon, hydrogen and a single oxygen atom for it to be both chiral and a ketone?

A 4 B 5

C 6 D 9

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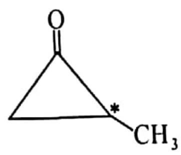
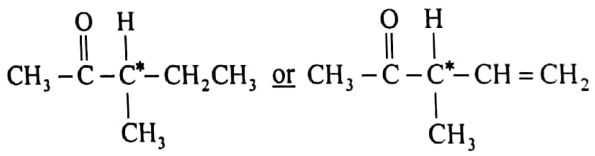


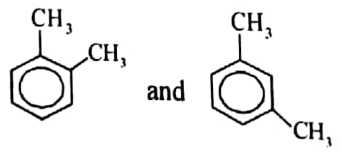
For a chiral aliphatic ketone, the smallest number of carbon atoms needed is 6.

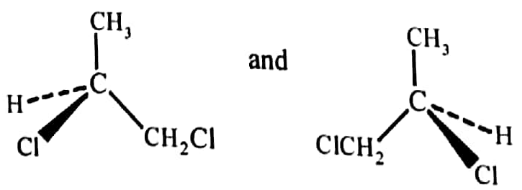


7. Which one of the following pairs do the isomers have identical boiling points?

A $CH_3CH_2CH_2CH_2OH$ and $(CH_3)_2CHCH_2OH$

B $CH_3(CH_2)_4CH_3$ and $(CH_3)_2CHCH(CH_3)_2$

C 

D 

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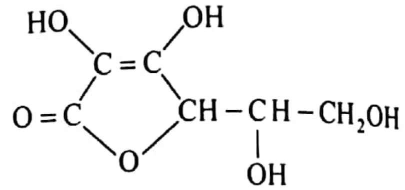
The two compounds in (D) are enantiomers and should therefore exhibit same physical and chemical properties. The only difference is their behaviour towards plane polarised light where the light is rotated in equal but opposite directions by the isomers.

8. The diagram shows the structure of vitamin C.



How many chiral centres are there in one molecule?

A 1 B 2

C 3 D 4

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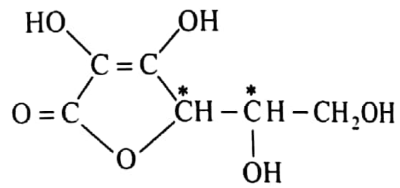
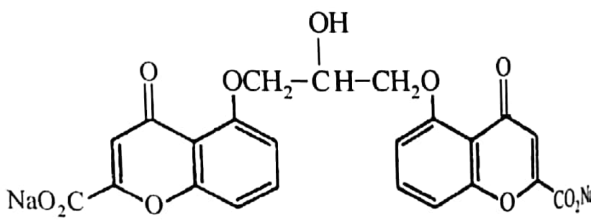


where * : chiral centre

9. The anti-asthma drug *Intal* contains disodium cromoglycate, which has the following structure



How many chiral centres are there in the molecule?

A 0 B 1

C 2 D 3

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There is no chiral centre. The C atom with an -OH group attached to it is achiral. The 2 bulky groups attached to it are equivalent.

10. Which hydrocarbon can form a monochloro-substitution derivative which shows both chirality and *cis-trans* isomerism?

A $CH_3CH{=}CH_2$
B $(CH_3)_2C{=}CH_2$
C $CH_3CH{=}C(CH_3)_2$
D $CH_3CH{=}CHCH_2CH_3$

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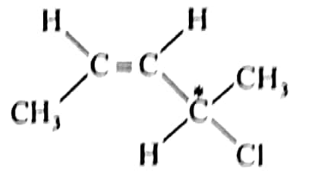
There are many possible monochloro-substitution derivatives of (D). Among these, the following derivative shows both chirality and *cis-trans* isomerism.



11. The compound of molecular formula $CH_3CH(NH_2)CO_2H$ exists in two forms.
What are these forms called?

A isotopes
B *cis-trans* isomers
C optical isomers
D structural isomers

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The two isomers are enantiomers (optical isomers) because they are non-superimposable mirror images of one another. The compound is chiral and it has a chiral centre. The enantiomers rotate plane polarised light in equal but opposite directions.

12. A compound **X** exhibits structural isomerism, the isomers being members of different homologous series.

To which pair of isomers could **X** belong?

A acylchlorides and carboxylic acids
B carboxylic acids and esters
C amino acids and ammonium salts
D amides and amino acids

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Carboxylic acids and esters exhibit structural isomerism, e.g. CH_3COOH and $HCOOCH_3$ are structural isomers.

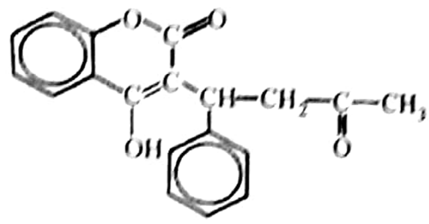
Option A is incorrect since acyl chloride has chlorine but carboxylic acid does not.

Option C is incorrect since anions of ammonium salts are not fixed but include anions such as chloride and sulfate which is absent in amino acids.

Option D is incorrect since amides contain only one O atom while amino acids contain two O atoms.

13. *Warfarin* is used as a rat poison.

Warfarin



How many chiral centres are present in the *Warfarin* molecule?

A 0 B 1
C 2 D 3

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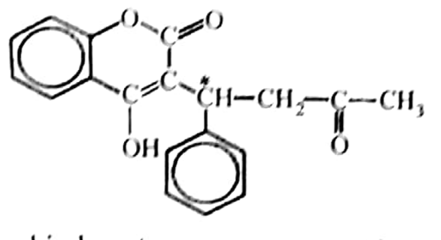

where * : chiral centre

14. *Use of the Data Booklet is relevant to this question.*

The setting agent used in the manufacture of chocolate mousse is an organic acid. It has the following features.

- It is dibasic.
- It is non-cyclic.
- It contains no C=C.
- It has a relative molecular mass of 146.

How many carbon atoms are in one molecule of this organic acid?

A 4 B 5

C 6 D 7

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Dibasic $\Rightarrow 2\times -CO_2H$

Non-cylic and no C=C $\Rightarrow HO_2C-C_nH_{2n}-CO_2H$

$\therefore (n+2)\times 12+(2n+2)\times 1+4\times 16=146$

$n=4$

Hence, there are 6 carbon atoms per molecule.

---

15. Which of the following amino acids contains two chiral carbon atoms?

A H_2NCHCO_2H with side chain $-CH_2-CH_2OH$

B H_2NCHCO_2H with side chain $-CHCH_3-CH_3$

C H_2NCHCO_2H with side chain $-CH_2-C_6H_5$

D H_2NCHCO_2H with side chain $-CHCH_3-CH_2-CH_3$

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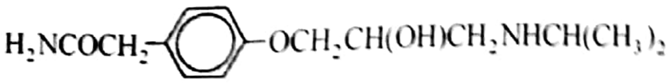
$$H_2N-\overset{H}{\underset{|}{\overset{|}{C^*}}}-CO_2H$$
$$H-\underset{|}{C^*}-CH_3$$
$$CH_2CH_3$$

where * : chiral centre

---

16. Beta-blockers are used for the treatment of angina and blood pressure disorders. One such beta-blocker is *atenolol*.



How many chiral centres are there in one molecule of *atenolol*?

A 0 B 1

C 2 D 3

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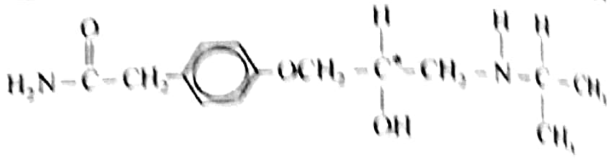

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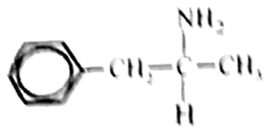
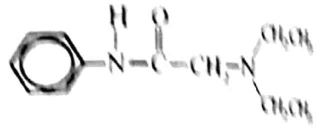
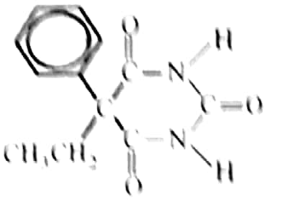
17. Many drugs show optical isomerism. The diagrams show the structure of three drugs.



amphetamine



lidocaine



phenobarbital

What is the total number of chiral carbon centres in these three structures?

A 1 B 2

C 3 D 4

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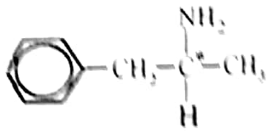

Lidocaine and phenobarbital do not contain chiral centres.

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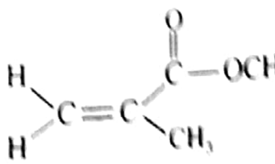
18. One of the chemicals used to make the hard outer covering of golf balls has the following structural formula.



Which of the following statements about this molecule is correct?

A It is a *cis* isomer.

B It is a *trans* isomer.

C It has only one chiral centre.

D It has only structural isomers.

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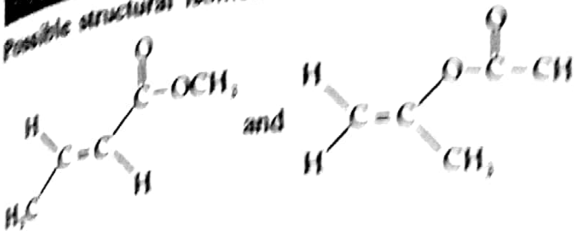
Possible structural isomers include



etc.

The compound is not capable of showing *cis-trans* isomerism and optical isomerism.

---

19. The isomers, citric acid and isocitric acid, are intermediates in the Krebs cycle of the oxidation of glucose in living cells.

citric acid	isocitric acid
CH_2CO_2H	CH_2CO_2H
$C(OH)CO_2H$	$CHCO_2H$
CH_2CO_2H	$CH(OH)CO_2H$

How many chiral centres does each acid possess?

	citric acid	isocitric acid
A	0	1
B	0	2
C	1	1
D	1	2

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In citric acid, the C marked with 'Δ' is not a chiral centre since there are 2 same CH_2CO_2H groups bonded to it.

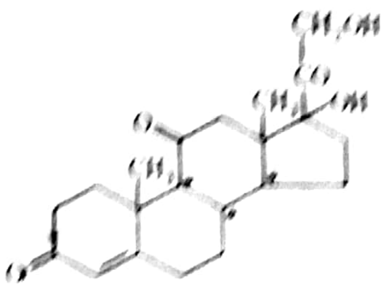
$$\begin{array}{l} CH_2CO_2H \\ | \\ {}^{\Delta}C(OH)CO_2H \\ | \\ CH_2CO_2H \end{array}$$

In isocitric acid, the chiral centres are marked with (*).

$$\begin{array}{l} CH_2CO_2H \\ | \\ {}^{*}CHCO_2H \\ | \\ {}^{*}CH(OH)CO_2H \end{array}$$

---

20. The drug *cortisone* has the formula shown.



In addition to those chiral centres marked by an asterisk (*), how many other chiral centres are present in the *cortisone molecule*?

A 0 **B** 1

C 2 **D** 3

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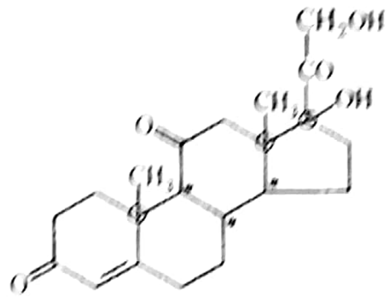
The additional chiral centres are circled.



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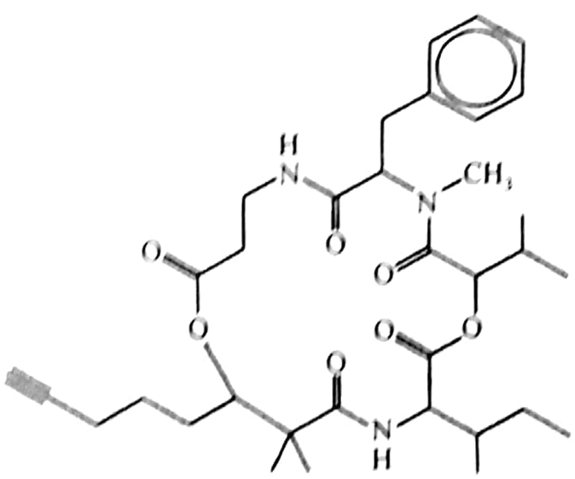
21. Yanucamide B can be extracted from a marine sponge.



yanucamide B

Which combination of the number of chiral centres and of ester linkages does it possess?

	number of chiral centres	number of ester linkages
A	4	2
B	4	3
C	5	2
D	5	3

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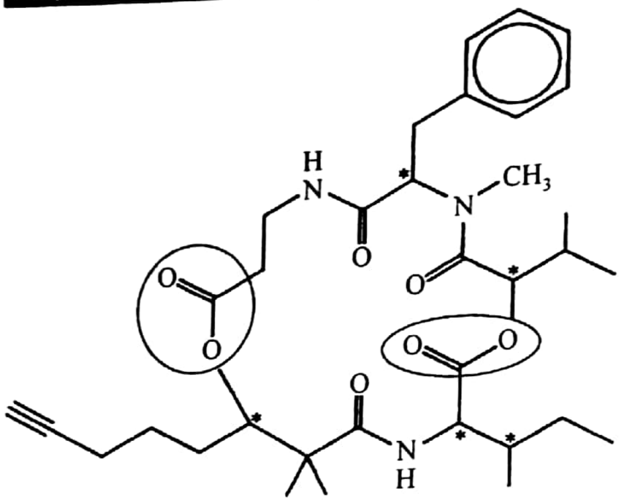

yanucamide B

22. The bond lengths in buta-1,3-diene differ from those which might be expected.

    The carbon-carbon bond length in ethane is 0.154 nm and in ethene 0.134 nm. The central single bond in buta-1,3-diene (C2–C3), however, is shorter than the single bond in ethane: it is 0.147 nm.

$$\overset{1}{CH_2} \overset{0.134\text{ nm}}{=\!=\!=} \overset{2}{CH} \overset{0.147\text{ nm}}{-\!-\!-} \overset{3}{CH} \overset{0.134\text{ nm}}{=\!=\!=} \overset{4}{CH_2}$$

    What helps to explain this C2–C3 bond length?

    A It is an sp^2–sp^2 overlap.

    B It is an sp^2–sp^3 overlap.

    C The electrons in the filled p orbitals on C2 and C3 repel each other.

    D The sp^2–sp^2 bonding is pulled shorter by a p–p (π-bond) overlap.

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The C2–C3 bond is a sp^2–sp^2 σ-bond. The p orbitals in C2 and C3 that are involved in the π bonding with C1 and C4 respectievly, can also have p–p (π) overlap. This gives rise to partial double bond character in C2–C3. Hence, its bond length is shorter than a single bond but longer than a normal C=C double bond.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

23. Solid enantiomers (optical isomers) possess the same

1 infra-red spectrum.

2 melting point.

3 chemical properties.

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Enantiomers share all the same properties (physical and chemical) except that they rotate plane polarised light in equal but opposite directions.

24. What will always be a characteristic of a compound containing a single carbon atom with four different groups bonded to it?

1 It will have an optical isomer.

2 It will have a chiral centre.

3 It will have a structural isomer.

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*1,*2. With 4 different groups bonded to it, the carbon is chiral. And when there is only 1 carbon atom, the compound will be optically active.

25. In what ways could two compounds of molecular formula $C_2H_2Br_2$ be related to each other?

1 structural isomers

2 *cis-trans* isomers

3 optical isomers

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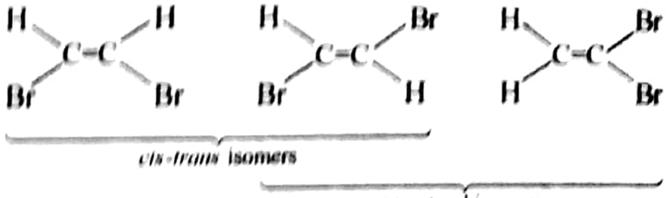
*1,*2.



cis-trans isomers

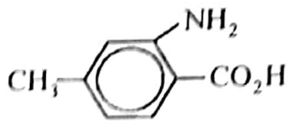
structural isomers

3. There is no chiral centre in the compound. The mirror images of the compounds are superimposable.

26. Which amino acids have optical isomers?

1 $CH_3CH(NH_2)CO_2H$

2 $HSCH_2CH(NH_2)CO_2H$

3 

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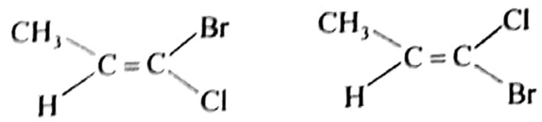
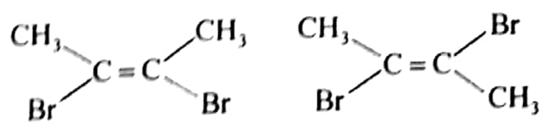
*1. $CH_3\overset{*}{C}H(NH_2)CO_2H$

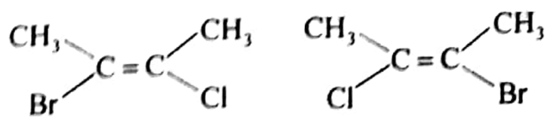
*2. $HSCH_2\overset{*}{C}H(NH_2)CO_2H$

3. There is no chiral centre in this molecule.

27. Which of the following pairs illustrate *cis-trans* isomerism?

1 

2 

3 

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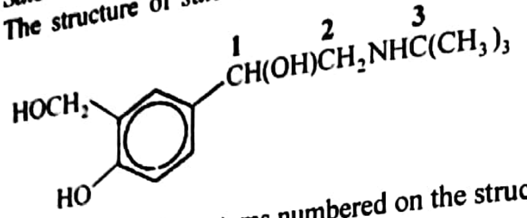
3. The two compounds are exactly the same.

---

28. *Salbutamol* is a widely used anti-asthmatic drug. The structure of *salbutamol* is



Which of the carbon atoms numbered on the structure are chiral?

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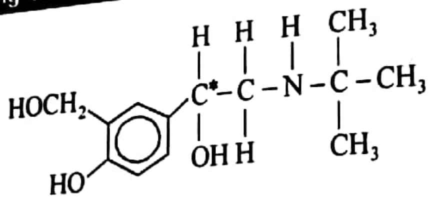

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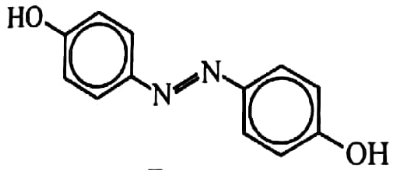
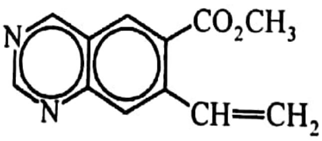
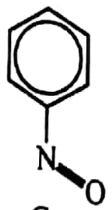
29. The three compounds E, F and G have the following structures.



E



F



G

Which statements about E, F and G are correct?

1 E and G have the same empirical formula.

2 E and F are isomers.

3 The M_r of F is exactly twice that of G.

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*1. The molecular formulae of E, F and G are $C_{12}H_{10}N_2O_2$, $C_{12}H_{10}N_2O_2$ and C_6H_5NO. Hence, they have the same empirical formula C_6H_5NO.

*2. Since E and F have the same molecular formula, they are isomers.

*3. From the molecular formula, it can be seen that the M_r of E and F are double that of G.

---

30. A non-cyclic organic compound has the molecular formula $C_4H_9O_2N$.

Which pair of functional groups could be present in this molecule?

1 one carboxylic acid group and one nitrile group

2 one carboxylic acid group and one amine group

3 one ester group and one amine group

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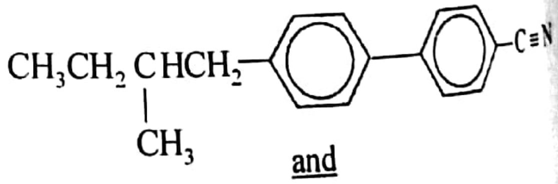
1. $(C_2H_8)(–CO_2H)(–C{\equiv}N)$
It is not possible to form a hydrocarbon chain C_2H_8. It has to be $(C_2H_4)(CO_2H)(C{\equiv}N)$.

*2. $(C_3H_6)(–CO_2H)(–NH_2)$

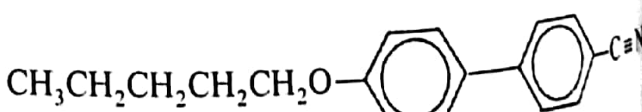
*3. $(C_3H_7)(-\overset{\overset{\displaystyle O}{\|}}{C}-O-)(–NH_2)$

---

31. The following compounds are used in liquid crystal displays in watches and electronic calculators.



and



Which of the following are correct statements about these molecules?

1 Both can exist in optically active forms.

2 Both have permanent dipoles.

3 Neither of them is a linear molecule.

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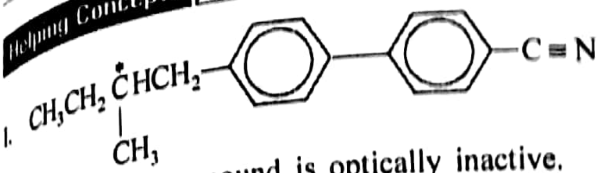
1. 

The second compound is optically inactive.

*2. Both the compounds are unsymmetrical and both contain some electron withdrawing groups (e.g. $-C\equiv N$). They do have permanent dipoles.

*3. Saturated C chains are non-linear. The shape at each carbon of the hydrocarbon chain is tetrahedral.

---

32. Bacteria have been suggested as a possible means of cleaning up oil spillages. Some bacteria contain enzymes that can insert one or more oxygen atoms into any carbon-hydrogen bond in an alkane. This converts a water-insoluble alkane into a water-soluble alcohol,

e.g. $CH_3CH_3 \rightarrow CH_3CH_2OH$.

Which of the following alcohols could be obtained by this process from $(CH_3)_2CHCH_2CH_3$?

1 $(CH_3)_2C(OH)CH(OH)CH_3$

2 $CH_3CH(OH)CH(CH_3)_2$

3 $CH_3CH_2CH(CH_2OH)_2$

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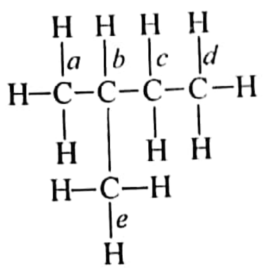

An oxygen may be inserted at *a*, *b*, *c* or/and *d*.

*1. Insertion at *b* and *c*.

*2. Insertion at *c*.

*3. Insertion at *a* and *e*.

TOPIC

14

Hydrocarbons

Key content that you will be examined on:

1. Alkanes (exemplified by ethane)
   (i) Free-radical reactions
2. Alkenes (exemplified by ethene)
   (i) Addition and oxidation reactions
3. Arenes (exemplified by benzene and methylbenzene)
   (i) Influence of delocalised π electrons on structure and properties
   (ii) Substitution reactions with electrophiles
   (iii) Oxidation of side-chain
4. Hydrocarbons as fuels

Topic 14

Hydrocarbons

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which reaction is not an electrophilic addition?

A $CH_2=CH_2 + HI \rightarrow CH_3CH_2I$

B $CH_3CH=CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$

C $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

D $CH_3CH=CH_2 + H_2O \xrightarrow{\text{conc } H_2SO_4} CH_3CH(OH)CH_3$

Helping Concepts *Exam Favourite Rating* ★★★

It is a nucleophilic addition reaction.

---

2. Benzene reacts with chlorine as shown.

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

Which term describes this type of reaction?

A electrophilic substitution

B free-radical substitution

C nucleophilic addition

D nucleophilic substitution

Helping Concepts *Exam Favourite Rating* ★★★

Arenes such as benzene undergo electrophilic substitution reactions.

---

3. A hydrocarbon, which is a liquid at room temperature, decolourises aqueous bromine. What could be the molecular formula of the compound?

A C_2H_2 B C_2H_4

C C_7H_{16} D $C_{10}H_{20}$

Helping Concepts *Exam Favourite Rating* ★★

Since the hydrocarbon decolourises aqueous bromine, it is likely to be unsaturated, i.e. an alkene (C_nH_{2n}). Being a liquid, the VDW forces must be relatively strong and hence the hydrocarbon should have a high relative molecular mass.

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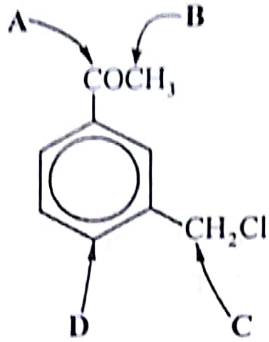
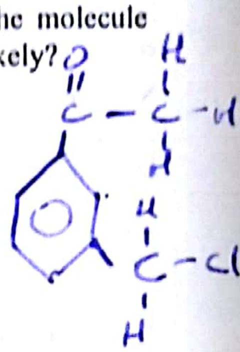
4. At which of the carbon atoms in the molecule below is electrophilic attack most likely?





Helping Concepts *Exam Favourite Rating* ★★★

The carbon atom of the benzene ring suffers electrophilic attack most readily due to the electron density in the ring.

A: nucleophilic addition

B: free radical substitution

C: nucleophilic substitution

~~Substitution~~ may occur at doubb bond ?

---

5. Which one of the following is a propagation step in the reaction between methane and chlorine when they are irradiated with light?

A $H\cdot + Cl_2 \rightarrow HCl + Cl\cdot$

B $CH_4 + Cl^+ \rightarrow CH_3Cl + H^+$

C $CH_4 + Cl^+ \rightarrow CH_3^+ + HCl$

D $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$

Helping Concepts *Exam Favourite Rating* ★★★

A propagation step involves the consumption of a radical and the production of another radical. Out of (A) and (D), (A) is not possible because $H\cdot$ are not present in the system because experimentally, H_2 gas is not detected which would otherwise have been formed if H· were present.

$$2H\cdot \rightarrow H_2 \text{ (termination step)}$$

6. Which substance in a vehicle exhaust results from incomplete combustion of a hydrocarbon fuel?

A CO B H_2O

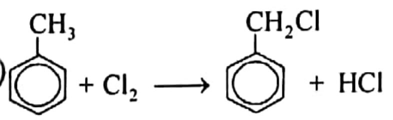
C N_2 D NO

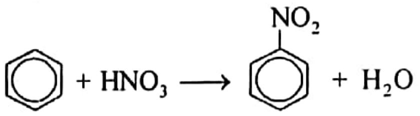
Helping Concepts Exam Favourite Rating ★★★

Incomplete combustion of hydrocarbon fuel will result in the release of C, CO and hydrocarbons.

NO is formed as a result of the combination of N_2 and O_2 at high temperatures, regardless of whether the combustion of the fuel is complete or not.

7. Which of the following represents a substitution reaction which proceeds by a free radical mechanism?

A 

B 

C $CH_3I + NH_3 \rightarrow CH_3\overset{+}{N}H_3I^-$

D $CH_2=CH_2 + HCl \rightarrow C_2H_5Cl$

Helping Concepts Exam Favourite Rating ★★★

Free radical substitution takes place at the methyl group of toluene. Thus, the compound behaves as an alkane when it reacts with Cl_2.

B: electrophilic substitution

C: nucleophilic substitution

D: electrophilic addition

8. *Use of the Data Booklet is relevant to this question.*

Which would be the easiest initiating step in a free-radical process (i.e. the one involving least energy)?

A $HCl \rightarrow H\cdot + Cl\cdot$

B $Cl_2 \rightarrow 2Cl\cdot$

C $CH_4 \rightarrow CH_3\cdot + H\cdot$

D $C_6H_5CH_3 \rightarrow C_6H_5CH_2\cdot + H\cdot$

Helping Concepts Exam Favourite Rating ★★★

The enthalpy change for each reaction corresponds to the bond energy.

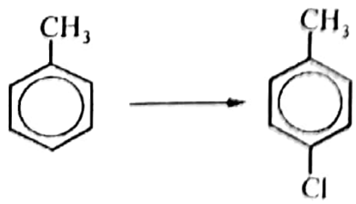
A: +431 kJ mol^{-1} (H–Cl)

B: +244 kJ mol^{-1} (Cl–Cl)

C: +410 kJ mol^{-1} (C–H)

D: +410 kJ mol^{-1} (C–H)

9. Which reagent and conditions are used to bring about the reaction shown?



A Cl_2 in the dark

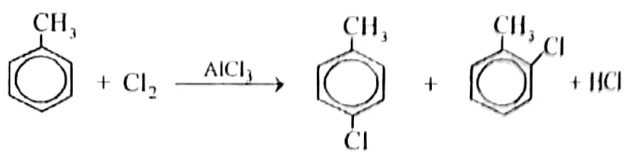
B Cl_2 with $AlCl_3$

C Cl_2 with ultraviolet light

D concentrated HCl heated under reflux

Helping Concepts Exam Favourite Rating ★★★

The reaction is an electrophilic sunstitution.



10. Samples of the gases CH_3Cl and Cl_2 are mixed together and irradiated with light.

Which compound is produced in trace amounts by a termination stage in the chain reaction?

A HCl

B $CH_2=CH_2$

C CH_2ClCH_2Cl

D CH_3CH_3

Helping Concepts *Exam Favourite Rating* ★★★

In one of the propagation steps, $CH_2Cl\cdot$ is generated:

$$CH_3Cl + Cl\cdot \rightarrow CH_2Cl\cdot + HCl$$

It is possible for trace CH_2ClCH_2Cl to be formed as shown by the termination step:

$$2CH_2Cl\cdot \rightarrow CH_2ClCH_2Cl$$

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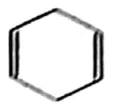
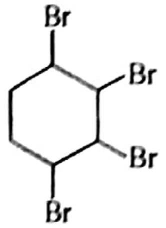
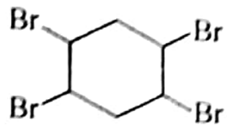
11. Cyclohexa-1,4-diene is treated with a solution of bromine in tetrachloromethane.

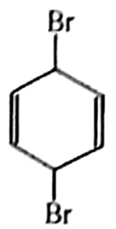


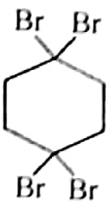
cyclohexa-1,4-diene

Which product is formed?

A 

B 

C 

D 

Helping Concepts *Exam Favourite Rating* ★★★

C=C double bonds undergoes electrophilic addition with bromine to give

```
 |    |
-C  - C-.
 |    |
 Br   Br
```

---

12. Which property of benzene may be directly attributed to the stability associated with its delocalised electrons?

A It has a low boiling point.

B It does not conduct electricity.

C Its enthalpy change of formation is positive.

D It tends to undergo substitution rather than addition reactions.

Helping Concepts *Exam Favourite Rating* ★★

Due to the extra resonance stability of the ring, benzene does not undergo addition in which the ring resonance would be destroyed. Undergoing substitution retains the aromatic system.

---

13. Which of the following is a correct statement about the two alkenes $CH_3CH_2CH{=}CH_2$ and $CH_3CH{=}CHCH_3$?

A Neither exhibits *cis-trans* (geometrical) isomerism.

B Neither may be polymerised.

C Neither reacts with bromine to give 1,4-dibromobutane.

D Neither reacts with hydrogen to form butane.

Helping Concepts *Exam Favourite Rating* ★★★

Upon reacting with Br_2, but-1-ene gives 1,2-dibromobutane and but-2-ene gives 2,3-dibromobutane.

---

14. What happens when one mole of ethane is mixed in the dark at room temperature with six moles of chlorine?

A There is no reaction.

B CH_3CH_2Cl and HCl are formed.

C CH_3CCl_3 and HCl are formed.

D CCl_3CCl_3 and HCl are formed.

Helping Concepts *Exam Favourite Rating* ★★

To undergo free-radical substitution, uv radiation or heating is required to initiate the reaction ($Cl_2 \rightarrow 2Cl\cdot$). Since the experiment is performed in the dark without heating (room temperature), there is no reaction.

---

15. A compound **V** is added to a solution of bromine in tetrachloromethane and the colour of the bromine is immediately discharged. Which one of the following could be compound **V**?

A benzene

B cyclohexane

C methylbenzene

D pentene

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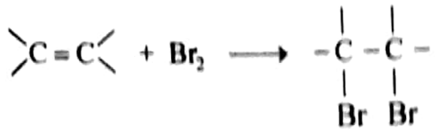
Decolourisation of Br_2 indicates the presence of an alkene (or a phenol).



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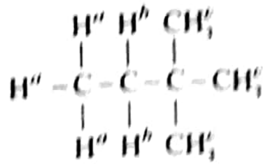
There are 3 different types of H atom that the Cl• can bond with.



16. What is the correct set of conditions for the conversion of benzene into nitrobenzene?

	acid	temperature
A	dilute HNO_3	100 °C
B	concentrated HNO_3	0 °C
C	concentrated HNO_3 and concentrated H_2SO_4	10 °C
D	concentrated HNO_3 and concentrated H_2SO_4	120 °C

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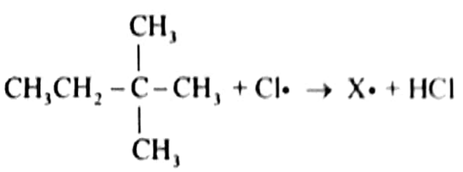
Both concentrated nitric acid and sulfuric acid needed to be used to generate the electrophilic NO_2^+. The usual temperature for nitration of benzene is about 50 °C, but this was not given as a choice.

(D) is incorrect since the boiling point of benzene is 80 °C so that at the high temperature of 120 °C, benzene would have boiled off. Also the high temperature may also cause more than one NO_2 to be substituted. Hence, (C) is selected as the answer.

17. When heated with chlorine, the hydrocarbon 2,2-dimethylbutane undergoes free radical substitution. In a propagation step, the free radical X• is formed by the loss of one hydrogen atom.



How many different forms of X• are theoretically possible?

A 1　　B 2

C 3　　D 4

18. When benzene is nitrated, concentrated nitric and sulfuric acids react to form an intermediate which attacks the benzene ring. Which one of the following represents this intermediate?

A NO^+　　B NO_2

C NO_2^-　　D NO_2^+

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The nitrating species is NO_2^+.

$$H_2SO_4 + HONO_2 \rightleftharpoons HSO_4^- + H_2ONO_2^+$$

$$H_2ONO_2^+ + H_2SO_4 \rightleftharpoons H_3O^+ + NO_2^+ + HSO_4^-$$

19. How many chiral compounds is it possible to prepare by subjecting ethane to repeated substitution by chlorine?

A 0　　B 1

C 2　　D 3

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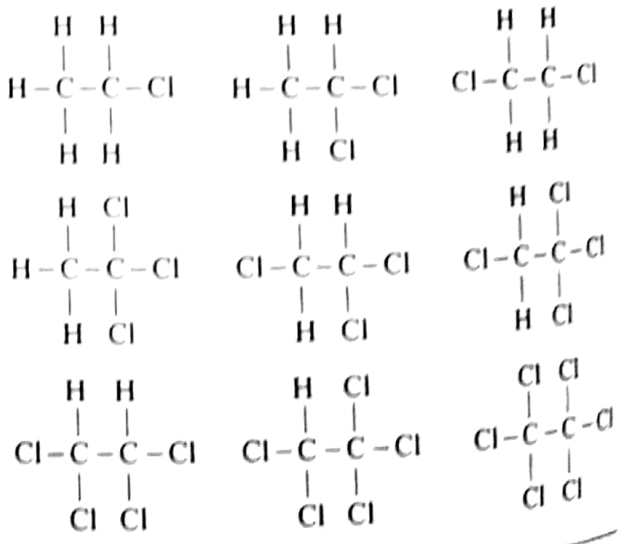
There are always at least 2 H or 2 Cl atoms attached to the same C atoms in all the products. The atoms are therefore never chiral. The possible products are:



20. Which is a correct statement about the intermediate complex, $[C_6H_6NO_2]^+$, formed during the mononitration of benzene?

A It is planar.
B It contains a chiral centre.
C It can exist in either a cis or a *trans* form.
D It contains only one tetrahedrally-bonded carbon atom.

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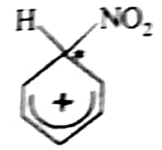

The carbon marked '•' is tetrahedral (i.e. not planar), and is not chiral.

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21. Nitrobenzene may be prepared by reacting benzene with a mixture of concentrated sulfuric and nitric acids.

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

Which of the following best explains the role of the sulfuric acid?

A removing the water produced
B forming an unstable complex with benzene
C protonating nitric acid
D acting as a solvent

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Concentrated H_2SO_4 acts as an acid and protonates the base, HNO_3.

$$\underset{conc}{H_2SO_4} + \underset{conc}{HNO_3} \rightleftharpoons HSO_4^- + H_2NO_3^+$$

$$H_2NO_3^+ \text{ (or } H_2ONO_2^+) + \underset{conc.}{H_2SO_4}$$

$$\rightleftharpoons H_3O^+ + NO_2^+ + HSO_4^-$$

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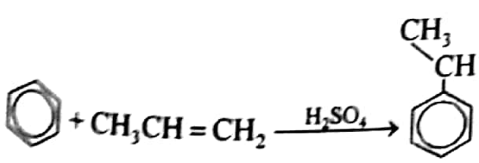
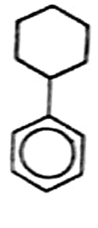
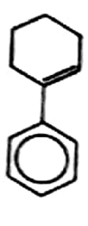
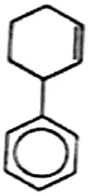
22. The first stage of the cumene process for the industrial production of phenol is as follows.

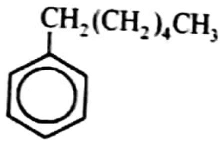


Which one of the following would be the product of the reaction, under similar conditions, between benzene and cyclohexene?

A


B


C


D


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The end result is that the C atom at the double bond is bonded directly to the benzene ring and the double bond itself is removed.

---

23. Which of the following reagents could best be used to distinguish between hex-1-ene and methylbenzene?

A $Ag(NH_3)_2^+$ in H_2O
B Br_2 in CCl_4
C I_2 in NaOH(aq)
D 2,4-dinitrophenylhydrazine in CH_3OH

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Being an alkene, hex-1-ene undergoes electrophilic addition readily with Br_2 in CCl_4 and decolourises it. Methylbenzene is unable to do so.

$$CH_3(CH_2)_3CH{=}CH_2 + Br_2 \rightarrow CH_3(CH_2)_3\underset{\displaystyle Br}{\underset{|}{C}}H-\underset{\displaystyle Br}{\underset{|}{C}}H_2$$

---

24. When bromine reacts with propene in an organic solvent at room temperature, what is the mechanism by which the bromine attacks the propene?

A electrophilic addition
B electrophilic substitution
C nucleophilic addition
D nucleophilic substitution

Topic 14 Hydrocarbons

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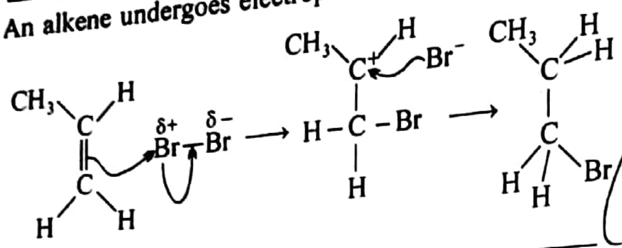
An alkene undergoes electrophilic addition with Br_2.



25. A sample of 1,2-dimethylbenzene is quantitatively oxidised to the corresponding dicarboxylic acid.

What is the mass of product formed from 1.00 g of 1,2-dimethylbenzene?

A 1.15 g **B** 1.28 g

C 1.57 g **D** 1.60 g

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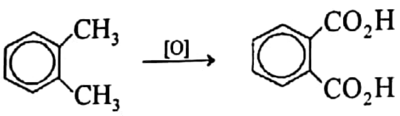
The phrase 'quantitatively oxidised' refers to 100% conversion.



M_r of 1,2-dimethylbenzene, $C_8H_{10} = (8\times12)+(10\times1) = 106$

M_r of acid, $C_8H_6O_4 = (8\times12)+(6\times1)+(4\times16) = 166$

106 g of 1,2-dimethylbenzene gives 166 g of acid.

1 g of 1,2-dimethylbenzene gives $\frac{166}{106}\times1 = 1.57$ g of acid.

26. Tetramethyl-lead(IV) increases the rate of the reaction of methane with chlorine.

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Why can tetramethyl-lead(IV) behave in this way?

A It is a source of methyl radicals.

B It releases $CH_3^+(g)$.

C It reacts with chloromethane and prevents equilibrium being established.

D Metal ions catalyse the reaction.

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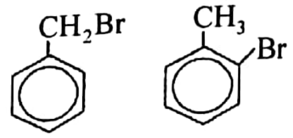
The Pb–C bond in $Pb(CH_3)_4$ is weak so that the radical, $CH_3\cdot$, is formed. Since methane reacts with chlorine via a free radical substitution mechanism, the presence of $CH_3\cdot$ would increase the rate of reaction greatly.

$$Pb(CH_3)_4 \xrightarrow{\text{heat}} Pb + 4CH_3\cdot$$

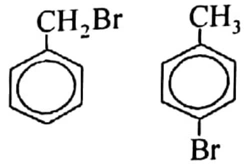
27. When methylbenzene is treated with bromine in the presence of a catalyst, a mixture of two monobromo isomers is formed.

What are the structure of these two isomers?

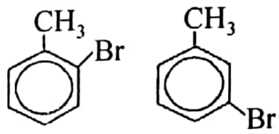
A



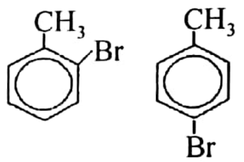
B



C



D



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–CH_3 group is 2,4-directing (or ortho- and para- directing). In the presence of a suitable catalyst (e.g. $FeBr_3$), electrophilic substitution occurs at C-2 and C-4.

28. Which hydrocarbon, on treatment with hot acidified potassium manganate(VII), would give ethanoic acid only?

A $CH_3CH{=}CH_2$

B $CH_3CH{=}CHCH_3$

C $(CH_3)_2C{=}CHCH_3$

D $(CH_3)_2C{=}C(CH_3)_2$

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A: $CH_3CH=CH_2 + 5[O] \rightarrow CH_3CO_2H + CO_2 + H_2O$

B: $CH_3CH=CHCH_3 + 4[O] \rightarrow 2CH_3CO_2H$

C: $(CH_3)_2C=CHCH_3 + 3[O] \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3CO_2H$

D: $(CH_3)_2C=C(CH_3)_2 + 2[O] \rightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

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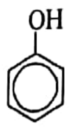
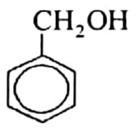
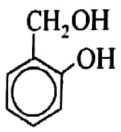
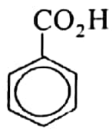
29. Which one of the following formulae represents the organic compound formed when methylbenzene is heated under reflux with alkaline potassium manganate(VII) solution and the mixture then acidified?

A 

B 

C 

D 

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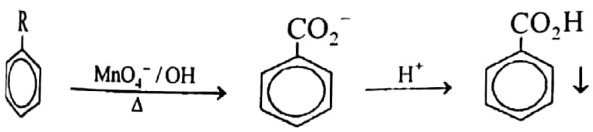

Alkybenzenes are readily oxidised by hot alkaline potassium manganate(VII) to yield benzoate ions. Acidification gives the benzoic acid as white precipitate.

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30. Two structural isomers of molecular formula C_6H_{14} are shown.

P $(CH_3)_2CHCH_2CH_2CH_3$

Q $CH_3CH_2CH(CH_3)CH_2CH_3$

P and Q react with chlorine to form monochloro compounds $C_6H_{13}Cl$.

How many possible **structural** isomers, each with formula $C_6H_{13}Cl$, could be produced by P and by Q?

	isomers formed by P	isomers formed by Q
A	5	3
B	5	4
C	6	3
D	6	4

Easy trick to so no. of isom

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P:
$$\overset{a}{C}H_3-\overset{b}{C}H(\overset{a}{C}H_3)-\overset{c}{C}H_2-\overset{d}{C}H_2-\overset{e}{C}H_3$$

Thre are 5 different carbon atoms in P.

Q:
$$\overset{a}{C}H_3-\overset{b}{C}H_2-\overset{c}{C}H(\underset{d}{C}H_3)-\overset{b}{C}H_2-\overset{a}{C}H_3$$

There are 4 different carbon atoms in Q.

MP

31. The compound hex-3-en-1-ol, **P**, has a strong 'leafy' smell of newly cut grass and is used in perfumery.

$$\underset{\textbf{P}}{CH_3CH_2CH=CHCH_2CH_2OH}$$

What is produced when P is treated with an excess of hot concentrated acidic $KMnO_4$?

A $CH_3CH_2CH(OH)CH(OH)CH_2CH_2OH$

B $CH_3CH_2CH=CHCH_2CO_2H$

C CH_3CH_2CHO and $OCHCH_2CH_2OH$

D $CH_3CH_2CO_2H$ and $HO_2CCH_2CO_2H$

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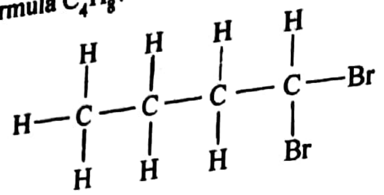
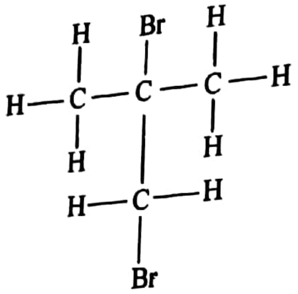
Oxidation at the C=C double bond and the 1° alcohol takes place.

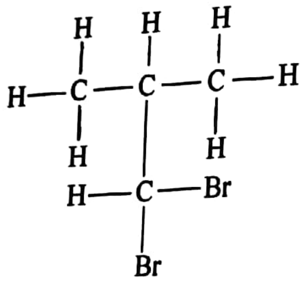
$$-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}- + 4[O] \rightarrow -\overset{OH}{\overset{|}{C}}=O + O=\overset{OH}{\overset{|}{C}}-$$

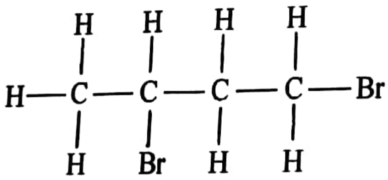
$$-\underset{|}{\overset{H}{\overset{|}{C}}}-OH + 2[O] \rightarrow -\overset{O}{\overset{\|}{C}}-OH + H_2O$$

32. Which of the following compounds could be formed by the action of bromine on an alkene of formula C_4H_8?

A 

B 

C 

D 

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An alkene undergoes electrophilic addition at the double bond with Br_2. The result is that a Br atom is each added to the adjacent carbon atoms of the double bond.

$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}=CH_2 + Br_2 \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}}(Br)-CH_2Br$$

(B)

33. Hydrogen iodide undergoes an addition reaction with propene forming 2-iodopropane. When propene is bubbled through iodine monochloride, ICl, dissolved in a suitable solvent, a similar reaction occurs.

Which product will be present in the greatest yield?

A $CH_3CH(Cl)CH_2Cl$

B $CH_3CH(I)CH_2I$

C $CH_3CH(Cl)CH_2I$

D $CH_3CH(I)CH_2Cl$

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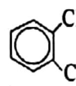
From the reaction between HI and CH_3–CH=CH_2, it shows that the H (which is $\delta+$) in H–I is bonded to the terminal C.

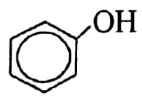
$$CH_3-CH{=}CH_2 + {}^{\delta+}H-I^{\delta-} \rightarrow CH_3-CH(I)-CH_3$$

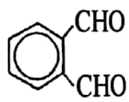
When CH_3–CH=CH_2 reacts with ICl, similarly, the I (which is $\delta+$) will be bonded to the terminal C.

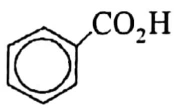
$$CH_3-CH{=}CH_2 + {}^{\delta+}I-Cl^{\delta-} \rightarrow CH_3-CH(I)-CH_2I$$

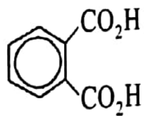
34. The aromatic compound  was made to react with an excess of hot aqueous alkaline potassium manganate(VII) and the product was treated with an excess of aqueous acid.

What is the most likely final product?

A 

B 

C 

D 

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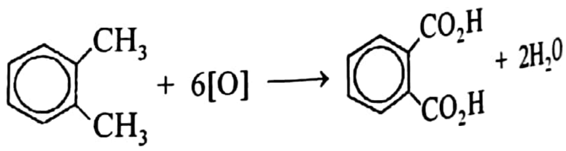
Alkylbenzenes are oxidised to the carboxylic acid at the side chain.



35. Aluminium chloride catalyses certain reactions by forming carbocations (carbonium ions) with chloroalkanes as shown in the following equation.

$$RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$$

This can occur because

A $AlCl_3$ is a covalent molecule.

B $AlCl_3$ exists as the dimer Al_2Cl_6 in the vapour.

C the aluminium atom in $AlCl_3$ has an incomplete octet of electrons.

D the chlorine atom in RCl has a vacant p orbital.

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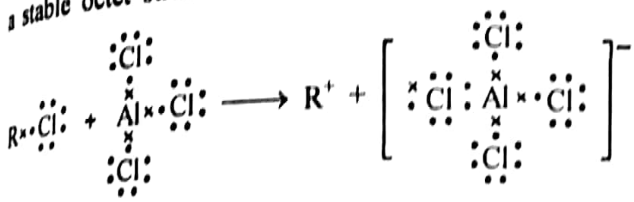
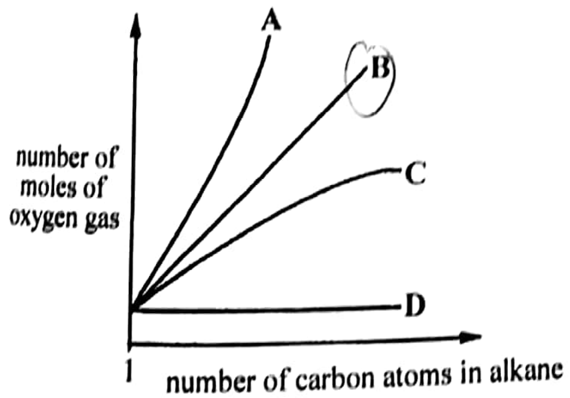
The Al atom has a sextet electronic configuration, 2 electrons short of an octet structure. This gives Al the ability to attract a pair of electrons from Cl to form a stable octet structure.



36. The complete combustion of alkanes to produce carbon dioxide and water is an important exothermic reaction.

Which line on the graph shows the relationship between the number of carbon atoms in the alkane and the number of moles of oxygen gas needed for complete combustion of the alkane?



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$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + (n+1)H_2O$$

Hence, the plot of graph should be a straight line graph with a positive slope of 3/2, and a y-intercept at 1/2.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

37. Which substances consist of planar molecules?

1 benzene
2 ethene
3 cyclohexene

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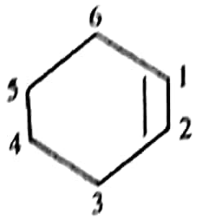
3.



The molecule is planar at C–1 and C–2. However, it is tetrahedral is C–3, C–4, C–5 and C–6.

38. Which pairs of compounds have the same empirical formula?

1 ethane and ethene
2 ethene and cyclohexane
3 cyclohexane and oct-1-ene

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The molecular formulae are

1. C_2H_6, $(CH_2)_2$
*2. $(CH_2)_2$, $(CH_2)_6$
*3. $(CH_2)_6$, $(CH_2)_8$

39. Which of the following are pollutants if released into the atmosphere?

1 nitrogen dioxide
2 sulfur dioxide
3 aerosol particles containing lead(II) oxide

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*1. NO_2 is formed as a result of the reaction between atmospheric N_2 and O_2 at high temperature.

*2. SO_2 is emitted when the petrol used is not desulfurised.

*3. PbO is emitted as a result of adding tetraethyl lead into petrol as an additive.

40. Which of the following molecules would be present in the photochemical chlorination of methane?

1 hydrogen
2 hydrogen chloride
3 dichloromethane

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1. $H\cdot$ radicals are never formed. Hence, H_2 cannot be found.

*2,*3. $Cl\cdot + CH_4 \rightarrow CH_3\cdot + \underline{HCl}$

$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$

$Cl\cdot + CH_3Cl \rightarrow CH_2Cl\cdot + \underline{HCl}$

$CH_2Cl\cdot + Cl_2 \rightarrow \underline{CH_2Cl_2} + Cl\cdot$ etc.

41. Which compounds can be obtained from ethene in a single reaction?

1 CH_3CH_3
2 $-\!\!(CH_2CH_2)\!\!-_n$
3 $HOCH_2CH_2OH$

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*1. $CH_2=CH_2 + H_2 \xrightarrow{Pt} CH_3CH_3$

*2. $nCH_2=CH_2 \rightarrow -\!\!(CH_2-CH_2)\!\!-_n$
Ethene undergoes addition polymerisation.

*3. $CH_2=CH_2 + [O] + H_2O \rightarrow \underset{OH}{CH_2}-\underset{OH}{CH_2}$

Ethene reacts with cold dilute alkaline $KMnO_4$ to give ethane-1,2-diol.

42. A catalytic converter is part of the exhaust system of modern cars.

Which reactions occur in a catalytic converter?

1 $2C_xH_y + (4x + y)NO \rightarrow 2xCO_2 + yH_2O + (2x + \frac{y}{2})N_2$

2 $2CO + 2NO \rightarrow 2CO_2 + N_2$

3 $CO_2 + NO \rightarrow CO + NO_2$

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A catalytic converter helps to convert unburnt hydrocarbon, carbon and carbon monoxide to carbon dioxide, and oxides of nitrogen to nitrogen gas.

MA

43. Which of the following statements suggests the presence of free radicals in the chlorination of methane?

1 Hydrogen chloride is present in the product.

2 The reaction proceeds most quickly in sunlight or ultraviolet light.

3 Ethane is present in small quantities in the product.

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1. The formation of HCl only suggests that the reaction is a substitution.

*2. $Cl_2 \xrightarrow{uv} 2Cl\cdot$ (initiation)

The presence of sunlight or uv light is a strong indication of a free radical reaction. The electromagnetic wave of a right frequency is used to cleave a particular bond to form radicals.

*3. $\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3CH_3$ (termination)

44. Bromine in an inert solvent is added separately to hexane, hexene, benzene and methylbenzene. In which of the following pairs will the observations be the same?

1 hexane and benzene

2 hexane and hexene

3 hexene and methylbenzene

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Br_2 does not react with hexane, benzene and methylbenzene. Addition of Br_2 to these solvents will colour them orange-brown. However, Br_2 undergoes electrophilic addition with hexene and the orange-brown colour of Br_2 will be discharged.

$$>C=C< + Br_2 \longrightarrow -\underset{Br}{\underset{|}{\overset{|}{C}}}-\underset{Br}{\underset{|}{\overset{|}{C}}}-$$

45. Which of the following hydrocarbons undergo substitution reactions to form only one monochloro-derivative?

1 cyclobutane

2 2,2-dimethylpropane $H_3C-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

3 2-methylpropane

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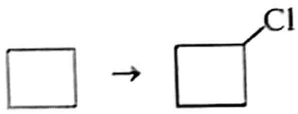
Symmetrical hydrocarbons form only 1 mono-chlorinated derivative.

*1. 

*2.
$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \rightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2Cl$$

3.
$$CH_3-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \rightarrow CH_3-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2Cl$$

and $CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

46. 2-methylbuta-1,3-diene can be polymerised to make synthetic rubbers. The structure of this monomer is shown below.

$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2$$

Which of the following statements about 2-methylbuta-1,3-diene are correct?

1 It decolourises aqueous bromine.

2 It is chiral (optically active).

3 It undergoes nucleophilic addition reactions.

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*1. Being an alkene, it readily undergoes electrophilic addition with aqueous Br_2.

$$CH_2=C(CH_3)-CH=CH_2 + 2Br_2 + 2H_2O \longrightarrow CH_2(Br)-C(CH_3)(OH)-CH(OH)-CH_2(Br) + 2Br^- + 2H^+$$

2. There is no chiral centre.

3. It does not undergo nucleophilic addition (but rather, it undergoes electrophilic addition).

47. Which statements about the complete combustion of an alkene, C_nH_{2n}, in oxygen are correct?

1 The volume of oxygen required is directly proportional to the number of carbon atoms present in the molecule.

2 The volume of gas produced at 25 °C is the same as for the complete combustion of an alkane with the same number of carbon atoms per molecule.

3 At 120 °C, the volume of steam produced is always twice the volume of carbon dioxide.

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$$C_nH_{2n} + \frac{3n}{2}O_2 \rightarrow nCO_2 + nH_2O$$

*1. The amount of O_2 (and hence its volume) is directly proportional to the number of carbon. If there are 5 carbon, the amount of O_2 required would be $5\times\frac{3}{2}=7.5$ mol.

*2. At 25 °C, CO_2 is the only gaseous product. Any hydrocarbon (C_nH_m) will always produce n moles of CO_2.

3. The volumes of CO_2 and H_2O at 120 °C are the same.

48. Long-chain alkanes are converted on an industrial scale into alky sulfates for use as detergents, e.g. sodium lauryl sulfate.

$$CH_3(CH_2)_{10}CH_2O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-ONa$$

sodium lauryl sulfate

Which of the following are properties of this substance?

1 It possesses both a water-attracting and a water-repelling part.

2 All the C–C–C bond angles are tetrahedral.

3 The alkyl chain is soluble in oil droplets.

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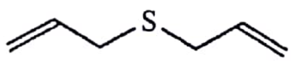
*1. The compound, $RSO_4^-Na^+$ has a long alkyl chain which is H_2O repelling and an anionic site which is H_2O attracting.

*2. All the C atoms are sp^3 hybridised and are singly bonded to four other atoms. Therefore, all the C–C–C bonds are tetrahedral.

*3. Being non-polar, the alkyl chain is soluble in organic oil droplets which are themselves non-polar.

49. *Use of the Data Booklet is relevant to this question.*

Diallyl sulfide ($M_r = 114$) can be isolated from garlic.



diallyl sulfide

Which statements about diallyl sulfide are correct?

1 On complete combustion, 0.10 g of diallyl sulfide produces 0.23 g of CO_2.

2 On complete combustion, 0.10 g of diallyl produces 21 cm^3 of SO_2 measured under room conditions.

3 0.10 g of diallyl sulfide reacts with excess bromine to produce 0.380 g of product.

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In 0.10 g, $n = \frac{0.10}{114} = 8.772\times10^{-4}$ mol.

In each diallyl sulfide molecule, there are 6 C, 1 S and 2 double bonds.

*1. $n_{CO_2} = 6 \times n$

$m_{CO_2} = 6n \times 44 = 0.23$ g

*2. $n_{SO_2} = n$

$V_{SO_2} = n \times 24\ dm^3 = 0.021\ dm^3 = 21\ cm^3$

*3. Each diallyl sulfide molecule undergoes electrophilic addition with 2 Br_2 to form the addition product.

M_r of the product $= 114 + 4(79.9)$
$= 433.6$

Hence, mass of product $= n \times 433.6$
$= 0.380$ g

50. Which compounds would be formed in the reaction of ethene with aqueous bromine in the presence of sodium chloride?

1 CH_2ClCH_2Cl
2 CH_2BrCH_2Cl
3 CH_2BrCH_2Br

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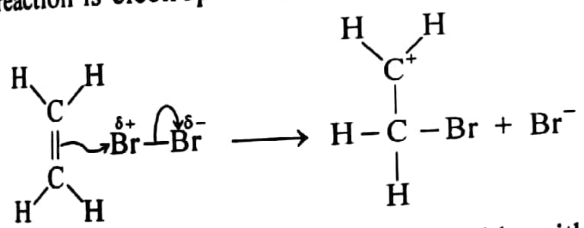
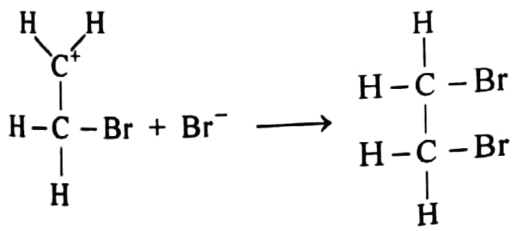
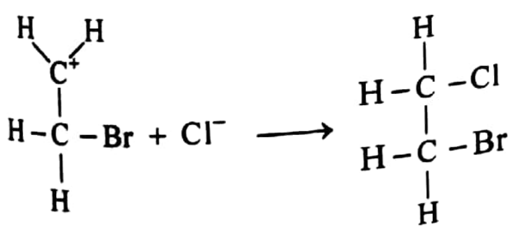
The reaction is electrophilic addition.

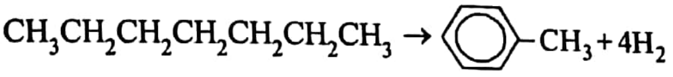


The bromonium ion formed is then attacked by either Br^- or Cl^- (from NaCl) and even H_2O.

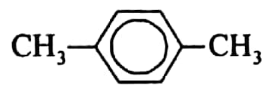




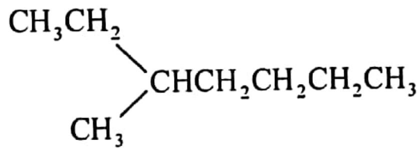
51. In an industrial process, heptane vapour is passed over a heated catalyst to make methylbenzene.

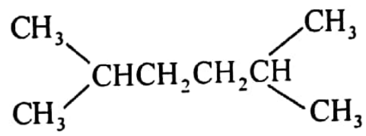


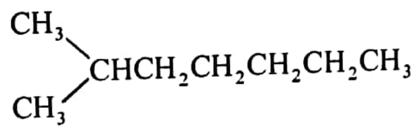
Using similar conditions, which of the C_8H_{18} isomers could give 1,4-dimethylbenzene?



1,4-dimethylbenzene

1 

2 

3 

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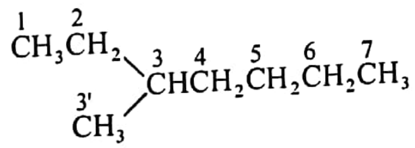
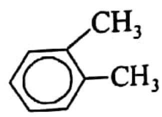
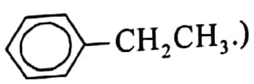
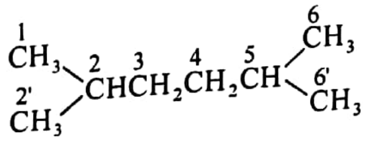
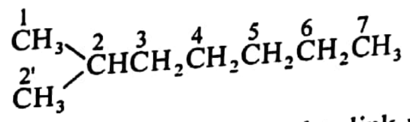
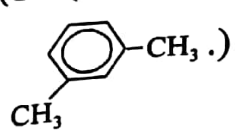
From the reaction, it can be seen that C-1 and C-6 are linked up to form the benzene ring system.

*1. 

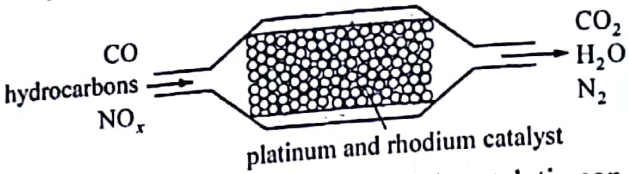
(C-2 and C-7 can also link up to form  and C-3' and C-7 can also link up to form .)

*2. 

3. 

(C-1 (or C-2') and C-6 can also link up to form .)

52. The diagram represents a section of a catalytic converter on the exhaust system of a car. Harmful gases are converted into carbon dioxide, nitrogen and water vapour.



Which processes take place in this catalytic converter?

1 Carbon monoxide and hydrocarbons react together.

2 Carbon monoxide and nitrogen oxide react together.

3 Platinum and rhodium catalyse redox reactions.

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$$2x(CO) + 2NO_x \rightarrow 2x(CO_2) + N_2$$

1,*2. Nitrogen oxides oxidises CO to CO_2 while itself is reduced to N_2.

*3. Pt and Rh are the active ingredients in the catalytic converter that help to catalyse the above redox reaction.

---

53. The sex-attractant of the house-fly is muscalure, the formula of which is given below.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_{12}CH_3$$

Which of the following statements about muscalure are correct?

1 It will decolourise bromine water.

2 It will be oxidised by cold aqueous alkaline $KMnO_4$ to give a diol.

3 It will be optically active.

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*1. Being an alkene, it undergoes electrophilic addition with aqueous bromine and hence decolourises it.

$$>C=C< + Br_2 + H_2O \rightarrow \begin{array}{c} | \quad | \\ -C-C- \\ | \quad | \\ Br \;\; OH \end{array} + Br^- + H^+$$

*2. As an alkene, it is oxidised by cold aqueous alkaline $KMnO_4$ to give a diol.

$$>C=C< + H_2O + [O] \rightarrow \begin{array}{c} | \quad | \\ -C-C- \\ | \quad | \\ OH \;\; OH \end{array}$$

MnO_4^- is reduced to MnO_2. The MnO_4^- is decolourised and a brown precipitate is formed.

3. There is no chiral centre in the compound and it is therefore achiral. Its mirror images are superimposable and hence it is optically inactive.

TOPIC 15

Halogen Derivatives

Key content that you will be examined on:

1. Halogenoalkanes and halogenoarenes
   (i) Nucleophilic substitution
   (ii) Elimination
2. Relative strength of the C–Hal bond

Halogen Derivatives

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which of these always applies to a nucleophile?

   A It attacks a double bond.
   B It has a lone pair of electrons.
   C It is a single atom.
   D It is negatively charged.

Helping Concepts *Exam Favourite Rating* ★

A nucleophile is one that is nucleus loving. It is electron rich and possesses at least a lone pair of electrons. It can be neutral or negatively charged.

2. Which of the following compounds could be prepared by reacting bromoethane with potassium cyanide and then reducing the product?

   A CH_3CH_3
   B $CH_3CH_2NH_2$
   C $CH_3CH_2CH_3$
   D $CH_3CH_2CH_2NH_2$

Helping Concepts *Exam Favourite Rating* ★★★

$$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$$
$$CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$$

3. Dichlorodifluoromethane, CCl_2F_2, is widely used in aerosol propellants and as a refrigerant.

   Which statement helps to explain why dichlorodifluoromethane is chemically inert?

   A The carbon-fluorine bond energy is large.
   B The carbon-fluorine bond has a low polarity.
   C Fluorine is highly electronegative.
   D Fluorine compounds are non-flammable.

Helping Concepts *Exam Favourite Rating* ★★

C–F bonds are very strong. A lot of energy is required to break the bonds and this is not favourable. Hence, CCl_2F_2 is chemically inert.

4. Which of the following reactions is the inorganic reagent acting as a nucleophile?

   A $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$
   B $CH_3CH=CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$
   C $CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3Cl^-$
   D $CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$

Helping Concepts *Exam Favourite Rating* ★★

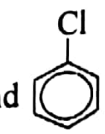
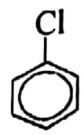
$$CH_3\overset{\delta+}{C}H_2-\overset{\delta-}{Br} + OH^- \longrightarrow Br^- + CH_3CH_2OH$$

OH^- is electron-rich and it acts as a nucleophile. It attacks the electron deficient carbon of C–Br.

B: Br_2 - electrophile (electrophilic addition)

C: HCl - acid (acid-base reaction)

5. Which pair of chlorine compounds are both unaffected by boiling aqueous sodium hydroxide?

   A $CHCl_3$ and $CH_3CHClCH_3$
   B CH_3Cl and $CH_3CHClCH_3$
   C CH_3Cl and 
   D CCl_4 and 

Helping Concepts *Exam Favourite Rating* ★★★

CCl_4 is not hydrolysed by OH^- or H_2O because C does not have any low lying vacant d-orbitals to be attacked by the nucleophile. On the other hand, the C–Cl bond in chlorobenzene is unusually strong due to the overlap between the p-orbital of Cl and π-orbitals of benzene. It is not hydrolysed by OH^-.

---

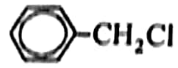
6. When a halogen compound **S** was boiled under reflux for some time with ethanolic silver nitrate, little or no precipitate was seen.

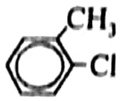
Which of the following formulae could represent **S**?

A $CH_3CH_2CHClCH_2CH_3$

B $CH_3CH_2CH_2COCl$

X

C 

D 

Helping Concepts *Exam Favourite Rating* ★★

The C–Cl bond in (D) is relatively stronger than in the others. In fact, it has partial double bond characteristics because a lone electron pair of Cl is able to delocalise into the benzene ring. (D) therefore does not lose the Cl atom easily to give Cl^- which can react with $AgNO_3$ to give AgCl precipitate.

---

7. Chlorofluorocarbons (CFCs) have been widely used in aerosol sprays, refrigerators and in making foamed plastics, but are now known to destroy ozone in the upper atmosphere.

What will not destroy ozone, and therefore can be used safely as a replacement for CFCs?

A $CHBr_3$

B CCl_3CBr_3

C $CHClFCClF_2$

D $CH_3CH_2CH_2CH_3$

Helping Concepts *Exam Favourite Rating* ★★

It is a hydrocarbon. It does not release reactive radicals that destroy the ozone layer.

---

8. Chlorofluoroalkanes, commonly known as CFCs, undergo homolytic fission by ultraviolet irradiation in the stratosphere.

Which radical could result from this irradiation of $CHFClCF_2Cl$?

A $CHFCl\dot{C}FCl$

F

HC−F−Cl−C−Cl

F

B $\dot{C}HClCF_2Cl$

C $\dot{C}HFCF_2Cl$

D $\dot{C}FClCF_2Cl$

Helping Concepts *Exam Favourite Rating* ★★★

C–F bond is stronger than C–Cl bond. To cleave the C–F bond, stronger radiation of shorter wavelength is needed. The uv radiation breaks the C–Cl bond.

---

9. 1,2-Dibromo-3-chloropropane (DBCP) has been used in the control of earthworms in agricultural land. Which of the following would be the best synthesis of this compound?

A $CH_3CH_2CH_2Cl + 2Br_2 \rightarrow DBCP + 2HBr$

B $CH_3CHBrCH_2Br + Cl_2 \rightarrow DBCP + HCl$

C $CH_2=CHCHBr_2 + HCl \rightarrow DBCP$

D $CH_2=CHCH_2Cl + Br_2 \rightarrow DBCP$

Helping Concepts *Exam Favourite Rating* ★★

$$CH_2=CHCH_2Cl + Br_2 \rightarrow CH_2BrCHBrCH_2Cl$$

A,B: No reaction (unless uv light is present).

C: $CH_2=CHCHBr_2 + HCl \rightarrow CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCHBr_2$

W)

10. In the upper atmosphere, chlorofluoroalkanes (CFCs) are broken down to give chlorine radicals but not fluorine radicals.

What is the best explanation for this?

A Fluorine is more electronegative than chlorine.

B The C–F bond is longer than the C–Cl bond.

C The C–F bond is stronger than the C–Cl bond.

D The chlorine atom is larger than the fluorine atom.

Helping Concepts *Exam Favourite Rating* ★★

C–F bond is stronger than C–Cl bond and thus C–F bond is more difficult to be cleaved. An electromagnetic wave of a shorter wavelength is required.

---

11. Chlorofluorocarbons (CFCs) have been widely used in aerosol sprays, refrigerators and in making foamed plastics, but are now known to destroy ozone in the upper atmosphere.

What will **not** destroy ozone, and therefore can be used as a replacement for CFCs?

A $CHBr_3$

B CCl_3CBr_3

C $CHClFCClF_2$

D $CH_3CH_2CH_2CH_3$

Helping Concepts *Exam Favourite Rating* ★★

It is a hydrocarbon which contains only C and H. It does not contain Cl and F.

---

12. Why does the reaction $C_2H_5X + OH^- \rightarrow C_2H_5OH + X^-$ take place more rapidly in aqueous solution when X is I than when X is Br?

A The I^- ion is a stronger nucleophile than Br^- ion.

B The I^- ion is less hydrated in solution than the Br^- ion.

C The C–Br bond is more polar than the C–I bond.

D The C–Br bond is stronger than the C–I bond.

Helping Concepts *Exam Favourite Rating* ★★★

Br is smaller than I. The p orbital of Br is less diffuse than the p orbital of I. Consequently, the overlap of C and Br orbitals is more effective and hence C–Br bond is stronger. This makes C–Br bond more difficult to be cleaved. Therefore, nucleophilic substitution for C_2H_5Br is less rapid.

---

13. Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon, C_4H_6.

From which pair of chlorobutanes was this hydrocarbon obtained?

A $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$

B $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$

C $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$

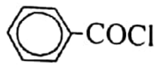
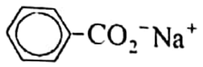
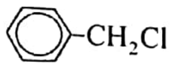
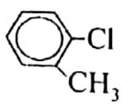
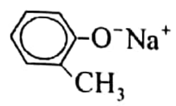
D $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CHClCH_3$

Helping Concepts *Exam Favourite Rating* ★★

Treatment of chlorobutane with ethanolic sodium hydroxide results in dehydrochlorination resulting in the formation of alkenes. Since the resultant hydrocarbon has a formula of C_4H_6, it has either 2 C=C bonds or 1 C≡C bond. The original chlorobutane must have lost 2 HCl molecules to form the 2 C=C bonds or 1 C≡C bond. Hence, the 2 original chlorobutanes should have 2 chlorine atoms each.

---

14. Which hydrolysis reaction, using NaOH(aq), will be the slowest?

	reactant	product
A	CH_3CH_2Cl	CH_3CH_2OH
B		
C		
D		

Helping Concepts *Exam Favourite Rating* ★★★

The lone pair of electrons of Cl delocalises into the benzene ring. The C–Cl bond has partial double bond character and is not readily broken. Hence, the compound does not readily undergoes hydrolysis which involves the cleavage of the C–Cl bond.

---

15. The anaesthetic *halothane*, $CF_3CHBrCl$, is made industrially as shown below.

$$CCl_2 = CHCl \xrightarrow[\text{stage 1}]{HF} CF_3CH_2Cl \xrightarrow[\text{stage 2}]{Br_2} CF_3CHBrCl$$

What type of reaction is occurring in stage 2?

A electrophilic addition

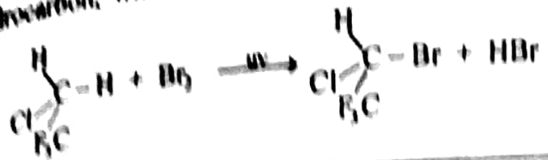
B electrophilic substitution

C free radical substitution

D nucleophilic addition

Helping Concepts Exam Favourite Rating ★★★

The reaction is similar to that of the bromination of a hydrocarbon, where uv is required.



16. What is the product of a nucleophilic substitution reaction between 2-iodobutane and sodium ethoxide?

OR

A $CH_3CH{=}CHCH_3$
B $CH_3CH_2CH(OCH_3)CH_2CH_3$
C $CH_3CH_2CH(CH_3)OCH_2CH_3$
D $(CH_3)_2CHCH_2OCH_2CH_3$

hp

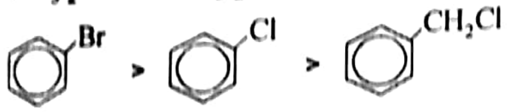
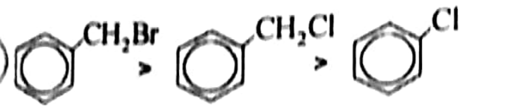
Helping Concepts Exam Favourite Rating ★★

$$CH_3CH_2{-}O^- + CH_3CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}I$$

$$\longrightarrow CH_3CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}O{-}CH_2CH_3 + I^-$$

hp

17. Which sequence shows the correct order of decreasing ease of hydrolysis?

A $CH_3CH_2Cl > CH_3CH_2Br > CH_3CH_2I$
B $(CH_3)_2CHCl > (CH_3)_2CHI > (CH_3)_2CHBr$
C 
D 

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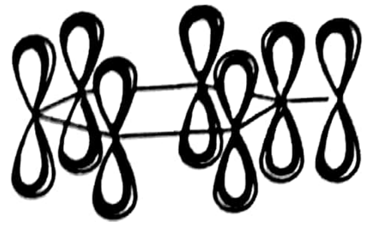
C–Br bond is weaker and hence easier to cleave than C–Cl bond. Therefore, $C_6H_5CH_2$–Br hydrolyses more readily than $C_6H_5CH_2$–Cl. In C_6H_5Cl, the C–Cl bond has partial double bond character due to the overlapping of p-orbital of Cl with the π-orbitals of benzene. Hence, it is difficult to cleave and C_6H_5Cl is the most difficult to be hydrolysed.

18. Which of the following chloro-compounds is least easily hydrolysed by hydroxide ion to give the product indicated?

A $C_2H_5Cl \rightarrow C_2H_5OH$
B $CH_3CHClCH_3 \rightarrow CH_3CH(OH)CH_3$
C $CH_3COCl \rightarrow CH_3CO_2H$
D $C_6H_5Cl \rightarrow C_6H_5OH$

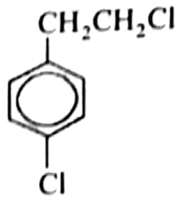
Helping Concepts Exam Favourite Rating ★★★

The C–Cl bond in C_6H_5Cl has partial double bond characteristics due to the delocalisation of a lone pair of electrons from chlorine into the benzene ring. This strengthens the C–Cl bond and makes it difficult to be broken.



Furthermore, the electron-rich benzene system makes the attack by OH^- difficult since like charges repel.

19. When compound V reacts with aqueous sodium hydroxide, what type of reaction occurs?



V

A base-catalysed elimination
B electrophilic addition
C electrophilic substitution
D nucleophilic substitution

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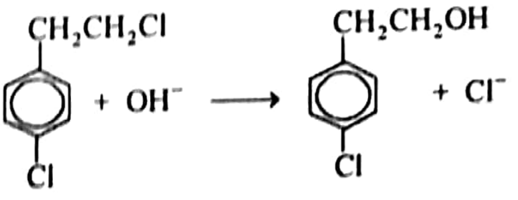
Nucleophilic substitution occurs at the alkyl chloride, giving rise to an alcohol while the aryl chloride remains unchanged.



20. Ethene reacts with aqueous bromine to give two products, CH_2BrCH_2Br and CH_2BrCH_2OH.

Which statement is correct for these products?

A Both products are obtained in this reaction by electrophilic substitution.

B Both products are obtained in this reaction by nucleophilic addition.

C Both products can be hydrolysed to form the same diol.

D Both products can form hydrogen bonds with water.

Helping Concepts | *Exam Favourite Rating* ★★

$$CH_2BrCH_2Br + 2OH^- \longrightarrow \underset{OH}{CH_2} - \underset{OH}{CH_2} + 2Br^-$$

$$CH_2BrCH_2OH + OH^- \longrightarrow \underset{OH}{CH_2} - \underset{OH}{CH_2} + Br^-$$

---

21. Chloroethane is converted into a carboxylic acid containing one more carbon atom through a two-stage process.

Which of the following compounds could be the intermediate in the synthesis of the carboxylic acid?

A CH_3CH_2OH

B $CH_3CH_2CH_2CN$

C $CH_3CH_2CO_2CH_3$

D CH_3CH_2CN

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In organic sythesis, cyanides (HCN or CN^-) are commonly employed in reactions whereby the number of carbon is increased, e.g. carbonyl and HCN (with a base) in nucleophilic addition; haloalkane (RX) and KCN in nucleophilic substitution.

$$C_2H_5Cl + CN^-(aq, alc) \rightarrow C_2H_5CN + Cl^-$$

$$C_2H_5CN + 2H_2O + H^+ \rightarrow C_2H_5CO_2H + NH_4^+$$

---

22. Bromomethane, CH_3Br, is used as a fumigant to destroy insect pests in grain that is to be stored. It can be made by reacting methanol with hydrogen bromide.

$$CH_3OH + HBr \rightarrow CH_3Br + H_2O$$

What type of reaction is this?

A condensation

B electrophilic substitution

C free radical substitution

D nucleophilic substitution

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$$CH_3-OH + H^+ \longrightarrow CH_3-OH_2^+$$

$$Br^- : \; \overset{\delta+}{C}H_3 - OH_2^+ \longrightarrow Br-CH_3 + H_2O$$

HBr is the nucleophile and it attacks the electron deficient C, i.e. a nucleophilic attack.

The overall reaction is a substitution.

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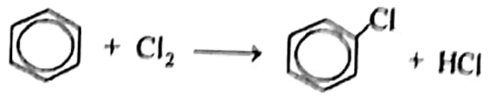
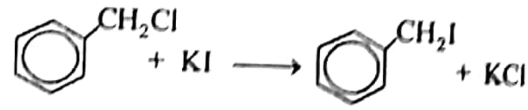
23. Which one of the following reactions is the inorganic reagent acting as a nucleophile?

A 

B $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$

C $CH_2=CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$

D 

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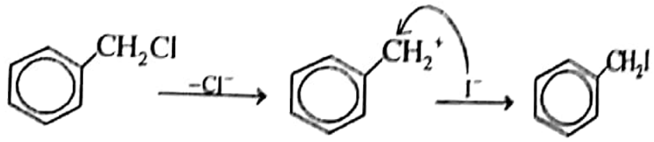
A nucleophile is one that is nucleus seeking. It usually has a lone electron pair or is negatively charged and is able to form a dative bond through donating the lone electron pair to the electron deficient site.



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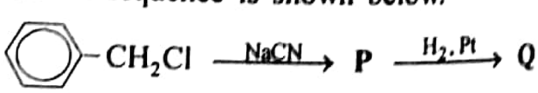
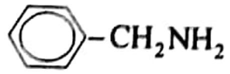
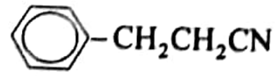
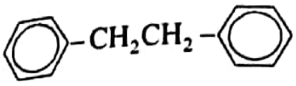
24. A reaction sequence is shown below.

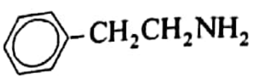


What would be the product Q?

A 

B 

C 

D 

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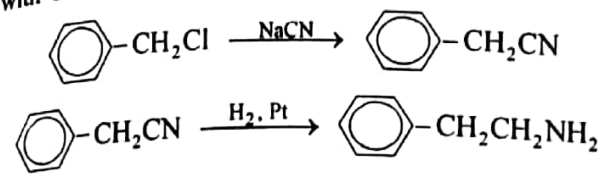
Benzyl chloride undergoes nucleophilic substitution with CN^- to give P, benzyl cyanide.



Reduction of benzyl chloride gives the corresponding amine, Q.

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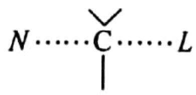
25. The diagram represents the transition state of an S_N2 reaction in which N is an anionic nucleophile and L the leaving group, but without any indication of the location of positive or negative charges.



Which is a possible combination of charges?

	charge on N	charge on L
A	$\delta-$	$\delta+$
B	$\delta-$	$\delta-$
C	$\delta+$	$\delta+$
D	$\delta+$	$\delta-$

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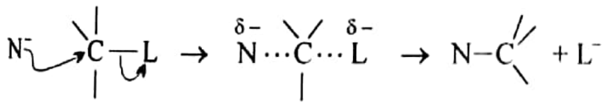

As N gradually forms a bond with C, it gradually loses its negative charge. At the same time, C–L bond gradually breaks and L acquire a partial negative charge, where it eventually leaves as L^-.

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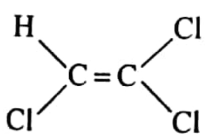
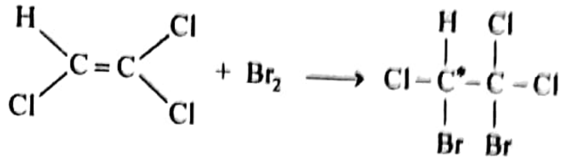
26. Trichloroethene is widely used as a dry-cleaning agent.



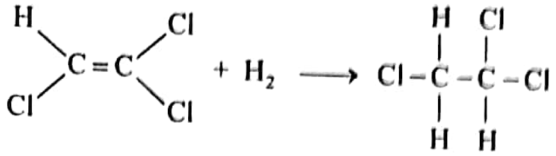
With which of the following does trichloroethene react to give a chiral product?

A H_2
B Br_2
C HCl
D NaOH(aq)

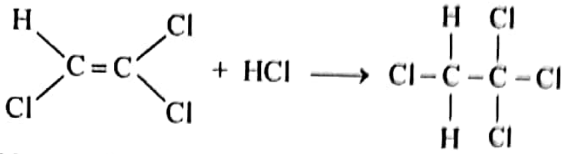
Helping Concepts *Exam Favourite Rating* ★★★



A:



C:



D: No reaction.

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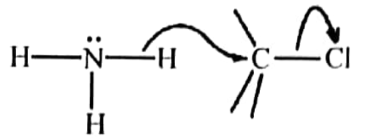
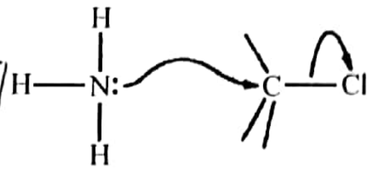
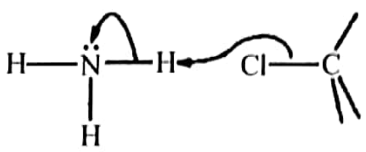
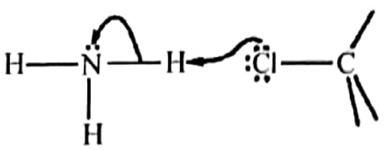
27. Which diagram correctly represents the transfer of electrons when ammonia reacts with a chloroalkane (alkyl chloride)?

A 

B 

C 

D 

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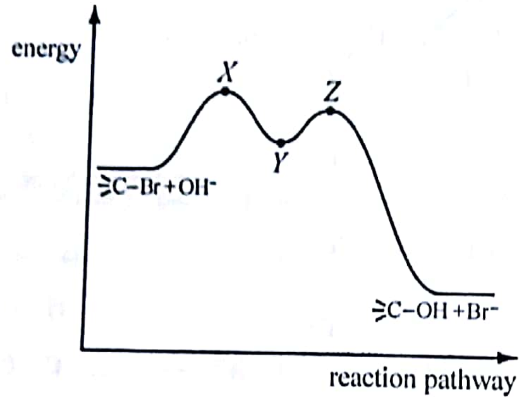
The reaction is a nucleophilic substitution whereby the lone electron pair of NH_3 (nucleophile) attacks the electron deficient C atom of C–Cl. The C–Cl bond elongates and breaks eventually with Cl^- (NOT Cl atom) as leaving group.

28. A bromoalkane, indicated here by $\rangle C-Br$, reacts with aqueous alkali with a mechanism which has the reaction pathway diagram below.



Which point in the diagram is correctly identified? (..... indicates a partial bond)

A X is $\rangle\overset{\delta+}{C}\cdots\overset{\delta-}{Br}$

B X is $C+$

C Y is $H\overset{\delta-}{O}\cdots C\cdots\overset{\delta-}{Br}$

D Z is $C+$

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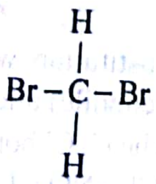
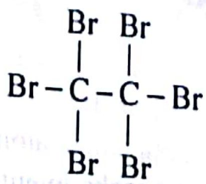
The energy profile shows an S_N1 mechanism.

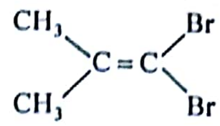
In step 1, in forming Y, the C–Br is gradually broken to form the carbocation.

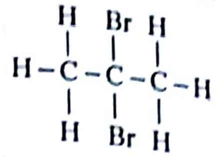
$$\rangle C-Br \rightarrow \underset{X}{\left[\rangle C^{\delta+}\cdots\cdots\overset{\delta-}{Br}\right]^{\ddagger}} \rightarrow \underset{Y}{C^{\oplus}} + Br^{\ominus}$$

29. Which compound could undergo an elimination reaction when treated with hot ethanolic potassium hydroxide?

A 

B 

C 

D 

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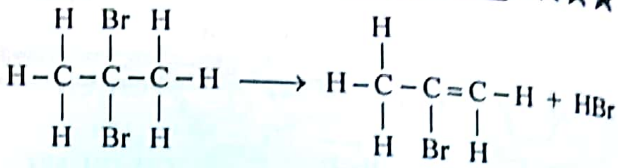
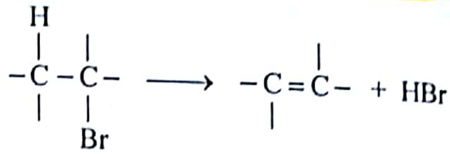


In order to undergo elimination, there must be a hydrogen atom bonded to the carbon atom adjacent to the carbon atom carrying the bromine atom.



30. Which reagent brings about a nucleophilic substitution of 4-(chloromethyl)phenol?

4-(chloromethyl)phenol

A $Br_2(aq)$

B $HNO_3(aq)$

C NH_3

D NO_2^+

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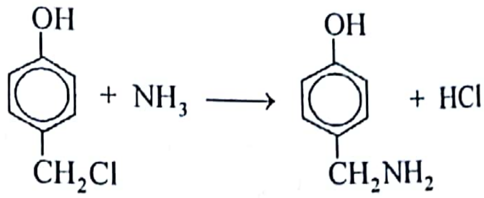
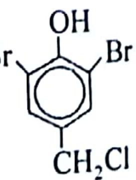
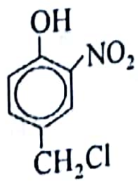
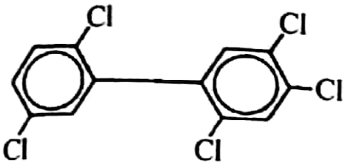


A: Electrophilic substitution: 

B,D: Electrophilic substitution: 

31. Polychlorinated biphenyls (PCBs) have been used as plasticisers and in electrical insulation coverings but they are now known to be environmentally harmful. One such PCB is shown below.



A suspension of this compound is stirred in aqueous sodium hydroxide. How many of the chlorine atoms in each molecule will be removed by hydrolysis?

A 0 **B** 1
C 2 **D** 3

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Cl bonded directly to the C of a benzene ring has partial C–Cl double bond character due to the overlap of the p-orbital of Cl and π-orbitals of the benzene ring. It is therefore difficult to cleave. Under the given conditions, no Cl will be substituted.

---

32. Under the Montreal Protocol, the use of chlorofluorocarbons is to be phased out. Fluorocarbons are often used to replace them. One chlorofluorocarbon which was widely used as a solvent is CCl_2FCClF_2 and large stocks of it remain. One process to use up these stocks is to convert it into the fluorocarbon CH_2FCF_3 by the following route.

$$CCl_2FCClF_2 \xrightarrow{\text{step 1}} CCl_3CF_3 \xrightarrow{\text{step 2}} CCl_2FCF_3 \xrightarrow{\text{step 3}} CH_2FCF_3$$

What type of reaction is step 1?

A elimination
B free radical substitution
C isomerisation
D nucleophilic substitution

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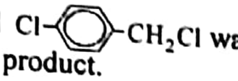
In step 1, one of the Cl atoms is substituted by F, while one of the F atoms is substituted by Cl.

---

33. Chlorine was passed into methylbenzene under reflux in the presence of aluminium chloride.

The compound  was found to be present in the product.

How is the mechanism for the formation of this product best described?

A electrophilic and free-radical substitution
B electrophilic and nucleophilic substitution
C nucleophilic and free-radical substitution
D nucleophilic substitution only

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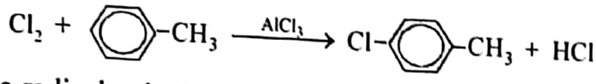
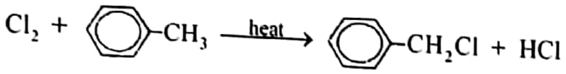
Electrophilic substitution:



Free-radical substitution:



---

34. An amine is produced in the following reaction.

$$C_2H_5I + 2NH_3 \rightarrow C_2H_5NH_2 + NH_4I$$

What is the mechanism?

A electrophilic addition
B electrophilic substitution
C nucleophilic addition
D nucleophilic substitution

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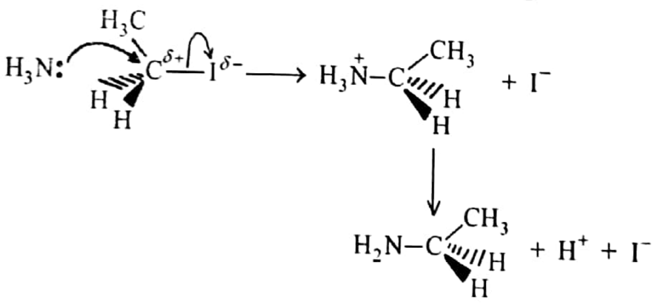

NH_3 has a lone pair of electrons on N. It acts as a nucleophile and attacks the electron deficient C to form a dative bond and the C–I cleaves heterolytically.

---

35. The reaction scheme outlines the production of one of the monomers of nylon 66 from compound **X**.

$$\text{compound X} \xrightarrow[\text{in ethanol}]{\text{KCN}} NCCH_2CH_2CH_2CH_2CN \xrightarrow{\text{reduction}} NH_2(CH_2)_6NH_2$$

Which compound could be **X**?

A $BrCH_2CH_2CH_2CH_2Br$

B $CH_2{=}CHCH{=}CH_2$

C $HOCH_2CH_2CH_2CH_2OH$

D $HO_2CCH_2CH_2CH_2CH_2CO_2H$

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Being a halogenoalkane, 1,4-dibromobutane undergoes nucleophilic substitution with CN^- to give the nitrile product.

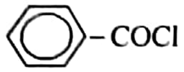
$$BrCH_2CH_2CH_2CH_2Br + 2CN^- \xrightarrow[\text{heat}]{\text{alcohol}} NCCH_2CH_2CH_2CH_2CN + 2Br^-$$

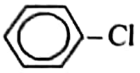
---

36. When a substance, Z, is shaken with aqueous silver nitrate at room temperature, there is no immediate precipitate.

In a second experiment, Z is boiled under reflux for some time with aqueous sodium hydroxide. The resulting solution is cooled and acidified with dilute nitric acid. When aqueous silver nitrate is now added, a white precipitate readily forms.

What could Z be?

A 

B 

C CH_3COCl

D $CH_3CH_2CH_2CH_2Cl$

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Z is not an acyl chloride (i.e. not (A) or (C)) as it does not readily form AgCl ppt. with aq. $AgNO_3$.

$$-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2O \rightarrow -\overset{\overset{\displaystyle O}{\|}}{C}-OH + Cl^-$$

$$Cl^- + Ag^+ \rightarrow AgCl\downarrow$$

Z is not an aryl chloride as it does not readily undergo hydrolysis with NaOH to form Cl^- (i.e. not (B)).

---

37. A mixture of 1 mol of bromobenzene and 1 mol of 2-bromopropane is heated under reflux for several hours with 2 mol of sodium hydroxide in aqueous solution.

How many moles of bromobenzene and 2-bromopropane are likely to remain?

	bromobenzene	2-bromopropane
A	1	1
B	1	0
C	0	1
D	0	0

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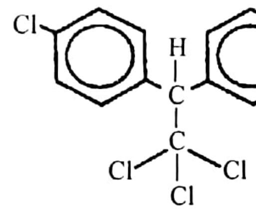
2-bromopropane undergoes nucleophilic substitution to form 2-propanol.

$$CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3 + OH^- \xrightarrow{\Delta} CH_3-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_3 + Br^-$$

Bromobenzene does not react with OH^-. The C–Br bond has partial double bond characteristic due to delocalisation of electrons from Br into the benzene ring. The C–Br bond is strong and is not cleaved.

---

38. DDT was widely used in the period from 1945 to 1980 to combat malaria by killing insects which spread the disease.



DDT

Which of the following statements about DDT is true?

A Its molecule contains a chiral carbon atom.

B Its molecule is strongly polar.

C It reacts with aqueous sodium hydroxide to give a compound containing two phenol groups.

D It gives an immediate precipitate when shaken with silver nitrate in ethanol.

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Cl groups are electron withdrawing and phenyl groups are electron donating. Therefore, the molecule should be strongly polar since there are so many Cl atoms.

D: DDT does not give an *immediate* precipitate with $AgNO_3$ in C_2H_5OH.

---

39. *Use of the Data Booklet is relevant to this question.*
2-bromopropane reacts with the following.

- an aqueous solution of sodium hydroxide to form organic product P
- an alcoholic solution of sodium hydroxide to form organic product Q
- an alcoholic solution of sodium cyanide to form organic product R

What is the order of increasing relative molecular masses, lowest to highest, of the organic products?

A P Q R
B Q P R
C Q R P
D R P Q

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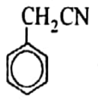
1. $CH_3-\underset{\underset{Br}{|}}{C}H-CH_3 \xrightarrow[\text{heat}]{\text{aq. }OH^-} CH_3-\underset{\underset{OH}{|}}{C}H-CH_3$ $(M_r = 60)$

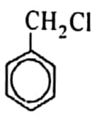
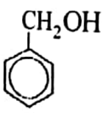
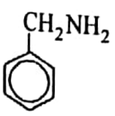
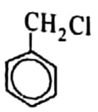
2. $CH_3-\underset{\underset{Br}{|}}{C}H-CH_3 \xrightarrow[\text{heat}]{\text{alcohol }OH^-} CH_3-CH=CH_2$ $(M_r = 42)$

3. $CH_3-\underset{\underset{Br}{|}}{C}H-CH_3 \xrightarrow[\text{heat}]{\text{alcohol }CN^-} CH_3-\underset{\underset{CN}{|}}{C}H-CH_3$ $(M_r = 69)$

40. Compond **Y** reacts with a reagent **Z** to form



What could **Y** and **Z** be?

	Y	Z
A		NaCN in ethanol
B		NaCN(aq)
C		HCN(aq)
D		HCN(aq)

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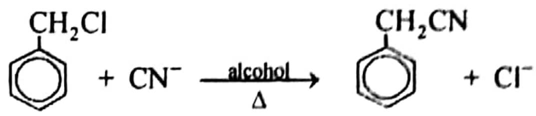

Chloromethylbenzene, being a halogenoalkane, undergoes nucleophilic substitution with CN^-.

In (B) and (C), the C–O and C–N bonds are strong and the compounds do not undergo substitution (where C–O and C–N bonds are cleaved).

In (D), HCN is a weak acid. The concentration of CN^- is very low.

41. If an organic halogeno-compound is heated with sodium, any halogen present in the compound is converted into the corresponding sodium halide.

$CH_2ClCHICO_2H$ is heated with sodium and the resultant residue dissolved in dilute nitric acid. Aqueous silver nitrate is then added to the mixture and finally concentrated ammonia is added dropwise, until present in excess.

Which observation is made when the ammonia is added?

A All the precipitate dissolves.
B All the precipitate remains.
C The precipitate appears less yellow.
D The precipitate appears more yellow

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Upon reaction with Na, NaI and NaCl will be formed. When $AgNO_3$ is added, AgI (yellow) and AgCl (white) precipitate will be formed. When concentrated NH_3 is added, AgCl will dissolve, leaving behind the yellow AgI precipitate.

$$AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$$

V. Imp

42. Under identical conditions, even though it proceeds by the same mechanism, reaction 1 is faster than reaction 2.

Reaction 1:

$CH_3CHBrCH_3 + NaCN \rightarrow CH_3CH(CN)CH_3 + NaBr$

Reaction 2:

$CH_3CHBrCH_3 + NaI \rightarrow CH_3CHICH_3 + NaBr$

What factor will explain this result?

A The C–I bond is a stronger bond than the C–Br bond.

B The C–N bond is a stronger bond than the C–I bond.

C The cyanide ion is a stronger nucleophile than the iodide ion.

D The cyanide ion is a weaker nucleophile than the iodide ion.

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Since same conditions are used for the same compound, $CH_3CHBrCH_3$, the difference in rate must be due to the difference in the property of CN^- and I^-. CN^- is a better nucleophile than I^-. I^- is larger than C (in CN^-) and its electron cloud is more diffuse. Hence, I^- is a poorer nucleophile and is less attracted to the electron deficient C in $CH_3CHBrCH_3$.

43. Experiments are carried out on three compounds.

X, $CH_3CH_2CH_2CH_2Cl$

Y, $CH_3CH_2CH_2COCl$, and

Z, C_6H_5Cl

To 0.010 mol samples of each X, Y and Z is added 10 cm^3 water and the samples are shaken and held at a fixed temperature for 24 hours.

An excess of aqueous silver nitrate is then added to each sample and the silver chloride produced is filtered off, washed, dried and weighed. The three samples of silver chloride weigh 0.000 g, 0.014 g and 1.430 g.

Which sequence of compounds matches these results?

	0.000 g	0.014 g	1.430 g
A	X	Y	Z
B	Y	Z	X
C	Z	X	Y
D	Z	Y	X

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Y readily undergoes hydrolysis to give Cl^-:

$$CH_3CH_2CH_2COCl + H_2O \rightarrow CH_3CH_2CH_2CO_2H + H^+ + Cl^-$$

X undergoes slight hydrolysis:

$$CH_3CH_2CH_2CH_2Cl + H_2O \rightleftharpoons CH_3CH_2CH_2CH_2OH + H^+ + Cl^-$$

Z does not undergo hydrolysis due to the partial double bond character of the C–Cl bond.

Hence, Y will give 0.1 mol of AgCl (=1.430 g), X will give less than 0.1 mol of AgCl and Z gives no AgCl.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** *to* **D** *should be selected on the basis of*

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

44. Which of the following would be suitable for use in a fire extinguisher?

1 $CBrF_3$

2 $CH_3(CH_2)_5CBr_3$

3 HF

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A suitable chemical would be one that does not support combustion, is not combustible (i.e. bonds are strong) and non-volatile. (2) is combustible due to the presence of C–C bonds, and (3) is volatile.

1 WP

45. Which of the following are properties of fluoroalkanes?

1 They are less reactive than the corresponding chloroalkanes.

2 They are non-flammable.

3 They may be used as aerosol propellants.

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*1. C–F bonds are stronger than C–Cl bonds. Hence, fluoroalkanes are more stable than the corresponding chloroalkanes since C–F bonds are very difficult to be broken.

*2. Due to the strong C–F bonds, they are not easily combustible (the bonds are difficult to be broken).

*3. Haloalkanes are commonly used as aerosol propellants.

46. For the reaction: WP

$$(CH_3)_3SiCl + C_2H_5O^- \rightarrow (CH_3)_3SiOC_2H_5 + Cl^-$$

which of the following statements are likely to be true?

1 It involves nucleophilic attack by $C_2H_5O^-$.

2 Cl^- is displaced by $C_2H_5O^-$.

3 The oxygen-carbon bond is not broken.

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*1. The reaction is a nucleophilic substitution whereby $C_2H_5O^-$ is acting as the nucleophile.

*2. The end result of the reaction is that Cl^- is substituted by $C_2H_5O^-$.

*3. The C–O bond in $C_2H_5O^-$ remains intact.

47. Chloroethane can be formed from bromoethane in two steps.

$$C_2H_5Br \xrightarrow{\text{step X}} C_2H_5OH \xrightarrow{\text{step Y}} C_2H_5Cl$$

Which statements about these steps are correct?

1 Step **X** involves a nucleophilic substitution.

2 Hot aqueous sodium hydroxide is the reagent in step **X**.

3 Hot aqueous sodium chloride is the reagent in step **Y**.

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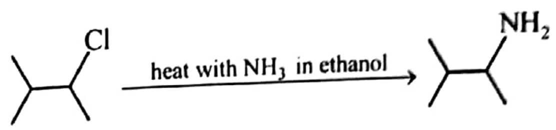
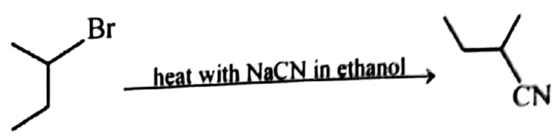
*1,*2. $C_2H_5Br + OH^-(aq) \xrightarrow{\text{heat}} C_2H_5OH + Br^-$

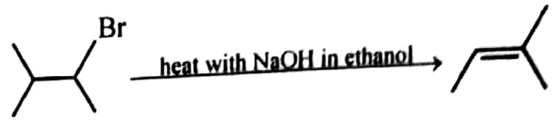
This is a nucleophilic substitution reaction.

3. To effect step **Y**, conc. HCl or PCl_5 is needed.

48. Which reactions would give the products stated?

1 

2 

3 

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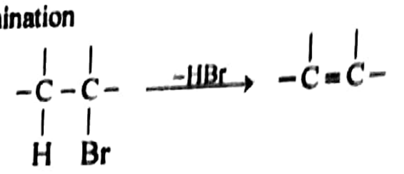
*1. Nucleophilic Substitution

$$R{-}Cl + NH_3 \rightarrow R{-}NH_2 + HCl$$

*2. Nucleophilic Substitution

$$R{-}Br + CN^- \rightarrow R{-}CN + Br^-$$

*3. Elimination



1 It is relatively unreactive.

2 The molecule has a chiral centre.

3 It may cause depletion of the ozone layer.

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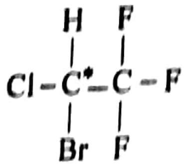
1. The C–Br bond is relatively easily broken.

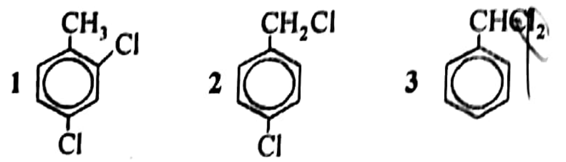
*2.



*3. Radicals can be formed by the homolytic cleavage of C–Br or C–Cl bond by uv light. The radicals formed can destroy the ozone layer.

49. A liquid L, $C_7H_6Cl_2$, gives a white precipitate when shaken for some time with cold ethanolic silver nitrate.

Which of the following structures could be L?



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1. Aryl chlorides do not undergo nucleophilic substitution to give Cl^- ions due to the strong C–Cl bond (partial double bond) which is not easily broken. This is due to the delocalisation of a lone pair of electrons of Cl into the benzene ring. Furthermore, the electron rich benzene system repels away the OH^- ion (like charges repel) and makes the attack difficult.

*2,*3. Both, being alkyl chlorides, react with alcohol to give Cl^- ions which forms white precipitate of AgCl with $AgNO_3$.

$$R-Cl + C_2H_5OH \rightarrow R-OC_2H_5 + HCl$$

$$HCl + AgNO_3 \rightarrow AgCl\downarrow + HNO_3$$

51. Bromoethene, $CH_2{=}CHBr$, is unreactive to nucleophiles whereas 3-bromopropene, $CH_2{=}CHCH_2Br$, is very reactive by comparison.

What could be a reason for the lack of reactivity of $CH_2{=}CHBr$?

1 The electrons of the bromine atom delocalise into the π bond.

2 The electrons of the π bond repel the attacking nucleophile.

3 The presence of the π bond prevents free rotation of the C–Br bond thus decreasing the reactivity.

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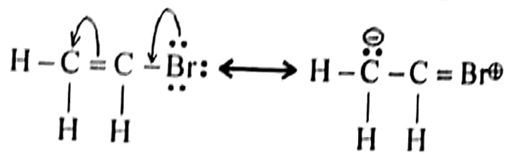
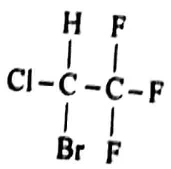
*1,*2.



The π electrons (electron rich) repels nucleophile away. This is further enhanced by the delocalisation of the electrons in Br into the π-bond system.

3. The π bond prevents the free rotation of the C–Br bond but does not implicate any attack by a nucleophile.

50. *Halothane* is a widely used anaesthetic.



Halothane

Which statements about *Halothane* are correct?

52. The chlorine free radical takes part in the destruction of the ozone layer.

Which statements about this free radical are correct?

1 It is formed by the heterolytic fission of the covalent bond in a chlorine - containing molecule.

2 It has a single unpaired electron.

3 It has the same electron arrangement as a chlorine atom.

Helping Concepts *Exam Favourite Rating* ★★

1. Free radicals are formed by homolytic cleavage of covalent bonds, not heterolytic fission (which would give ions).

$$A - A \longrightarrow A\cdot + \cdot B$$

*2. Free radicals are species that contain odd (or lone or unpaired) electron(s).

*3. Cl free radicals are actually Cl atoms!

---

53. During the preparation of many organic compounds by-products are formed. This usually occurs because the reagents can react in more than one way depending on the conditions used or because the products formed may react with the reactants.

Propan-1-ol is produced by the reaction between 1-bromopropane and aqueous sodium hydroxide.

$$CH_3CH_2CH_2Br + NaOH$$
$$\rightarrow CH_3CH_2CH_2OH + NaBr$$

What could be a by-product of this reaction?

1 $CH_3CH{=}CH_2$

2 $CH_3CH_2CH_2ONa$

3 $CH_3CH(OH)CH_3$

Helping Concepts *Exam Favourite Rating* ★

*1. $CH_3CH_2CH_2Br$ can undergo elimination to form $CH_3CH{=}CH_2$, especially when more alcohol is formed to provide the alcoholic medium.

2. In aqueous medium, RO^-Na^+ is unstable and will readily be converted to ROH.

$$RO^-Na^+ + H_2O \rightarrow ROH + NaOH$$

3. The rearrangement of the alcohol (from $CH_3CH_2CH_2OH$ to $CH_3CH(OH)CH_3$) is possible in acidic condition (but not in alkaline condition).

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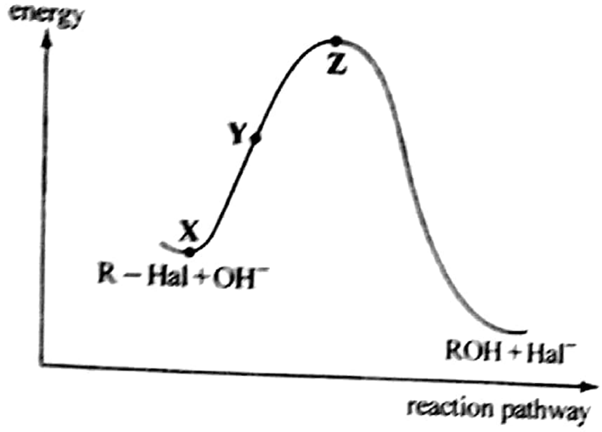
54. Halogenoalkanes react with aqueous alkali. One mechanism of this reaction has the energy profile shown below.



Which of the following statements are correct?

1 The reaction is an example of nucleophilic substitution.

2 Between **X** and **Z**, the C–Hal bond will be lengthening.

3 The energy difference between **X** and **Y** represents the activation energy.

Helping Concepts *Exam Favourite Rating* ★★★

$$\underset{X}{Hal - R} \leftarrow {}^-OH \rightarrow \underset{Z}{[Hal \cdots R \cdots OH]^-} \rightarrow Hal^- + ROH$$

*1,*2. The reaction follows an S_N2 mechanism whereby the C–OH bond is gradually formed to form the activated complex **Z**.

3. The activation energy of the reaction is the difference between energies at **X** and **Z**.

TOPIC 16

Hydroxy Compounds

Key content that you will be examined on:

1. Alcohols (exemplified by ethanol)
   - (i) Formation of halogenoalkanes
   - (ii) Reaction with sodium; oxidation; dehydration
   - (iii) The tri-iodomethane test
2. Phenol
   - (i) Its acidity; reaction with sodium
   - (ii) Nitration of, and bromination of, the aromatic ring

Hydroxy Compounds

Topic 16

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which compound reacts with ammonia?

A bromoethane
B chlorobenzene
C ethanol
D phenol

NH L

Helping Concepts *Exam Favourite Rating* ★★★

C_2H_5Br undergoes nucleophilic substitution reaction with NH_3.

$$C_2H_5Br + NH_3 \rightarrow C_2H_5NH_2 + HBr$$

2. In which of these processes is at least one product a gas at room temperature and pressure?

A dehydration of ethanol
B esterification of ethanoic acid by ethanol
C oxidation of ethanal by $H^+/Cr_2O_7^{2-}$
D substitution of ethanol by hydrogen bromide

Helping Concepts *Exam Favourite Rating* ★★

$$C_2H_5OH(l) \xrightarrow{-H_2O} C_2H_4(g)$$

3. Which reagent gives a colourless homogeneous solution when added to phenol?

A aqueous bromine
B aqueous sodium carbonate
C aqueous sodium hydroxide
D aqueous sodium hydroxide and benzoyl chloride

Helping Concepts *Exam Favourite Rating* ★★

Phenol is acidic enough to react with OH^- to give an ionic salt which is soluble in water.

$$C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$$

4. Which reagent could detect the presence of added alcohol in a petrol consisting mainly of a mixture of alkanes and alkenes?

A Na
B Br_2 (in CCl_4)
C $KMnO_4$(aq)
D 2,4-dinitrophenylhydrazine

Helping Concepts *Exam Favourite Rating* ★★★

Alkanes and alkenes, being hydrocarbons, are inert towards Na. However, an alcohol can act as an acid to give H_2 gas when reacting with Na.

$$2ROH + 2Na \rightarrow 2RO^-Na^+ + H_2$$

5. Which inorganic reagent may be used to distinguish between phenol and methanol?

A alkaline aqueous I_2
B aqueous $NaHCO_3$
C $K_2Cr_2O_7$ in dilute H_2SO_4
D Na

up

Helping Concepts *Exam Favourite Rating* ★★★

Options A and B are incorrect since both phenol and methanol do not react with alkaline aqueous iodine and aqueous $NaHCO_3$.

Option C is *correct* since only methanol is oxidised and it turns orange $Cr_2O_2^{2-}$ to green Cr^{3+}.

Option D is incorrect since both phenol and methanol react with sodium to give H_2.

6. Which one of the following pairs of reagents **cannot** be used to prepare CH_3CH_2Cl?

A $CH_2{=}CH_2 + HCl$
B $CH_2{=}CHCl + H_2$
C $CH_3CH_2OH + HCl$
D $CH_3CH_2OH + Cl_2$

Helping Concepts *Exam Favourite Rating* ★★★

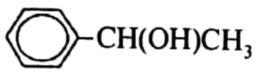
Cl_2 cannot substitute the –OH group. Instead, it may undergo free radical substitution at the alkyl chain under suitable conditions to give chloroethanols.

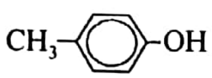
A: $CH_2=CH_2 + HCl \rightarrow CH_3CH_2Cl$
B: $CH_2=CHCl + H_2 \rightarrow CH_3CH_2Cl$
C: $CH_3CH_2OH + HCl \rightarrow CH_3CH_2Cl + H_2O$

7. Which of the following dissolves in water to give an acidic solution?

A $CH_3CH_2CH_2CH_2OH$

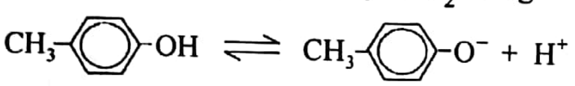
B
$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ CH_3 \end{array}$$

C 

D 

Helping Concepts *Exam Favourite Rating* ★★★

Being a phenol, it ionises partially in H_2O to give H^+.



8. A compound **X** is optically active. One mole of **X** liberates one mole of hydrogen when it reacts with sodium.

What could be the formula of **X**?

A $CH_3CH(OH)CHO$
B $CH_3CH(OH)CO_2H$
C $HOCH_2CH(CH_3)CH_2OH$
D $HOCH_2CH_2CO_2H$

Helping Concepts *Exam Favourite Rating* ★★★

X contains 2 –OH groups (either alcohol or carboxylic acid).

$$\begin{array}{c} H \\ | \\ CH_3-C^*-CO_2H \\ | \\ OH \end{array} + 2Na \rightarrow \begin{array}{c} H \\ | \\ CH_3-C^*-CO_2^-Na^+ \\ | \\ O^-Na^+ \end{array} + H_2$$

Option D is not optically active.

9. In its reaction with sodium, 1 mol of a compound **X** gives 1 mol of $H_2(g)$.

Which compound might **X** be?

A $CH_3CH_2CH_2CH_2OH$
B $(CH_3)_3COH$
C $CH_3CH_2CH_2CO_2H$
D $CH_3CH(OH)CO_2H$

Helping Concepts *Exam Favourite Rating* ★★★

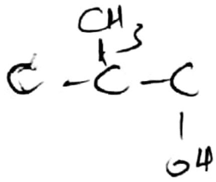
$$R-OH + Na \rightarrow R-O^-Na^+ + \tfrac{1}{2}H_2$$
$$R-CO_2H + Na \rightarrow R-CO_2^-Na^+ + \tfrac{1}{2}H_2$$

1 mol of –OH group or –COOH group each gives $\frac{1}{2}$ mol of H_2. Hence, to form 1 mol of H_2, 2 mol of –OH, 2 mol of $-CO_2H$ or 1 mol of –OH and 1 mol of $-CO_2H$ are required.

10. An alcohol X with molecular formula $C_4H_{10}O$ is oxidised by acidified potassium dichromate(VI) solution and also produces a pale yellow precipitate with alkaline aqueous iodine.

Which compound could be X?

A butan-1-ol
B butan-2-ol
C 2-methylpropan-1-ol
D 2-methylpropan-2-ol



Helping Concepts *Exam Favourite Rating* ★★

X is likely a 1° or 2° alcohol (that can be oxidised) and contains the $\begin{array}{c} -CH-CH_3 \\ | \\ OH \end{array}$ group to react with I_2/NaOH to form the yellow CHI_3.

11. Which compound reacts with its own oxidation product (an oxidation which involves no loss of carbon) to give a sweet-smelling liquid?

A propanal

B propanoic acid

C propanone

D propan-1-ol

up

Helping Concepts *Exam Favourite Rating* ★★★

As a 1° alcohol, propan-1-ol is oxidised to propanoic acid.

$$CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CO_2H + H_2O$$

Propan-1-ol and propanoic acid react when heated in the presence of conc. H_2SO_4 to form an ester, propyl propanoate.

$$CH_3CH_2CO_2H + CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} CH_3CH_2CO_2CH_2CH_2CH_3 + H_2O$$

---

12. In the following sequence of reactions, what is the mechanism of each step?

$$CH_3OH \xrightarrow[\text{step 1}]{\text{HBr, heat}} CH_3Br \xrightarrow[\text{step 2}]{(CH_3)_3P} (CH_3)_4P^+Br^-$$

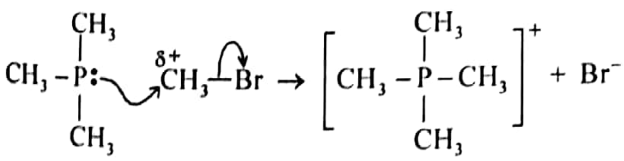
	step 1	step 2
A	electrophilic substitution	electrophilic substitution
B	electrophilic substitution	nucleophilic substitution
C	nucleophilic substitution	electrophilic substitution
D	nucleophilic substitution	nucleophilic substitution

Helping Concepts *Exam Favourite Rating* ★★★

Both steps are S_N.

1: Br^- is the nucleophile.

2: $(CH_3)_3P$: is the nucleophile.



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13. An aqueous solution of compound Q is weakly acidic. When an alkaline solution of Q is shaken with benzoyl chloride, a solid derivative is obtained.

What could Q be?

A $C_6H_5CO_2H$

B C_6H_5OH

C $C_6H_5CH_2OH$

D $C_6H_5NH_2$

Helping Concepts *Exam Favourite Rating* ★★★

Phenol is a weak acid in water.

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

It undergoes esterification with an acid chloride in alkaline medium.

$$C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$$

$$C_6H_5O^- + C_6H_5COCl \rightarrow C_6H_5COOC_6H_5 + Cl^-$$

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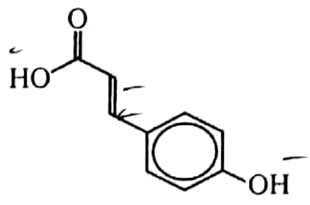
14. *Para*-coumaric acid is an antioxidant in coffee.



para-coumaric acid

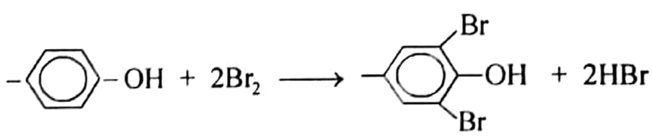
When treated with aqueous bromine, what is the maximum number of bromine atoms that can be incorporated into a molecule of *para*-coumaric acid?

A 2 **B** 4

C 5 **D** 6

Helping Concepts *Exam Favourite Rating* ★★★

$$>C{=}C< + Br_2 \longrightarrow -\underset{Br}{\overset{|}{C}}-\underset{Br}{\overset{|}{C}}-$$



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15. Which one of the following correctly describes the acid-base properties of phenol?

A an acid, stronger than carbonic acid

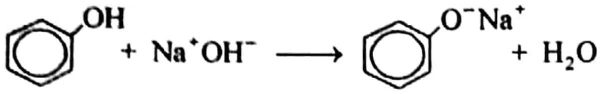
B an acid, weaker than carbonic acid

C a neutral compound

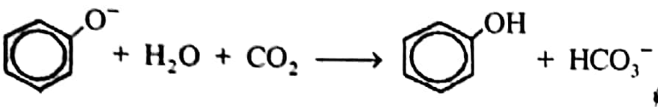
D a base, weaker than ammonia

Helping Concepts *Exam Favourite Rating* ★★★

Phenol is an acid because it reacts with NaOH to form sodium phenoxide (salt) and H_2O.



However, it is unable to release CO_2 from Na_2CO_3. Hence, it is an acid weaker than H_2CO_3. In fact, bubbling CO_2 into a solution of phenoxide yields phenol.



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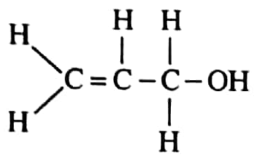
16. Prop-2-en-1-ol (allyl alcohol) has the following structure.



Which reagent would react with prop-2-en-1-ol to form a product that could exist as optical isomers?

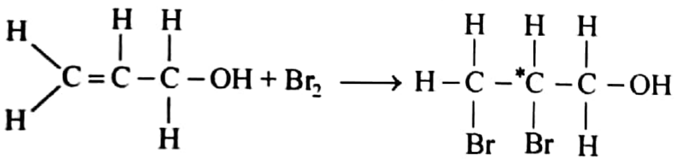
A bromine

B hydrogen and nickel

C phosphorus pentachloride

D sodium

Helping Concepts *Exam Favourite Rating* ★★★



C* is chiral and the product is optically active.

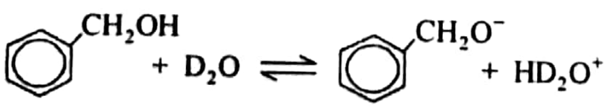
---

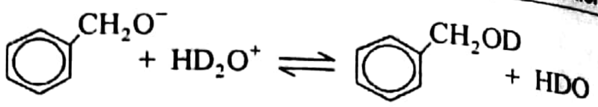
17. How many hydrogen atoms in a molecule of phenylmethanol, $C_6H_5CH_2OH$, may be substituted by deuterium by dissolving the alcohol in an excess of D_2O?

A 1 **B** 2

C 3 **D** 8

Helping Concepts *Exam Favourite Rating* ★





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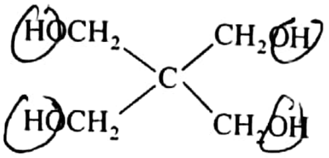
18. Pentaerythritol is an intermediate in the manufacture of paint.



pentaerythritol

What deduction about pentaerythritol can be made from this structure?

A It gives a precipitate with Tollens' reagent.

B It is chiral.

C It is dehydrated to an alkene by concentrated sulfuric acid.

D It is soluble in water.

Helping Concepts *Exam Favourite Rating* ★★

The molecule is highly polar due to the presence of 4 –OH groups. Hence, it is soluble in H_2O (through hydrogen bonding).

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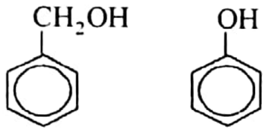
19. Which one of the following reagents can be used to distinguish between the two compounds shown below?



A aqueous bromine

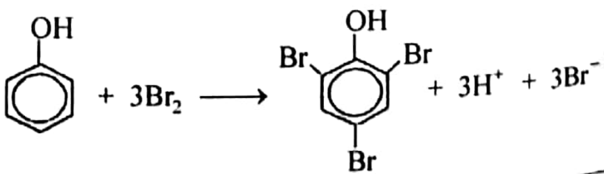
B ethanoic anhydride

C ethanoyl chloride

D dilute hydrochloric acid

Helping Concepts *Exam Favourite Rating* ★★★

In phenol, the benzene ring is activated by the –OH group towards electrophilic substitution. It decolourises Br_2 and forms a white precipitate readily with aqueous Br_2 at room temperature but benzyl alcohol is unable to do so.



20. Ethene reacts with aqueous bromine to give the two products, CH_2BrCH_2Br and CH_2BrCH_2OH.

Which statement is correct for these products?

A Both products possess an overall dipole.

B Both products can be hydrolysed to form the same diol.

C Both products are obtained in this reaction by electrophilic substitution.

D Both products are obtained in this reaction by nucleophilic addition.

Helping Concepts *Exam Favourite Rating* ★★

$CH_2BrCH_2Br + 2OH^- \rightarrow CH_2OHCH_2OH + 2Br^-$

$CH_2BrCH_2OH + OH^- \rightarrow CH_2OHCH_2OH + Br^-$

A: CH_2BrCH_2Br has no overall dipole because it is a symmetrical molecule.

C,D: The products are obtained in this reaction by electrophilic addition.

---

21. A mixture is made by adding together one mole of sodium hydroxide, one mole of phenol (C_6H_5OH) and one mole of hexan-1-ol ($C_6H_{13}OH$), each solute being in aqueous solution.

Which organic species are present in this final solution?

A mainly C_6H_5OH and $C_6H_{13}OH$

B mainly $C_6H_{13}OH$ and $C_6H_5O^-Na^+$

C mainly C_6H_5OH and $C_6H_{13}O^-Na^+$

D approximately equal quantities of C_6H_5OH, $C_6H_5O^-Na^+$, $C_6H_{13}OH$ and $C_6H_{13}O^-Na^+$

Helping Concepts *Exam Favourite Rating* ★★

Hexan-1-ol is not acidic enough to react with NaOH. Hence, it remains as hexan-1-ol. Phenol is acidic enough to react with NaOH to give the phenoxide.

$$C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$$

---

22. If $\frac{1}{10}$ mol of ethanol, $\frac{1}{8}$ mol of potassium bromide and $\frac{1}{6}$ mol of sulfuric acid were used to prepare bromoethane, what is the maximum mass of bromoethane which could be formed?

[M_r: ethanol, 46; bromoethane, 109]

A $\frac{109}{10}$ g

B $\frac{109}{8}$ g

C $\frac{109}{6}$ g

D $\frac{109}{10 \times 46}$ g

Helping Concepts *Exam Favourite Rating* ★★★

$$C_2H_5OH + KBr \xrightarrow{H^+} C_2H_5Br + KOH$$

C_2H_5OH is the limiting agent.

Amount of C_2H_5Br formed $= \frac{1}{10}$ mol

$\therefore$ Mass of C_2H_5Br formed $= \frac{1}{10} \times 109 = \frac{109}{10}$ g

Note: H_2SO_4 is added to catalyse the reaction and to remove the KOH formed and hence shifts the equilibrium to the right.

---

23. In a preparation of ethene, ethanol is added a drop at a time to a heated reagent **Y**. The impure ethene is washed by being bubbled through a solution **Z** and then collected.

What are reagent **Y** and solution **Z** likely to be?

	reagent Y	solution Z
A	acidified $K_2Cr_2O_7$	dilute NaOH
B	concentrated H_2SO_4	dilute H_2SO_4
C	concentrated H_2SO_4	dilute NaOH
D	ethanolic NaOH	concentrated H_2SO_4

Helping Concepts *Exam Favourite Rating* ★★

Y should be **concentrated H_2SO_4** and it serves as a dehydrating agent. Ethene is evolved and it is passed through dilute NaOH to remove any acid before it is collected.

$$C_2H_5OH \xrightarrow[\Delta]{\text{conc } H_2SO_4} C_2H_4 + H_2O$$

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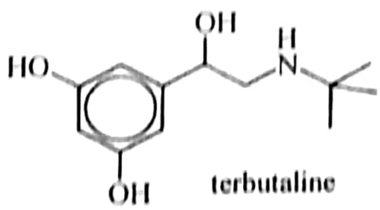
24. Terbutaline is a fast acting bronchodilator which may be used to treat asthma.



terbutaline

Which statement about terbutaline is correct?

A Terbutaline is hydrolysed by dilute H_2SO_4 to give a carboxylic acid and an amine.

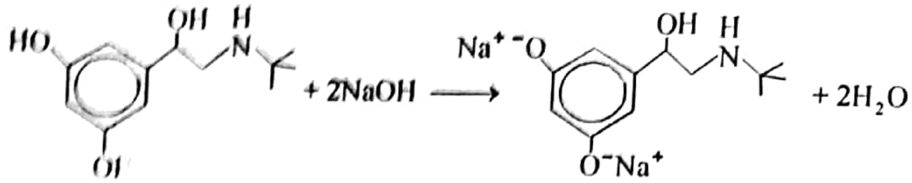
B Terbutaline reacts with NaOH(aq) to form $C_{12}H_{17}NO_3Na_2$.

C The molecular formula of terbutaline is $C_9H_{13}NO_3$.

D The molecule contains six lone pairs of electrons.

Helping Concepts *Exam Favourite Rating* ★★★

As a phenol, terbutaline functions as an acid and reacts with NaOH to form the phenoxide.



A: It is not an amide and hence does not undergo hydrolysis with H_2SO_4.

C: Its formula is $C_{12}H_{19}NO_3$.

D: It has 7 lone pairs of electrons. 2 l.p. on each of the 3 O and 1 on N.

---

25. Propan-1-ol, C_3H_7OH, is dehydrated by passing its vapour over hot aluminium oxide to give a hydrocarbon.

Which structural formula represents the product obtained when the hydrocarbon reacts with bromine?

A $\begin{array}{c} H\ \ H\ \ H \\ H-C-C-C-Br \\ H\ \ H\ \ H \end{array}$ B $\begin{array}{c} H\ \ Br\ \ H \\ H-C-C-C-H \\ H\ \ H\ \ H \end{array}$

C $\begin{array}{c} H\ \ H\ \ Br \\ H-C-C-C-Br \\ H\ \ H\ \ H \end{array}$ D $\begin{array}{c} H\ \ Br\ \ Br \\ H-C-C-C-H \\ H\ \ H\ \ H \end{array}$

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$$CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{Al_2O_3} CH_3CH=CH_2 + H_2O$$

$$CH_3CH=CH_2 + Br_2 \longrightarrow CH_3\underset{\displaystyle Br}{CH}-\underset{\displaystyle Br}{CH_2}$$

---

26. Which of the following isomers of $C_5H_{11}OH$ gives, on dehydration, the greatest number of different alkenes?

A $CH_3-CH_2-\underset{\displaystyle CH_3}{CH}-CH_2OH$

B $CH_3-CH_2-CH_2-\underset{\displaystyle OH}{CH}-CH_3$

C $CH_3-CH_2-\underset{\displaystyle OH}{CH}-CH_2-CH_3$

D $CH_3-\underset{\displaystyle CH_3}{CH}-CH_2-CH_2OH$

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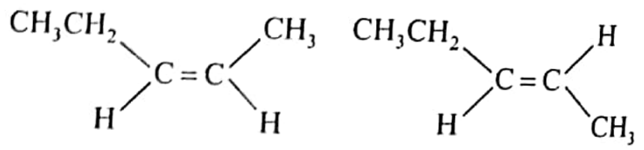
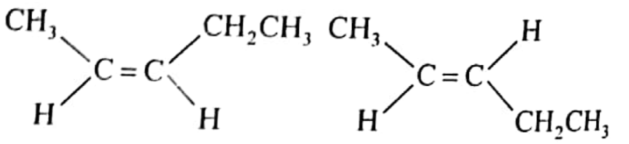
A: $CH_3CH_2\underset{\displaystyle CH_3}{C}=CH_2$

B: $CH_3CH_2CH_2CH=CH_2$



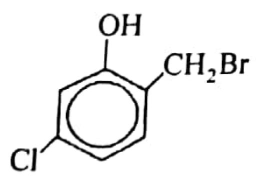
C:



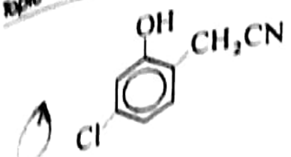
D: $CH_3\underset{\displaystyle CH_3}{CH}CH=CH_2$

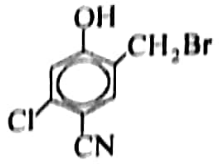
---

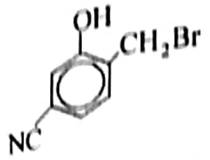
27. A compound has the following structure.

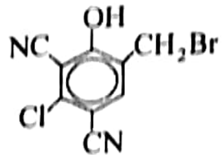


Which compound is obtained by nucleophilic substitution when a cyanide ion reacts with this compound?

A 

B 

C 

D 

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The compound behaves as a bromoalkane and CN^- attacks the alkyl chain.

$$R-X + CN^- \rightarrow R-CN + X^-$$

---

28. Which set of alcohols correctly shows a primary, a secondary and a tertiary alcohol?

	primary	secondary	tertiary
A	CH_2OH	CH_2OH	CH_2OH
	|	|	|
	CH_2	$CHOH$	$CHOH$
	|	|	|
	CH_3	CH_3	CH_2OH
B	CH_2OH	CH_3	CH_3
	|	|	|
	CH_3-C-H	CH_3-C-OH	CH_3-C-H
	|	|	|
	CH_3	CH_3	CH_2OH
C	CH_2OH	CH_2OH	CH_2OH
	|	|	|
	CH_3-C-H	CH_3-C-CH_2OH	CH_3-C-CH_2OH
	|	|	|
	H	H	CH_2OH
D	H	CH_3	CH_3
	|	|	|
	CH_3-C-OH	CH_3-C-OH	CH_3-C-OH
	|	|	|
	H	H	CH_3

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A: 1°, (1°, 2°), (1°, 2°, 1°)

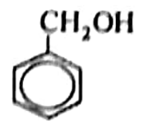
B: 1°, 3°, 1°

C: 1°, (1°, 1°), (1°, 1°, 1°)

---

29. Many alcohols are oxidised by warming with acidified potassium dichromate(VI).

Which alcohol resists this oxidation?

A 

B $CH_3-C(H)(CH_3)-CH_2OH$

	CH_2OH
	|
B	CH_3-C-H
	|
	CH_3

	CH_3		H
	|		|
C	CH_3-C-OH	D	CH_3CH_2-C-OH
	|		|
	CH_3		CH_3

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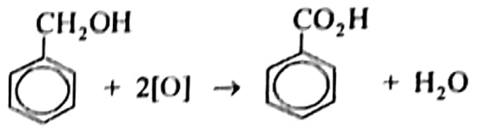
Tertiary (3°) alcohols are resistant to oxidation.

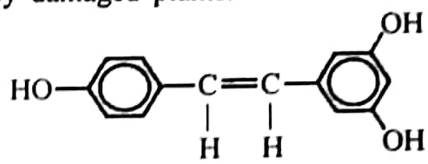


$$CH_3-\underset{CH_3}{\overset{CH_2OH}{C}}-H + 2[O] \rightarrow CH_3-\underset{CH_3}{\overset{CO_2H}{C}}-H + H_2O$$

$$CH_3CH_2-\underset{CH_3}{\overset{H}{C}}-OH + [O] \rightarrow CH_3CH_2-\underset{CH_3}{C}=O + H_2O$$

---

30. *Reversatrol* is an insect repellent which is emitted by damaged plants.



Reversatrol

Which reagent, in its reactions with *Reversatrol*, shows both electrophilic addition and electrophilic substitution?

A bromine

B ethanoyl chloride

C hydrogen bromine

D steam

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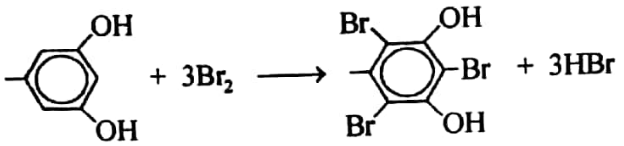
$>C=C<$ undergoes electrophilic addition with Br_2.

$$>C=C< + Br_2 \longrightarrow -\underset{Br}{\overset{|}{C}}-\underset{Br}{\overset{|}{C}}-$$

Phenols undergo electrophilic substitution with Br_2.



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31. Ethyl ethanoate is a very important solvent in industry. Currently, researchers are investigating ways of producing the ester from cheap, low grade ethanol by the following process.

$$CH_3CH_2OH \xrightarrow{\text{step 1}} CH_3CHO$$

$$\xrightarrow{\text{step 2}} CH_3CH_2O\underset{\underset{OH}{|}}{C}HCH_3$$

$$\xrightarrow{\text{step 3}} CH_3CH_2OCOCH_3$$

What types of reaction are steps 1 and 3?

	step 1	step 2
A	elimination	esterification
B	elimination	isomerisation
C	oxidation	esterification
D	oxidation	oxidation

Helping Concepts *Exam Favourite Rating* ★★

In step 1, the 1° alcohol is oxidised to an aldehyde.

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$

In step 3, the –OH group is oxidised to a C=O group.

$$CH_3CH_2-O-\underset{\underset{OH}{|}}{C}HCH_3 + [O]$$

$$\longrightarrow CH_3CH_2-O-\underset{\underset{O}{\|}}{C}-CH_3 + H_2O$$

---

32. In the sequence of the Krebs cycle, which metabolises glucose into useful energy, fumaric acid is converted into oxaloacetic acid by a two-step process involving the intermediate T.

$$\underset{\text{fumaric acid}}{HO_2CCH{=}CHCO_2H} \xrightarrow{\text{step 1}} T$$

$$\xrightarrow{\text{step 2}} \underset{\text{oxaloacetic acid}}{HO_2CCOCH_2CO_2H}$$

Each of these metabolic steps could be achieved in the laboratory by a single reagent.

What could be the reagent for step 1 and for step 2?

	step 1	step 2
A	cold acidified $KMnO_4$	H_2 with Pt catalyst
B	H_2 with Pt catalyst	hot acidified $KMnO_4$
C	HBr	hot acidified $KMnO_4$
D	steam and H_2SO_4	hot acidified $KMnO_4$

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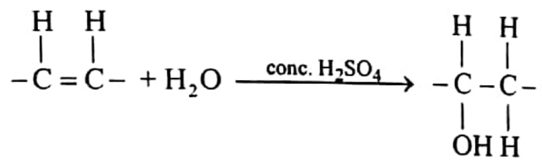
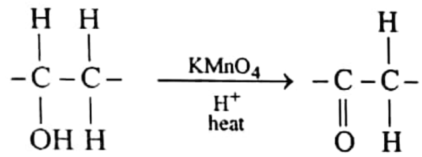
There is an insertion of an O atom into the compound. The oxaloacetic acid has a ketone group. Hence, the intermediate T, is likely a 2° alcohol which is oxidised to form the ketone.



T

The 2° alcohol can be obtained by hydration across the C=C double bond.



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33. An account in a student's notebook read:

'An excess of aqueous bromine was added to aqueous phenol in a test-tube. 2,4,6-tribromophenol was produced as a creamy-white precipitate suspended in a yellow alkaline solution.'

Which statement in this account must have been **incorrect**?

A The precipitate is not 2,4,6-tribromophenol, but a mixture of 2- and 4-bromophenol.

B The precipitate obtained is not creamy-white, but yellow.

C The resultant solution is not alkaline, but acidic.

D The resultant solution is not yellow, but purple.

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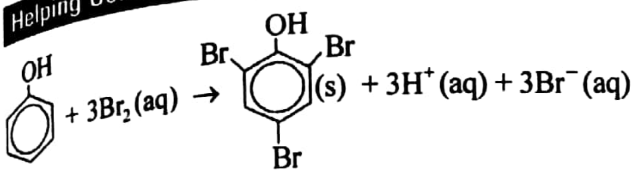

The reaction generates H^+ and hence the solution formed should be acidic, **not** alkaline.

---

34. The molecular formula of a sugar is $C_6H_{12}O_6$. Its structure consists of an unbranched chain of carbon atoms, each of which has an oxygen atom bonded to it. It does not contain any carbon-carbon double bonds.

How many moles of sodium react with 1 mol of the sugar and how many moles of gaseous hydrogen are formed?

	moles of sodium	moles of gaseous hydrogen
A	5	2.5
B	5	5
C	6	3
D	6	6

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The sugar has the following skeleton structure with an unbranched chain of C, and with each C bonded to O.

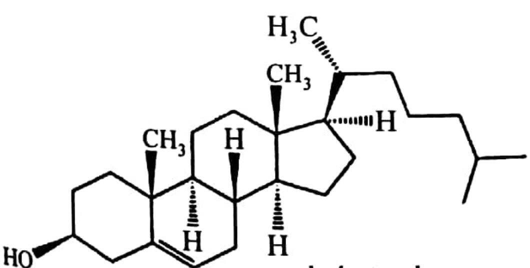
```
C – C – C – C – C – C
|   |   |   |   |   |
O   O   O   O   O   O
```

However, it is a 2 H short of a saturated molecule. Hence, it is not a hexa-ol but a penta-ol with a $>C=O$.

$$C_6H_7(OH)_5 + 5Na \rightarrow C_6H_7(O^-Na^+)_5 + \tfrac{5}{2}H_2$$

---

35. The diagram shows the structure of the naturally-occurring molecule cholesterol.



cholesterol

Cholesterol reacts with cold, dilute acidified $KMnO_4$.

Four students made claims about this reaction.

W The cyclohexene ring becomes saturated.

X The cyclohexene ring is broken open.

Y The number of chiral centres increases by 1.

Z The number of chiral centres increases by 2.

Which students' claims are correct?

A W and Y

B W and Z

C X and Y

D X and Z

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$$>C=C< \longrightarrow -\underset{OH}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

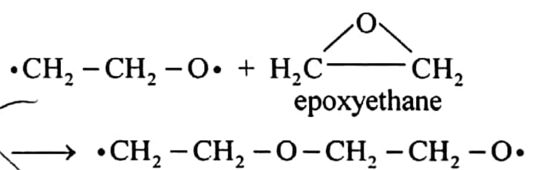
W, X: The cyclohexene ring becomes saturated as the π bond is broken. However, the σ bond is not broken. Hence, the ring is not broken.

Y, Z: The 2 C at the double bond become chiral centre upon reaction with $KMnO_4$. The number of chiral centres increases by 2.

---

36. Non-ionic detergents can be made by reaction of epoxyethane, in an excess, with a C_{11} alcohol.

A possible mechanism involves homolytic fission of a C–O bond in epoxyethane giving rise to a 'double-ended' free radical that initiates a chain reaction. The first propagation step is as follows.



After termination of the reaction with an alcohol, what is a possible formula of such a non-ionic detergent?

A $(CH_3(CH_2)_{10}O)_{10}CH_2CH_2OH$

B $CH_3(CH_2)_{10}O(OCH_2CH_2)_{10}OH$

C $CH_3(CH_2)_{10}O(CH_2CH_2O)_{10}H$

D $CH_3(CH_2)_{10}O(CH_2CH_2O)_{10}OH$

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The base polymeric chain is

$$-\!\!\left(CH_2-CH_2-O\right)\!\!-_n$$

The chain is likely to abstract a H from the alcohol or bond with the O of the alcohol.

In (B) and (D), there are extra O atom in the formula.

Note: O–O bond is weak and hence not likely to be formed.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

37. Which alcohols on oxidation with acidified potassium dichromate(VI) give an organic product which causes an effervescence when reacted with sodium carbonate?

1 butan-1-ol

2 2-methylpropan-1-ol

3 2-methylpropan-2-ol

CH_3
$H_2C-C-CH_2$
OH

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A 1° alcohol is oxidised to a carboxylic acid which can then react with Na_2CO_3 to form CO_2.

(3) is a 2° alcohol.

$$R-CH_2OH + 2[O] \rightarrow RCO_2H + H_2O$$

---

38. Which of the following compounds will react with sodium metal to release hydrogen and also with ethanoyl chloride to release hydrogen chloride?

1 CH_3CH_2OH

2 $CH_3CH(OH)CH_3$

3 C_6H_5OH

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The compound contains an –OH group, e.g. alcohol, phenol.

$$2R-OH + 2Na \rightarrow 2RO^-Na^+ + H_2\uparrow$$
$$R-OH + CH_3COCl \rightarrow R-OCOCH_3 + HCl\uparrow$$

---

39. Which observations will be obtained with the compound $CH_3CH(OH)CH_3$?

1 a yellow precipitate with alkaline aqueous iodine

2 fumes of HCl gas with PCl_5

3 an orange precipitate with a solution of 2,4-dinitrophenylhydrazine

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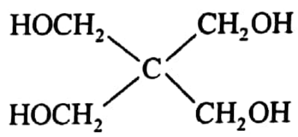
*1. The alcohol contains the $CH_3-\underset{\displaystyle H}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-$ group and hence gives a positive result for triiodomethane test, i.e. I_2/NaOH, heat. Yellow precipitate of CHI_3 would be obtained.

*2 $R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$

3. It is not a carbonyl compound.

---

40. Pentaerythritol is an intermediate in the manufacture of paint.



Pentaerythritol

Which of the following statements about pentaerythritol are correct?

1 It decolourises acidified potassium manganate(VII) on warming.

2 It reacts with metallic sodium.

3 Its empirical formula is CH_3O.

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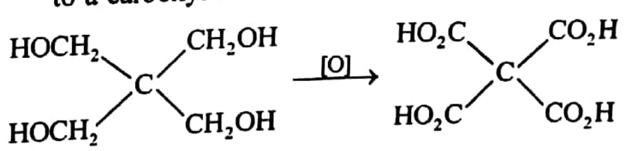
*1. Being a primary alcohol, it can be readily oxidised to a carboxylic acid.



*2. Being an alcohol, it gives H_2 with Na.

$$R-OH + Na \rightarrow R-O^-Na^+ + \tfrac{1}{2}H_2$$

3. Its molecular and empirical formulae are $C_5H_{12}O_4$.

Topic 16 Hydroxy Compounds

41. By varying the conditions of the reaction between propan-1-ol, $CH_3CH_2CH_2OH$, and concentrated sulfuric acid, which of the following compounds can be obtained?

1 $CH_3CH{=}CH_2$
2 $CH_3CH_2CH_2OCH_2CH_2CH_3$
3 $CH_3CH_2CH_2HSO_4$

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*1. Elimination (dehydration):

$$CH_3CH_2CH_2OH \xrightarrow[170\ °C]{conc.\ H_2SO_4} CH_3CH{=}CH_2 + H_2O$$

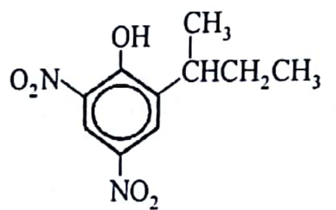
*2. Nucleophilic substitution:

$$2CH_3CH_2CH_2OH \xrightarrow[140\ °C]{conc.\ H_2SO_4} CH_3CH_2CH_2OCH_2CH_2CH_3 + H_2O$$

*3. Nucleophilic substitution:

$$CH_3CH_2CH_2OH + \underset{excess}{conc.\ H_2SO_4} \xrightarrow[0\ °C]{} CH_3CH_2CH_2OSO_3H + H_2O$$

42. *Binapacryl* is used as a fungicide.



Binapacryl

Which of the following statements about *Binapacryl* are correct?

1 Its aqueous solution is acidic.
2 It can exist in optically active forms.
3 It reacts with ethanol in the presence of concentrated sulfuric acid to give an ester.

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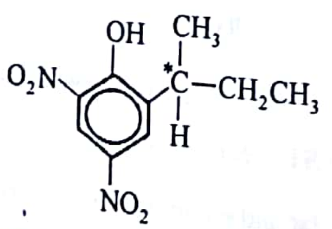

where * : chiral centre

*1. The phenol group is acidic.
*2. There is a chiral C and the compound is non-superimposable with its mirror image.
3. There is no –COOH or –COCl group.

43. When aqueous bromine is added to aqueous phenol, a creamy-white precipitate is obtained. What does this show?

1 A hydroxy group makes the benzene ring more susceptible to electrophilic attack.
2 2-bromophenol is insoluble in water.
3 Phenol is unsaturated.

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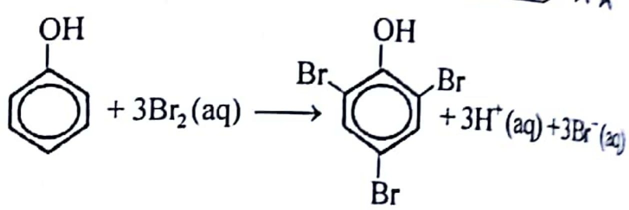

*1. A hydroxy group activates the benzene ring by resonance. The lone pair of electrons of oxygen delocalises into the benzene ring and enhances the electron density of the ring. This makes the ring more susceptible to attack by an electrophile.
2. The white precipitate is 2,4,6-tribromophenol, not 2-bromophenol.
3. The reaction is a substitution. It does not show that phenol is unsaturated (otherwise it will undergo addition instead).

44. Mevalonic acid is an intermediate in the biosynthesis of cholesterol. The acid has a number of functional groups related to this activity.

$$HO_2CCH_2\overset{\overset{OH}{|}}{C}(CH_3)CH_2CH_2OH$$

Which properties does mevalonic acid have?

1 It has only one chiral carbon atom.
2 It can be esterified both by ethanoic acid and by ethanol, in the presence of H^+ ions.
3 It contains both primary and secondary alcohol groups.

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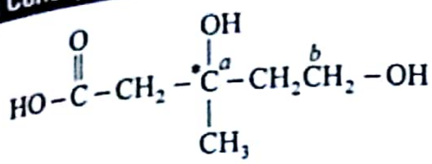
*1.


*2. It is a carboxylic acid and an alcohol. It therefore undergoes esterification with an alcohol and a carboxylic acid respectively.

$$R-\overset{O}{\overset{\|}{C}}-OH + R'-OH \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O$$

3. Carbon *a* - tertiary alcohol
Carbon *b* - primary alcohol

---

45. During the preparation of many organic compounds, by-products are formed. This usually occurs because the reagents can react in more than one way, depending on the conditions used, or because the products formed may react with the reactants.

1-bromopropane may be prepared by slowly adding concentrated sulfuric acid to a mixture of propan-1-ol and sodium bromide, and keeping the reaction mixture cool.

$$CH_3CH_2CH_2OH + HBr$$
$$\rightarrow CH_3CH_2CH_2Br + H_2O$$

What could be a by-product of this reaction if the temperature is allowed to rise?

1 $CH_3CH{=}CH_2$
2 $CH_3CH(Br)CH_3$
3 Br_2

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*1. The alcohol can undergo dehydration with conc. H_2SO_4, especially when heated.

$$CH_3-\underset{H}{\underset{|}{C}H}-\underset{OH}{\underset{|}{C}H_2} \xrightarrow{-H_2O} CH_3-CH{=}CH_2$$

*2. The product from 1 can further react with HBr (electrophilic addition) to form the more stable 2° product.

*3. Br^- can be oxidised by conc. H_2SO_4 to form Br_2.

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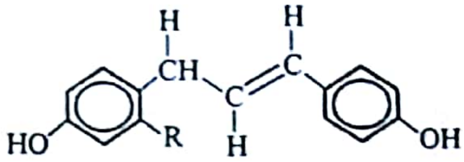
46. The compound shown is secreted by a parasitic plant to enable it to recognise its host before settling and growing on it.



Which reagents would react with this compound?

1 aqueous sodium hydroxide
2 aqueous bromine
3 aqueous sodium carbonate

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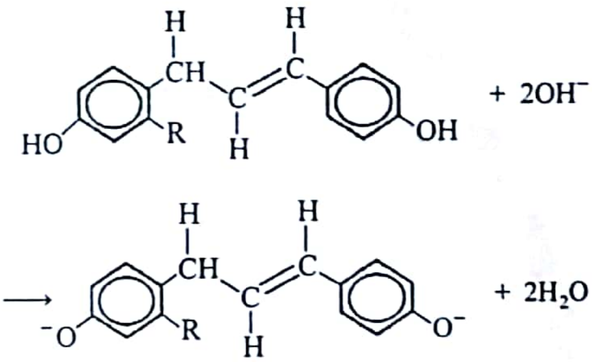
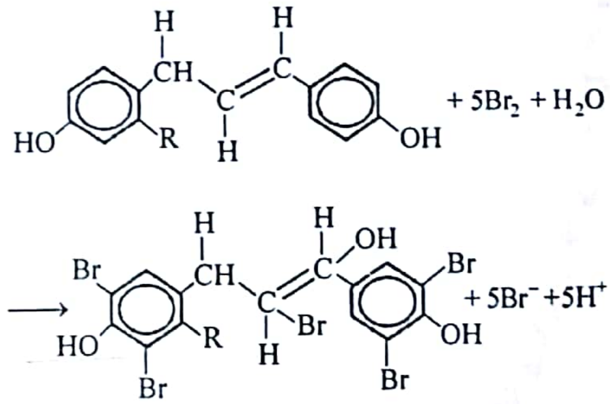
The compound is a phenol and it contains a double bond. Phenol is acidic enough to react with NaOH-neutralisation.

*1.


*2. The compound undergoes electrophilic addition at the double bond and electrophilic substitution at the phenolic rings.



3. There is no reaction. Phenol is not acidic enough to react with Na_2CO_3.

TOPIC

17

Carbonyl Compounds

Key content that you will be examined on:

1. Aldehydes (exemplified by ethanal)
   (i) Oxidation to carboxylic acid
   (ii) Reaction with hydrogen cyanide
   (iii) Characteristic tests for aldehydes
2. Ketones (exemplified by propanone and phenylethanone)
   (i) Reaction with hydrogen cyanide
   (ii) Characteristic tests for ketones

Topic 17

Carbonyl Compounds

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which reagent gives the same visible result with propanal and with propan-2-ol?

A 2,4-dinitrophenylhydrazine reagent

B acidified potassium dichromate(VI)

C concentrated sulfuric acid

D Tollens' reagent

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Both can be oxidised and hence cause a colour change from orange to green.

$$CH_3CHO + [O] \rightarrow CH_3CO_2H$$

$$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

2. When propanal reacts with Tollens' reagent, what are the principal inorganic and organic products?

A Ag and $CH_3CH_2CH_2OH$

B Ag and $CH_3CH_2CO_2H$

C $AgNO_3$ and $CH_3CH_2CO_2H$

D Ag_2O and $CH_3CH_2CO_2H$

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Tollens' reagent $[Ag(NH_3)_2]^+$ is reduced to Ag while aldehydes are oxidised to carboxylic acid.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$

$$\rightarrow CH_3CH_2CO_2^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

3. Which reagent could be used to distinguish between

$CH_3CH(OH)CH_2CHO$ and $CH_3COCH_2CH_2OH$?

A acidified potassium dichromate(VI)

B dilute sulfuric acid

C 2,4-dinitrophenylhydrazine

D Fehling's reagent

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$CH_3CH(OH)CH_2$**CHO** is an aldehyde and it gives a brick-red precipitate, Cu_2O, when heated with Fehling's solution.

Both compounds are alcohols (1° and 2° respectively) and they can be oxidised by $K_2Cr_2O_7$.

Both compounds are carbonyls (aldehyde and ketone respectively) and they form an orange precipitate with 2,4-DNPH. Both do not react with dilute H_2SO_4.

4. Compound **X** changes the colour of acidified sodium dichromate(VI) from orange to green. 1 mol of **X** reacts with 2 mol of HCN(g).

What could **X** be?

A $CH_3COCH_2COCH_3$

B $CH_3CH_2CH_2CHO$

C $H_2C{=}CHCH_2CHO$

D $OHCCH_2CH_2CHO$

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Since 1 mol of **X** reacts with 2 mol of HCN, there are 2 carbonyl functional groups per molecule of **X**. **X** contains either an aldehyde group or 1°/2° alcohol group since it is oxidised by $Cr_2O_7^{2-}$.

(A) is a diketone and does not undergo oxidation. (B) and (C) have only 1 carbonyl group.

5. The product of the reaction between propanone and hydrogen cyanide is hydrolysed under acidic conditions.

What is the formula of the final product?

A $CH_3CH(OH)CO_2H$

B $CH_3CH_2CH(OH)CO_2H$

C $CH_3CH_2CH_2CO_2H$

D $(CH_3)_2C(OH)CO_2H$

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$$CH_3COCH_3 + HCN \rightarrow \underset{\displaystyle CN}{CH_3\underset{|}{C}(OH)CH_3}$$

$$\underset{\displaystyle CN}{CH_3\underset{|}{C}(OH)CH_3} + 2H_2O + H^+ \rightarrow \underset{\displaystyle COOH}{CH_3\underset{|}{C}(OH)CH_3} + NH_4^+$$

6. The table shows the results of simple tests on a compound **S**.

reagent	result
2,4-dinitrophenylhydrazine	positive
Tollens' reagent	negative
alkaline aqueous iodine	positive

From the result of the tests, what could **S** be?

A CH_3CHO

B CH_3COCH_3

C CH_3CH_2CHO

D $CH_3CH(OH)CH_3$

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The results show that S

1. is a carbonyl compound;
2. is not an aldehyde; and
3. has $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-$ group.

(A) and (C) give positive result with Tollens' reagent.
(C) does not give a positive result with I_2/NaOH.
(D) does not give a positive result with 2,4-DNPH.

7. Which statement about ethanal and propanone is **incorrect**?

A Both may be prepared by the oxidation of an alcohol.

B Both change the colour of warm acidified potassium dichromate(VI) from orange to green.

C Both react with 2,4-dinitrophenylhydrazine reagent.

D Both give a positive tri-iodomethane (iodoform) test.

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Propanone, being a ketone, does not undergo oxidation. Ethanal is an aldehyde and hence reduces orange dichromate(VI) to chromium(III).

8. Glucose can be represented by the formula $CH_2OH(CHOH)_4CHO$.
How many moles of ethanoyl chloride would react with one mole of glucose?

A 1 **B** 2

C 4 **D** 5

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Only the OH groups react with acid chloride to give an ester.

$$R-OH + R'COCl \rightarrow R-O-\overset{\displaystyle O}{\overset{\|}{C}}-R' + HCl$$

9. How many structural isomers with the molecular formula C_4H_8O can reduce a solution containing $Ag(NH_3)_2^+$ ions (Tollens' reagent) to form a silver mirror?

A 1 **B** 2

C 3 **D** 4

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To reduce Tollens' reagent, C_4H_8O should be an aldehyde, i.e. C_3H_7CHO.

$$CH_3CH_2CH_2CHO \qquad \underset{\displaystyle CH_3}{CH_3\underset{|}{C}HCHO}$$

10. Which reaction yields a carbon compound incorporating deuterium, D? [D = ^2H]

A $CH_3CH_2CN \xrightarrow[D_2O]{NaOD}$

B $CH_3CD(OD)CO_2H \xrightarrow[heat]{acidified\ KMnO_4}$

C $CH_3COCl_3 \xrightarrow[D_2O]{NaOD}$

D $(CH_3)_3COH \xrightarrow[\text{heat}]{\text{conc. } D_2SO_4}$

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The reaction results in the formation of CH_3COO^- and CDI_3. If H_2O is used instead, CHI_3 will be obtained. The reaction is part of the tri-iodomethane test.

$$CH_3COCH_3 \xrightarrow{I_2/OH^-} CH_3COCI_3$$
$$\xrightarrow{OH^-} CH_3COO^- + CHI_3$$

In (B), X=Y=CH_3CH_2; in (D), X=Y=H. (C) does not undergo nucleophilic addition with HCN.

11. The compound C_3H_7Br undergoes a sequence of reactions as follows:

$$C_3H_7Br \xrightarrow{OH^-(aq)} X \xrightarrow{\text{acidified } K_2Cr_2O_7} Y \xrightarrow{\text{Tollens' reagent}} Z + \text{silver mirror}$$

What could be the formulae for **X**, **Y** and **Z**?

	X	Y	Z
A	$CH_3CH_2CH_2OH$	$CH_3CH_2CO_2H$	CH_3CH_2CHO
B	$CH_3CH_2CH_2OH$	$CH_3CH(OH)CH_2OH$	CH_3CO_2H
C	$CH_3CH_2CH_2OH$	CH_3CH_2CHO	$CH_3CH_2CO_2H$
D	$CH_3CH(OH)CH_3$	CH_3COCH_3	CH_3CO_2H

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The positive result with Tollens' reagent suggests that Y is an aldehyde.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$
$$\rightarrow CH_3CH_2CO_2^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

12. Which compound on reaction with hydrogen cyanide produces a compound with a chiral centre?

A CH_3CHO
B $CH_3CH_2COCH_2CH_3$
C $CH_3CO_2CH_3$
D HCHO

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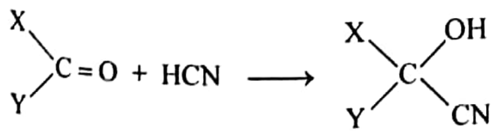

To have a chiral carbon, X and Y have to be different.

13. Which of the following reagents will distinguish between benzaldehyde, C_6H_5CHO, and phenylethanone, $C_6H_5COCH_3$?

A aqueous bromine
B aqueous diamminesilver(I) ions
C 2,4-dinitrophenylhydrazine
D aqueous iron(III) chloride

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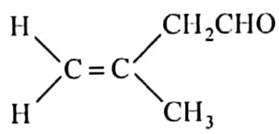
C_6H_5CHO, being an aldehyde, reduces $[Ag(NH_3)_2]^+$ (Tollens' reagent) to give a silver mirror whereas $C_6H_5COCH_3$, being a ketone, is unable to.

$$C_6H_5CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$
$$\rightarrow C_6H_5CO_2^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

14. Compound **P** displays *cis-trans* isomerism and gives a red-brown precipitate with Fehling's solution.

What is **P**?

A



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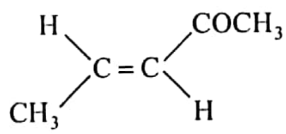

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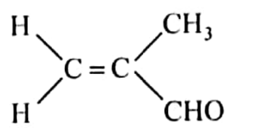

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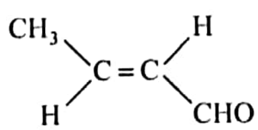

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(A) and (C) do not exhibit *cis-trans* isomerism.

(B) is a ketone and does not reduce Fehling's solution.

(D) is an aldehyde and it gives brick-red ppt. of Cu_2O when heated with Fehling's solution.

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15. Which one of the following compounds will give a precipitate of tri-iodomethane (iodoform) when reacted with iodine and aqueous sodium hydroxide?

A C_6H_5CHO

B $(CH_3)_3COH$

C CH_3CO_2H

D $CH_3CH_2CH(OH)CH_3$

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Positive iodoform test indicates the presence of

$$-\underset{|}{\overset{OH}{C}}HCH_3 \text{ or } -\overset{O}{\overset{\|}{C}}CH_3 .$$

$$CH_3CH_2-\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_3 + 4I_2 + 6OH^-$$

$$\longrightarrow CH_3CH_2-\overset{O}{\overset{\|}{C}}-O^- + 5I^- + CHI_3\downarrow + 5H_2O$$

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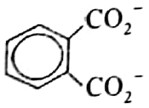
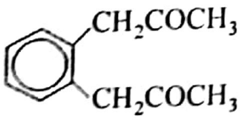
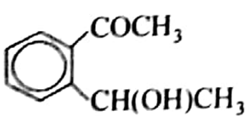
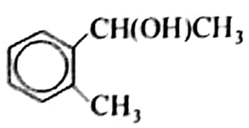
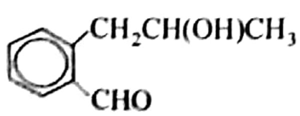
16. Which compound will react with alkaline aqueous iodine to give  ?

A 

B 

C 

D 

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$$R-COCH_3 \xrightarrow{I_2/OH^-} R-CO_2^- + CHI_3$$

$$R-\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow{I_2/OH^-} R-CO_2^- + CHI_3$$

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17. Which one of the following can a solution of iodine in aqueous sodium hydroxide be used to distinguish between members of the pair?

A CH_3CHO and CH_3COCH_3

B CH_3CH_2CHO and CH_3COCH_3

C CH_3CH_2OH and $CH_3CH_2CH(OH)CH_3$

D CH_3OH and CH_3CH_2CHO

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I_2/NaOH gives a positive iodoform test with a compound that has $CH_3-\overset{OH}{\overset{|}{C}}H-$ or $CH_3-\overset{O}{\overset{\|}{C}}-$ group but not others.

$$CH_3COCH_3 + 3I_2 + 4OH^-$$

$$\rightarrow CH_3CO_2^- + CHI_3 + 3H_2O + 3I^-$$

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18. Oxidation of an alkene **X** gives a diol; further oxidation gives a diketone. Which one of the following could be **X**?

A $(CH_3)_2C{=}C(CH_3)_2$

B $CH_3CH{=}C(CH_3)_2$

C $(CH_3)_2CHCH{=}CH_2$

D $C_6H_5CH{=}CHC_6H_5$

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To form a diketone, the carbon atoms at the double bond must be both **mono**-substituted.

$$C_6H_5CH=CHC_6H_5 \rightarrow C_6H_5\underset{OH}{\underset{|}{C}}H\underset{OH}{\underset{|}{C}}HC_6H_5$$

$$\rightarrow C_6H_5\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}C_6H_5$$

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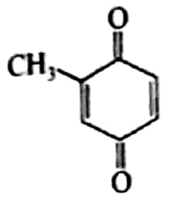
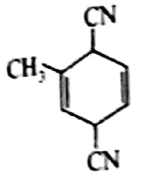
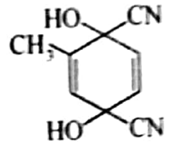
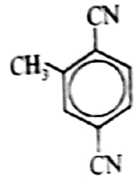
19. The unsaturated diketone shown is excreted by the bombardier beetle.

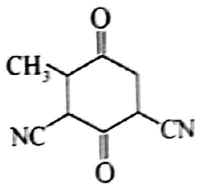


What is formed when this compound reacts with hydrogen cyanide?

A 

B 

C 

D 

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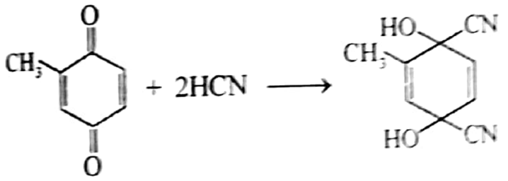
With HCN, nucleophilic addition occurs at the C=O bond to give cyanohydrin:



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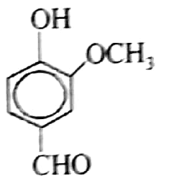
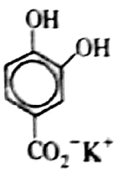
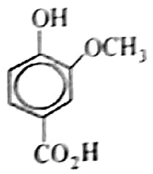
20. *Vanillin* is the main constituent of vanilla flavouring.

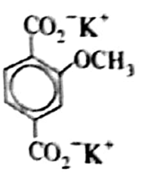


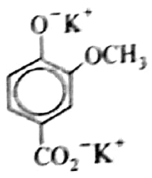
Vanillin

What is the product of its reaction with $KMnO_4$ in aqueous KOH?

A 

B 

C 

D 

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$-OCH_3$ (ether) remains unaffected. Phenol is acidic enough to react with KOH to form the phenoxide.

Aldehydes are readily oxidised to give carboxylate ($-COO^-$) in alkaline medium.

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21. Which one of the following pairs of compounds can the members be distinguished by means of Tollens' test (the use of a solution containing $Ag(NH_3)_2^+$)?

A HCHO and CH_3CHO

B CH_3CHO and CH_3COCH_3

C CH_3COCH_3 and $C_6H_5COCH_3$

D CH_3COCH_3 and $CH_3CO_2CH_3$

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CH_3CHO, being an aldehyde, reduces $[Ag(NH_3)_2]^+$ to form a Ag mirror. CH_3COCH_3 is a ketone and it does not reduce Tollens' reagent.

$$R-CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$
$$\rightarrow R-CO_2^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

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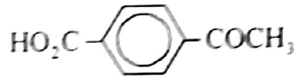
22. The diagram shows the structure of a compound.



It is suggested that this compound

1 gives a precipitate when warmed with Fehling's solution;

2 gives an orange precipitate with 2,4-dinitrophenylhydrazine.

Which suggestions are correct?

A 1 only

B 2 only

C both 1 and 2

D neither 1 nor 2

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1: The compound is a ketone (not aldehyde) and hence does not react with Fehling's solution.

2: The compound is a carbonyl and it reacts with 2,4-DNPH to form an orange ppt.

23. 2,3-dihydroxypropanal, $HOCH_2CH(OH)CHO$, and 1,3-dihydroxypropanone, $HOCH_2COCH_2OH$, may each be prepared by the mild oxidation of $HOCH_2CH(OH)CH_2OH$.

Which statement is correct for **both** 2,3-dihydroxypropanal **and** 1,3-dihydroxypropanone?

A They are chiral.

B They give a silver precipitate with Tollens' reagent.

C They give a yellow precipitate with alkaline aqueous iodine.

D They have the same empirical formula.

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A: The ketone is achiral.

B: The ketone shows negative result with Tollen's reagent.

C: Both show no yellow ppt.

D: The empirical formula is CH_2O.

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24. Which of the following reagents will give similar results for both butanone and butanal?

A acidified aqueous potassium dichromate(VI).

B an alkaline solution containing complexed Cu^{2+} ions (Fehling's solution)

C iodine and aqueous sodium hydroxide

D 2,4-dinitrophenylhydrazine reagent

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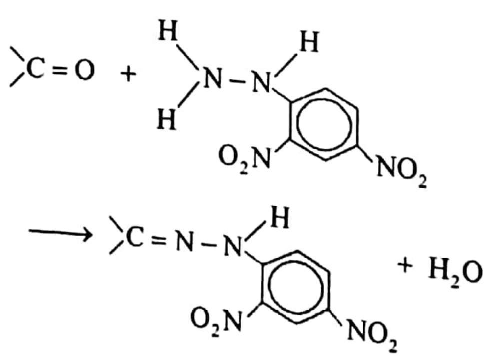
2,4-dinitrophenylhydrazine reacts with a carbonyl to give orange precipitates of 2,4-dinitrophenylhydrozone irrespective of whether the carbonyl is a ketone or an aldehyde.



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25. The production of light by animals and plants is known as bioluminescence. It sometimes involves the following reaction:

$$CH_3(CH_2)_8CHO \xrightarrow{\text{enzyme}} CH_3(CH_2)_8CO_2H$$

Which reagent could be used in the laboratory to carry out this conversion?

A acidified $Na_2Cr_2O_7$

B concentrated H_2SO_4

C KOH in ethanol

D $LiAlH_4$ in ether

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The process is an oxidation. A suitable oxidising agent has to be used.

$$R-CHO + [O] \rightarrow R-CO_2H$$

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26. Hydrogen cyanide adds to ketones. The table shows the relative rates of reaction under different conditions.

condition	*relative rate*
aqueous solution	slow
acidified solution	virtually zero
alkaline solution	very rapid

Which of the following is likely to be involved in the rate-determining step of the reaction?

A CN^- **B** OH^-

C H^+ **D** HCN

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$$HCN \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H^+ + CN^-$$

In an aqueous solution, HCN is weakly ionised to CN^- and the addition reaction is slow. Addition of acid suppresses the ionisation (no CN^-) and there is virtually no reaction. On the other hand, in the alkaline medium, the equilibrium shifts to the right and produces large quantity of CN^-. The reaction becomes very rapid.

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27. A compound **Q**, $C_4H_{10}O$, gives the compound **R**, C_4H_8O, on oxidation. **R** gives a yellow precipitate on warming with alkaline aqueous iodine.

Which of the following could be Q?

A $CH_3CH_2CH_2CH_2OH$

B $(CH_3)_2CHCH_2OH$

C $CH_3CH_2CH(OH)CH_3$

D $(CH_3)_3COH$

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Q is an alcohol and **R** is a ketone. Since **R** gives positive tri-iodomethane test, **R** is a methyl ketone,

i.e. $X-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$. Therefore, Q is $X-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$.

$$CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{C}HCH_3 + [O] \rightarrow CH_3CH_2\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 + H_2O$$

$$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + 3I_2 + 4OH^-$$

$$\rightarrow CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + 3I^- + CHI_3\downarrow + 3H_2O$$

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28. The exhaled breath of diabetics contains propanone.

A medical student wishes to test for diabetes by asking patients to bubble their breath through a reagent.

Which reagent could give a positive result?

A alkaline aqueous iodine

B aqueous bromine

C Fehling's reagent

D Tollens' reagent

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Propanone contains $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-$ group. Hence, it gives a positive tri-iodomethane test.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3I_2 + 4OH^-$$

$$\xrightarrow{heat} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + CHI_3 + 3I^- + 3H_2O$$

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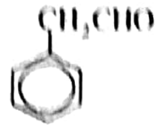
29. Smoke from a bonfire contains a compound that causes irritation to the eyes. This compound readily decolourises aqueous bromine and produces a precipitate of silver when bubbled into Tollens' reagent.

What is a possible structure of the compound?

A $CH_2=CHCH_2OH$ **B** $CH_2=CHCHO$

C  **D** 

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The functional groups present in the compound are C=C bond (readily decolourises aqueous Br_2) and aldehydic group (–CH=O). Only the compound shown in (B) has both these groups present.

---

30. Ethanal can react with ammonia as shown.

$$CH_3CHO + NH_3 \rightarrow CH_3CH(OH)NH_2$$

Which type of chemical reaction takes place?

A addition-elimination

B electrophilic addition

C free radical addition

D nucleophilic addition

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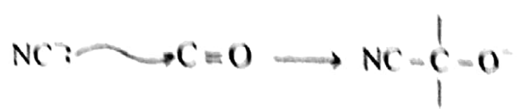
The reaction is basically that of an addition, with NH_3 functioning as a nucleophile and attacking the electron deficient carbonyl carbon.

This reaction is similar to that of a carbonyl and HCN in the presence of a base.



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31. Almond essence is used to flavour foods. A student tested a sample of almond essence using 2,4-dinitrophenylhydrazine reagent and obtained coloured crystals which had a sharp melting point.

Which class of compound gives this positive result?

A alcohols
B aldehydes
C amines
D carboxylic acids

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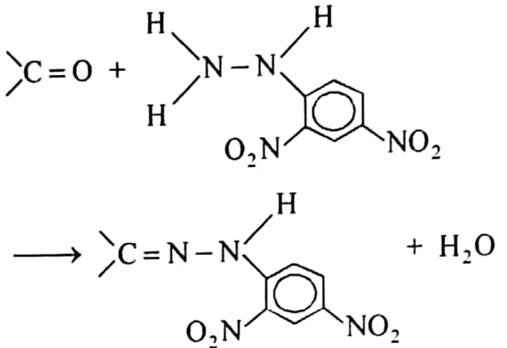
Carbonyl compounds (aldehydes and ketones) give bright coloured ppt. with 2,4-DNPH.



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32. One of the earliest biotechnological processes, developed by Weizmann in 1911, was the conversion of starch into propanone and butan-1-ol.

Which reagent could be used to confirm the presence of propanone in a propanone/butan-1-ol mixture?

A Na
B I_2 in NaOH(aq)
C acidified $K_2Cr_2O_7$(aq)
D $AgNO_3$(aq) with an excess of NH_3(aq)

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$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3I_2 + 4OH^-$$
$$\longrightarrow CH_3CO_2^- + 3I^- + CHI_3 + 3H_2O$$

Butan-1-ol, $CH_3CH_2CH_2CH_2OH$, does not contain CH_3–CHOH group and therefore does not give a yellow precipitate of CHI_3 with I_2/NaOH.

---

33. An organic compound has the following properties:

it gives a positive tri-iodomethane (iodoform) test;
it is readily oxidised to ethanoic acid;
it does not react with Fehling's reagent.

Which compound would give these results?

A CH_3CH_2CHO
B CH_3CH_2OH
C $CH_3CH_2COCH_3$
D $CH_3CH_2COCH_2CH_3$

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CH_3CH_2OH contains $CH_3-\underset{}{\overset{|}{C}}H-OH$ group.

$$CH_3CH_2OH + 4I_2 + 6OH^-$$
$$\rightarrow HCO_2^- + CHI_3 + 5I^- + 5H_2O$$

CH_3CH_2OH is a primary alcohol.

$$CH_3CH_2OH + 2[O] \rightarrow CH_3CO_2H + H_2O$$

CH_3CH_2OH is not an aldehyde and hence is not oxidised by Fehling's solution.

---

34. 4-Methylpentan-2-one, MIBK, is a solvent used in a glue:

$$(CH_3)_2CHCH_2COCH_3$$
MIBK

When the glue is tested, which result could be due to the presence of MIBK?

A It gives an orange precipitate on boiling with Fehling's solution.
B It is oxidised and gives a green colouration on warming with aqueous potassium chromate(VI).
C It gives a yellow precipitate on warming with alkaline aqueous iodine.
D It gives a sweet-smelling liquid on warming with benzoic acid.

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MIBK is a ketone that contains the $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ group. Thus, it gives a positive result with the tri-iodomethane test where a yellow CHI_3 precipitate is formed.

$$-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3I_2 + 4OH^- \rightarrow -\overset{\overset{\displaystyle O}{\|}}{C}-O^- + CHI_3 + 3H_2O + 3I^-$$

---

35. The structures for two alarm pheromones for ants are given.

$CH_3CH_2CH_2CH{=}CHCHO$
and $CH_3CH_2CH(CH_3)COCH_2CH_3$

Which characteristic applies to both compounds?

A Both can be obtained by the oxidation of alcohols.

B Both decolourise aqueous bromine.

C Both decolourise dilute alkaline potassium manganate(VII)

D Both show optical isomerism.

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$$CH_3CH_2CH_2CH{=}CHCH_2OH + [O] \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} CH_3CH_2CH_2CH{=}CHCHO + H_2O$$

$$CH_3CH_2CH(CH_3)CH(OH)CH_2CH_3 + [O] \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} CH_3CH_2CH(CH_3)COCH_2CH_3 + H_2O$$

B: The aldehyde decolourises $Br_2(aq)$ since it is also an alkene, but the ketone does not.

$$>C=C< + H_2O + Br_2 \longrightarrow -\underset{Br}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

C: The aldehyde and alkene are oxidised, but not the ketone.

D: The aldehyde does not show optical isomerism.

Propene, being electron rich, repels CN^-. It readily suffers electrophilic attack instead.

---

36. Why does hydrogen cyanide add to propanone but not to propene?

A The addition product formed with propene would not be stable.

B Propanone is more susceptible to nucleophilic attack than propene.

C Propanone is more susceptible to electrophilic attack than propene.

D Propanone is more susceptible to free radical attack than propene.

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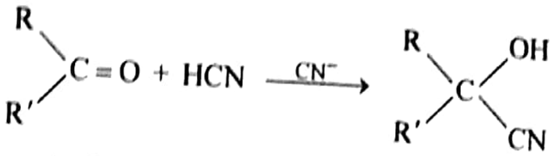
Propanone (a ketone) undergoes nucleophilic addition readily with HCN due to the presence of a partial positive charge on the carbon of the carbonyl. This electron deficient carbon suffers nucleophilic attack by CN^-.

$$CH_3-\overset{\overset{O^{\delta-}}{||}}{\underset{\delta+}{C}}-CH_3 + :CN^- \xrightarrow{H^+} CH_3-\underset{CN}{\overset{OH}{C}}-CH_3$$

37. Cyanohydrins can be mde from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.



In a similar reaction, $^-CH_2CO_2CH_3$ ions are generated from $CH_3CO_2CH_3$ by strong bases.

Which compound can be made from an aldehyde and $CH_3CO_2CH_3$?

A $CH_3CH(OH)CO_2CH_3$

B $CH_3CO_2CH_2CH(OH)CH_3$

C $CH_3CH_2CH(OH)CH_2CO_2CH_3$

D $(CH_3)_2C(OH)CH_2CO_2CH_3$

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The overall reaction shows the addition of HA across C=O.

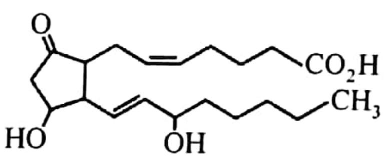
$$>C=O + HA \longrightarrow -\overset{A}{\overset{|}{C}}-OH$$

When $CH_3CO_2CH_3$ is used where A = $-CH_2CO_2CH_3$, the product would be

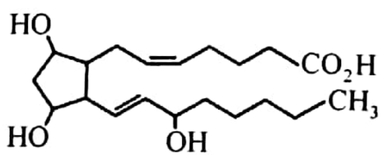
$$-\overset{CH_2CO_2CH_3}{\overset{|}{C}}-OH \quad \text{i.e.} \quad -\overset{|}{C}(OH)CH_2CO_2CH_3.$$

---

38. PGE_2 and $PGF_{2\alpha}$ are two prostaglandins, both with pharmacological activity.



PGE_2



$PGF_{2\alpha}$

Which reagent will convert PGE_2 into $PGF_{2\alpha}$ efficiently?

A H_2/Ni B H_2/Pt

C H_2O/H^+ D $NaBH_4$

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The C=O group in PGE_2 can be reduced to form C–OH group in $PGE_{2\alpha}$ by a suitable reducing agent ($NaBH_4$) without affecting the C=C double bond and –COOH group.

H_2/Ni and H_2/Pt will reduce C=O and also hydrogenate C=C double bond.

H_2O/H^+ does not reduce C=O and it will hydrate the C=C double bond to form $\begin{array}{cc} | & | \\ -C- & C- \\ | & | \\ H & OH \end{array}$.

39. Which reaction will occur without a colour change being observed?

A phenylethanal, $C_6H_5CH_2CHO$, + Fehling's reagent

B phenylethene, $C_6H_5CHCH_2$, + cold dilute acidified potassium manganate(VII)

C phenol, C_6H_5OH, + aqueous sodium hydroxide

D phenol, C_6H_5OH, + dilute nitric acid

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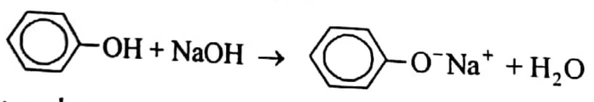
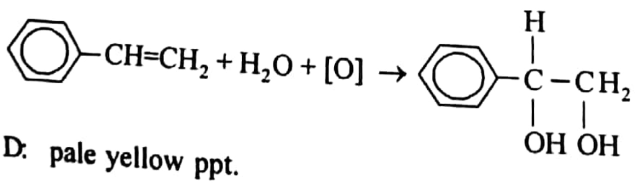
There is an acid-base reaction and there is no colour change during the reaction.

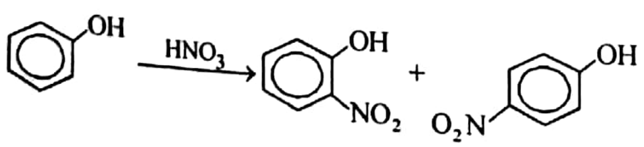


A: red ppt.

B: decolourisation of $KMnO_4$



D: pale yellow ppt.



40. One industrial preparation of ethanoic acid is the direct carbonylation of methanol using a rhodium catalyst.

$$CH_3OH + CO \xrightarrow[\text{catalyst}]{\text{rhodium}} CH_3CO_2H$$

Which compound could be expected to produce $\begin{array}{l} CO_2H \\ | \\ HC-CH_2CO_2H \\ | \\ CH_2CO_2H \end{array}$ by this method.

A $\begin{array}{l} OH \\ | \\ HC-CO_2H \\ | \\ CH_2OH \end{array}$

B $\begin{array}{l} CH_2OH \\ | \\ HC-CH_2CO_2H \\ | \\ CH_2CO_2H \end{array}$

C $\begin{array}{l} OH \\ | \\ HC-CH_2CO_2H \\ | \\ CO_2H \end{array}$

D $\begin{array}{l} OH \\ | \\ HC-CH_2CO_2H \\ | \\ CH_2OH \end{array}$

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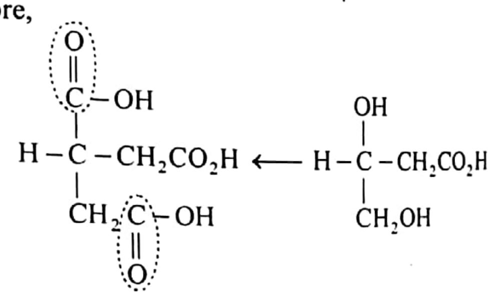
From the given equation, the overall result is the insertion of a carbonyl group into the C–O bond,

i.e. $-\overset{|}{\underset{|}{C}}-OH + CO \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-OH.$

Therefore,



41. Butanedione, $CH_3COCOCH_3$, is a yellow liquid which is responsible for the cheese-like smell in cheese and from unwashed feet.

How does butanedione reacts with 2,4-dinitrophenylhydrazine reagent and Fehling's reagent?

	2,4 - dinitrophenylhydrazine	Fehling's
A	positive	positive
B	positive	negative
C	negative	positive
D	negative	negative

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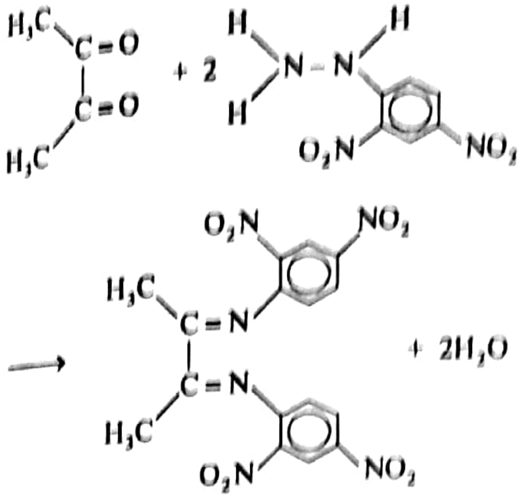
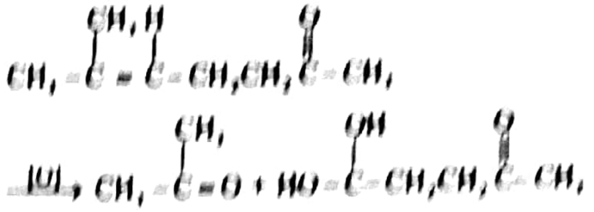
$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$$

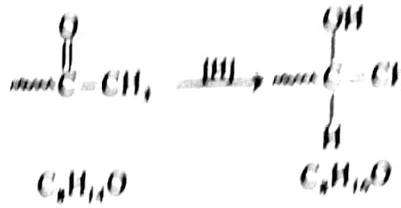
Butanedione is a diketone. It gives an orange precipitate with 2,4-dinitrophenylhydrazine but shows no reaction with Fehling's reagent.



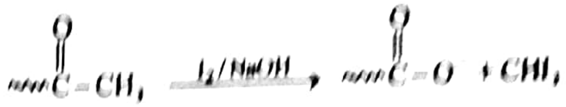
(B)



(C) The ketone is reduced to an alcohol while the alkene is not affected.



(D)



($CH_3CO_2^-$ is not formed.)

42. Cattle suffering from stress produce 6-methylhept-5-en-2-one, which repels mosquitos.

$$(CH_3)_2C=CHCH_2CH_2COCH_3$$

6-methylhept-5-en-2-one

Which property will 6-methylhept-5-en-2-one possess?

A Addition of $Br_2(aq)$ produces a chiral compound.

B Prolonged heating with acidified concentrated $KMnO_4$ produces $HO_2CCH_2CO_2H$.

C Reduction by a methanolic solution of $NaBH_4$ produces a compound $C_8H_{18}O$.

D Warming with alkaline aqueous I_2 produces CH_3CO_2H.

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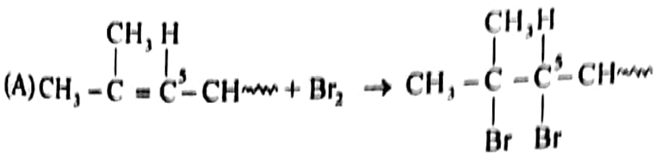


The compound is an alkene and it undergoes electrophilic addition with Br_2. C^5 in the product formed is a chiral centre.

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

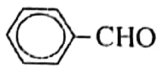
The responses A to D should be selected on the basis of

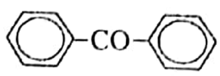
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

43. Which carbonyl compounds could be easily oxidised to carboxylic acids that are readily soluble in cold water?

1 CH_3CH_2CHO

2 

3 

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*1. $CH_3CH_2CHO + [O] \rightarrow CH_3CH_2CO_2H$
$CH_3CH_2CO_2H$ readily dissolves in H_2O.

2. Although C_6H_5CHO, an aldehyde, can be oxidised to $C_6H_5CO_2H$, the acid does not readily dissolve in H_2O due to the presence of the large hydrophobic benzene ring.

3. The ketone is not readily oxidised to an acid.

---

44. How can the rate of reaction between ethanal and aqueous hydrogen cyanide be increased?

1 by irradiation with ultraviolet light

2 by a rise in temperature

3 by the addition of a small quantity of aqueous sodium cyanide

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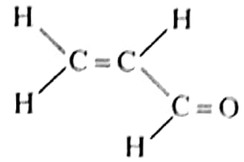
1. The reaction does not proceed via a free radical mechanism and so the rate of reaction will not be increased by irradiation with uv light.

*2. A rise in temperature increases the proportion of molecules having energy greater than or equal to the activation energy. This increases the rate of successful collision and hence the rate of reaction.

*3. The rate of reaction is increased as CN^- acts as a catalyst and increases the rate of reaction.

---

45. *Acrolein* is produced in photochemical smog. It has a strong smell, irritates eyes and mucous membranes and is carcinogenic.



acrolein

What can be deduced from this structure?

1 All bond angles are approximately 120°.

2 It will undergo electrophilic addition reactions.

3 It will undergo nucleophilic addition reactions.

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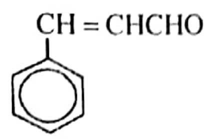
*1. The shape w.r.t. to each C is trigonal planar (3 regions of electron cloud). Hence, the bond angles are all 120°.

*2. Electrophilic addition occurs at the C=C double bond.

*3. Nucleophilic addition occurs at the C=O double bond.

---

46. Cinnamaldehyde is an essential oil with the distinctive odour of cinnamon.



cinnamaldehyde

Which of the following statements about cinnamaldehyde is correct.

1 It is optically active.

2 It decolourises aqueous bromine.

3 It reacts with 2,4-dinitrophenylhydrazine reagent.

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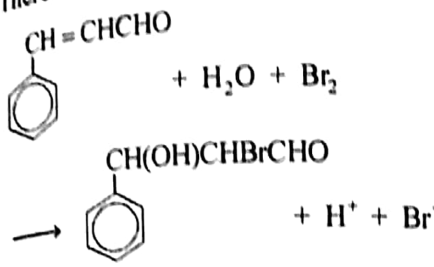
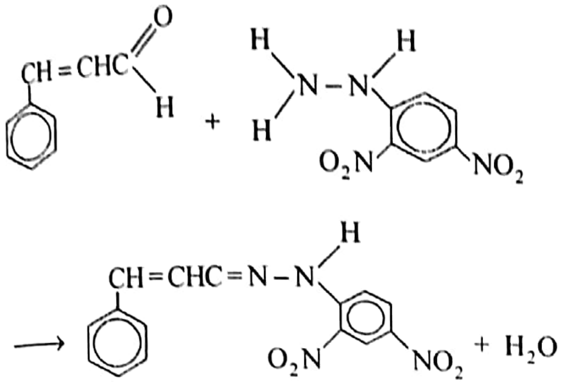
Cinnamaldehyde contains a double bond and an aldehyde group.

1. There is no chiral centre.

*2. 

*3. 

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47. Citral, which occurs in lemongrass oil, has the following structural formula.

$$\underset{\displaystyle CH_3}{\underset{|}{CH_3\,C}}=CHCH_2CH_2\,\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle H}{\underset{|}{CH\,C}}=O$$

From this, it can be deduced that citral will

1 decolourise dilute aqueous potassium manganate(VII).

2 give a silver mirror with aqueous diammine silver(I) ions (Tollens' reagent).

3 give a sweet smelling oil with ethanoic acid, when heated under reflux with a drop of concentrated sulfuric acid.

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The functional groups present in citral are double bonds and aldehyde. Therefore, it is expected that:

*1. Both the functional groups are oxidised by $KMnO_4$ to acids.

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CHCH_2CH_2\,\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle H}{\underset{|}{CH\,C}}=O+8[O]$$

$$\rightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O+O=\underset{\displaystyle OH}{\underset{|}{C}}-CH_2CH_2\,\underset{\displaystyle CH_3}{\underset{|}{C}}=O+2CO_2+H_2O$$

*2. The aldehyde reduces Tollens' reagent to Ag.

3. It is unable to form ester with ethanoic acid since it contains no –OH group.

---

48. Deuterium, D, is the ${}^{2}_{1}H$ isotope of hydrogen. Which reactions could give an organic compound having a chiral centre?

1 $CH_3COCH_3 \xrightarrow[\text{NaCN in } D_2O]{DCN,}$

2 $CH_3CH=CHCH_3 \xrightarrow{DBr}$

3 $CH_3CHO \xrightarrow[D_2O]{NaBD_4}$

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1. Nucleophilic addition:

$$CH_3COCH_3 \xrightarrow{DCN} CH_3-\overset{\displaystyle OD}{\overset{|}{\underset{\displaystyle CN}{\underset{|}{C}}}}-CH_3$$

*2. Electrophilic addition:

$$CH_3CH=CHCH_3 \xrightarrow{DBr} CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle D}{\underset{|}{{}^{*}C}}}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C^{*}}}}}-CH_3$$

There are 2 chiral centres.

*3. Reaction:

$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow[D_2O]{NaBD_4} CH_3-\overset{\displaystyle OD}{\overset{|}{\underset{\displaystyle D}{\underset{|}{C^{*}}}}}-H$$

---

49. Which of the following reagents react in a similar manner both with ethanal and with benzaldehyde?

1 alkaline aqueous iodine

2 a solution of 2,4-dinitrophenylhydrazine

3 aqueous diamminesilver ions (Tollens' reagent)

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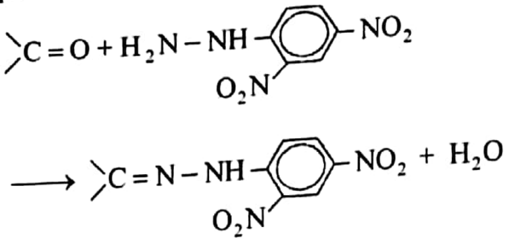
1. Ethanal gives a yellow precipitate of CHI_3, but benzaldehyde does not.

$$CH_3CHO + 3I_2 + 4OH^-$$
$$\rightarrow CHI_3\downarrow + HCO_2^- + 3I^- + 3H_2O$$

*2. Both being carbonyl compounds, give orange precipitates with 2,4-dinitrophenylhydrazine.

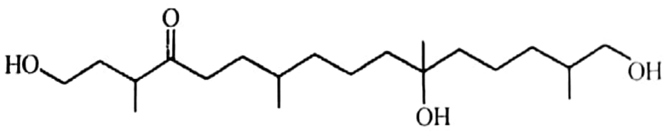


*3. Both being aldehydes, reduce Tollens' reagent to give silver mirrors.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$
$$\rightarrow RCOO^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

---

50. The mould *Phytophthora* damages many plants, destroying agricultural crops such as potatoes. A hormone-like compound called alpha 1 regulates the reproduction of all species of *Phytophthora*. The structure of alpha 1 is now known, giving scientists a key to the possible future eradication of the mould.



alpha 1

Which will react with alpha 1?

1 Cl_2(g)/light
2 $SOCl_2$
3 H_2/Pt

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The compound has the following functional groups:

–OH (alcohol)

O=C< (ketone)

*1. The alkyl chain can undergo free radical substitution with Cl_2/uv.

*2. The –OH groups will react to give –Cl.

$$R\text{–}OH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$

*3. The O=C< group can be reduced to form an alcohol.

$$O{=}C\langle + H_2 \xrightarrow{Pt} HO\text{–}\overset{|}{\underset{|}{C}}\text{–}H$$

---

51. All of the following reagents react with ethanal, CH_3CHO.

Which reagents give a product that retains the C–C= structure?

1 2,4-dinitrophenylhydrazine reagent
2 ethanolic hydrogen cyanide
3 lithium tetrahydridoaluminate(III), $LiAlH_4$

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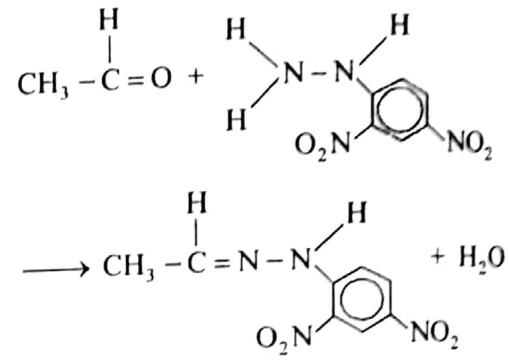
*1.

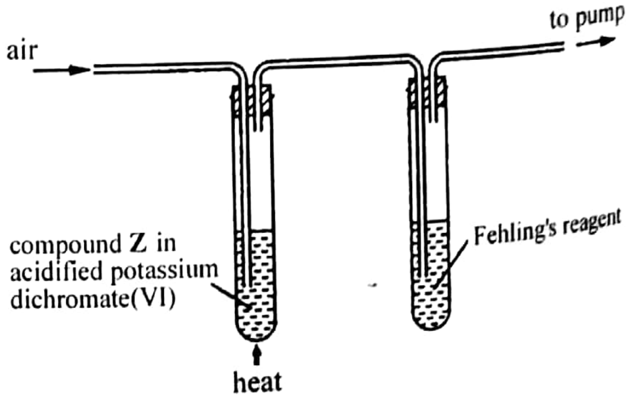


2.
$$CH_3-\overset{H}{\overset{|}{C}}=O + HCN \longrightarrow CH_3-\overset{H}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-OH$$

3.
$$CH_3-\overset{H}{\overset{|}{C}}=O + 2[H] \xrightarrow{LiAlH_4} CH_3-CH_2-OH$$

---

52. When the apparatus below was used with compound **Z**, a brick-red precipitate formed in the right-hand tube.



Which compound could be **Z**?

1 $CH_3CH(OH)CH_3$
2 $CH_3CH_2CH_2OH$
3 CH_3OH

Helping Concepts *Exam Favourite Rating* ★★★

1. $CH_3CH(OH)CH_3$ is a 2° alcohol and it gives CH_3COCH_3, a ketone, upon oxidation by $Cr_2O_7^{2-}$ and it has no effect on the Fehling's reagent.

*2, *3. Both are 1° alcohols and give aldehydes upon oxidation. The aldehydes formed give a brick-red ppt. of Cu_2O with Fehling's solution.

---

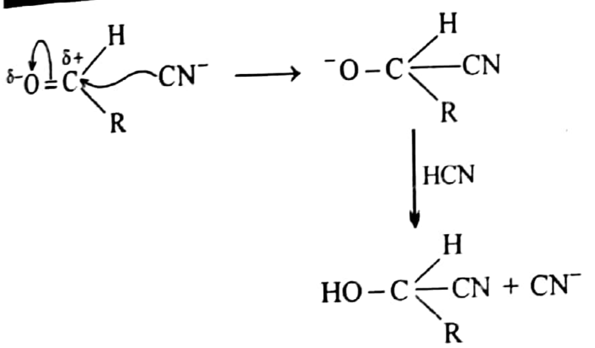
53. In the reaction between an aldehyde and HCN catalysed by NaCN, which of the following statements about the reaction mechanism are true?

1 A new carbon-carbon bond is formed.

2 In the intermediate, the oxygen carries a negative charge.

3 The last stage involves the formation of a hydrogen-oxygen bond.

Helping Concepts *Exam Favourite Rating* ★★



A new C–C bond is formed in the 1st step, resulting in the formation of the intermediate with a negative charge on oxygen. The last step involves the abstraction of a proton from HCN to form the O–H bond, yielding the product.

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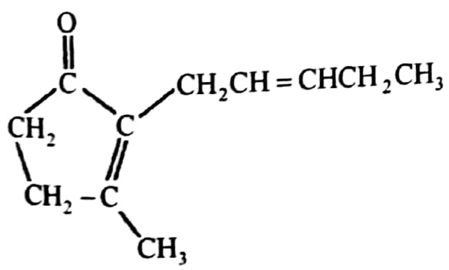
54. Jasmone is the active ingredient of Jasmine. It is extracted from Jasmine flowers for perfume.



jasmone

Which of the following reagents, when added to jasmone, would show a change of colour?

1 dilute acidified potassium manganate(VII)

2 bromine

3 Fehling's or Tollens' reagent

Helping Concepts *Exam Favourite Rating* ★★★

*1. $>C=C< + [O] + H_2O \rightarrow -\underset{OH}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$

$KMnO_4$ would be decolourised.

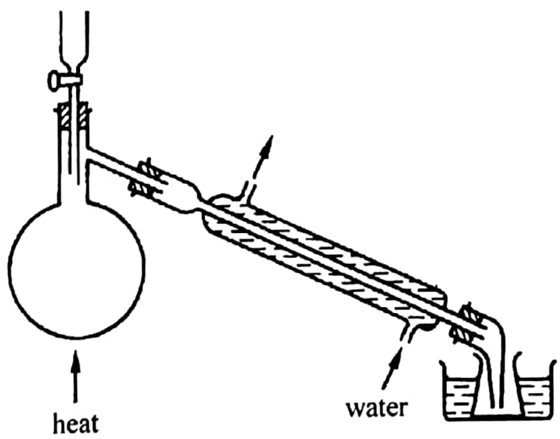
*2. $>C=C< + Br_2 \rightarrow -\underset{Br}{\overset{|}{\underset{|}{C}}}-\underset{Br}{\overset{|}{\underset{|}{C}}}-$

Br_2 would be decolourised.

3. Jasmone is a ketone (not an aldehyde) and it shows no reaction with Fehling's and Tollens' reagents.

---

55. The diagram shows some laboratory apparatus.



Which preparations could this apparatus be used for?

1 bromoethane, from ethanol, sodium bromide and concentrated sulfuric acid

2 ethanal, from ethanol, sodium dichromate(VI) and sulfuric acid

3 1,2-dibromoethane, from bromine and ethene

Helping Concepts *Exam Favourite Rating* ★★★

*1. $Br^- + CH_3CH_2OH + H^+ \rightarrow CH_3CH_2Br + H_2O$

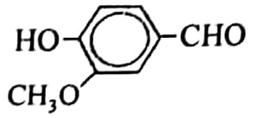
CH_3CH_2Br is the most volatile among all the reactants and products. Hence, it can be distilled off and be collected.

*2. $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$
Once CH_3CHO is formed, it is distilled off immediately because it is the most volatile (unlike CH_3CH_2OH, it is not capable of H-bonding). However, ethanal has a very low boiling point and ice-cold H_2O has to be used to condense it.

3. Ethene is a gas!

---

56. Vanillin is the active ingredient of vanilla.



vanillin

Which of the following will be observed with vanillin?

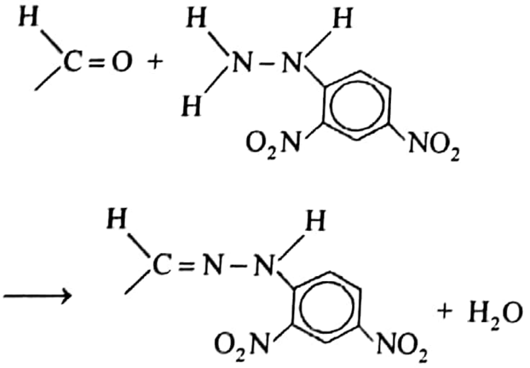
1 Warm acidified potassium dichromate(VI) turns green.
2 2,4-dinitrophenylhydrazine reagent gives a coloured precipitate.
3 A yellow precipitate is formed on warming with aqueous, alkaline iodine.

Helping Concepts *Exam Favourite Rating* ★★★

*1. –CHO group is oxidised to –COOH where $Cr_2O_7^{2-}$ is reduced to green Cr^{3+}.

$$RCHO + [O] \rightarrow RCO_2H$$

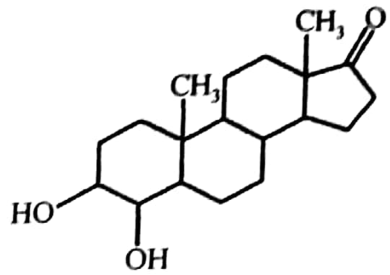
*2.



3. $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-$ group and $CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-$ group are absent.

---

57. The steroid shown is an intermediate compound obtained during the synthesis of *Formestane* which is used in the treatment of breast cancer.



Which statements about this compound are correct?

1 It reacts with hydrogen cyanide in a nucleophilic addition reaction.
2 It can be oxidised by warm acidified potassium dichromate(VI) to a carboxylic acid.
3 It will react with Fehling's solution.

Helping Concepts *Exam Favourite Rating* ★★★

*1. The carbonyl group undergoes nucleophilic addition with HCN.

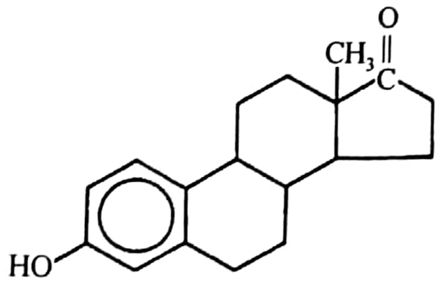
$$>C=O + HCN \xrightarrow{\text{base}} -\overset{|}{\underset{\underset{\displaystyle CN}{|}}{C}}-OH$$

2. The 2° alcohol groups are oxidised to ketones, not carboxylic acid.

3. It does not contain an aldehyde group. Hence, it does not react with Fehling's solution.

---

58. The sex hormone, oestrone, has the structure shown below.



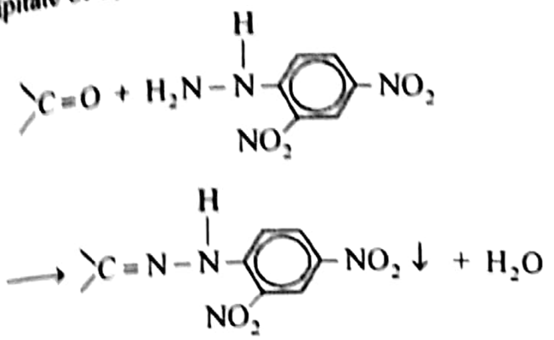
Which of the following reactions would oestrone be expected to undergo?

1 It gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent.
2 It gives hydrogen with metallic sodium.
3 It forms an ester with ethanoyl chloride.

Helping Concepts *Exam Favourite Rating* ★★★

The functional groups present are ketone and phenol.

*1. The carbonyl reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate of 2,4-dinitrophenylhydrazone.



*2. Being a phenol, it acts as an acid and releases H_2 on reacting with a reactive metal.

$$2ArOH + Na \rightarrow 2ArO^-Na^+ + H_2\uparrow$$

*3. Although unable to form an ester with a carboxylic acid, it does react with an activated acid, e.g. ethanoyl chloride to give an ester.

$$ArOH + CH_3COCl \rightarrow CH_3COOAr + HCl\uparrow$$

---

59. Compounds **P** and **Q** have the following formulae:

$HOCH_2CH(OH)CHO$ (**P**) $HOCH_2COCH_2OH$ (**Q**)

Which of the following statements apply to these compounds?

1 **P** can be directly oxidised to **Q**.

2 **P** and **Q** can both be reduced to $HOCH_2CH(OH)CH_2OH$.

3 Both **P** and **Q** react with ethanoyl chloride to form esters.

Helping Concepts *Exam Favourite Rating* ★★★

1. **P** cannot be directly oxidised to **Q** because both the two alcohol groups and the aldehyde group would be oxidised.

$$HO-CH_2-CH(OH)-C(=O)-H \rightarrow HOOC-C(=O)-COOH$$

The product may be further oxidised to CO_2 and H_2O.

*2. The aldehyde group in **P** and the ketone group in **Q** would be reduced.

$$HO-CH_2-CH(OH)-C(=O)-H \rightarrow HO-CH_2-CH(OH)-CH_2(OH)$$

$$HO-CH_2-C(=O)-CH_2-OH \rightarrow HO-CH_2-CH(OH)-CH_2-OH$$

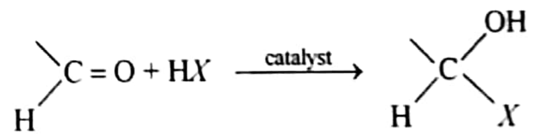
*3. Both **P** and **Q** are alcohols and they react with ethanoyl chloride to form esters.

$$HO-CH_2-CH(OH)-CHO + 2CH_3COCl \rightarrow CH_3C(=O)-O-CH_2-CH(O-C(=O)-CH_3)-CHO + 2HCl$$

$$HO-CH_2-C(=O)-CH_2OH + 2CH_3COCl \rightarrow CH_3-C(=O)-O-CH_2-C(=O)-CH_2-O-C(=O)-CH_3 + 2HCl$$

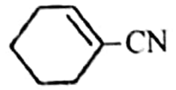
---

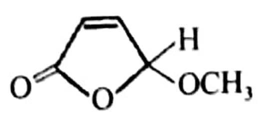
60. There is a range of reactions of the aldehyde group which have the pattern

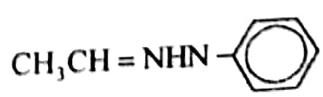


of which the formation of a cyanohydrin (where X = CN) is one.

Which compounds could be obtained by such an addition to an aldehyde group, followed by a dehydration?

1 

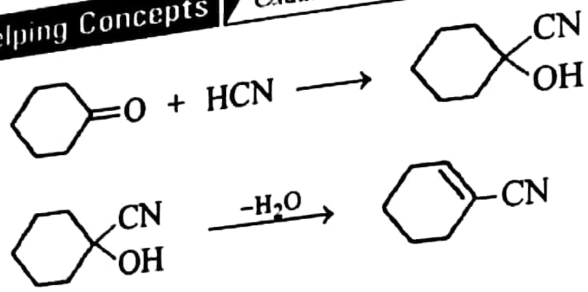
2 

3 

Topic 17 Carbonyl Compounds

Helping Concepts *Exam Favourite Rating* ★

*1.



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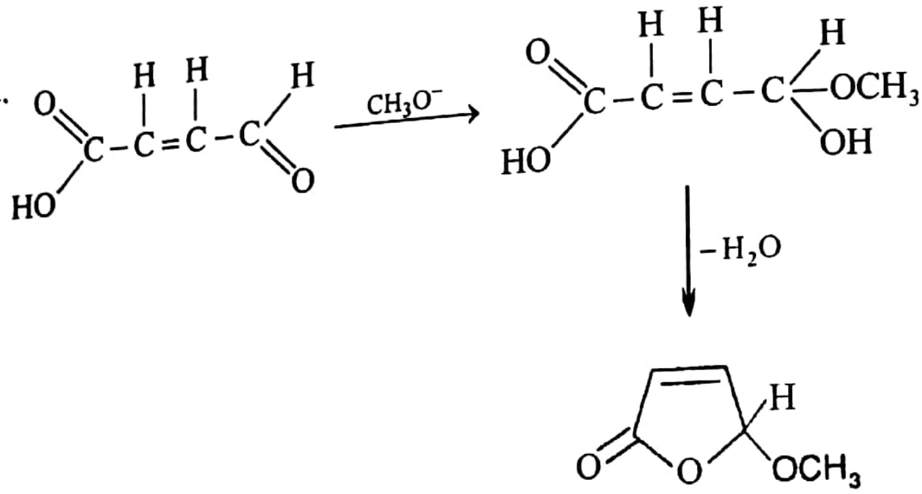
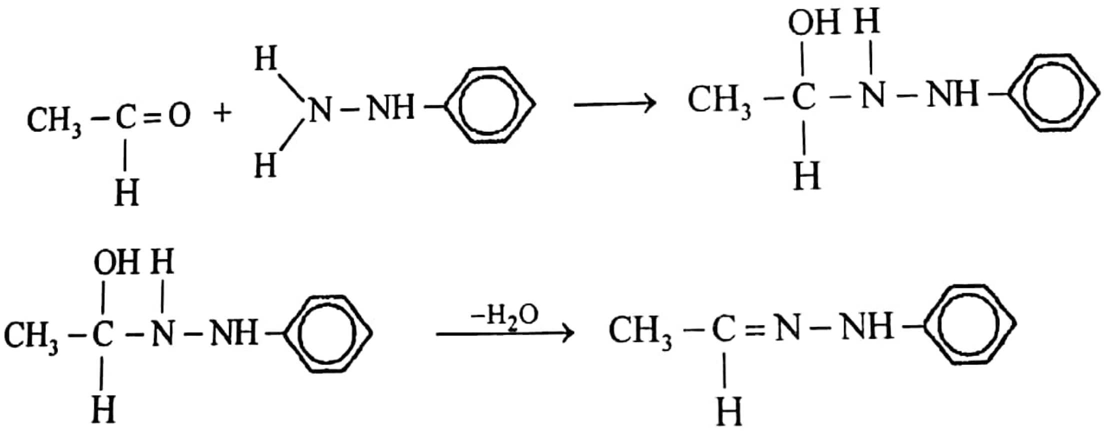


*3.



TOPIC 18

Carboxylic Acids and Derivatives

Key content that you will be examined on:

1. Carboxylic acids (exemplified by ethanoic acid and benzoic acid)
   (i) Formation from primary alcohols and nitriles
   (ii) Salt, ester and acyl chloride formation
2. Acyl chlorides (exemplified by ethanoyl chloride)
   (i) Ease of hydrolysis compared with alkyl and aryl chlorides
   (ii) Reaction with alcohols, phenols and primary amines
3. Esters (exemplified by ethyl ethanoate and phenyl benzoate)
   (i) Formation from carboxylic acids and from acyl chlorides
   (ii) Hydrolysis (under acidic and under basic conditions)

Topic 18

Carboxylic Acids and Derivatives

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which class of compounds is commonly used for the artificial flavourings in jams?

   A aldehydes
   B carboxylic acids
   C esters
   D ketones

Helping Concepts *Exam Favourite Rating* ★★

Esters are sweet-smelling organic substances that are commonly used as artificial flavourings.

2. Which compound is a product of the hydrolysis of $CH_3CO_2C_3H_7$ by boiling aqueous sodium hydroxide?

   A C_3H_8
   B CH_3OH
   C C_3H_7OH
   D $C_3H_7CO_2^-Na^+$

Helping Concepts *Exam Favourite Rating* ★★★

$$CH_3CO_2C_3H_7 + OH^- \xrightarrow{heat} CH_3CO_2^- + HOC_3H_7$$

3. Which compound reacts with its own oxidation product (an oxidation which involves no loss of carbon) to give a sweet-smelling liquid?

   A propanal
   B propanoic acid
   C propanone
   D propan-1-ol

not aldehyde?

Helping Concepts *Exam Favourite Rating* ★★★

$$CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CO_2H + H_2O$$

$$CH_3CH_2CH_2OH + CH_3CH_2CO_2H \xrightarrow[heat]{H^+} CH_3CH_2CO_2CH_2CH_2CH_3 + H_2O$$

4. Ethanoic acid has a pK_a of 4.7.

   What will have a higher pK_a value?

   A $ClCH_2CO_2H$
   B $C_6H_5CO_2H$
   C C_6H_5OH
   D HCO_2H

Helping Concepts *Exam Favourite Rating* ★★★

A weaker acid has a higher pK_a value.
C_6H_5OH (phenol) is a weaker acid than CH_3CO_2H (ethanoic acid).

5. What is the product of the reaction between phenylmethanol, $C_6H_5CH_2OH$, and ethanoyl chloride, CH_3COCl?

   A $C_6H_5CH_2Cl$
   B $C_6H_5CH_2COCl$
   C $C_6H_5COCH_3$
   D $C_6H_5CH_2OCOCH_3$

Helping Concepts *Exam Favourite Rating* ★★★

$$C_6H_5CH_2OH + CH_3COCl$$

$$\rightarrow C_6H_5CH_2O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + HCl$$

6. Which reaction does **not** produce benzoic acid?

   A the hydrolysis of $C_6H_5CO_2CH_2CH_3$
   B the hydrolysis of C_6H_5CN

C the oxidation of $C_6H_5CH_3$

D the oxidation of C_6H_5OH

Helping Concepts *Exam Favourite Rating* ★★

A: $C_6H_5CO_2CH_2CH_3 + H_2O \xrightarrow[heat]{H^+} C_6H_5CO_2H + CH_3CH_2OH$

B: $C_6H_5CN + 2H_2O + H^+ \xrightarrow[heat]{} C_6H_5CO_2H + NH_4^+$

C: $C_6H_5CH_3 + 3[O] \rightarrow C_6H_5CO_2H + H_2O$

D: No reaction.

---

7. Which of the following compounds gives an immediate precipitate with aqueous silver nitrate?

A CH_3COCl

B CH_3CCl_3

C $CH_3CH_2CH_2Cl$

D $ClCH_2CO_2H$

Helping Concepts *Exam Favourite Rating* ★★★

Ethanoyl chloride hydrolyses readily in H_2O giving HCl.

The Cl^- ion released forms white precipitate of AgCl with $AgNO_3$.

$$CH_3COCl + H_2O \rightarrow CH_3COOH + H^+ + Cl^-$$

$$Cl^- + Ag^+ \rightarrow AgCl\downarrow$$

---

8. Which set of reagents could be used to prepare phenyl benzoate in the laboratory?

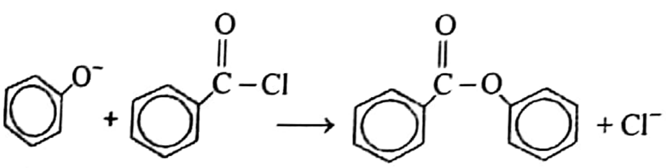
A chlorobenzene and sodium benzoate

B phenol and benzoic acid

C sodium phenate and benzoic acid

D sodium phenate and benzoyl chloride

Helping Concepts *Exam Favourite Rating* ★★★



(B) and (C) are wrong because benzoic acid cannot be used. An activated acid, e.g. benzoyl chloride has to be used.

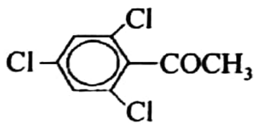
---

9. Which compound is most readily hydrolysed by water?

A CH_3COCH_2Cl

B $C_6H_5CH_2COCl$

C $CH_3CHClCO_2H$

D 

Helping Concepts *Exam Favourite Rating* ★★★

Acyl chlorides are more easily hydrolysed than alkyl (options A and C) and aryl chlorides (option D).

$$C_6H_5CH_2COCl + H_2O \rightarrow C_6H_5CH_2CO_2H + HCl$$

---

10. Which of the following, in aqueous solution of equal concentration, has the lowest pH?

A chloroethanoic acid

B ethanoic acid

C ethylamine

D phenol

Helping Concepts *Exam Favourite Rating* ★★★

Arrange the compounds in increasing acidity:

ethylamine < phenol < ethanoic acid < chloroethanoic acid

$ClCH_2CO_2H$ is a stronger acid than CH_3CO_2H because Cl is electronegative and is electron withdrawing by inductive effect. It therefore helps to disperse the negative charge on the carboxylate anion and stabilises it.

$$HA \rightleftharpoons H^+ + A^-$$

Hence, chloroethanoic acid dissociates to a greater extent and is the strongest acid, producing the highest $[H^+]$.

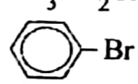
---

11. In which compound is the carbon-halogen bond hydrolysed most readily by aqueous sodium hydroxide?

A CH_3CH_2F

B CH_3CH_2Cl

C CH_3COBr

D 

Helping Concepts *Exam Favourite Rating* ★★★

Being an acyl bromide (acid bromide), CH_3COBr readily undergoes hydrolysis in aqueous OH^-.

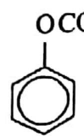
$$CH_3COBr + 2OH^- \xrightarrow{\text{cold}} CH_3CO_2^- + Br^- + H_2O$$

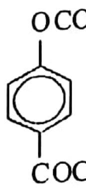
Both (A) and (D) do not undergo hydrolysis because the C–F bond and C–Br bond (with partial double bond characteristic due to delocalisation of electrons from Br into the benzene ring) are too strong to be cleaved. CH_3CH_2Cl undergoes hydrolysis upon heating.

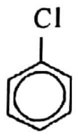
$$CH_3CH_2Cl + OH^- \xrightarrow{\text{heat}} CH_3CH_2OH + Cl^-$$

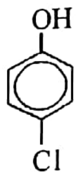
---

12. What is the product when phenol is treated with an excess of ethanoyl chloride?

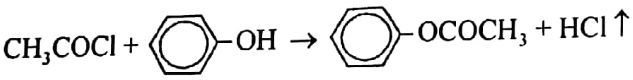
A 

B 

C 

D 

Helping Concepts *Exam Favourite Rating* ★★★



It is not possible to produce an ester by reacting phenol with a carboxylic acid.

---

13. Which materials are best used for the preparation of phenyl benzoate in the laboratory?

A C_6H_5Cl and $C_6H_5CO_2H$ only

B C_6H_5Cl, $C_6H_5CO_2H$ and NaOH

C C_6H_5OH, C_6H_5COCl and NaOH

D C_6H_5OH, $C_6H_5CO_2H$ and H_2SO_4

Helping Concepts *Exam Favourite Rating* ★★

In the laboratory, C_6H_5COCl is slowly added into a mixture of C_6H_5OH and NaOH in the cold.

$$C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$$

$$C_6H_5O^- + C_6H_5COCl \rightarrow C_6H_5CO_2C_6H_5 + Cl^-$$

Unlike alcohol, C_6H_5OH does not form an ester with a carboxylic acid. An acid chloride has to be used.

---

14. A food chemist wants to create the odour of pineapples for a product. An ester with this odour has the formula $C_3H_7CO_2C_2H_5$.

Which pair of reactants would produce this ester?

A C_2H_5Cl and $C_3H_7CO_2H$

B C_2H_5OH and C_2H_5COCl

C C_2H_5OH and $C_3H_7CO_2H$

D C_3H_7OH and C_2H_5COCl

Helping Concepts *Exam Favourite Rating* ★★★

$$C_3H_7CO_2H + C_2H_5OH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} C_3H_7CO_2C_2H_5 + H_2O$$

The products of the other options are

A: No reaction.

B: $C_2H_5CO_2C_2H_5$

D: $C_2H_5CO_2C_3H_7$

---

15. A compound **X** has the properties below:

it is a liquid at room temperature and atmospheric pressure;

it does not mix completely with water;

it does not decolourise acidified potassium manganate(VII).

What could **X** be?

A ethane

B ethanoic acid

C ethanol

D ethyl ethanoate

carboxylic acids are totally miscible with water.

Helping Concepts *Exam Favourite Rating* ★★

(A) is gas. (B) and (C) are totally miscible with H_2O (through hydrogen bonding with H_2O).

---

16. When an organic compound **X** was treated with phosphorus pentachloride, fumes of hydrogen chloride were evolved. When **X** was warmed with acidified aqueous potassium dichromate(VI), the solution turned green.

Which of the following was **X**?

A CH_3CH_2CHO
B $CH_3CH_2CO_2H$
C $CH_3CH(OH)CH_3$
D CH_3COCH_3

Helping Concepts *Exam Favourite Rating* ★★★

The reactions show that X has –OH group (alcohols or acids) and it is reducing (alcohols are more reducing than acids).

$$CH_3CH(OH)CH_3 + PCl_5 \rightarrow CH_3CHClCH_3 + POCl_3 + HCl$$

$$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

---

17. Which pair of reaction *could* have the same common intermediate?

W $CH_3CH_2CH_3 \rightarrow$ intermediate $\rightarrow (CH_3)_2CHCN$
X $CH_3CH(OH)CH_3 \rightarrow$ intermediate $\rightarrow (CH_3)_2C(OH)CN$
Y $CH_3CH{=}CH_2 \rightarrow$ intermediate $\rightarrow CH_3CH(OH)CH_3$
Z $CH_3CO_2CH_2CH_2CH_3 \rightarrow$ intermediate $\rightarrow CH_3CH_2CH_2Br$

A W and X
B W and Y
C X and Z
D Y and Z

Helping Concepts *Exam Favourite Rating* ★★★

W: $CH_3CH_2CH_3 \xrightarrow[uv]{Cl_2} CH_3CH(Cl)CH_3 \xrightarrow[heat]{KCN} CH_3CH(CN)CH_3$

Y: $CH_3CH{=}CH_2 \xrightarrow{HCl} CH_3CH(Cl)CH_3 \xrightarrow[heat]{aq.\ NaOH} CH_3CH(OH)CH_3$

---

18. An organic compound will decolourise dilute acidified aqueous potassium manganate(VII) on warming, but will not decolourise bromine water.

What could the organic compound be?

A butane
B ethanol
C ethene
D ethanoic acid

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Neither (A) nor (D) react with $KMnO_4$ and Br_2(aq). (C) reacts with both $KMnO_4$ and Br_2(aq).

$$CH_2{=}CH_2 + [O] + H_2O \xrightarrow{MnO_4^-} CH_2(OH){-}CH_2(OH)$$

$$CH_2{=}CH_2 + Br_2 + H_2O \rightarrow CH_2(Br){-}CH_2(OH) + H^+ + Br^-$$

Ethanol is oxidised by $KMnO_4$ but has no reaction with Br_2(aq).

$$CH_3CH_2OH + 2[O] \longrightarrow CH_3CO_2H + H_2O$$

---

19. Which compound reacts with each of

- cold NaOH(aq);
- CH_3OH under reflux with concentrated H_2SO_4;
- PCl_5?

A $ClCOCOCl$
B $ClCOCO_2CH_3$
C $HOCH_2CO_2CH_3$
D HO_2CCO_2H

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It contains the $-CO_2H$ group and hence can react with each of the 3 sets of reagents.

$$R-CO_2H + NaOH \rightarrow R-CO_2^-Na^+ + H_2O$$

$$R-CO_2H + CH_3OH \xrightarrow[heat]{conc.\ H_2SO_4} RCO_2CH_3 + H_2O$$

$$R-CO_2H + PCl_5 \rightarrow R-COCl + POCl_3 + HCl$$

(A) and (B) do not react with PCl_5.
(C) does not react with NaOH and CH_3OH.

---

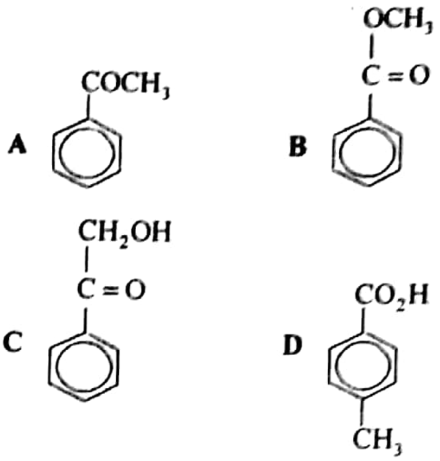
20. A compound **R** has all of the following properties:

it is neutral;

it gives an orange precipitate with 2,4-dinitrophenylhydrazine;

it evolves hydrogen chloride when treated with PCl_5 in the cold.

What could **R** be?



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Option A (ketone) does not give HCl with PCl_5.

Option B (ester) does not react with 2,4-DNPH and PCl_5.

Option D (acid) is not neutral and does not react with 2,4-DNPH.

---

21. Why is chloroethanoic acid, $ClCH_2CO_2H$, a stronger acid than ethanoic acid?

A Chlorine releases electrons and destabilises the $ClCH_2CO_2^-$ anion.

B Chlorine releases electrons and stabilises the $ClCH_2CO_2^-$ anion.

C Chlorine withdraws electrons and destabilises the $ClCH_2CO_2^-$ anion.

D Chlorine withdraws electrons and stabilises the $ClCH_2CO_2^-$ anion.

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$$HA \rightleftharpoons H^+ + A^-$$

When the A^- formed is more stable, the equilibrium lies more to the right. More HA dissociate and hence it is a stronger acid. The presence of Cl withdraws the negative charge by inductive effect since Cl is electronegative. This disperses the negative charge and hence stabilises the anion.

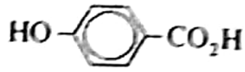
---

22. One mole of an organic compound **X** is reacted with an excess of PCl_5 and two moles of hydrogen chloride are formed. Which of the following compounds could be **X**?

A $CH_3CH{=}CHCH_3$

B $C_6H_5CH_2Cl$

C $HOCH_2CO_2H$

D 

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Both alcohols and carboxylic acids react with PCl_5 to give white fumes of HCl.

$$R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$$

$$R-COOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$$

However, phenol does not react with PCl_5.

$$HOCH_2COOH + 2PCl_5$$
$$\rightarrow ClCH_2COCl + 2POCl_3 + 2HCl$$

The formation of 2 moles of HCl per mole of **X** shows that there are 2 aliphatic –OH groups (alcohol or carboxylic acid) per molecule of **X**.

---

23. How many moles of hydrogen chloride are evolved when an excess of PCl_5 is added to one mole of citric acid?

$$HO-\underset{\displaystyle CH_2CO_2H}{\overset{\displaystyle CO_2H}{\underset{|}{\overset{|}{C}}}}-CH_2CO_2H$$

citric acid

A 0 **B** 1

C 3 **D** 4

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Both the –OH and –COOH groups react with PCl_5.

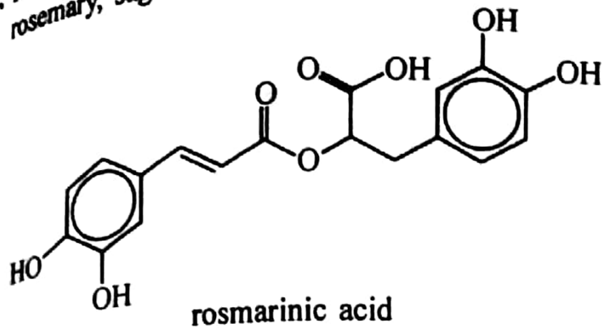
$$R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$$

$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

$$HO-\underset{\displaystyle CH_2CO_2H}{\overset{\displaystyle CO_2H}{\underset{|}{\overset{|}{C}}}}-CH_2CO_2H + 4PCl_5$$

$$\longrightarrow Cl-\underset{\displaystyle CH_2COCl}{\overset{\displaystyle COCl}{\underset{|}{\overset{|}{C}}}}-CH_2COCl + 4POCl_3 + 4HCl$$

24. Rosmarinic acid occurs in culinary herbs such as rosemary, sage and thyme.



rosmarinic acid

How many moles of NaOH(aq) will react with one mole of rosmarinic acid when the acid is heated under reflux with an excess of NaOH(aq)?

A 4
B 5
C 6
D 7

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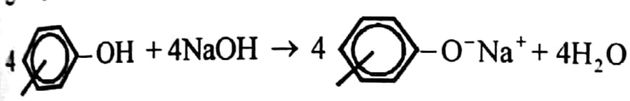
The functional groups that will react with NaOH are phenols, carboxylic acid and ester. Each of these groups react in 1 : 1 ratio with NaOH.



$$-\overset{O}{\overset{\|}{C}}-O- + NaOH \rightarrow -\overset{O}{\overset{\|}{C}}-O^-Na^+ + HO^-$$

$$-\overset{O}{\overset{\|}{C}}-OH + NaOH \rightarrow -\overset{O}{\overset{\|}{C}}-O^-Na^+ + H_2O$$

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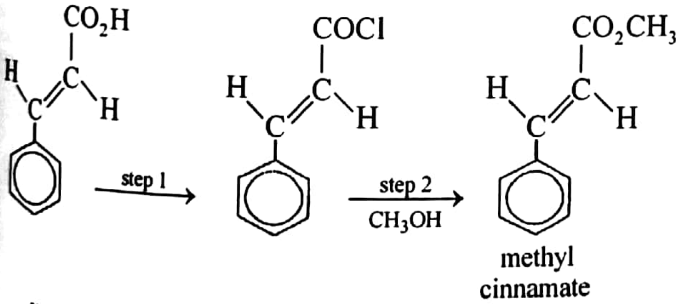
$$R-CO_2H + PCl_5 \rightarrow R-COCl + HCl + POCl_3$$

25. The *matsutake* mushroom is a delicacy added to many Janpanese foods. The spicy aroma of this mushroom is due to methyl cinnamate, which can be prepared in the laboratory according to the following reaction sequence.



Which reagent could be used in step 1?

A $AlCl_3$
B CH_3Cl
C HCl
D PCl_5

26. An ester P with a fruity odour has the following structural formula:

$$CH_3C(=O)OCH_2CH_2CH(CH_3)_2$$

What compounds are produced when P is hydrolysed using hydrochloric acid?

A CH_3COCl and $(CH_3)_2CHCH_2CH_2OH$
B CH_3CHO and $(CH_3)_2CHCH_2CH_2OH$
C CH_3CO_2H and $(CH_3)_2CHCH_2CHO$
D CH_3CO_2H and $(CH_3)_2CHCH_2CH_2OH$

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An ester undergoes hydrolysis to give an acid and an alcohol.

$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2CH(CH_3)_2 + H_2O \xrightarrow[\text{heat}]{H^+} CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-CH_2CH_2CH(CH_3)_2$$

27. Malic acid occurs in apples.

$$H-\underset{CO_2H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2CO_2H$$

malic acid

Which substance will react with all three –OH groups present in the malic acid molecule?

A ethanol in the presence of concentrated sulfuric acid
B potassium hydroxide
C sodium
D sodium carbonate

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The three –OH groups are from the alcohol and carboxylic acids functional groups. Na will react with all the three OH groups.

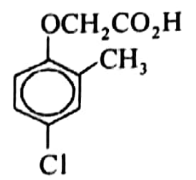
$$R-OH + Na \rightarrow R-O^-Na^+ + \tfrac{1}{2}H_2$$

$$R'-CO_2H + Na \rightarrow R'-CO_2^-Na^+ + \tfrac{1}{2}H_2$$

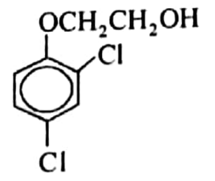
Ethanol does not undergo esterification with the alcohol. Alcohol is not acidic enough to react with KOH and Na_2CO_3.

---

28. MCPA and 2,4-D are two widely-used selective weedkillers.



MCPA



2,4-D

Which of the following reagents will distinguish MCPA from 2,4-D?

A acidified $AgNO_3(aq)$
B Fehling's solution
C I_2 in NaOH(aq)
D $Na_2CO_3(aq)$

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MCPA is a carboxylic acid and readily releases CO_2 on reacting with Na_2CO_3.

$$2R-COOH + Na_2CO_3 \rightarrow 2RCOO^-Na^+ + CO_2\uparrow + H_2O$$

2,4-D is an alcohol and is too weak an acid to react with Na_2CO_3.

---

29. 2-Bromopropane, $(CH_3)_2CHBr$, may be used as the starting point for making $(CH_3)_2CHCO_2H$.

Which of the following sequences would be most suitable?

A $(CH_3)_2CHBr \rightarrow (CH_3)_2CHOH \rightarrow (CH_3)_2CHCO_2H$

B $(CH_3)_2CHBr \rightarrow (CH_3)_2CHCN \rightarrow (CH_3)_2CHCO_2H$

C $(CH_3)_2CHBr \rightarrow (CH_3)_2CHOH \rightarrow (CH_3)_2CHCN \rightarrow (CH_3)_2CHCO_2H$

D $(CH_3)_2CHBr \rightarrow (CH_3)_2CHCN \rightarrow (CH_3)_2CHOH \rightarrow (CH_3)_2CHCO_2H$

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The product has one more C atom. The use of a cyanide is necessary.

$$(CH_3)_2CHBr + CN^- \xrightarrow[\text{heat}]{S_N} (CH_3)_2CHCN + Br^-$$

$$(CH_3)_2CHCN + H^+ + 2H_2O \xrightarrow[\text{heat}]{\text{hydrolysis}} (CH_3)_2CHCO_2H + NH_4^+$$

---

30. Citric acid, which causes the sharp taste of lemon juice, has the following formula.

$$\begin{array}{c} CH_2CO_2H \\ | \\ HO-C-CO_2H \\ | \\ CH_2CO_2H \end{array}$$

What reacts completely with 1 mol of citric acid?

A 3 mol of $PCl_5(s)$
B 4 mol of HCl(g)
C 4 mol of Na(s)
D 4 mol of NaOH(aq)

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Both the $-CO_2H$ and $-OH$ groups react with PCl_5 and Na.

$$-CO_2H + Na \rightarrow -CO_2^-Na^+ + \frac{1}{2}H_2$$

$$-OH + Na \rightarrow -O^-Na^+ + \frac{1}{2}H_2$$

$$-CO_2H + PCl_5 \rightarrow -COCl + POCl_3 + HCl$$

$$-OH + PCl_5 \rightarrow -Cl + POCl_3 + HCl$$

Hence, each citric acid molecule reacts with 4 PCl_5 and 4 Na.

However, only $-CO_2H$ reacts with NaOH. $-OH$ does not react with NaOH and therefore, each citric acid molecule reacts with 3 NaOH.

$$-CO_2H + NaOH \rightarrow -CO_2^-Na^+ + H_2O$$

---

31. The acarid mite releases *lardolure* to attract other mites to a host: this chemical can be destroyed by hydrolysis with acid.

$$CH_3CH_2CH_2[CH(CH_3)CH_2]_3CH(CH_3)O-\overset{\displaystyle H}{\underset{\underset{\displaystyle O}{\|}}{C}}$$

A simplified formula for *lardolure* may be written as $RCH(CH_3)O-\underset{\underset{O}{\|}}{C}-H$.

What are the products of its hydrolysis?

A $RCH{=}CH_2 + HCO_2H$

B $RCH_2CH_3 + CO_2$

C $RCH(CH_3)CO_2H + HCO_2H$

D $RCH(CH_3)OH + HCO_2H$

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$$RCH(CH_3)O-\underset{\underset{O}{\|}}{C}H + H_2O \xrightarrow[\text{heat}]{H^+} RCH(CH_3)OH + HCOOH$$

Lardolure is an ester. Hydrolysis yields an alcohol and an acid.

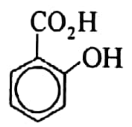
---

32. A compound **U** liberates carbon dioxide from aqueous sodium hydrogencarbonate. When **U** is added to aqueous bromine, the colour of the bromine is rapidly discharged. What could **Q** be?

A $HOCH_2CO_2H$

B CH_3CO_2H

C CH_3CO_2Na

D 

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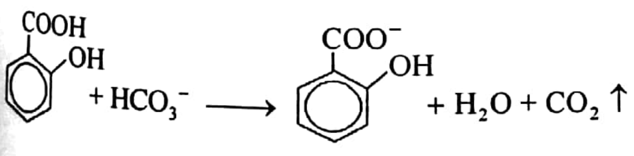
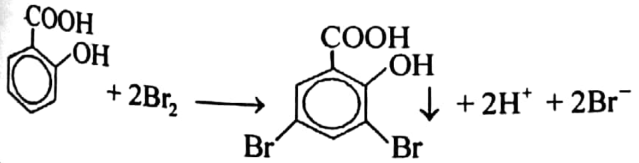
Reaction with $NaHCO_3$ indicates the presence of -COOH and reaction with Br_2 indicates the presence of a phenol (or an alkene).





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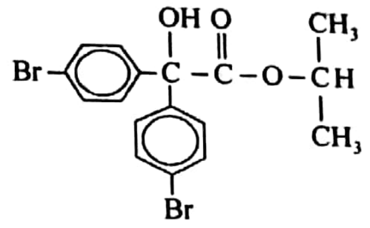
33 Acarol is sold as an insecticide for use on fruit and vegetables.



Acarol

The final stage in its manufacture is an esterification.

Which alcohol is used to form the ester?

A di(4-bromophenyl)methanol

B methanol

C propan-1-ol

D propan-2-ol

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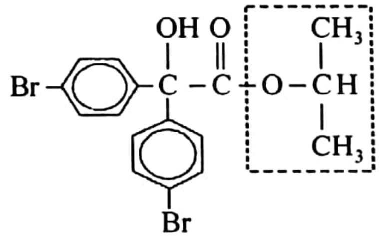
$$RCO_2H + R'OH \rightarrow RCO_2R' + H_2O$$



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34. Which procedure gives the best yield of ethyl ethanoate, $CH_3CO_2C_2H_5$, starting from ethanoic acid, CH_3CO_2H, and ethanol, C_2H_5OH?

A reacting CH_3CO_2H with $SOCl_2$, then adding C_2H_5OH

B reacting C_2H_5OH with $SOCl_2$, then adding CH_3CO_2H

C refluxing a mixture of CH_3CO_2H and C_2H_5OH with NaOH(aq)

D refluxing C_2H_5OH with concentrated H_2SO_4, then adding CH_3CO_2H

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The best yield of an ester is obtained by reacting the corresponding acid chloride and alcohol. Reacting CH_3CO_2H with $SOCl_2$ yields CH_3COCl which reacts with C_2H_5OH to give the required ester $CH_3CO_2C_2H_5$.

Option B is incorrect since C_2H_5OH reacts with $SOCl_2$ to give C_2H_5Cl which does not react with CH_3CO_2H.

Option C is incorrect since refluxing CH_3CO_2H and C_2H_5OH with aqueous NaOH yields no ester as CH_3CO_2H is converted into its salt $CH_3CO_2^-Na^+$.

Option D is incorrect since refluxing C_2H_5OH with concentrated sulfuric acid may bring about dehydration. Also, reaction of an alcohol with a carboxylic acid in the presence of concentrated acid to form an ester is a reversible reaction, so the reaction is not completed.

---

35. An ester with an odour of banana has the following formula.

$$CH_3CO_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

In which of the following will the substances react together to produce this ester?

A $CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CO_2H + CH_3OH$

B $CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2COCl + CH_3OH$

C $CH_3COCl + CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2OH$

D $CH_3CO_2H + CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2Cl$

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$$CH_3COCl + HOCH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

$$\longrightarrow CH_3CO_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3 + HCl\uparrow$$

A,B: $CH_3O\underset{\underset{\displaystyle O}{\|}}{C}CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$

D: No reaction.

---

36. Citric acid, which causes the sharp taste of lemon juice, has the following formula.

$$\begin{array}{c} CH_2CO_2H \\ | \\ HO-C-CO_2H \\ | \\ CH_2CO_2H \end{array}$$

What reacts completely with 1 mol of citric acid?

A 3 mol of $PCl_5(s)$

B 4 mol of $HCl(g)$

C 4 mol of $Na(s)$

D 4 mol of $NaOH(aq)$

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Citric acid contains 3 –COOH and 1 alcoholic –OH groups. These groups react with 1 Na each:

$$RCOOH + Na \rightarrow RCOO^-Na^+ + \tfrac{1}{2}H_2$$

$$ROH + Na \rightarrow RO^-Na^+ + \tfrac{1}{2}H_2$$

Hence, a total of 4 mol of Na is needed per mol of citric acid.

Option A is incorrect since –COOH and alcoholic –OH groups react with 1 PCl_5 each:

$$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$$

$$ROH + POCl_3 \rightarrow RCl + POCl_3 + HCl$$

Hence, 4 mol of PCl_5 are needed per mol of citric acid.

Option B is incorrect since –COOH does not react with HCl(g).

Option D is incorrect since alcoholic –OH does not react with aqueous NaOH. Hence, only 3 mol of aqueous NaOH is needed per mol of citric acid.

---

37. When a substance **X** is shaken with aqueous silver nitrate at room temperature, there is no immediate precipitate. However, when **X** is boiled under reflux for some time with aqueous sodium hydroxide, cooled, acidified with dilute nitric acid and aqueous silver nitrate added, a white precipitate readily forms.

What could **X** be?

A CH_3COCl

B C_6H_5Cl

C $CH_3CH_2CH_2CH_2Cl$

D C_6H_5COCl

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Being a chloroalkane, it does not undergo hydrolysis readily in H_2O to give Cl^-. However, upon heating with aqueous NaOH, nucleophilic substitution takes place and Cl^- is formed.

$$R-Cl + OH^- \rightarrow R-OH + Cl^-$$

Addition of $AgNO_3$ gives AgCl precipitate.

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

(A) and (D) give immediate precipitate with $AgNO_3$ due to rapid hydrolysis in H_2O.

$R-COCl + H_2O \rightarrow RCO_2H + H^+ + Cl^-$

(B) does not undergo hydrolysis at all even when heated with aqueous NaOH because the C–Cl has partial double bond character due to the delocalisation of electrons from Cl into benzene ring.

---

38. A compound **Y** is boiled with aqueous sodium hydroxide and the resulting mixture cooled and acidified with dilute sulfuric acid. The final products include a compound $C_3H_6O_2$ and an alcohol. This alcohol gives a positive tri-iodomethane (iodoform) test.

Which formula could represent **Y**?

A $CH_3CH_2COOCH_3$
B $CH_3CH_2COOCH_2CH_3$
C $CH_3CH_2OCOCH_3$
D $HOCH_2CH_2COCH_2CH_3$

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Y is likely to be an ester which gives a carboxylic acid ($C_3H_6O_2$) and an alcohol upon hydrolysis.

$$RCO_2R' + H_2O \xrightarrow{H^+} RCO_2H + R'OH$$

From the formula, the acid is $C_2H_5CO_2H$.

Since the alcohol gives a positive tri-iodomethane test, it should contain $-\underset{\displaystyle CH_3}{\underset{|}{C}H}-OH$ group.

Hence, the ester is $CH_3CH_2CO_2\underset{\displaystyle R''}{\underset{|}{C}}HCH_3$.

In this case, $R'' = H$.

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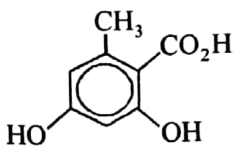
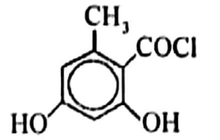
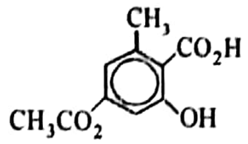
39. Orsellinic acid occurs in lichens.

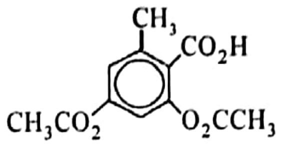


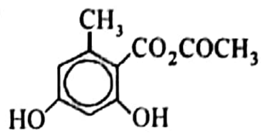
Orsellinic acid

Which of the following formulae represents the product of its reaction with ethanoyl chloride?

A


B


C


D


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Ethanoyl chloride reacts readily with active H (e.g. H in –OH group) to give HCl.

$$R-OH + CH_3COCl \rightarrow R-OCOCH_3 + HCl$$

If the –COOH were to be acylated, then the –OH group should also be acylated too since the O of the –OH group is more basic than that of the –COOH group. Hence, option C is incorrect.

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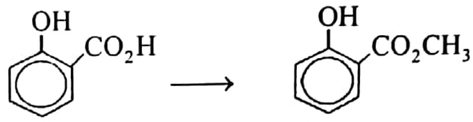
40. A manufacturer wishes to make methyl salicylate, the aromatic liniment of oil of wintergreen, from salicylic acid.



salicylic acid   methyl salicylate

How is this esterification of salicylic acid best achieved?

A mixing it with cold ethanoyl chloride
B warming it with anhydrous methanol
C heating it under reflux with aqueous methanol
D heating it under reflux with methanol and a little concentrated sulfuric acid

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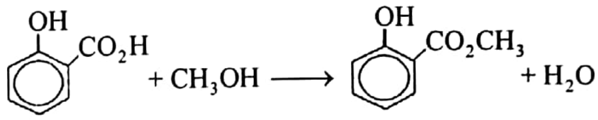
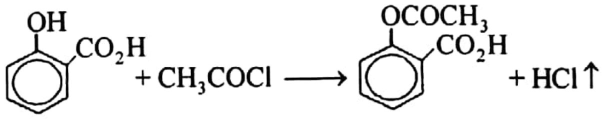


The reaction is esterification. Concentrated H_2SO_4 is needed as a catalyst.

A: The use of ethanoyl chloride leads to esterification of phenol.



41. Which of the following gives the correct order of acid strength (strongest first) for ethanoic acid, chloroethanoic acid, and phenol?

	strongest	$\longrightarrow$	weakest
A	CH_3CO_2H	C_6H_5OH	CH_2ClCO_2H
B	CH_3CO_2H	CH_2ClCO_2H	C_6H_5OH
C	CH_2ClCO_2H	C_6H_5OH	CH_3CO_2H
D	CH_2ClCO_2H	CH_3CO_2H	C_6H_5OH

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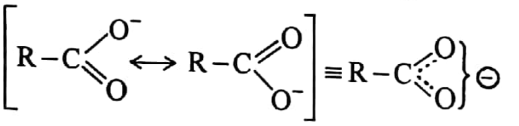
$$HA \rightleftharpoons H^+ + A^-$$

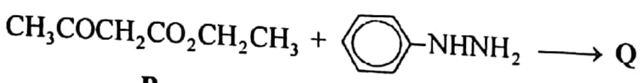
The strength of an acid depends on the stability of the anion, A^- formed. The more stable the anion, A^-, the greater is the dissociation to give H^+ and the stronger is the acid. HA.

Carboxylic acids are generally stronger acids than phenol due to the extensive delocalisation of electrons in the carboxylate anion. This helps to disperse the negative charge and hence stabilises it.



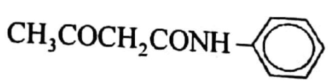
However, CH_2ClCO_2H is a stronger acid than CH_3CO_2H because of the presence of the electronegative Cl atom. It is electron withdrawing by inductive effect and this further disperses the negative charge in $CH_2ClCO_2^-$ and therefore further stabilises it with respect to $CH_3CO_2^-$.

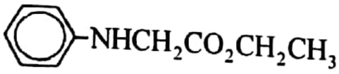
42. The first stage in the synthesis of *Antipyrine*, a drug used in reducing fever, is the reaction between compound **P** and phenylhydrazine.

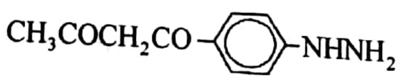


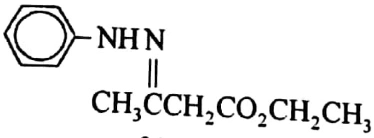
P phenylhydrazine

What will be the product **Q** of this first stage?

A 

B 

C 

D 

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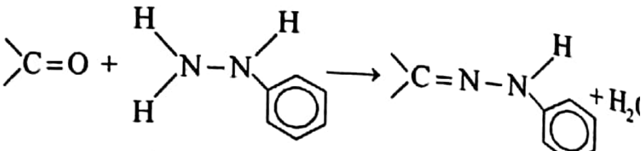
The carbonyl functional group reacts with phenylhydrazine to form a condensation product, phenylhydrazone.

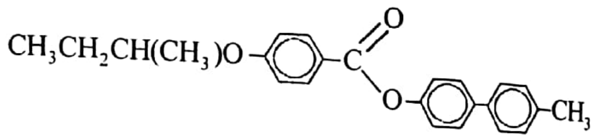


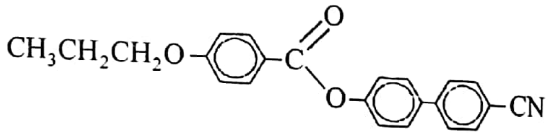
The ester functional group does not react.

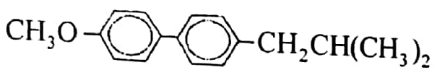
43. The display of a digital watch needs a liquid crystal which is

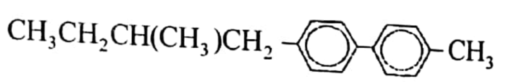
(i) stable to acidic hydrolysis;
(ii) stable to alkaline hydrolysis;
(iii) chiral.

Which of the following compounds, all of which form liquid crystals, meets these requirements?

A 

B 

C 

D 

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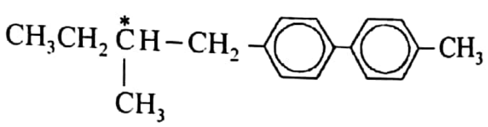
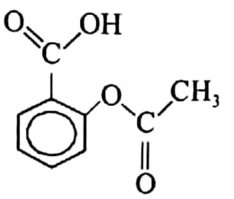
Both (A) and (B) can be hydrolysed ($-\overset{O}{\overset{\|}{C}}-O-$ and $-CN$); (B) and (C) do not contain a chiral centre. (D) is a hydrocarbon and is therefore stable in both acids and alkalis.

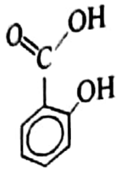


44. Aspirin has the following structure.



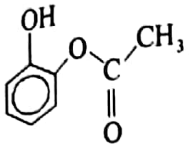
When aspirin is hydrolysed by acid present in the stomach, what products are formed?

A



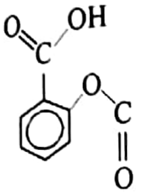
$+ CH_3CO_2H$

B



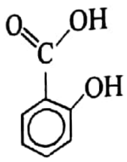
$+ HCO_2H$

C



$+ CH_3OH$

D



$+ CO_2 + CH_3OH$

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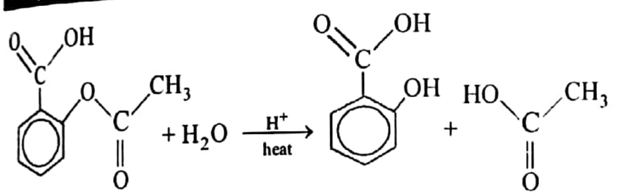
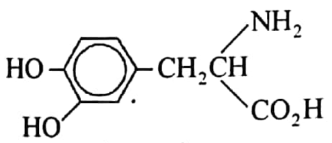


The ester is hydrolysed to give a phenol and ethanoic acid.

---

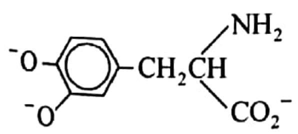
45. Dopamine is a neurotransmitter: its absence from the human brain might lead to Parkinson's disease.



dopamine

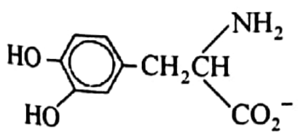
What is produced when dopamine is dissolved in aqueous sodium hydroxide?

A



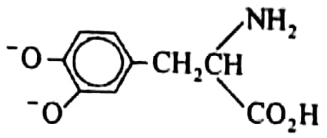
$+ 3Na^+$

B



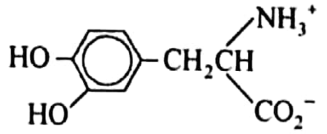
$+ Na^+$

C



$+ 2Na^+$

D



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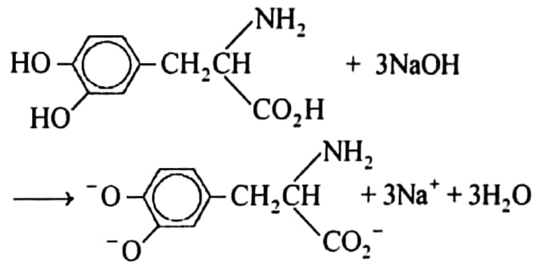
Both the phenolic group and the carboxylic acid groups are acidic.



---

46. One gram of each of the following compounds was heated with NaOH(aq), and then dilute HNO_3(aq) and $AgNO_3$(aq) were added.

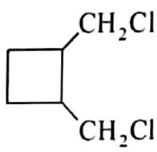
Which compound will produce the largest mass of AgCl(s)?

A CH_3COCl

C_2H_3OCl

$M_r = 78.5$

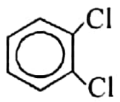
B



$C_6H_{10}Cl_2$

$M_r = 153$

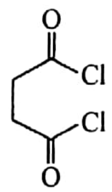
C



$C_6H_4Cl_2$

$M_r = 147$

D



$C_4H_4O_2Cl_2$

$M_r = 155$

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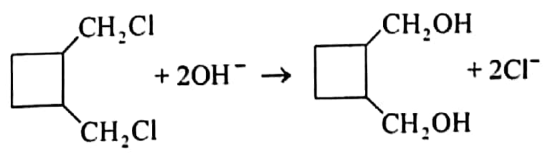
A: $CH_3COCl + 2OH^- \rightarrow CH_3CO_2^- + Cl^- + H_2O$

$n_{Cl^-} = \frac{1}{78.5}$ mol

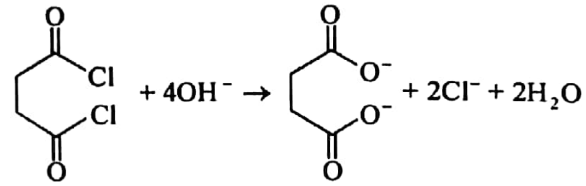
B:



$n_{Cl^-} = 2 \times \frac{1}{153}$ mol

C: No reaction with NaOH.

D:

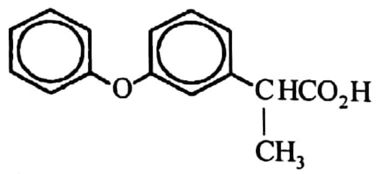


$$n_{Cl^-} = 2 \times \frac{1}{155} \text{ mol}$$

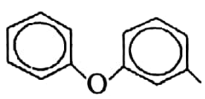
Since (D) produces the highest amount of Cl^-, it will form the largest mass of AgCl.

---

47. *Fenoprofen* is an anti-arthritic agent.



Which of the following could be part of a sequence for synthesising *Fenoprofen*.

[In the sequences below, R = ]

	Step 1	Step 2
A	$RCHBrCH_3 \xrightarrow[\text{heat}]{\text{NaCN(ethanolic)}}$ intermediate	$\xrightarrow[\text{heat}]{H^+(aq)}$ *Fenoprofen*
B	$RCH(CH_3)_2 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-(aq)}$ intermediate	$\xrightarrow{H^+(aq)}$ *Fenoprofen*
C	$R\underset{\displaystyle CH_3}{\underset{\vert}{C}}HOCOCH_3 \xrightarrow[\text{warm}]{I_2,\ OH^-(aq)}$ intermediate	$\xrightarrow{H^+(aq)}$ *Fenoprofen*
D	$RCH(OH)CH_3 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-(aq)}$ intermediate	$\xrightarrow{H^+(aq)}$ *Fenoprofen*

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$$R\underset{\displaystyle CH_3}{\underset{\vert}{C}}HBr + CN^- \xrightarrow{\text{heat}} R\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCN + Br^-$$

$$R\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCN + 2H_2O + H^+ \xrightarrow{\text{heat}} R\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCO_2H + NH_4^+$$

C: No reaction.

D: $RCH(OH)CH_3 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-} R-\overset{\displaystyle O}{\overset{\Vert}{C}}-CH_3 \xrightarrow{H^+,\ \text{heat}}$ no reaction

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

48. Which of the following reacts with ethanoyl chloride, CH_3COCl, to form an ester?

1 C_6H_5OH

2 $C_6H_5CH_2OH$

3 $C_6H_5CO_2H$

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*1. $C_6H_5OH + CH_3COCl \xrightarrow{OH^-} CH_3CO_2C_6H_5 + Cl^- + H^+$

*2. $C_6H_5CH_2OH + CH_3COCl \longrightarrow CH_3CO_2CH_2C_6H_5 + Cl^- + H^+$

3. $C_6H_5CO_2H$ is an acid and it does not react with an acid chloride to form ester.

---

49. Malic acid, $HO_2CCH(OH)CH_2CO_2H$, is found in apples.

Which properties does malic acid have?

1 It can form esters both with ethanoic acid and with ethanol.

2 Its molecule contains a secondary alcohol group.

3 Its molecule has one chiral centre.

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*1. Both –OH and –COOH are present. The –OH group can react with an acid and the –COOH group can react with an alcohol to form esters.

*2. OH is attached to a carbon with two other C atoms attached.

*3. $$HO_2C-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle H}{|}}{C^*}}-CH_2-CO_2H$$

---

50. Which of the following statements are true for concentrated sulfuric acid?

1 It oxidises ethanoic acid.

2 It dehydrates methanoic acid.

3 It is reduced by potassium iodide.

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1. CH_3COOH is not oxidised by concentrated H_2SO_4.

*2. $HCO_2H \xrightarrow{\text{conc. } H_2SO_4} CO\uparrow + H_2O$

HCO_2H, unlike other carboxylic acids, is readily dehydrated to give CO (and oxidised to CO_2).

*3. $8I^- + \underset{\text{conc.}}{H_2SO_4} + 8H^+ \rightarrow 4I_2 + H_2S + 4H_2O$

Other products of S are also formed, e.g. SO_2 and S.

---

51. Which of the following substances are oxidised by hot acidified aqueous potassium managate (VII)?

1 ethanoic acid

2 ethanal

3 ethane-1-2-diol

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1. Ethanoic acid is not oxidised by $KMnO_4$.

*2. Aldehydes are oxidised to carboxylic acids.

$$CH_3CHO + [O] \rightarrow CH_3CO_2H$$

*3. Ethane-1,2-diol is a primary alcohol and can therefore be oxidised.

$$\underset{\underset{\displaystyle OH}{|}}{CH_2}-\underset{\underset{\displaystyle OH}{|}}{CH_2} + 2[O] \rightarrow H-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-H + 2H_2O$$

$$H-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-H + 2[O] \rightarrow HO-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-OH$$

$$HO-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-OH + [O] \rightarrow 2CO_2 + H_2O$$

Note: $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \xrightarrow{60\,°C} 10CO_2 + 2Mn^{2+} + 8H_2O$

52. Sodium benzoate (sodium benzenecarboxylate) can be prepared by refluxing aqueous sodium hydroxide with

1 methylbenzene and sodium manganate(VII).
2 phenyl benzoate.
3 phenyl ethanoate.

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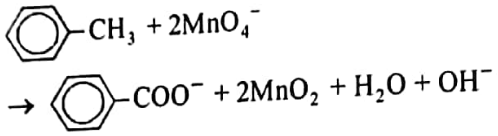
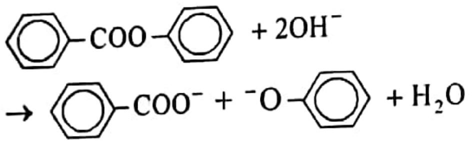
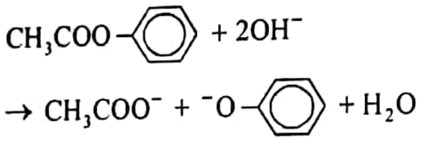
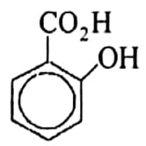
*1.


*2.


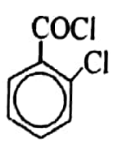
3.


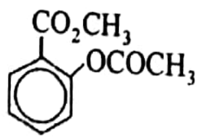
53. The diagram shows the structure of salicylic acid.

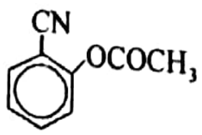


salicylic acid

Which compounds give salicylic acid on acid hydrolysis?

1


2


3


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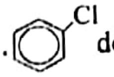
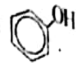
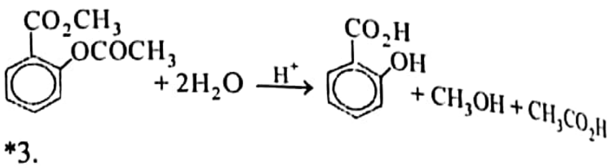
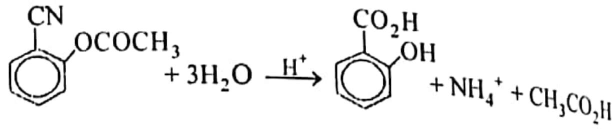
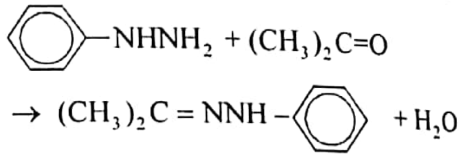
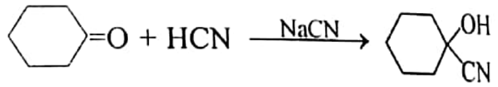
1.  does not undergo hydrolysis to give .

*2.


*3.


54. Which transformations involve a nucleophile?

1


2


3 $CH_3CH_2COCl + NH_3 \rightarrow CH_3CH_2CONH_2 + HCl$

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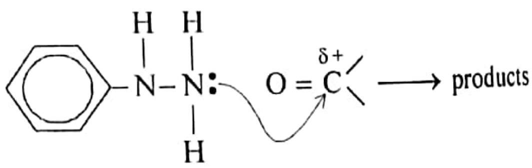
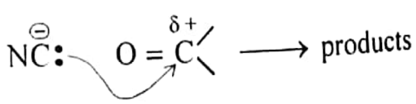
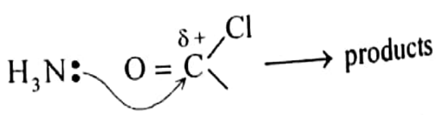
*1. The lone pair of electron on N makes the substance a nucleophile.



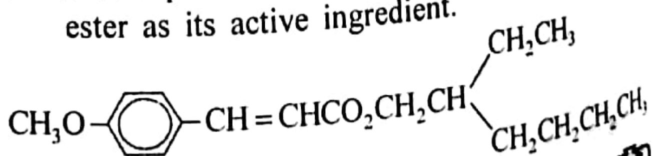
*2. The :CN^- functions as the nucleophile.



*3. The :NH_3 functions as the nucleophile.

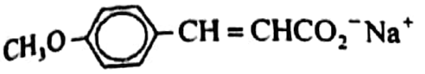


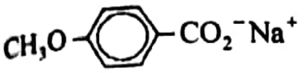
55. A sun protection cream contains the following ester as its active ingredient.



What are the products of its partial or total hydrolysis by aqueous sodium hydroxide?

1 $CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2OH$

2 

3 

Helping Concepts *Exam Favourite Rating* ★★

*1,*2. The ester on hydrolysis by aqueous NaOH gives an alcohol and a carboxylate salt.

3 This compound cannot be obtained from the ester by hydrolysis as its formation requires oxidative cleavage of the C=C bond.

---

56. Which compounds may be prepared from $C_6H_5CHBrCH_3$ by the action of sodium hydroxide under different conditions?

1 $C_6H_5CO_2Na$

2 $C_6H_5CH(OH)CH_3$

3 $C_6H_5CH{=}CH_2$

Helping Concepts *Exam Favourite Rating* ★★★

1. To get $C_6H_5CO_2H$ from $C_6H_5CHBrCH_3$, a methyl group needs to be removed and this cannot be brought about by the action of NaOH on $C_6H_5CHBrCH_3$.

*2,*3. A halogenoalkane can be dehydrohalogenated to give the corresponding alkene by reacting it with alcoholic NaOH or be converted to the corresponding alcohol by reacting it with aqueous NaOH. Hence,

$$C_6H_5CHBrCH_3 \xrightarrow[\Delta]{\text{alcoholic NaOH}} C_6H_5CH{=}CH_2$$
$$C_6H_5CHBrCH_3 \xrightarrow[\Delta]{\text{aq. NaOH}} C_6H_5CH(OH)CH_3$$

---

57. A sex attractant produced by butterflies and moths has the following structural formula.

$$CH_3CO_2(CH_2)_6CH{=}CH(CH_2)_3CH_3$$

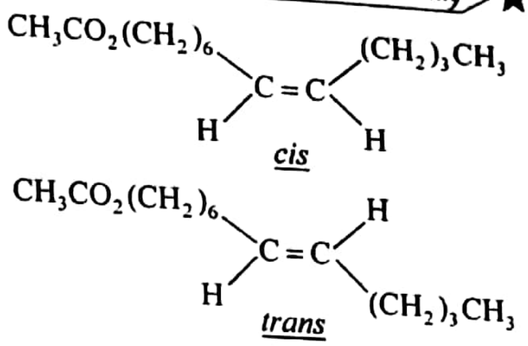
Which properties of this sex attractant can be deduced from this structure?

1 It could exist as *cis-trans* isomers.

2 It can be hydrolysed by dilute hydrochloric acid to give ethanoic acid.

3 It undergoes an electrophilic addition with bromine.

Helping Concepts *Exam Favourite Rating* ★★

*1. 

*2. The ester group is hydrolysed.

$$CH_3CO_2(CH_2)_6CH{=}CH(CH_2)_3CH_3 + H_2O$$
$$\rightarrow CH_3CO_2H + HO(CH_2)_6CH{=}CH(CH_2)_3CH_3$$

*3. Being an alkene, it undergoes electrophilic addition with Br_2.

$$>C{=}C< + Br_2 \longrightarrow -\underset{Br}{\underset{|}{\overset{|}{C}}}-\underset{Br}{\underset{|}{\overset{|}{C}}}-$$

---

58. Nail varnish consists of a mixture of pigments, gloss, plasticizer and adhesive dissolved in a suitable solvent. A common solvent is a mixture of propanone and pentyl ethanoate, $CH_3CO_2(CH_2)_4CH_3$.

Which reagents will give a yellow or orange precipitate with this solvent?

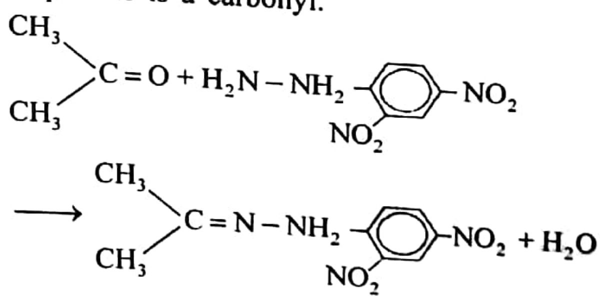
1 2,4-dinitrophenylhydrazine reagent

2 alkaline aqueous iodine

3 Fehling's reagent

Helping Concepts *Exam Favourite Rating* ★★★

*1. Propanone is a carbonyl.



*2. Propanone has the $CH_3-\overset{O}{\overset{\|}{C}}-$ group.

3. There is no aldehyde.

---

59. Mevalonic acid is an intermediate in the biosynthesis of cholesterol, and is shown below.

$$HO_2CCH_2\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}CH_2CH_2OH$$

Which properties does mevalonic acid have?

1 It has only one chiral carbon atom.

2 It can be esterified both by ethanoic acid and by ethanol, in the presence of H^+ ions.

3 It contains both primary and secondary alcohol groups.

Helping Concepts *Exam Favourite Rating* ★★

*1. $$HO_2CCH_2-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C^*}}-CH_2CH_2OH$$

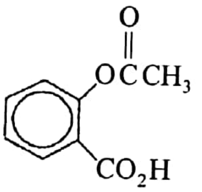
The carbon marked '*' is chiral.

*2. It contains both alcohol and carboxylic acid groups and hence can undergo esterification with a carboxylic acid and an alcohol respectively.

3. It contains a 1° and a 3° alcohols.

---

60. Aspirin, an analgesic, has the structural formula shown below:



Which of the following properties does aspirin possess?

1 It has a chiral carbon atom.

2 It forms a salt on reaction with cold, aqueous sodium hydroxide.

3 The ethanoyl group is removed on heating with aqueous sodium hydroxide.

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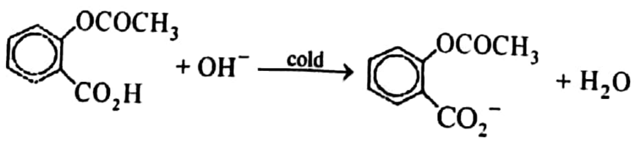
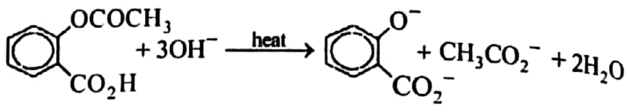
1. There is no chiral carbon.

*2. 

*3. The ester group is hydrolysed.



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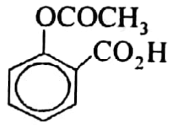
61. The compound *Aspirin* has the structure shown.



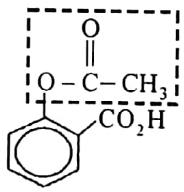
Which statements about *Aspirin* are correct?

1 It is an ester.

2 It dissolves in aqueous sodium carbonate, liberating carbon dioxide.

3 It can be prepared by the action of ethanoyl chloride on 2-hydroxybenzoic acid.

Helping Concepts *Exam Favourite Rating* ★★★

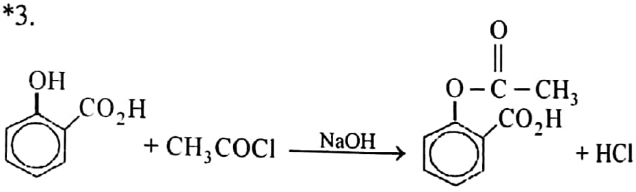


*1. It is an ester (see the above dotted box).

*2. It is a carboxylic acid and hence it reacts with Na_2CO_3 to give CO_2.

$$2R-CO_2H + CO_3^{2-} \rightarrow 2R-CO_2^- + CO_2 + H_2O$$

*3.



---

62. In a beehive, the queen bee secretes the substance below to cause worker bees to begin constructing royal colony cells.

$$CH_3CO(CH_2)_5CH{=}CHCO_2H$$

queen bee substance

From the structure shown, which of the following statements are true?

1 It gives a positive test with Fehling's solution (alkaline Cu^{2+} solution).

2 It gives a positive tri-iodomethane (iodoform) test.

3 It could exist as *cis-trans* isomers.

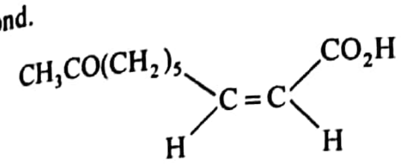
Helping Concepts | Exam Favourite Rating ★★★

The functional groups present are ketone, double bond and carboxylic acid.

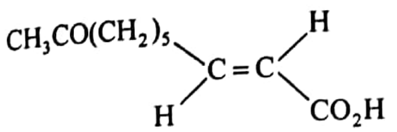
1. It is not an aldehyde.

*2. It contains $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-$ group.

*3. Different groups are bonded to the C at the double bond.



cis



trans

TOPIC 19

Nitrogen Compounds

Key content that you will be examined on:

1. Amines (exemplified by ethylamine and phenylamine)
   (i) Their formation
   (ii) Salt formation
   (iii) Other reactions of phenylamine
2. Amides (exemplified by ethanamide)
   (i) Their formation from acyl chlorides
   (ii) Their hydrolysis
3. Amino acids (exemplified by aminoethanoic acid)
   (i) Their acid and base properties
   (ii) Zwitterion formation
4. Proteins
   (i) Protein structure: primary; secondary; tertiary; quaternary structures
   (ii) The hydrolysis of protein
   (iii) Denaturation of proteins

Nitrogen Compounds

Topic 19

Exam Favourite Rating: ★Might be tested ★★Likely to be tested ★★★Always tested

Section A

1. Which of the following compounds is **least** soluble in water?

   A $CH_3CH(NH_2)CO_2H$

   B $CH_3CH(OH)CH_3$

   C $CH_3CH_2CH_2NH_2$

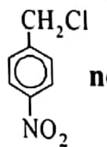
   D $C_6H_5NH_2$

Helping Concepts *Exam Favourite Rating* ★★

(A), (B) and (C) readily form H-bonding with water. (D) has a comparatively large carbon skeleton (hydrophobic) and the delocalisation of the nitrogen lone pair into the benzene ring reduces its tendency to hydrogen-bond with water.

---

2. Which type of reaction does the compound



not undergo?

   A electrophilic addition

   B electrophilic substitution

   C free radical substitution

   D nucleophilic substitution

Helping Concepts *Exam Favourite Rating* ★★

Although unsaturated, benzene ring is resonance stabilised and hence does not readily undergo electrophilic addition. The compound undergoes electrophilic substitution at the benzene ring, free radical substitution at $-CH_2-$, nucleophilic substitution at $-CH_2Cl$, and reduction at $-NO_2$.

---

3. What is produced when propanenitrile, CH_3CH_2CN, reacts with hydrogen using a palladium catalyst?

   A CH_3CONH_2

   B $CH_3CH_2NH_2$

   C CH_3NH_2 and CH_4

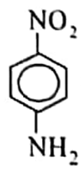
   D $CH_3CH_2CH_2NH_2$

Helping Concepts *Exam Favourite Rating* ★★★

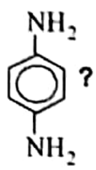
$$CH_3CH_2CN + 2H_2 \xrightarrow{Pd} CH_3CH_2CH_2NH_2$$

---

4. Which of the following would be used in a school laboratory to convert



into



?

   A concentrated aqueous ammonia

   B carbon monoxide in the presence of platinum

   C iron and concentrated nitric acid

   D tin and concentrated hydrochloric acid

Helping Concepts *Exam Favourite Rating* ★★

The process requires a reducing agent and (D) is commonly employed.

---

5. What stabilises the α-helix of proteins?

   A disulfide bridges and hydrogen bonding

   B disulfide bridges only

   C hydrogen bonding only

   D van der Waals' forces only

Helping Concepts *Exam Favourite Rating* ★

The α-helix of proteins is stabilised by hydrogen bonds between the N–H group of one amino acid unit and the C=O group of another along the main chain.

---

6. When phenylamine is treated with aqueous hydrochloric acid and the solution is then evaporated, what is the formula of the product?

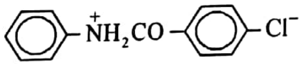
A $C_6H_5N_2^+Cl^-$
B C_6H_5Cl
C $C_6H_5NH_3^+Cl^-$
D C_6H_5NHCl

Helping Concepts *Exam Favourite Rating* ★★★

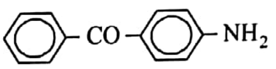
Phenylamine functions as a base and reacts with HCl to give an ionic salt, phenylammonium chloride.

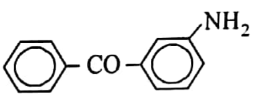
$$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^+Cl^-$$

7. What is the most likely product of reaction between phenylamine and benzoyl chloride?

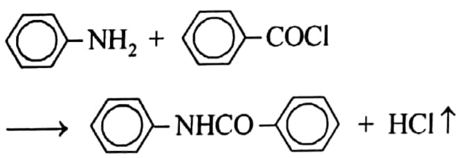
A 

B 

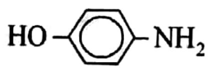
C 

D 

Helping Concepts *Exam Favourite Rating* ★★★



8. Which of the following would form an aqueous solution with the highest pH?

A C_2H_5OH
B $C_2H_5NH_2$
C CH_3CO_2H
D 

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(A), an alcohol, is neutral in water.

(C), an acid, has the lowest pH among the 4 compounds.

(B) and (D) are both amines. Thus, their aqueous solutions have pH > 7. However, (B) is a stronger base than (D) due to the electron donating $-C_2H_5$ group by inductive effect. This increases the availability of the lone electron pair on nitrogen for protonation. In addition, in (D), the lone electron pair on nitrogen is delocalised into the benzene ring and this renders the lone electron pair less available for protonation. Hence, (D) is a weaker base than (B).

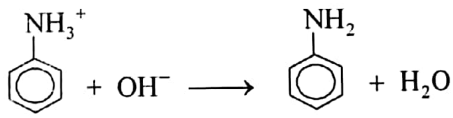
9. After the reduction of nitrobenzene to phenylamine, using tin and concentrated hydrochloric acid, an excess of sodium hydroxide is added.

What is the purpose of the sodium hydroxide?

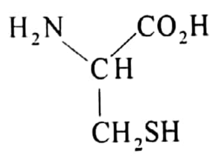
A to dry the product
B to liberate phenylamine
C to lower the boiling point for subsequent distillation
D to precipitate tin(II) hydroxide

Helping Concepts *Exam Favourite Rating* ★★

Before adding NaOH, the product exists in cationic form.



10. Proteins containing the amino acid cysteine often form disulfide bridges.



cysteine

Which type of reaction is involved in the formation of disulfide bridges from cysteine?

A condensation　　B hydrolysis
C oxidation　　D reduction

Helping Concepts *Exam Favourite Rating* ★★

In forming a disulfide linkage, H is removed. Hence, it is an oxidation process.

$$-SH + HS- \xrightarrow{-2H} -S-S-$$

11. A liquid **P** is sparingly soluble in water but dissolves readily in cold hydrochloric acid. Evaporation of this solution yields a crystalline solid. Which of the following could be **P**?

A $C_6H_5COCH_3$
B $C_6H_5CO_2H$
C C_6H_5CN
D $C_6H_5NH_2$

Helping Concepts *Exam Favourite Rating* ★★★

$C_6H_5NH_2$ is capable of H-bonding with water and hence is soluble in water. However, the hydrophobic benzene ring reduces its solubility in H_2O. Being a base, it reacts with HCl to form an ionic salt which is the crystalline solid.

$$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^+Cl^-$$

---

12. Which of the following compounds gives
(i) fumes of HCl with PCl_5;
(ii) NH_3 when heated with NaOH(aq)?

A $HOCH_2CH_2NH_2$
B $HOCH_2CONH_2$
C $HOCH_2\underset{\substack{|\\ NH_2}}{C}HCO_2H$
D $NH_2CH_2CO_2H$

Helping Concepts *Exam Favourite Rating* ★★★

(i) indicates that the compound contains at least an -OH group or –COOH group whilst (ii) suggests that it is either an ammonium salt or a primary amide.

$$R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl\uparrow$$
$$R-CONH_2 + OH^- \rightarrow R-CO_2^- + NH_3\uparrow$$

---

13. Which of the following reagents reacts only with the acid group of the amino acid $H_2NCH_2CO_2H$?

A HCl(aq) B HNO_2(aq)
C C_2H_5OH D C_6H_5COCl

Helping Concepts *Exam Favourite Rating* ★★★

$$H_2NCH_2CO_2H + C_2H_5OH \xrightarrow{\text{esterification}} H_2NCH_2CO_2C_2H_5 + H_2O$$

All (A), (B) and (D) react with the $-NH_2$ groups:

A: $H_2NCH_2CO_2H + H^+ \rightarrow H_3\overset{+}{N}CH_2CO_2H$

B: $H_2NCH_2CO_2H + HNO_2$
$\rightarrow HO-CH_2CO_2H + N_2 + H_2O$

D: $H_2NCH_2CO_2H + C_6H_5COCl$
$\rightarrow C_6H_5CONHCH_2CO_2H + HCl$

---

14. Which sequence shows the nitrogen compounds in decreasing order of basic strength?

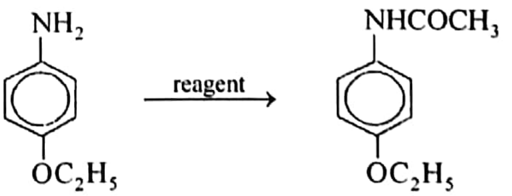
	most basic	$\longrightarrow$	least basic
A	$C_2H_5NH_2$	NH_3	$(C_2H_5)_2NH$
B	$C_2H_5NH_2$	$(C_2H_5)_2NH$	$C_6H_5NH_2$
C	$(C_2H_5)_2NH$	NH_3	$C_6H_5NH_2$
D	$C_6H_5NH_2$	NH_3	$C_2H_5NH_2$

Helping Concepts *Exam Favourite Rating* ★★

The strength of a base depends on how readily available its lone pair of electrons is for protonation. Alkylamines such as $(C_2H_5)_2NH$ are more basic than NH_3 because the electron-donating alkyl group makes the lone pair of electrons on N more available. Arylamines such as $C_6H_5NH_2$ are less basic than NH_3 since the lone pair of electrons on N can delocalise into the benzene ring so that it is less available. Thus, $(C_2H_5)_2NH$ is more basic than NH_3 which is more basic than $C_6H_5NH_2$.

---

15. The painkiller *Phenacetin* can be made from compound **X**.



X **Phenacetin**

What could be the reagent?

A CH_3COCH_3
B CH_3COCl
C CH_3CONH_2
D $CH_3CO_2CH_2CH_3$

Helping Concepts *Exam Favourite Rating* ★★★

The reaction involves the substitution of a H from the amino group by CH_3CO. Hence, it is an acylation.

$$RNH_2 + CH_3COCl \rightarrow RNHCOCH_3 + HCl$$

---

16. Which of the following statements explains why $C_6H_5NH_2$ is a weaker base than CH_3NH_2?

A $C_6H_5NH_2$ is sparingly soluble in water.
B The CH_3 group is smaller than the C_6H_5 group.
C The lone pair of electrons on the nitrogen in $C_6H_5NH_2$ is delocalised over the benzene ring.
D The benzene ring in $C_6H_5NH_2$ is electron-releasing.

Helping Concepts *Exam Favourite Rating* ★★

The basicity of an amine depends on the availability of the lone pair of electrons of nitrogen for donation to an acid.

In $C_6H_5NH_2$, the lone electron pair of N is able to delocalise into the benzene ring, making it less susceptible to donation to an acid. Therefore, it is a weaker base. In ethylamine, $CH_3CH_2NH_2$, the ethyl group is electron-donating by inductive effect and this enhances the availability of lone pair for donation.

---

17. The same carboxylic acid is obtained either by the hydrolysis of a nitrile **P** or by the oxidation of an alcohol **Q**.

Which of the following pairs could be **P** and **Q**?

	P	Q
A	CH_3CH_2CN	CH_3CH_2OH
B	$(CH_3)_2CHCN$	$(CH_3)_3COH$
C	$C_6H_5CH(CH_3)CN$	$C_6H_5CH_2CH(OH)CH_3$
D	$C_6H_5CH_2CN$	$C_6H_5CH_2CH_2OH$

Helping Concepts *Exam Favourite Rating* ★★★

$$RCN + 2H_2O + H^+ \rightarrow RCO_2H + NH_4^+$$
$$R'CH_2OH + 2[O] \rightarrow R'CO_2H + H_2O$$

Therefore, $R = R'$ and the alcohol should be a primary alcohol with the same number of C atoms as there is in the nitrile.

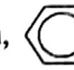
---

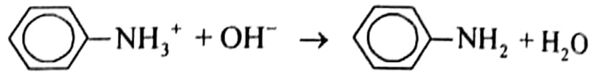
18. After the reduction of nitrobenzene to phenylamine using tin and concentrated hydrochloric acid, an excess of sodium hydroxide is added.

What is the purpose of the sodium hydroxide?

A to dry the product
B to liberate the phenylamine
C to lower the boiling point for subsequent distillation
D to precipitate tin(II) hydroxide

Helping Concepts *Exam Favourite Rating* ★★

In acid medium, $-NH_3^+$ is formed. The addition of NaOH, is to liberate $-NH_2$ from this salt (via an acid-base reaction).



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19. A solid compound **X** dissolved readily in water to give a weakly alkaline solution. On evaporation of the water, **X** was recovered unchanged.

Which of the following could **X** be?

A $CH_3NH_3^+Cl^-$ **B** $CH_3O^-Na^+$
C $C_6H_5O^-Na^+$ **D** $C_6H_5NH_2$

Helping Concepts *Exam Favourite Rating* ★★

$C_6H_5O^-Na^+$ dissolves in H_2O with partial hydrolysis, giving an alkaline solution.

$$C_6H_5O^-Na^+ + H_2O \rightleftharpoons C_6H_5OH + OH^- + Na^+$$

On evaporation of H_2O, the salt is recovered.

(A) gives an acidic solution in H_2O; hydrolysis of (B) is not reversible; (D) is a liquid.

---

20. The reduction of a nitrile produced a compound of formula $C_3H_7NH_2$. Which of the following compounds would be produced if the same nitrile was hydrolysed by heating with dilute hydrochloric acid?

A CH_3CONH_2
B $CH_3CH_2NH_2$
C $(CH_3)_2CHCO_2H$
D $CH_3CH_2CO_2H$

Helping Concepts *Exam Favourite Rating* ★★★

The given nitrile is C_2H_5CN.

$$C_2H_5CN + 4[H] \rightarrow C_3H_7NH_2$$

The acidic hydrolysis of C_2H_5CN would give C_2H_5COOH and NH_4^+ (partial hydrolysis would give $C_2H_5CONH_2$ instead).

$$C_2H_5CN + 2H_2O + H^+ \xrightarrow{\Delta} C_2H_5CO_2H + NH_4^+$$

---

21. The amino acid serine has the structure shown below:

$$HOCH_2\underset{}{C}HCO_2H \text{ with } NH_2 \text{ on the central C}$$

What is the zwitterion formed by serine?

A $HOCH_2CH(NH_2)CO_2^-$

B $HOCH_2CH(\overset{+}{N}H_3)CO_2H$

C $HOCH_2CH(\overset{+}{N}H_3)CO_2^-$

D $^-OCH_2CH(\overset{+}{N}H_3)CO_2H$

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Serine is an amino acid. In general, the formula of a zwitterion of an amino acid is $R-CH(\overset{+}{N}H_3)-CO_2^-$.

---

22. Benzenediazonium chloride is prepared by reacting phenylamine dissolved in concentrated hydrochloric acid with aqueous sodium nitrite, keeping the temperature below 10 °C.

Which of the following occurs if the temperature rises above 10 °C?

A loss of phenylamine

B loss of hydrogen chloridre

C decomposition of benzenediazonium chloride

D crystalisation of benzenediazonium chloride

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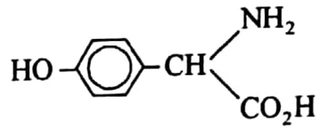
Benzenediazonium chloride is unstable to heat. N_2 is readily evolved when the salt is warmed.

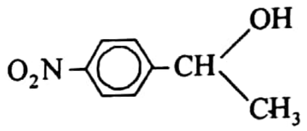
$$ArN_2^+ + H_2O \rightarrow ArOH + H^+ + N_2\uparrow$$

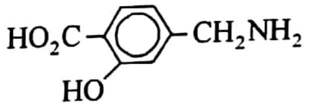
---

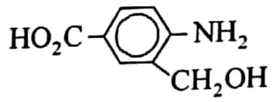
23. A product P isolated from a naturally-occurring source is established as having a molecular formula of $C_8H_9NO_3$. It possesses a chiral centre and it forms a zwitterion.

Which of the following structures could be P?

A 

B 

C 

D 

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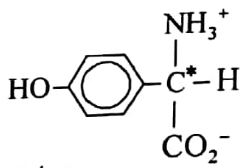

where ∗: chiral centre

---

24. With which of the following reagents do phenylamine and phenol have similar reactions?

A $Br_2(aq)$ B $HCl(aq)$

C $HNO_2(aq)$ D $NaOH(aq)$

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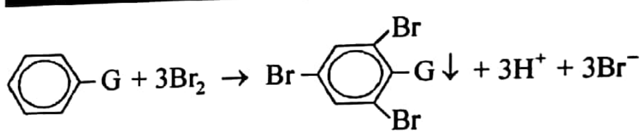


where G = OH, NH_2.

Both reactions are electrophilic substitution.

B: Only $C_6H_5NH_2$ reacts to give a salt.

$$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^+Cl^-$$

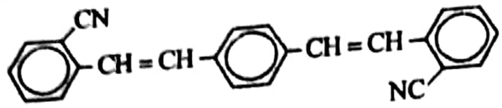
C: Only $C_6H_5NH_2$ reacts to five a benzenediazonium salt.

$$C_6H_5NH_2 + HNO_2 + H^+ \rightarrow C_6H_5N_2^+ + 2H_2O$$

D: Only C_6H_5OH reacts to give a salt.

$$C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$$

25. A compound used as an optical brightener in detergents has the following formula.



Which of the following is likely to be a property of this compound?

A It is readily soluble in water.

B The molecules exist as *cis-trans* isomers.

C It reduces aqueous $Ag(NH_3)_2^+$ to silver.

D It is hydrolysed by hot dilute sulfuric acid to give an amine.

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Different groups are bonded to the same C atoms of the double bonds. The compound can therefore exists as *cis-trans* isomers.

---

26. A dipeptide of structure

$H_2NCH_2CONHCH(CH_3)CO_2H$

was isolated after partial hydrolysis of an animal protein.

Which form would be predominant at pH 2?

A $H_2NCH_2CONHCH(CH_3)CO_2^-$

B $H_2NCH_2CONHCH(CH_3)CO_2H$

C $H_3\overset{+}{N}CH_2CONHCH(CH_3)CO_2^-$

D $H_3\overset{+}{N}CH_2CONHCH(CH_3)CO_2H$

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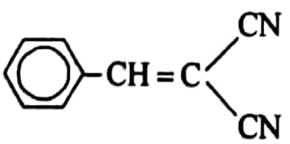
At pH=2 (acidic), the predominant form is the cationic form.

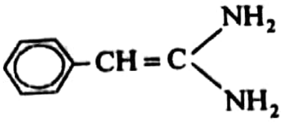
$$H_3\overset{+}{N}CH_2CONHCH(CH_3)CO_2^- + H^+$$
$$\rightarrow H_3\overset{+}{N}CH_2CONHCH(CH_3)CO_2H$$

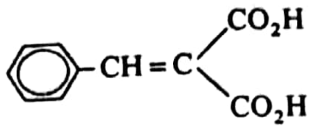
---

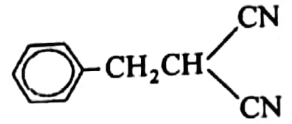
27. CS has the structure shown below, is an active component of 'tear gas' and is readily hydrolysed.

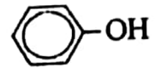


Which of the following is a possible hydrolysis product of CS?

A 

B 

C 

D 

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$$R-CN + 2H_2O \rightarrow R-CO_2H + NH_3$$

---

28. When aqueous bromine is added to a solution of phenylamine, the colour of the bromine disappears. Which of the following statements explains this observation?

A Phenylamine oxidises Br_2 to Br.

B The NH_2 of phenylamine is substituted by Br.

C The NH_2 group of phenylamine reacts with Br_2.

D Bromine replaces hydrogen in the benzene ring.

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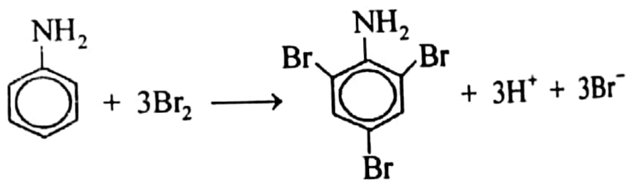

The lone pair of electrons of N delocalises into the benzene ring and this renders the benzene ring highly activated towards electrophilic substitution at 2– and 4– positions.

---

29. Some aminoethanoic acid is dissolved in a buffer solution of pH=9.0. Which of the following gives the structure of the two main forms of aminoethanoic acid at this pH?

A $\overset{+}{N}H_3CH_2CO_2H$ and $NH_2CH_2CO_2H$

B $\overset{+}{N}H_3CH_2CO_2H$ and $\overset{+}{N}H_3CH_2CO_2^-$

C $\overset{+}{N}H_3CH_2CO_2H$ and $NH_2CH_2CO_2^-$

D $\overset{+}{N}H_3CH_2CO_2^-$ and $NH_2CH_2CO_2^-$

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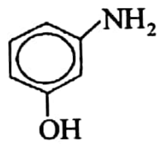
$$H_3\overset{+}{N}CH_2CO_2H \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H_3\overset{+}{N}CH_2CO_2^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H_2NCH_2CO_2^-$$

$\xrightarrow{\text{increasing pH}}$

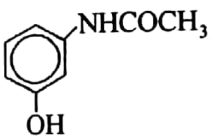
At pH 9, the zwitterion and the anion exist predominantly. At even higher pH, the anionic form becomes the main species present.

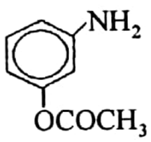
---

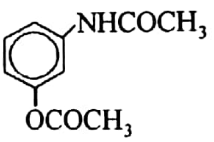
30. The compound below reacts with ethanoyl chloride.

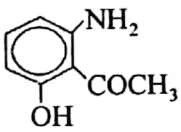


What is the formula of the product when the ethanoyl chloride is in excess?

A 

B 

C 

D 

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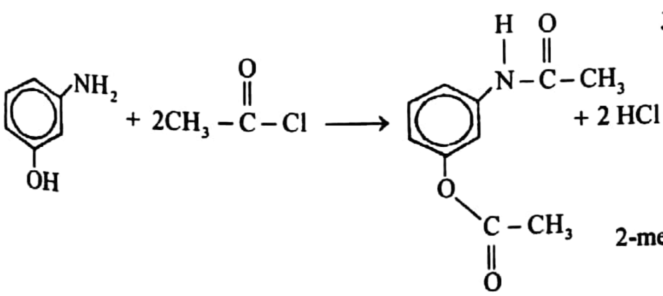
Both the –NH_2 and –OH groups undergo acylation to form an amide and an ester respectively.

$$Ar-NH_2 + CH_3COCl \rightarrow Ar-NHCOCH_3 + HCl$$

$$Ar-OH + CH_3COCl \rightarrow Ar-OCOCH_3 + HCl$$

Therefore, the overall reaction is



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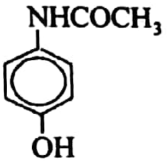
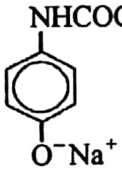
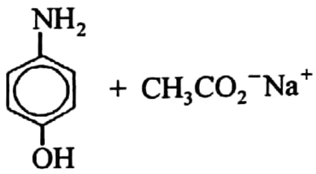
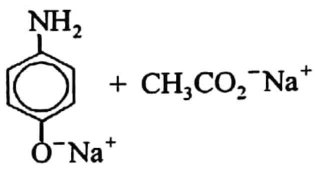
31. *Paracetamol* is a pain-killing drug.

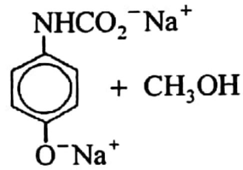


What are the products from its reaction with an excess of boiling aqueous NaOH?

A 

B 

C 

D 

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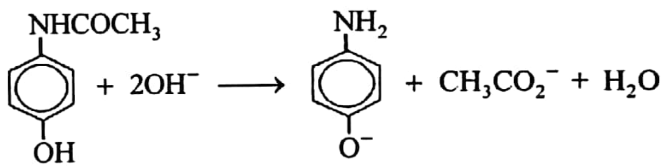
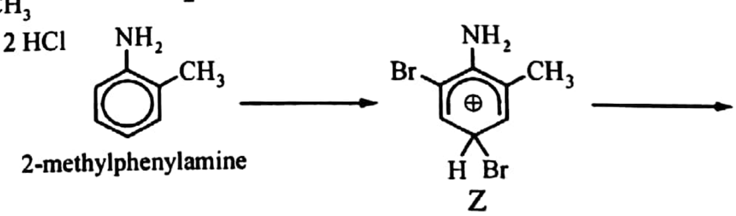


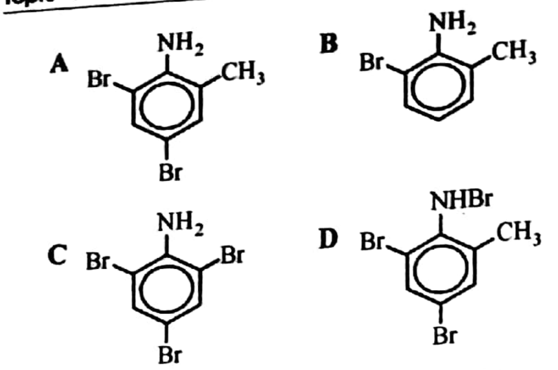
The amide is hydrolysed to an amine (R–NH_2) and a carboxylate ion. Phenol is acidic enough to react with NaOH to form a salt (phenate).

---

32. When 2-methylphenylamine reacts with an excess of Br_2(aq), one of the intermediates is cation Z.



What is the final product of this reaction?



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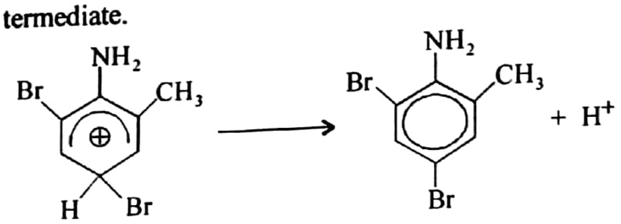
The last step involves the ejection of H^+ from the intermediate.



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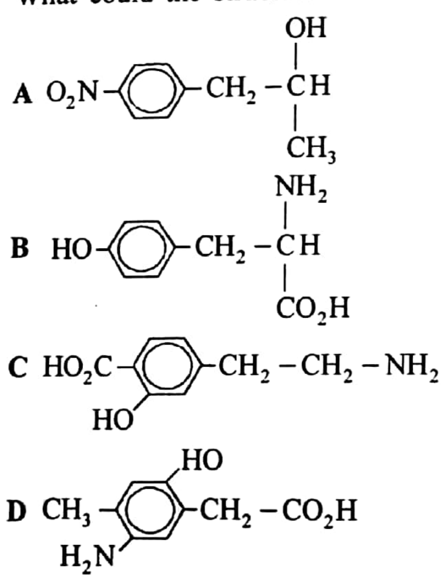
33. A product P, isolated from a naturally-occurring source, has a molecular formula of $C_9H_{11}NO_3$. It possesses a chiral centre and it forms a zwitterion.

What could the structure of **P** be?



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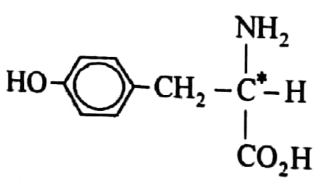
P should be an amino acid since it forms a zwitterion. The chiral centre is marked '*'.



34. Which of the following pairs of substances react together, forming an organic product that gives a neutral solution in water?

A CH_3CO_2H and NaOH

B C_6H_5OH and Na

C $C_6H_5NH_2$ and HCl

D CH_3COCH_3 and $LiAlH_4$

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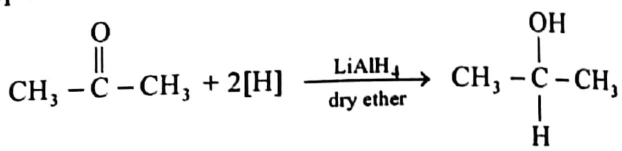
$LiAlH_4$ reduces ketones (and aldehydes) to their respective alcohols, which are neutral in H_2O.



A: $CH_3CO_2^-Na^+$, pH > 7

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$$

B: $C_6H_5O^-Na^+$, pH > 7

$$C_6H_5O^- + H_2O \rightleftharpoons C_6H_5OH + OH^-$$

C: $C_6H_5NH_3^+Cl^-$, pH < 7

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

---

35. Why are amides, $RCONH_2$, less basic than amines, RNH_2?

A Amides form a zwitterion in which the nitrogen atom carries a positive charge.

B Amides have a resonance structure involving the movement of a pair of electrons from the nitrogen atom to the oxygen atom.

C Electrons on the nitrogen atom move on to the C–N bond giving it some double bond character so that it is more difficult to break.

D The amide carbonyl group withdraws electrons from the NH_2 group to make the hydrogen atoms acidic.

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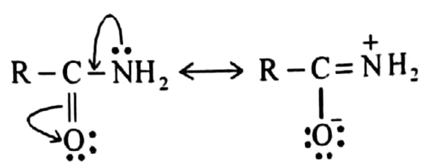

The lone pair of electrons on N is involved in delocalisation as shown above. Hence, it is less available for protonation, i.e. it is less basic compared to an amine.

36. Peptide P contains seven amino acid residues. When P is partially hydrolysed, the following dipeptide and tripeptide fragments are produced.

ala-gly
lys-ser
ser-gly-ala
met-ala
gly-lys

What could be the structure of peptide P?

A ala-gly-met-ala-lys-ser-gly
B lys-ser-gly-ala-gly-met-ala
C met-ala-gly-lys-ser-gly-ala
D ser-gly-ala-met-ala-gly-lys

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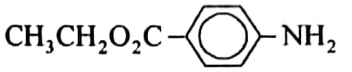
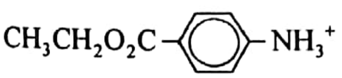
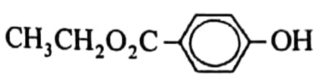
met-ala
ala-gly
gly-lys
lys-ser
ser-gly-ala

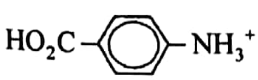
37. Benzocaine is a local anaesthetic, often used in suntan lotions to relieve pain.

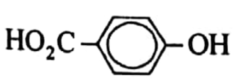


When benzocaine is heated with concentrated hydrochloric acid under reflux, what is the final product?

A 

B 

C 

D 

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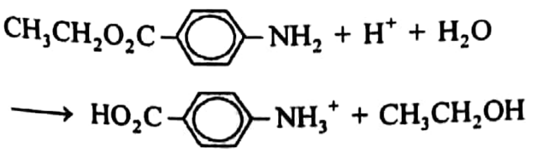
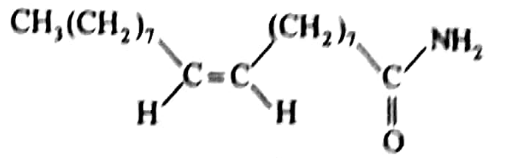
The ester functional group is hydrolysed to give a carboxylic acid and ethanol while the amine group, $-NH_2$, is protonated by the acid to give $-NH_3^+$.



38. A 'sleep factor', isolated from animal tissues, acts as a signal to the brain that it is time to sleep. It has been identified as *cis*-octadec-9-enoamide.



cis-octadec-9-enoamide

Which reagent would not readily destroy this molecule?

A dilute potassium manganate(VII)
B hydrogen with a platinum catalyst
C Tollens' reagent
D warm aqueous sodium hydroxide

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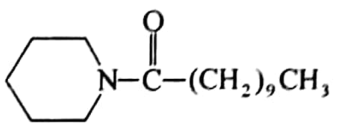
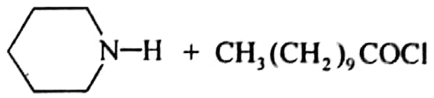
Cis-octadec-9-enoamide is not an aldehyde and hence does not react with Tollens' reagent. Options A and B are incorrect since a diol is formed with cold dilute $KMnO_4$ and H_2 is added across the C=C and C=O bonds respectively. Option D is incorrect since the amide functional group is hydrolysed by warm aqueous NaOH.

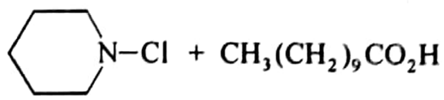
39. Acylpiperidines such as compound X are being studied as mosquito repellents.

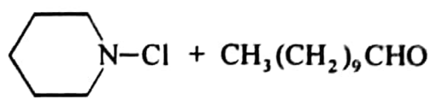


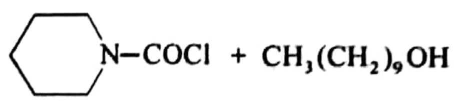
X

Which pair of compounds would produce X when reacted together?

A 

B 

C 

D 

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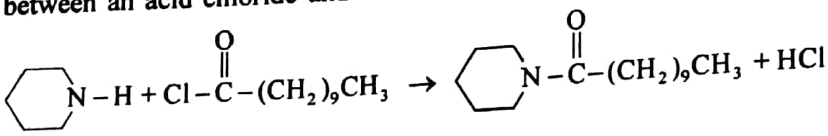
X is an amide and it can be formed by the reaction between an acid chloride and an amine.



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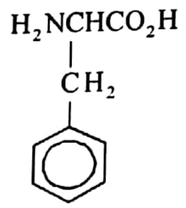
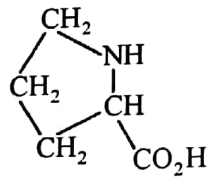
40. Which amino acid residue cannot form a hydrogen bond to stabilise the peptide α-helix and so causes a 'bend' in the regular shape?

A H_2NCHCO_2H with side chain CH_2SH
cysteine

B H_2NCHCO_2H with side chain $CH_2CH_2CO_2H$
glutamic acid

C 
phenylalanine

D 
proline

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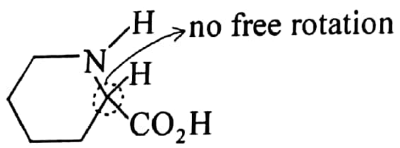
In proline, the α-amino acid group is locked in a ring structure and prevents free rotation at the α-carbon.



This structure is more rigid than the other α-amino acids and hence is not able to stabilise the peptide α-helix and causes a 'bend' in the regular shape.

---

41. Partial hydrolysis of insulin, the hormone essential for carbohydrate metabolism, gives the following tripeptide.

$$\begin{array}{c} \qquad\qquad\quad CH_2CH_2CO_2H \\ \qquad\qquad\quad | \\ (CH_3)_2CHCH(NH_2)CONH\,CHCONHCH(CH_3)CO_2H \end{array}$$

Which compound could be obtained by further hydrolysis of this tripeptide?

A $CH_3CH(CO_2H)_2$

B $(CH_3)_2CHCH(NH_2)CONH_2$

C $H_2NCONHCHCO_2H$ with side chain $CH_2CH_2CO_2H$

D $H_2NCHCONHCH(CH_3)CO_2H$ with side chain $CH_2CH_2CO_2H$

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$$\begin{array}{c} \quad\qquad\qquad\qquad O \;\; H \;\; CH_2CH_2CO_2H \\ (CH_3)_2CHCH(NH_2)\!\vdots\!\overset{}{C}-N\!\vdots\!CH\!\vdots\!C-N\!\vdots\!CH(CH_3)CO_2H \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad O \;\; H \end{array}$$

Hydrolysis takes place at either or both amide linkages as shown above. The amino acids obtained upon hydrolysis are:

1. Complete Hydrolysis:

$$(CH_3)_2CHCH(NH_2)-CO_2H$$

$$H_2N-CH(CH_2CH_2CO_2H)-CO_2H$$

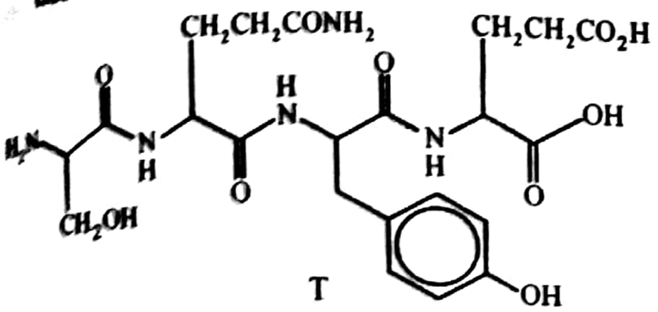
$$H_2N-CH(CH_3)CO_2H$$

2. Partial Hydrolysis:

$$(CH_3)_2CHCH(NH_2)-C(=O)-NH-CH(CH_2CH_2CO_2H)-CO_2H$$

$$H_2N-CH(CH_2CH_2CO_2H)-C(=O)-NH-CH(CH_3)CO_2H$$

42. The diagram shows the structure of the tetrapeptide T.



T

When 0.1 mole of T is heated under reflux with NaOH(aq) until no further reaction occurs, how many moles of NaOH will react?

A 0.4 B 0.5

C 0.6 D 0.7

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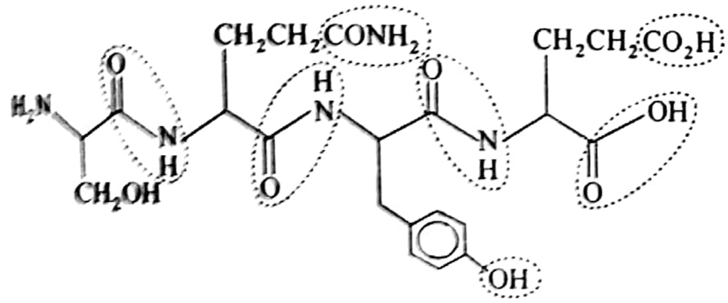
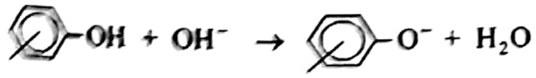


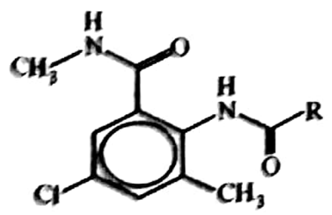
There are 4 amide bonds, 2 $-CO_2H$ and 1 phenolic groups. Hence, 1 mole of T will react with 7 moles of OH^-.

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}- + OH^- \rightarrow -\overset{O}{\overset{\|}{C}}-O^- + H-\overset{H}{\overset{|}{N}}-$$

$$-\overset{O}{\overset{\|}{C}}-OH + OH^- \rightarrow -\overset{O}{\overset{\|}{C}}-O^- + H_2O$$



43. An insecticide, J, has been developed for killing pests that attack fruit such as grapes, apples and peaches. Its structure is shown below, where R is an inert group.

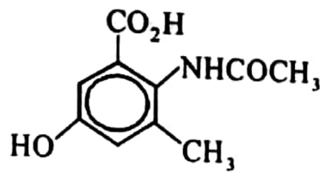


J

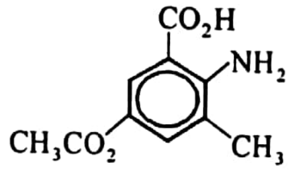
J is heated with aqueous NaOH under reflux, the solution neutralised and the product K isolated. K is then warmed with CH_3COCl in an inert solvent, to produce L.

What is the final product L?

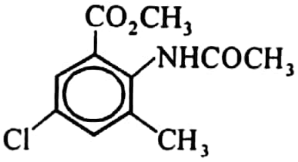
A



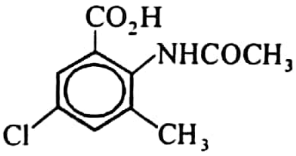
B



C



D



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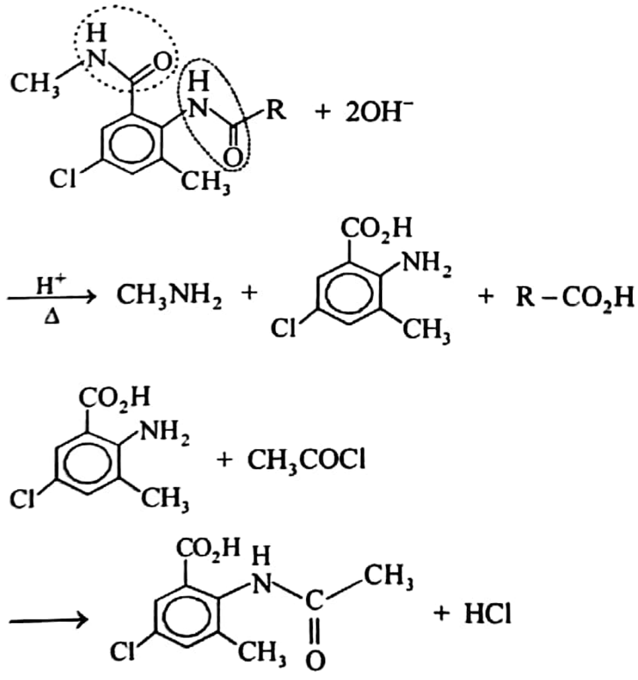

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

44. In which aspects of protein structure can hydrogen bonding occur?

1 the primary structure
2 the secondary structure
3 the tertiary structure

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*2. In a secondary structure, there are hydrogen bonds between N–H and C=O.

*3. In a tertiary structure, there are hydrogen bonds between $-CH_2OH$, $-CO_2H$, $-NH_2$ groups.

---

45. Which changes in bonding occur during the reaction of ethylamine with ethanoyl chloride?

1 A hydrogen-chlorine bond is formed.
2 A carbon-chlorine bond is broken.
3 A carbon-nitrogen bond is broken.

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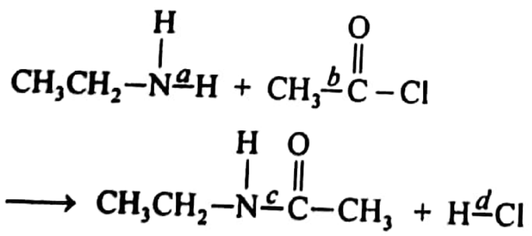

Bonds *a* and *b* are broken while bonds *c* and *d* are formed.

---

46. Which of the following pairs of substances evolve ammonia when mixed in aqueous solution and heated?

1 $(NH_4)_2SO_4$ and $Ca(OH)_2$
2 CH_3CONH_2 and NaOH
3 $C_6H_5NH_2$ and HNO_2

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*1. $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(\ell)$

*2. $RCONH_2(s) + OH^-(aq) \rightarrow RCOO^-(aq) + NH_3(g)$

3. $ArNH_2 \xrightarrow{HNO_2} ArN_2^+ \xrightarrow{H_2O} ArOH$

---

47. Which compounds liberate ammonia when boiled with aqueous sodium hydroxide?

1 $CH_3CH_2NH_2$
2 $CH_3CH_2CONH_2$
3 $CH_3CH_2CO_2NH_4$

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1. $CH_3CH_2NH_2$ is an amine and does not react with aqueous NaOH.

*2. $CH_3CH_2CONH_2$ is an amide and hydrolyses in hot aqueous NaOH to give sodium propanoate and ammonia.

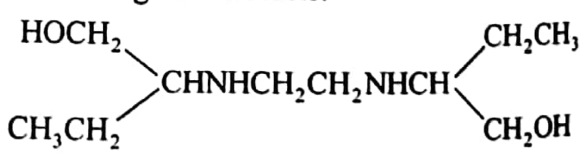
$$CH_3CH_2CONH_2 + OH^- \xrightarrow[\Delta]{} CH_3CH_2CO_2^- + NH_3$$

*3. $CH_3CH_2CO_2NH_4$ is an ammonium salt and the NH_4^+ present reacts with aqueous NaOH on boiling to give ammonia gas.

$$CH_3CH_2CO_2NH_4 + OH^- \xrightarrow[\Delta]{} CH_3CH_2CO_2^- + NH_3 + H_2O$$

---

48. Ethambutol has been used since 1960 as a drug for treating tuberculosis.



Which reagents, under suitable conditions, could convert it into an organic compound containing a halogen?

1 hydrogen bromide
2 alkaline aqueous iodine
3 ethanoyl chloride

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*1. HBr reacts with alcoholic OH to substitute in Br for OH so that an organic compound containing a halogen can be formed.

$$R-OH + HBr \rightarrow R-Br + H_2O$$

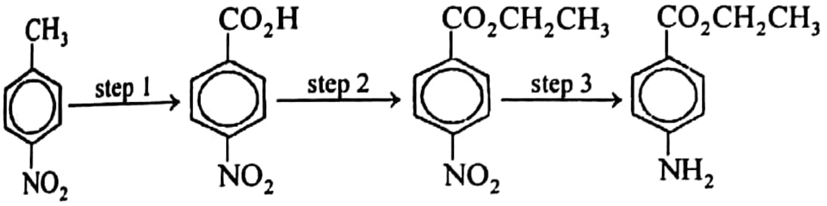
2. The molecule does not react with alkaline aqueous iodine since it does not contain the $-CH_3C{=}O$ or $-(CH_3)CHOH$ functional groups.

3. Ethanoyl chloride reacts with alcoholic OH to give an ester and HCl but not an organic compound containing a halogen.

$$R-OH + CH_3COCl \rightarrow R-OCOCH_3 + HCl$$

---

49. Many sunburn ointments contain benzocaine which relieves the pain caused by sunburn. It can be made in the laboratory by using the following reaction scheme.



Which of the following statements about this reaction scheme are correct?

1 Step 1 is an oxidation.

2 Step 2 is an esterification.

3 Step 3 is a reduction.

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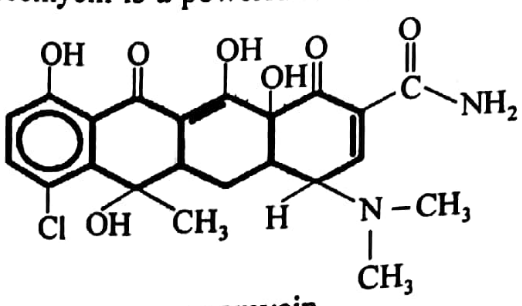
*1. Oxygen is added into the system.

*2. An ester is formed from the $-COOH$ group.

*3. $-NO_2$ is reduced to $-NH_2$: removal of oxygen, addition of hydrogen.

---

50. Aureomycin is a powerful antibiotic.



aureomycin

What functional groups are present in its molecular structure?

1 secondary alcohol

2 tertiary alcohol

3 ketone

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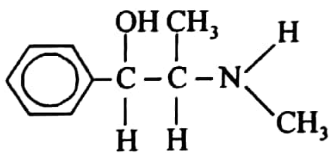
1,*2. There is no 2° alcohol group. The OH groups present are one phenol and three 3° alcohol groups.

3. There are two ketone groups: one on the ring next to the benzene and one on the extreme right ring.

---

51. The structure of the alkaloid ephedrine is shown below.



Which of the following will be properties of the alkaloid?

1 It has two chiral carbon atoms.

2 When warmed, it will be oxidised by acidified $KMnO_4$ solution.

3 It will form a salt on reaction with hydrochloric acid.

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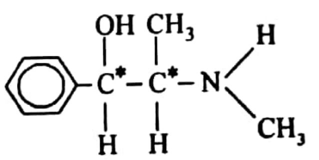
*1.



where *: chiral centre

*2. The compound is a secondary alcohol. It can be oxidised by acidified $KMnO_4$ to a ketone.

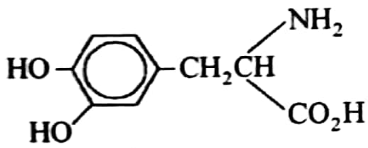
$$R-\underset{\displaystyle OH}{\underset{|}{C}}HR' + [O] \rightarrow R-\underset{\displaystyle O}{\underset{\|}{C}}-R' + H_2O$$

*3. Being an amine, it acts as a base and reacts with HCl to form a salt.

$$\underset{\substack{|\\ CH_3}}{R-NH} + HCl \rightarrow \underset{\substack{|\\ CH_3}}{R-NH_2^+Cl^-}$$

---

52. *Dopamine* is a drug used in the treatment of Parkinson's disease.



dopamine

Which of the following statements about this compound are correct?

1 It can exist in optically active forms.

2 One mole will react with three moles of sodium hydroxide to form a salt.

3 It can exist as a zwitterion in aqueous solution.

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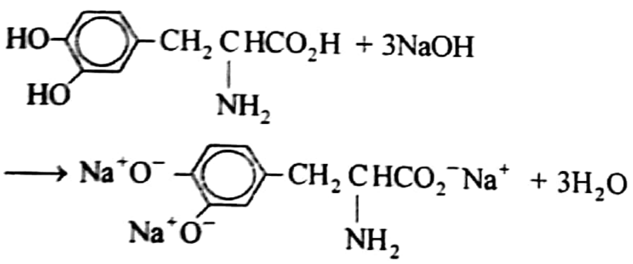
*1.

$$R-CH_2-\overset{\substack{NH_2\\ |}}{\underset{\substack{|\\ CO_2H}}{C^*}}-H$$

where $*$: chiral centre

The compound has a chiral centre and it is non-superimposable with its mirror image.

*2. Both the two phenolic groups and the carboxylic group act as acids and they react with NaOH to form a salt and H_2O.

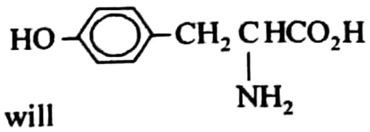


*3. Being an amino acid, it can exist as a zwitterion in aqueous solution.

$$\underset{\substack{|\\ {}^+NH_3}}{R-CHCO_2^-}$$

---

53. The amino-acid tyrosine has the structural formula shown below.



Tyrosine will

1 exist as a pair of optical isomers.

2 react with hydrochloric acid to form a salt.

3 react with aqueous sodium hydroxide to form a salt.

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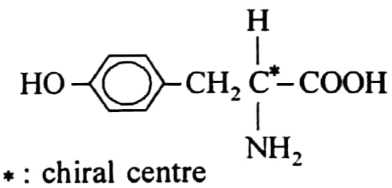
*1.



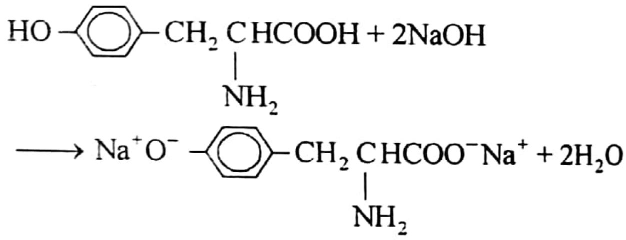
where $*$: chiral centre

The mirror images are non-superimposable.

*2. The amino group ($-NH_2$) is basic and reacts with HCl to form a salt.

$$R-NH_2 + HCl \rightarrow RNH_3^+Cl^-$$

*3. The phenolic group and the carboxylic group are acidic and they react with NaOH to form a salt and H_2O.



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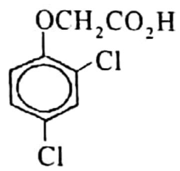
54. The compound *2,4-D* is used as a weedkiller.



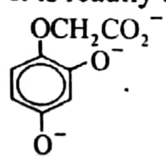
2,4-D

Which of the following statements about this compound are correct?

1 It can be esterified by ethanol in the presence of H^+ ions.

2 It can exist as a zwitterion.

3 It is readily attacked by aqueous alkali to form



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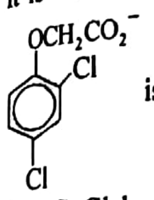
*1. 2,4-D is a carboxylic acid. It can therefore undergo esterification with an alcohol in the presence of H^+ ions.

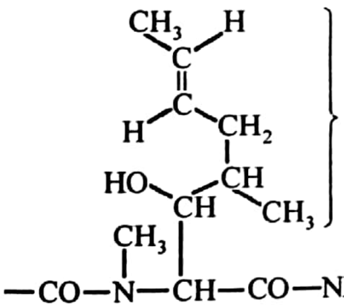
$$R-COOH + C_2H_5OH \xrightarrow[\text{heat}]{H^+} R-COOC_2H_5 + H_2O$$

2. It is not an amino acid.

3.  is formed.

The C–Cl bond is not broken due to its partial double bond characteristic as a result of the overlap of the p-orbital of Cl with the π-orbitals of benzene ring. Hence, it does not undergo nucleophilic substitution with OH^-.

55. Cyclosporin A is used in human kidney transplant operations as an immunosuppressor. It is a peptide.



side chain

Which reagents react with the side-chain shown?

1 ethanoyl chloride

2 aqueous bromine

3 dilute potassium manganate(VII)

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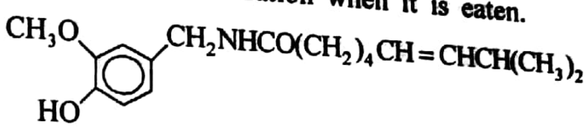
The side chain contains a $>C=C<$ double bond and a 2° OH group.

*1. $R-OH + CH_3COCl \rightarrow CH_3COOR + HCl$

*2. $>C=C< + Br_2 + H_2O \rightarrow -\underset{OH}{\underset{|}{\overset{|}{C}}}-\underset{Br}{\underset{|}{\overset{|}{C}}}- + H^+ + Br^-$

*3. $>C=C< + [O] + H_2O \xrightarrow{KMnO_4} -\underset{OH}{\underset{|}{\overset{|}{C}}}-\underset{OH}{\underset{|}{\overset{|}{C}}}-$

56. Capsaicin is the substance in chilli peppers which causes the hot sensation when it is eaten.



capsaicin

The CH_3O- group is inert.

Which reactions will capsaicin undergo?

1 Addition of bromine in an organic solvent causes three atoms of bromine to be incorporated into the molecule.

2 On heating with NaOH(aq), two moles of NaOH are used up per mole of capsaicin.

3 On heating under reflux with acidified concentrated $KMnO_4$, $(CH_3)_2CHCHO$ is a product.

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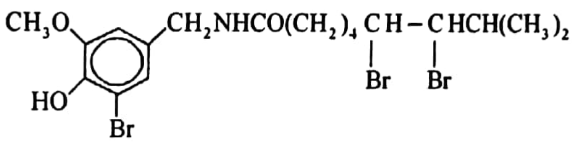
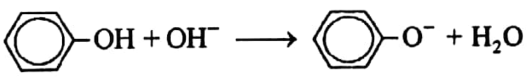
*1. Capsaicin undergoes electrophilic substitution at the benzene ring and electrophilic addition at the C=C double bond. The product formed is



*2. The phenol undergoes acid-base reaction while the amide is hydrolysed.

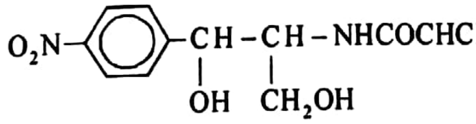


$$-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}- + OH^- \longrightarrow -\overset{H}{\overset{|}{N}}-H + {}^-O-\overset{O}{\overset{\|}{C}}-$$

One mole each of OH^- is needed for each reaction.

3. An aldehyde is not formed as a product as it can be further oxidised to a carboxylic acid by $KMnO_4$.

57. Chloramphenicol is an antibiotic secreted by certain bacteria; it has a large number of functional groups.



Which of the following deductions about the reactions of chloramphenicol can be made from this structure?

1 It gives a pale yellow precipitate with alkaline aqueous iodine.

2 It undergoes alkaline hydrolysis, one product of which contains an amino group and the other a carboxylate ion.

3 It decolourises acidified potassium manganate (VII) on warming.

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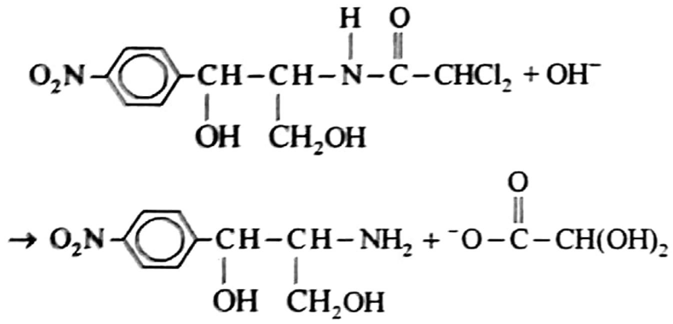
1. There is no $CH_3-\overset{|}{C}H-OH$ or $CH_3-\overset{|}{C}=O$ group present.

*2.

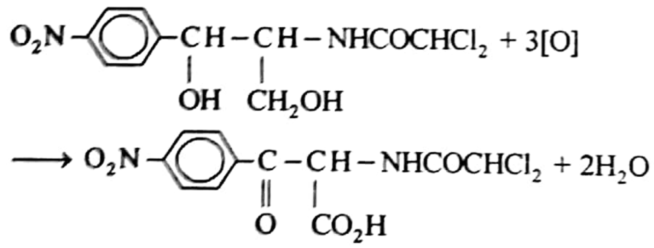


Note: The carboxylate ion undergoes dehydration readily:

$$^{-}O-\overset{\overset{\displaystyle O}{\|}}{C}-CH(OH)_2$$

$$\rightarrow {}^{-}O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-OH+H_2O$$

*3. The alcohol groups are oxidised.



ANSWERS

ANSWERS

Topic 1 Atoms, Molecules and Stoichiometry

1. D	2. D	3. B	4. A	5. B
6. C	7. A	8. B	9. D	10. C
11. D	12. B	13. B	14. A	15. B
16. A	17. B	18. D	19. B	20. D
21. D	22. C	23. B	24. B	25. B
26. C/D	27. B	28. D	29. C	30. B
31. D	32. C	33. A	34. C	35. D
36. C	37. C	38. D	39. C	40. B
41. C	42. C	43. C	44. C	45. D
46. A	47. B	48. B	49. B	50. B
51. A	52. A			

Topic 2 Atomic Structure

1. B	2. D	3. D	4. D	5. B
6. D	7. D	8. B	9. A	10. B
11. D	12. B	13. C	14. B	15. D
16. D	17. B	18. B	19. A	20. D
21. B	22. B	23. C	24. A	25. D
26. D	27. C	28. C	29. A	30. B
31. C	32. A	33. B	34. D	35. A
36. B	37. D	38. A	39. B	40. A
41. B	42. B	43. D	44. B	45. B
46. C	47. A	48. D	49. A	50. D
51. D				

Topic 3 Chemical Bonding

1. A	2. D	3. A	4. D	5. C
6. A	7. D	8. D	9. C	10. A
11. D	12. C	13. A	14. D	15. A
16. D	17. D	18. B	19. D	20. B
21. B	22. D	23. D	24. D	25. A
26. B	27. B	28. D	29. D	30. D
31. C	32. D	33. C	34. A	35. C

36. A	37. C	38. D	39. D	40. B
41. A	42. D	43. D	44. D	45. A
46. C	47. D	48. A	49. D	50. B
51. B	52. C	53. C	54. A	55. C
56. C	57. C	58. D	59. B	60. C
61. C	62. B	63. C	64. A	65. C
66. D	67. A	68. C	69. D	70. A
71. D	72. A	73. C	74. D	75. C
76. A	77. D	78. D	79. C	80. B
81. C	82. B	83. A	84. A	85. B
86. D	87. C			

Topic 4 The gaseous State

1. D	2. A	3. B	4. D	5. D
6. D	7. A	8. C	9. C	10. D
11. A	12. C	13. C	14. B	15. A
16. D	17. A	18. C	19. A	20. D
21. C	22. A	23. B	24. A	25. D
26. B	27. D			

Topic 5 Chemical Energetics

1. A	2. A	3. D	4. B	5. C
6. A	7. A	8. A	9. B	10. A
11. C	12. D	13. D	14. A	15. A
16. A	17. C	18. D	19. C	20. B
21. A	22. B	23. A	24. B	25. C
26. C	27. B	28. D	29. C	30. B
31. C	32. A	33. C	34. C	35. D
36. B	37. C	38. D	39. D	40. C
41. C	42. D	43. D	44. C	45. B
46. B	47. D	48. C	49. A	50. A
51. B				

Topic 6 Electrochemistry

1. A	2. D	3. C	4. D	5. D
6. B	7. A	8. D	9. D	10. B
11. C	12. B	13. A	14. A	15. D
16. D	17. C	18. B	19. D	20. C
21. A	22. D	23. C	24. C	25. B
26. D	27. D	28. D	29. C	30. D

31. A	32. D	33. C	34. D	35. A
36. D	37. C	38. D	39. D	40. A
41. D	42. D	43. B	44. C	45. D
46. B	47. A	48. D	49. D	50. D
51. B	52. B	53. B	54. D	55. D
56. A	57. C	58. C	59. C	60. B
61. B	62. C	63. C		

Topic 7 Equilibria

1. A	2. B	3. C	4. B	5. B
6. D	7. C	8. C	9. B	10. A
11. A	12. D	13. D	14. B	15. B
16. D	17. D	18. D	19. B	20. B
21. A	22. D	23. A	24. D	25. C
26. D	27. A	28. D	29. C	30. D
31. D	32. A	33. B	34. A	35. C
36. C	37. C	38. B	39. A	40. D
41. B	42. D	43. B	44. D	45. C
46. D	47. A	48. D	49. A	50. C
51. B	52. A	53. D	54. B	55. D
56. D	57. B	58. D	59. B	60. B
61. B	62. D	63. C	64. C	65. B

Topic 8 Reaction Kinetics

1. B	2. D	3. D	4. C	5. C
6. C	7. B	8. D	9. A	10. C
11. D	12. C	13. C	14. A	15. B
16. D	17. C	18. B	19. D	20. B
21. C	22. D	23. B	24. B	25. B
26. D	27. B	28. C	29. A	30. C
31. B	32. C	33. B	34. D	35. A
36. A	37. D	38. B	39. C	40. C
41. B	42. D	43. D	44. D	45. B
46. D	47. B	48. B	49. C	50. B
51. A	52. B	53. B		

Topic 9 The Periodic Table: Chemical Periodicity

1. A	2. D	3. A	4. D	5. B
6. D	7. B	8. D	9. B	10. C
11. D	12. D	13. C	14. A	15. C

16. D	17. D	18. B	19. A	20. B
21. C	22. D	23. B	24. C	25. C
26. B	27. C	28. B	29. B	30. C
31. C	32. D	33. C	34. B	35. A
36. A	37. D	38. D	39. B	40. A
41. D	42. C	43. C	44. A	45. B
46. D	47. A	48. C	49. B	50. C
51. B	52. A	53. B	54. C	55. D
56. A	57. B			

Topic 10 Group II

1. B	2. C	3. B	4. D	5. A
6. B	7. D	8. C	9. D	10. D
11. A	12. D	13. A	14. B	15. B
16. C	17. B	18. A	19. C	20. D
21. B	22. C	23. A	24. C	25. B
26. A	27. D	28. A	29. C	30. A
31. C	32. B	33. C	34. B	35. C
36. B	37. A	38. D	39. D	40. D
41. B	42. B	43. B	44. D	45. B
46. C	47. B	48. A		

Topic 11 Group VII

1. C	2. D	3. C	4. D	5. B
6. C	7. C	8. B	9. A	10. C
11. A	12. C	13. B	14. D	15. D
16. A	17. B	18. A	19. C	20. D
21. D	22. A	23. D	24. C	25. B
26. D	27. D	28. B	29. C	30. D
31. C	32. C	33. B	34. D	35. A
36. A	37. B	38. A	39. C	40. C
41. B				

Topic 12 An Introduction to the Chemistry of Transition Elements

1. D	2. A	3. B	4. C	5. C
6. C	7. D	8. D	9. D	10. D
11. A	12. C	13. C	14. C	15. D
16. C	17. C	18. A	19. C	20. C
21. D	22. D	23. B	24. D	25. B
26. D	27. C	28. D	29. B	30. B

31. C	32. B	33. D	34. D	35. B
36. D	37. C	38. B	39. B	40. B

Topic 13 Organic Chemistry: Introductory Topics

1. C	2. D	3. D	4. C	5. B
6. A	7. D	8. B	9. A	10. D
11. C	12. B	13. B	14. C	15. D
16. B	17. A	18. D	19. B	20. D
21. C	22. D	23. A	24. B	25. B
26. B	27. B	28. D	29. A	30. C
31. C	32. A			

Topic 14 Hydrocarbons

1. C	2. A	3. D	4. D	5. D
6. A	7. A	8. B	9. B	10. C
11. B	12. D	13. C	14. A	15. D
16. C	17. C	18. D	19. A	20. D
21. C	22. A	23. B	24. A	25. C
26. A	27. D	28. B	29. D	30. B
31. D	32. B	33. C	34. D	35. C
36. B	37. B	38. C	39. A	40. C
41. A	42. B	43. C	44. D	45. B
46. D	47. B	48. A	49. A	50. C
51. B	52. C	53. B		

Topic 15 Halogen Derivatives

1. B	2. D	3. A	4. D	5. D
6. D	7. D	8. C	9. D	10. C
11. D	12. D	13. B	14. D	15. C
16. C	17. D	18. D	19. D	20. C
21. D	22. D	23. D	24. D	25. B
26. B	27. B	28. A	29. D	30. C
31. A	32. D	33. A	34. D	35. A
36. D	37. B	38. B	39. B	40. A
41. D	42. C	43. C	44. D	45. A
46. A	47. B	48. A	49. C	50. C
51. B	52. C	53. D	54. B	

Topic 16 Hydroxy Compounds

1. A	2. A	3. C	4. A	5. C
6. D	7. D	8. B	9. D	10. B
11. D	12. D	13. B	14. B	15. B
16. A	17. A	18. D	19. A	20. B
21. B	22. A	23. C	24. B	25. D
26. B	27. A	28. D	29. C	30. A
31. D	32. D	33. C	34. A	35. B
36. C	37. B	38. A	39. B	40. B
41. A	42. B	43. D	44. B	45. A
46. B				

Topic 17 Carbonyl Compounds

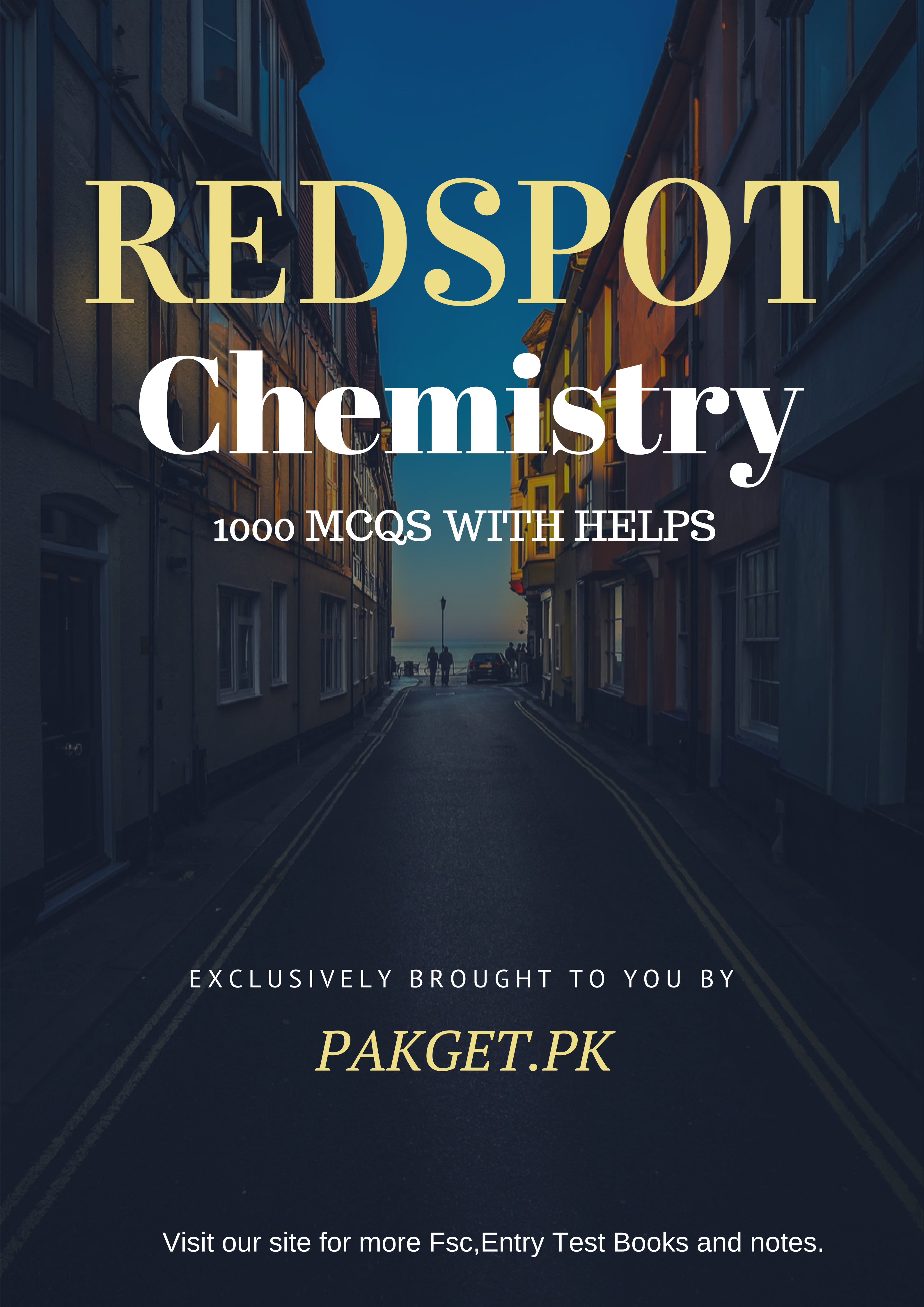
1. B	2. B	3. D	4. D	5. D
6. B	7. B	8. D	9. B	10. C
11. C	12. A	13. B	14. D	15. D
16. B	17. B	18. D	19. B	20. D
21. B	22. B	23. D	24. D	25. A
26. A	27. C	28. A	29. B	30. D
31. B	32. B	33. B	34. C	35. A
36. B	37. C	38. D	39. C	40. D
41. B	42. A	43. D	44. C	45. A
46. C	47. B	48. C	49. C	50. A
51. D	52. C	53. A	54. B	55. B
56. B	57. D	58. A	59. C	60. A

Topic 18 Carboxylic Acids and Derivatives

1. C	2. C	3. D	4. C	5. D
6. D	7. A	8. D	9. B	10. A
11. C	12. A	13. C	14. C	15. D
16. C	17. B	18. B	19. D	20. C
21. D	22. C	23. D	24. C	25. D
26. D	27. C	28. D	29. B	30. C
31. D	32. D	33. D	34. A	35. C
36. C	37. C	38. B	39. D	40. D
41. D	42. D	43. D	44. A	45. A
46. D	47. A	48. B	49. A	50. C
51. C	52. B	53. C	54. A	55. B
56. C	57. A	58. B	59. B	60. C
61. A	62. C			

Topic 19 Nitrogen Compounds

1. D	2. A	3. D	4. D	5. C
6. C	7. B	8. B	9. B	10. C
11. D	12. B	13. C	14. C	15. B
16. C	17. D	18. B	19. C	20. D
21. C	22. C	23. A	24. A	25. B
26. D	27. B	28. D	29. D	30. C
31. C	32. A	33. B	34. D	35. B
36. C	37. C	38. C	39. A	40. D
41. D	42. D	43. D	44. C	45. B
46. B	47. C	48. D	49. A	50. C
51. A	52. A	53. A	54. D	55. A
56. B	57. C			



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