1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
D	D	C	D	B	B	A	D	C	C	D	A	C	B	A
16	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
D	C	D	D	B	C	D	C	B	D	A	C	B	C	B

Q1(D)

Options A and B are incorrect as X is a cation while both options show anions.

No. of e^- in Ne atom = 10

	protons	neutrons	electrons
$^{23}Na^+$	11	12	10
$^{24}Mg^{2+}$	12	12	10

Thus, cation X is $^{24}Mg^{2+}$ since it has the same number of neutrons as protons.

Q2(D)

Statement 1 is incorrect as a longer covalent bond generally results in a smaller bond energy.

Statement 2 is incorrect as I in HI has a larger nuclear charge than Cl in HCl but HI has a lower bond energy than HCl.

Statement 3 is correct as more energy is required to overcome a greater attraction between shared pair of electons and the nuclei of the bonded atoms.

Q3(C)

Statement 1 is incorrect as H_2S has stronger permanent dipole-permanent dipole forces of attraction than H_2Se and hence a higher boiling point. This is so as the H−S bond is more polar than the H−Se bond due to greater electronegativity difference between H and S than H and Se since S is more electronegative than Se.

Statement 2 is correct as H_2O has less number of electrons and hence a smaller and less polarizable electron cloud, resulting in weaker instantaneous dipole-induced dipole forces of attraction than H_2Se.

Statement 3 is correct as the H−O bond is more polar than the H−S bond due to greater electronegativity difference between H and O than H and S since O is more electronegative than S.

Q4(D)

There are four bond pairs of electrons on N and no lone pair of electrons, hence the bond angle is 109°.

There are four bond pairs of electrons on C in CH_2 and no lone pair of electrons, hence the bond angle is 109°.

There are three bond pairs of electrons on N and no lone pair of electrons, hence the bond angle is 120°.

Q5(B)

Element	Electronic configuration	
$_{11}$Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$	1 unpaired electron
$_{12}$Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$	0 unpaired electron
$_{13}$Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$	1 unpaired electron
$_{14}$Si	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$	2 unpaired electrons
$_{15}$P	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	3 unpaired electrons
$_{16}$S	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$	2 unpaired electrons
$_{17}$Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	1 unpaired electron
$_{18}$Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	0 unpaired electron

Total 10 single unpaired electrons

Q6(B)

Option A is incorrect as the highest possible oxidation state of P is +5 and PCl_5 contains 85.1% by mass of chlorine.

Option B is correct as the highest possible oxidation state of Si is +4 and SiO_2 contains 53.2% by mass of oxygen.

Option C is incorrect as the highest possible oxidation state of P is +5 and P_4O_{10} contains 56.3% by mass of oxygen.

Option D is incorrect as the highest possible oxidation state of S is +6 and SO_3 contains 59.9% by mass of oxygen.

Q7(A)

$$A_r = \frac{69.3 \times 58 + 26.7 \times 60 + 1.20 \times 61 + 3.80 \times 62 + 1.00 \times 64}{69.3 + 26.7 + 1.20 + 3.80 + 1.00}$$

= 58.8

Note: Do not assume that relative abundances are percentages and do not assume that the relative abundances will always add up to 100. They do not add up to 100 in this case and students who made these assumptions would have incorrectly chosen option C.

Q8(D)

$$\left| \text{lattice energy} \right| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$$

q_+ = charge on cation
q_- = charge on anion
r_+ = radius of cation
r_- = radius of anion
$(r_+ + r_-)$ = inter-ionic distance

The least negative value (exothermic) for lattice energy will belong to a compound with smallest cationic and anionic charges as well as the largest cationic and anionic radii.

Since K^+ has a smaller charge than Ca^{2+} and peroxide anion, O_2^{2-}, has a larger anionic radius than oxide anion, O^{2-}, potassium peroxide (option D) will have the least negative value for lattice energy.

Q9(C)

Since $[SOCl_2]$ changed from 0.016 mol dm^{-3} to 0.002 mol dm^{-3} (0.016 ÷ 2 ÷ 2 ÷ 2) after 24 hours, each half-life is 24 ÷ 3 = 8 hours. A total of 4 half-lives are required to decrease $[SOCl_2]$ from 0.016 mol dm^{-3} to 0.001 mol dm^{-3} (0.016 ÷ 2 ÷ 2 ÷ 2 ÷ 2), thus a total of 32 hours is needed.

Q10(C)

When Q is in large excess, the reaction exhibits pseudo-order kinetics and given that the graph of [P] against time has a constant half-life, this means that the reaction is pseudo-first-order of reaction with respect to P.

When [P] remained constant and the [Q] × 2.4, the initial rate of reaction × 2.4^2 approximately. Hence, the reaction is 2nd order with respect to Q.

rate = $k[P]^1[Q]^1$, substituting in values for 1st expt,
$4.76 \times 10^{-4} = k\,[0.02][0.025]^2$
k = 38.1

Q11(D)

Activation energy remains constant even as temperature changes.

As temperature decreases, the maximum of the Boltzmann distribution curve displaces to the left and takes on a smaller value. Thus, the number of particles with kinetic energy greater than or equals to activation energy will be lower.

Q12(A)

Statement 1 is incorrect as the heterogenous catalyst (Fe) forms weak bonds with the reacting molecules and these bonds are very much weaker than the covalent bonds within the reacting molecules.

Statement 2 is incorrect as Fe is acting as a heterogenous catalyst and its mode of action does not change oxidation state unlike the mode of action for homogeneous catalysts

Q13(C)

Since the vessel has a fixed volume of 1.00 dm^3, concentration is directly proportional to amount of gas.

	H_2 +	CO_2 ⇌	H_2O +	CO
initial / mol dm^{-3}	0.01	0.01	0	0
change / mol dm^{-3}	−x	−x	+x	+x
equilibrium / mol dm^{-3}	0.01−x	0.01−x	x	x

$K_c = \frac{x^2}{(0.01-x)^2} = 0.123$

$x = 0.00026$ mol dm^{-3}

$[H_2(g)]_{eqm} = 0.01-x = 0.01-0.00026$

$= 0.0074$ mol dm^{-3}

Q14(B)

Electronegativity increases across the period, thus P has the highest electronegativity than Si than Al than Mg.

Atomic radius decreases across the period, thus P has the smallest atomic radius (0.110 nm) than Si (0.117 nm) than Al (0.143 nm) than Mg (0.160 nm).

Since the atomic radius of Si is closer to P than Al, option D is incorrect and option B is correct.

Q15(A)

A reducing agent undergoes oxidation and hence the metal will be the reducing agent in the reaction and since all elements have oxidation state = 0, a greater change in the magnitude of the oxidation number for the reducing agent depends on the magnitude of oxidation state of the cation.

Option A is correct as the cation has a large magnitude of charge than the anion.

Q16(D)

Statement 1 is incorrect as a pH of 13 at the end of experiment would mean $[OH^-] = 0.1$ mol dm^{-3} which is the same as the initial $[OH^-]$ before mixing. This is not possible as some of the OH^- would have reacted and there is also mixing with another solution, causing total volume to increase. When calculated, the pH at the end of the experiment is 12.2.

Statement 2 is correct as $pH = pKa + \lg\frac{[salt]}{[acid]}$ and $\frac{[salt]}{[acid]} = 1$ since half the acid has been transformed to an equal amount of salt.

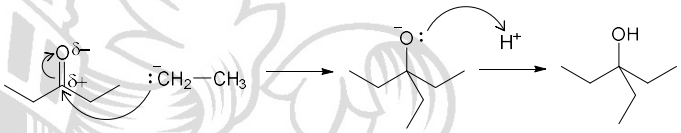
Q17(C)

KOH will react with some of the C_2H_5COOH to give $C_2H_5COO^-$ resulting in a buffer solution.

$pH = -\lg(1.35 \times 10^{-5}) + \lg(\frac{\frac{10.0}{1000}\times 0.20}{\frac{25.0}{1000}\times 0.15 - \frac{10.0}{1000}\times 0.20}) = 4.93$

Q18(D)

The reaction of a negatively charged carbon atoms with a carbonyl compound, to give an alcohol with more carbon atoms is nucleophilic addition, similar to the reaction of $:CN^-$ with carbonyl compounds.



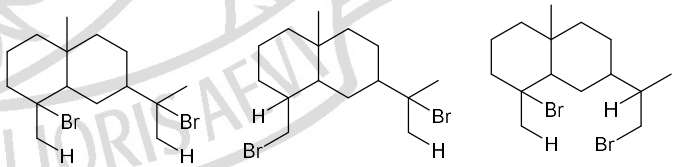
While the $C_2H_5^-$ anion functions as a nucleophile, option D is the closest as a Lewis base also donates it's lone pair electrons.

A	Incorrect. $C_2H_5^-$ is **not** electrophile, as it is donating, not accepting an electron pair.
B	Incorrect. $C_2H_5^-$ does not generate OH^- in this reaction as there is no water.
C	Incorrect. $C_2H_5^-$ is not a H^+ acceptor.
D	Correct, $C_2H_5^-$ donates its lone pair electrons in the reaction.

Q19(D)

Options A and B are incorrect as there is no change in the number of H atoms when it should have increased by two when 2 moles of HBr iadded to ß−selinene.

There are 3 possible products that are tertiary bromoalkanes:



Q20(B)

As the 2° carbocation has more electron-donating methyl groups, it is more stable than the 1° carbocation and this explains why 2-bromopropane is the main product.

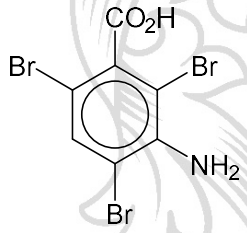
1	Correct
2	For a carbocation which is planar, steric hindrance does not factor so much into its reactivity. It is more important to consider the stability of the carbocations, and the more stable one will be made in larger proportions.
3	Incorrect as the methyl group has an electron-donating effect.

Q21(C)

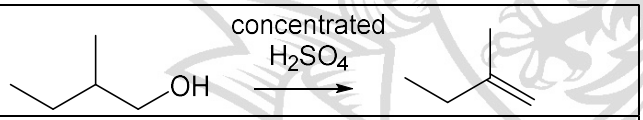
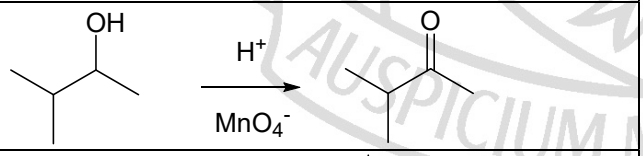
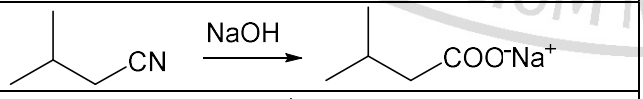
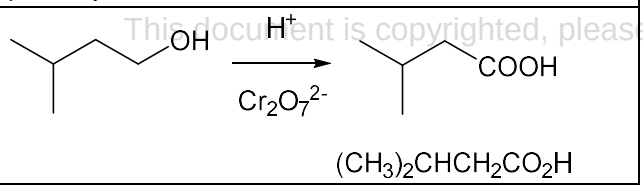
From the molecular formula of the product, 3 moles of Br_2 reacted with 1 mole of Y. Thus, the reactant should be a phenol or phenylamine with 2-, 4- and 6-positions relative to the −OH or $-NH_2$ available for substitution.

Options A and B are incorrect as they already have a substituent on the 4−position relative to the −OH or $-NH_2$, while option D has a substituent on the 2-position relative to the $-NH_2$.

Option C is correct answer and the product has this structure.



Q22(D)

A	
B	
C	
D	

Q23(C)

A	Incorrect. Ethoxide is **less stable** than phenoxide, as ethyl group is electron-donating and intensifies the negative charge on O^- in ethoxide, while phenoxide is more stable as lone pair of electrons of O^- in phenoxide is delocalised into the benzene π electron cloud.
B	Incorrect as the electron-donating ethyl group intensifies negative charge on O^- in ethoxide, making it less stable than hydroxide. Thus, ethanol is less acidic than water, and has a lower *K*a and **higher** p*K*a.
C	Correct.
D	Incorrect. Phenol has a **higher** *K*a value than ethanol since ethoxide is **less stable** than phenoxide (see option A).

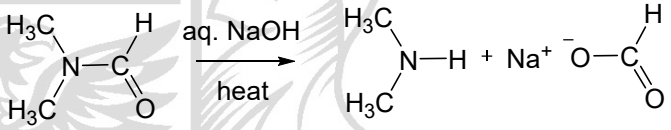
Q24(B)

In the reaction between $LiAlH_4$ and propanone, it can be considered a nucleophilic reaction where the "H^-" hydride acts as a nucleophile to react with electron deficient carbonyl carbon in the ketone.

1	Correct.
2	Incorrect. Propene has electron rich C=C group and no electron deficient $C^{\delta+}$ atoms and is unlikely to react with nucleophiles.
3	Incorrect. Reduction of propanone gives propanol.

Q25(D)

Amide hydrolysis takes place.



Q26(A)

Addition of hydroxide deprotonates the zwitterion of the amino acid in water to increase the concentration of the organic anion.

Q27(C)

$Q = IT = nF$

$5 \times 20.0 \times 60 = n(96500)$

$n = 0.06218$ mol of electrons

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

$n(Cu) = 0.06218 \div 2 = 0.03109$ mol

$m(Cu) = 0.03109 \times 63.5 = 1.97$ g

Q28(B)

Standard electrode potentials are measured under standard conditions: 1 bar for gases, 1 mol dm^{-3} for solutes, at a temperature of 298 K.

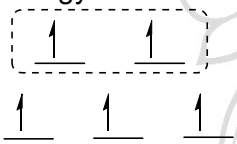
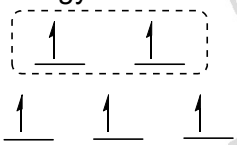
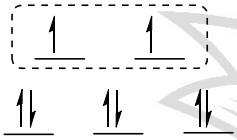
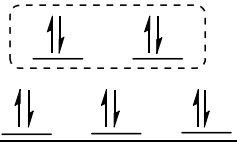
$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $\quad E^\ominus = +1.07$ V -------(1)

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\quad E^\ominus = +1.23$ V -------(2)

$E^\ominus_{cell} = +1.23 - (+1.07) = +0.16$ V > 0 (spontaneous)

1	Correct. Using a oxygen pressure smaller than 1 atm (since air only has 21% of oxygen) will cause position of eqm 1 to lie more to the left, $E(O_2/H_2O)$ to be less positive than +1.23 V and result $E_{cell} < 0$.
2	Correct. Even if a reaction is thermodynamically feasible, it could be kinetically unfavourable due to high activation energy.
3	Incorrect. If the $[Br^-] > 1$ mol dm^{-3} , the position of eqm 2 will lie more to the left, $E(Br_2/Br^-)$ to be less positive, making E_{cell} more positive and the reaction should still be spontaneous.

Q29(C)

A	Incorrect. Mn^{2+}, five 3d electrons, two in higher energy 3d orbitals 
B	Incorrect. Fe^{3+}, five 3d electrons, two in higher energy 3d orbitals 
C	Correct. Ni^{2+}, eight 3d electrons, two in higher energy 3d orbitals 
D	Incorrect. Cu^+, ten 3d electrons, four in higher energy 3d orbitals 

Q30(B)

From the data booklet,

	$E^\ominus$ / V
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26

SO_2 is a reducing agent and gets oxidised,

$E^\ominus_{anode} = +0.17$ V

Since for feasible reactions,

$E_{cell}^\ominus = E^\ominus_{cathode} - E^\ominus_{anode} = E^\ominus_{cathode} - (+0.17) > 0$

The vanadium half-reactions with $E^\ominus_{cathode} > +0.17$ will take place. Hence VO_2^+ is first reduced to VO^{2+}, which is reduced to V^{3+}. V^{3+} is not reduced to V^{2+} and the final oxidation state of V is +3.

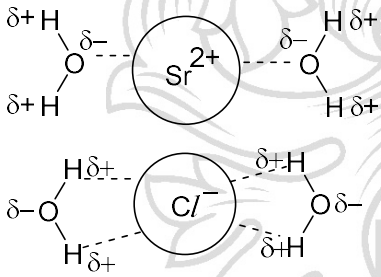
Question 1

(a)(i) $SrCO_3 \longrightarrow SrO + CO_2$

(a)(ii) Ca^{2+} ion has a smaller size, greater charge density and greater polarising power than Sr^{2+}. Thus, Ca^{2+} will polarize the CO_3^{2-} ion and weaken the C−O covalent within the CO_3^{2-} ion to a greater extent. Hence, less energy is required to break the C−O bond of CO_3^{2-} in $CaCO_3$, and it has a lower thermal decomposition temperature.

(b)(i) Between $SrCl_2$ particles: Ionic bonds
Between H_2O molecules: Hydrogen bonds

(b)(ii)



Note: All relevant dipoles should be labelled, and correctly oriented to the oppositely charged ion. As there are two δ+ dipoles on both H atoms of a water molecule, both should be aligned to the Cl^- ion and form ion-dipole interaction.

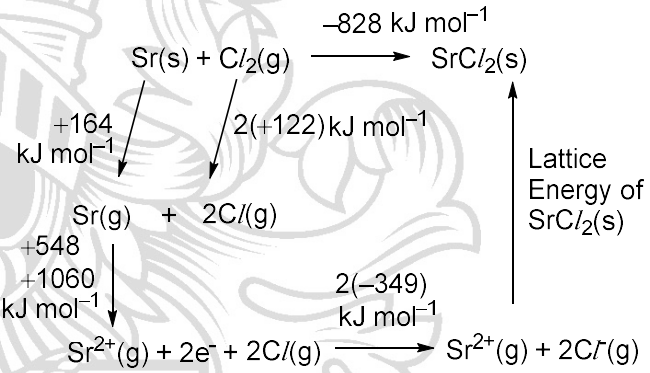
(c)(i) The entropy of a system is a measure of the disorder in the system. The more disordered the system is, the larger is its entropy.

(c)(ii) When $SrCl_2(s)$ dissolves, the Sr^2 and Cl^- ions dissociate and this increases the number of particles, increasing the disorder and entropy of the system.
The aqueous ions are mobile and free to move, compared to being held in fixed positions in solid state. The mobility of the aqueous ions increases the disorder and entropy of the system.

(c)(iii) The water molecules become bound to the ions via ion-dipole interactions formed during hydration of the ions. The orderly arrangement of water molecules about the ions decreases disorder and entropy.

(d) The standard enthalpy change of hydration of an ion is the energy released when 1 mole of gaseous ions is dissolved in water to form 1 mole of aqueous ions under standard conditions (i.e. 1 bar and 298 K).

(e)(i)



By Hess' Law
$-828 = +164 + 2(+122) + 548 + 1060 + 2(-349) + LE$
$LE = -2150 \text{ kJ mol}^{-1}$ (3 s.f.)

(e)(ii) $\Delta H^{\ominus}_{solution} = -LE + \sum \Delta H^{\ominus}_{hydration}$
$\Delta H^{\ominus}_{solution} = +2146 + (-1480) + 2(-364)$
$\Delta H^{\ominus}_{solution} = -62 \text{ kJ mol}^{-1}$

(f) The dissolution of CaF_2 requires high activation energy so that under room temperature conditions of 298K, there is insufficient energy to overcome activation energy requirements, making the process kinetically unfavourable.

Question 2

(a) An ideal gas consists of particles of negligible volume. In other words, the size of the gas particles is negligible compared to the volume of the container.
Collisions between the gas particles are perfectly elastic, there is no loss of overall kinetic energy upon collision.

(b)

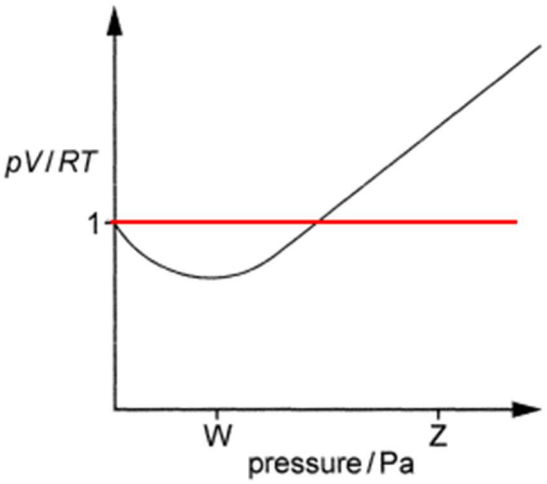


Fig. 2.1

(c) At very high pressures, the volume of gas is small, thus the molecular size and volume of gas particles is not negligible, resulting in 1 mol of a real gas occupying a larger volume than 1 mol of an ideal gas, thus $\frac{pV}{RT} > 1$, and positive deviation is observed.

(d) CO is polar as it has a net dipole with O more electronegative than C. Thus, CO molecules have permanent dipole−permanent dipole interactions in addition to instantaneous dipole–induced dipole (i.d.−i.d.) interactions. N_2 is non-polar and only has i.d.−i.d. interactions.
Hence, there are stronger intermolecular forces of attraction between CO molecules, causing 1 mol of CO to occupy a smaller volume than 1 mol of N_2, resulting in a lower pV/RT value for CO than N_2.

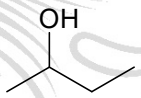
Question 3

(a) $pV = nRT = (m/M_r)RT$
$101325(250 \times 10^{-6}) = (0.500/M_r)(8.31)(273+93)$
$25.33 = 1520.7/M_r$
$M_r = 60.0$
A has a hydroxy group (OH), $M_r = 17.0$
Hence the remaining C_xH_y has $M_r = 60.0 - 17.0 = 43.0$, corresponding to C_3H_7
A is C_3H_7OH

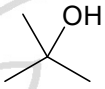
(b)(i) B and C Mr = 74 and both have one OH group.
M_r of $C_xH_y = 74 - 17 = 57$
$C_xH_y = C_4H_9$

Test 1: **B** has a 2° OH with a methyl group. It is oxidized to a ketone C=O, **C** cannot be oxidized, probably has a 3° OH

Test 2: **B** has $-CH(OH)CH_3$ in its structure. **C** does not have $-CH(OH)CH_3$ in its structure.



B



C

(b)(ii) $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightleftharpoons 2Cr^{3+} + 7H_2O$

(b)(iii) Triiodomethane, CHI_3

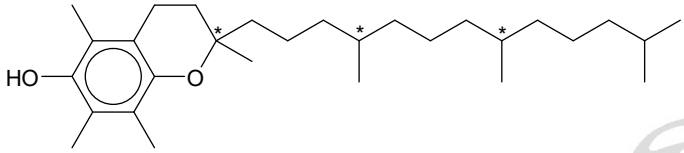
(c) In aqueous solution, Cr^{3+} exists as an octahedral complex $[Cr(H_2O)_6]^{3+}$. The presence of the H_2O ligands causes the splitting of the five originally degenerate 3d orbitals in the Cr^{3+} ion into two sets of slightly different energy levels.

Since the 3d subshell is partially filled (Cr^{3+}: [Ar] $3d^3$), the electrons from the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d orbitals.

Such d-d transitions are responsible for the colour observed in $Cr^{3+}(aq)$. The colour observed is the complement of the colour absorbed.

Question 4

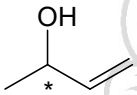
(a)



(b)(i) enzyme

(b)(ii) **F** and **G** are enantiomers. **F** is able to bind to **H,** as the structure of F is complementary to the shape of the active site on **H**, to form the enzyme−substrate complex, and proceed to react. **G** has a different 3D shape to **F**, thus **G** is not complementary to the shape of the active site on **H**, and unable to bind. Hence there is no reaction with **G**.

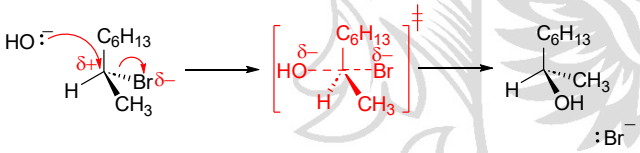
(c)(i)



J

(c)(ii) **J** and **K** are enantiomers. With separate sample of **J** and **K**, examine the rotation of plane-polarised light. The two compounds will rotate plane-polarised light in opposite directions.

(d)(i)



(d)(ii) S_N2 nucleophilic substitution

(e)(i)

Table 4.1

halogenoalkane sample	time for precipitate to appear/s	identity of halogen	colour of precipitate
L	38	I	yellow
M	76	Br	cream
N	512	Cl	white

(e)(ii) From Data Booklet,

Bond	Bond energy /kJ mol^{-1}
C−C*l*	340
C−Br	280
C−I	240

The higher the C-X bond energy, the slower the rate of nucleophilic substitution reaction. Hence the time taken for white AgC*l* precipitate to form is longest, with the highest C−C*l* bond energy and slowest rate, while time taken for AgI to form is shortest, with the lowest C−I bond energy and fastest rate.

(f)(i) $CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$

(f)(ii) The C−C*l* bond in chlorobenzene has partial double character, as the p orbital containing the lone pair of electrons on the C*l* atom overlaps with the π electron cloud of the benzene ring, resulting in a lone pair of electrons of C*l* delocalising into the benzene ring. This results in a stronger C−C*l* bond.

For the H_2O nucleophile to react with the benzene C atom bonded to C*l*, it needs to approach from the opposite side of the C−C*l* bond, which is sterically hindered by the rest of the benzene ring carbon atoms, impeding nucleophilic substitution.

(f)(iii) The carbon of the acyl group in CH_3COCl has a higher $\delta+$ charge (or is more electron deficient) as it is bonded to two electronegative atoms (O and C*l*). The carbon bonded to the chlorine atom in CH_3CH_2Cl has lower $\delta+$ charge (or is less electron deficient) as it is bonded to only one electronegative atom(C*l*). Hence, CH_3COCl can attract nucleophiles more easily and is more susceptible to nucleophilic attack with water.

Question 5

(a)(i) $HIn^{2-} + Ca^{2+} \longrightarrow H^+ + [In{-}Ca]^-$

(a)(ii) Seawater with X is pink before addition of $EDTA^{4-}$ and permanent blue colour remains at end of titration.

(b) From titration 2, under pH 12,
$n(EDTA^{4-}) = n(Ca^{2+})$
$= 8.00/1000(0.00375) = 3.00 \times 10^{-5}$ mol
in 3 cm^3 of seawater from Ocean 1
$[Ca^{2+}]$ in ocean 1, **V** $= 3.00 \times 10^{-5} /(3/1000)$
$= 0.0100$ mol dm^{-3}

From titration 1, under pH 10, both Ca^2 and Mg^2 are available to form complex and titrated with $EDTA^{4-}$.
$n(EDTA^{4-})$ = total $n(M^{2+})$
$= 16.80/1000(0.00375) = 6.3 \times 10^{-5}$ mol in 1 cm^3 of seawater from Ocean 1
Total $[M^{2+}] = 6.3 \times 10^{-5}/(1/1000)$
$= 0.0630$ mol dm^{-3}
Hence $[Mg^{2+}]$ in Ocean 1, **U** $= 0.0630 - 0.0100$
$= 0.0530$ mol dm^{-3}

(c)(i) SO_4^{2-}

(c)(ii) M_r of $BaSO_4 = 137.3 + 32.1 + 4(16.0)$
$= 233.4$
$n(BaSO_4) = 0.658/233.4 = 0.0028192$ mol $= n(SO_4^{2-})$
$[SO_4^{2-}] = 0.\ 0028192\ /(100/1000)$
$= 0.0282$ mol dm^{-3}

(d)(i) The K_{sp} of $Ca(OH)_2$ is much larger than the K_{sp} of $Mg(OH)_2$ and both of them have the same formula type. The given $[Mg^{2+}]$ is also much higher than $[Ca^{2+}]$. At pH 12, ionic product (I.P.) of $Mg(OH)_2$, exceeds its $K_{sp,}$ so the Mg^{2+} do not remain in solution but forms $Mg(OH)_2$ precipitate. Conversely, at pH 12, the I.P. of $Ca(OH)_2$ does not exceed its K_{sp} and no precipitate is formed, so Ca^2 remains in solution.

(d)(ii) After precipitation at pH 12,
I.P. $= K_{sp} = [Mg^{2+}][OH^-]^2$
$[OH^-] = 10^{-2}$ mol dm^{-3}
$[Mg^{2+}] = 1.1 \times 10^{-11}/10^{-2}$
$[Mg^{2+}] = 1.1 \times 10^{-9}$
% of Mg^{2+} remaining in solution
$= (1.1 \times 10^{-9}/0.0480) \times 100\%$
$= 2.29 \times 10^{-6}$ %

Question 6

(a) at pH = 8.2, $[H^+] = 10^{-8.2} = 6.3096 \times 10^{-9}$
At pH = 8.1, $[H^+] = 10^{-8.1} = 7.9433 \times 10^{-9}$
% change in $[H^+]$
$= (7.9433 - 6.3096)/6.3096 \times 100\%$
$= 25.9\%$

(b) $p(CO_2)$ in atm $= (4.2 \times 10^{-4})(1.009/1.013)$
$= 4.183 \times 10^{-4}$ atm
$K_{solubility} = [CO_2]$ in water / $p(CO_2) = 0.034$
$[CO_2]$ in water $= 0.034 \times 4.183 \times 10^{-4}$
$= 1.422 \times 10^{-5}$ mol kg^{-1}
$= 1.42 \times 10^{-5}$ mol dm^{-3}

(c)(i) As amount of CO_2 gas increases in the atmosphere, CO_2 concentration in sea water also increases proportionately. This causes the position of equilibrium in reaction 6.1 shifts to the right to reduce CO_2 concentration, increasing H^+ concentration. To counteract the increase in H^+ concentration, reaction position of equilibrium in reaction 6.2 shifts left, partially offsetting the increase in H^+ concentration thus maintaining the pH in seawater.

(c)(ii) $K_1 = [HCO_3^-][H^+]/[CO_2]$
$K_2 = [CO_3^{2-}][H^+]/[HCO_3^-]$
$K_3 = [HCO_3^-]^2/[CO_3^{2-}][CO_2]$
By observation, $K_3 = K_1/ K_2$
$K_3 = 1.45 \times 10^{-6} / (1.10 \times 10^{-9})$
$= 1.32 \times 10^3 = 1320.$
K_3 has no units since K_1/ K_2 has equal number of concentration terms in the numerator and denominator.

(c)(iii) At pH = 8.1, $[H^+] = 10^{-8.1} = 7.9433 \times 10^{-9}$
From reaction 6.1,
$[HCO_3^-]/[CO_2] = K_1/[H^+] = 182.5$
HCO_3^- is more abundant than CO_2
From reaction 6.2,
$[CO_3^{2-}]/[HCO_3^-] = K_2/[H^+] = 0.1385$
HCO_3^- is more abundant than CO_3^{2-}
Hence, HCO_3^- is most abundant inorganic carbon species at pH 8.1.

OR

$pK_1 = -\lg(1.45 \times 10^{-6}) = 5.839$
$pK_2 = -\lg(1.10 \times 10^{-9}) = 8.959$
Since $pK_1 < pH < pK_2$, the most abundant inorganic carbon species at pH 8.1 is HCO_3^-.

Note: The 2nd approach is analogous to determining the predominant form of an amino acid at different pH.

(d) With increasing T, pK_2 decreases, thus K_2 increases. Position of equilibrium of reaction 6.2 has shifted more to the right with increasing T to favour the forward endothermic reaction.

Question 1

(a) Down group 17 from chlorine to iodine, the electron clouds of the halogens become larger and more polarisable. Hence, more energy is required to overcome the increasing strength of the instantaneous dipole-induced dipole (id-id) interactions between the halogen molecules down the group, leading to decreasing volatility from chlorine to iodine.

(b) From Data Booklet,

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V

$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $E^\ominus = +1.07$ V

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

Experiment 1

$E^\ominus_{cell} = +1.36 - (+1.07) = +0.29V > 0$ V (spontaneous)

$Cl_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$

Final solution is orange in colour due to production of $Br_2(aq)$.

Experiment 2

$E^\ominus_{cell} = +1.36 - (+0.54) = +0.82V > 0$ V (spontaneous)

$Cl_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$

Final solution is brown in colour due to production of $I_2(aq)$.

Experiment 3

$E^\ominus_{cell} = +0.54 - (+1.07) = -0.53V < 0$ V (non-spontaneous)

No reaction occurs.

Final solution remains brown due to the presence of $I_2(aq)$.

Note: Observation in experiment 3 should be included.

(c) In **A**, there are 4 π bonds and hence 8 π electrons thus **A** is not aromatic since there is no [4n+2] π electrons (where n = 0,1,2,3).

In **B**, there are 5 π bonds and hence 10 π electrons thus **B** is aromatic since there [4n+2] π electrons (where n = 2).

(d) The N and C atoms in pyrrole are sp^2-hybridised. One sp^2 hybrid orbital each from N or C atom undergoes head-on overlap form C–C / C–N σ bonds. Each unhybridised p-orbital of N or C atoms overlaps side-on to form a continuously π electron cloud, delocalising the π electrons over the entire bent structure.

(e) Pyrrolidine is the most basic as there are two electron-donating alkyl groups bonded to the N atom, making the lone pair of electrons on N more readily available for coordination to H^+.

Pyrrole is less basic than pyrrolidine as lone pair of electrons on N is delocalised as part of the aromatic ring in pyrrole, making it less available for coordination to a H^+.

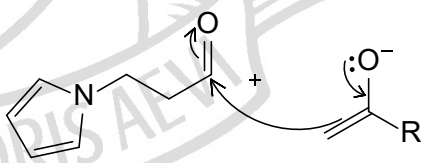
γ-lactam is the least basic as the overlap between the π electron cloud of the C=O and the orbital containing the lone pair of electrons on N causes the delocalisation of the lone pair of electrons into the π electron cloud of the C=O, making it unavailable for coordination to H^+.

(f)(i) secondary amide, secondary alcohol, carboxylic acid, fluorobenzene, benzene

Note: There is no alkene and amine functional group in atorvastatin as the C=C and N atom are part of the pyrrole functional group.

(f)(ii) Nucleophilic addition

(f)(iii)

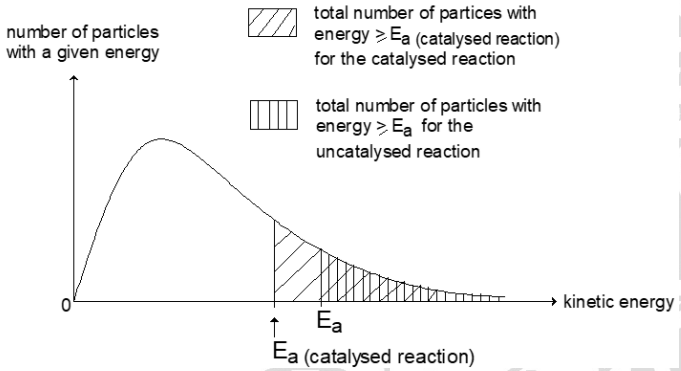


Question 2

(a)(i) $2NO(g) + 2CO(g) \xrightarrow{P} 2CO_2(g) + N_2(g)$

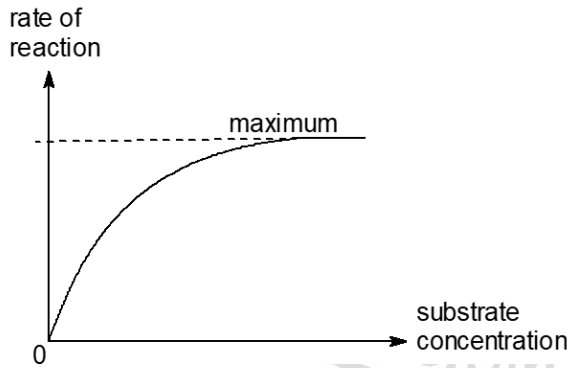
(a)(ii) Platinum acts as a heterogenous catalyst in this reaction as it is in a different phase (solid) from the gaseous reactants.

(b)



A catalyst increases the rate of a reaction by providing an alternative reaction pathway, one of lower activation energy ($E_{a\ (catalysed\ reaction)}$) than the uncatalysed reaction. As such, significantly more reactant molecules have energy greater than or equal to the activation energy for the catalysed reaction. This is as shown by the larger shaded area for the catalysed reaction in the above diagram. This results in an increase in effective collision frequency and hence an increase in the rate of the reaction. An alternative reaction pathway of lower activation energy also results in a larger rate constant k and hence an increase in the reaction rate.

(c)



At low substrate concentration, not all of the active sites of the enzymes are occupied thus, the rate of the reaction increases with increasing substrate concentration until a maximum is reached.

At high substrate concentration, the active sites of the enzyme become saturated with substrate. Further increase in the concentration of the substrate will not have any effect on the reaction rate.

(d)(i) rate equation for the reverse reaction of step 1: rate = k_r[ES]

rate equation of step 2: rate = k_2[ES]

(d)(ii)

rate of formation of ES = rate of breakdown of ES

$$k_f[E][S] = k_r[ES] + k_2[ES]$$

$$k_f[E][S] = (k_r + k_2)[ES]$$

$$[ES] = \frac{k_f}{k_r+k_2}[E][S]$$

(d)(iii)

$$[ES] = \frac{k_f}{k_r+k_2}[E][S]$$

$$\frac{k_r+k_2}{k_f} = \frac{[E][S]}{[ES]}$$

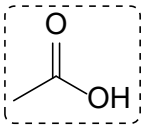
$$k_m = \frac{[E][S]}{[ES]}$$

(e)

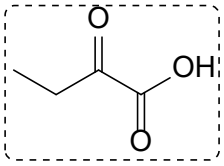
test	deductions
1	**F** ($C_{11}H_{14}O$) underdoes <u>reduction</u> to form **G** ($C_{11}H_{22}O$) → increase in 8 hydrogen atoms **G** contains a <u>secondary alcohol</u> from the reduction of ketone in the 2-cylcopenten-1-one structure → account for increase in 2 hydrogen atoms. The remaining increase in 6 hydrogen atoms is from the reduction of <u>3 C=C bonds</u> in **F** since **F** has only 2 different functional groups and only 1 O atom.
2	**F** ($C_{11}H_{14}O$) undergoes <u>electrophilic addition</u> to form **H** ($C_{11}H_{14}OBr_6$) → increase in 6 bromine atoms. **F** contains <u>3 C=C bonds</u>.
3	**F** undergoes <u>condensation</u> with 2,4-DNPH → **F** contains a <u>carbonyl</u> functional group.
4	**F** <u>does not undergo oxidation</u> with Fehling's reagent → **F** <u>does not contain an aliphatic aldehyde</u>
5	**F** undergoes <u>oxidative cleavage / strong</u> oxidation to form **J**, **K** and **L**. **J**, **K** and **L** undergoes <u>acid-base reaction</u> with $Na_2CO_3(aq)$ → they contain <u>−COOH</u>

	K and **L** undergo <u>condensation</u> with 2,4-DNPH and are formed from the oxidative cleavage of C=C → they contain <u>ketone</u> functional group. Since **L** contains 5 carbon atoms, it comes from the 2-cyclopenten-1-one structure.

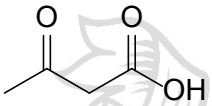
J:



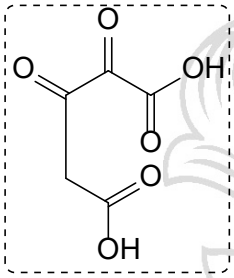
K:



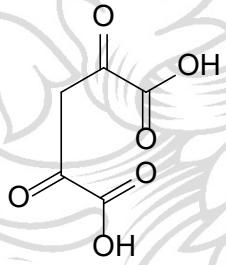
or



L:

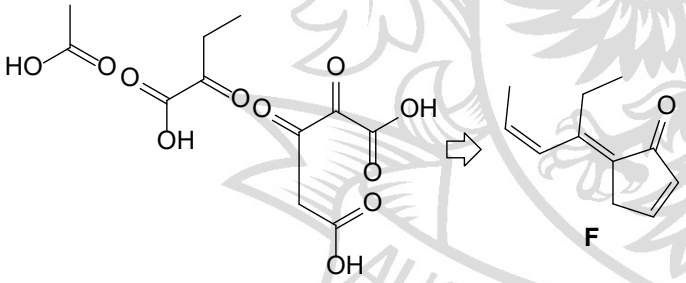


or

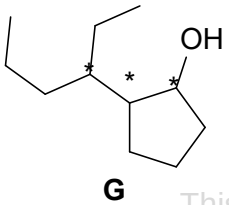


There are many possible structures of **F** and hence **G** and **H**, depending on which structures of **K** and **L** are used and how they are "joined" together. Check that the proposed structure of <u>**G** must have three chiral centres</u> and <u>**F** should display cis-trans isomerism</u> and <u>does not contain a chiral centre</u>.

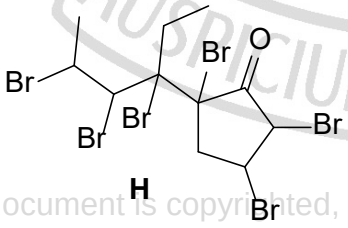
Using the circled structures as an example,



F

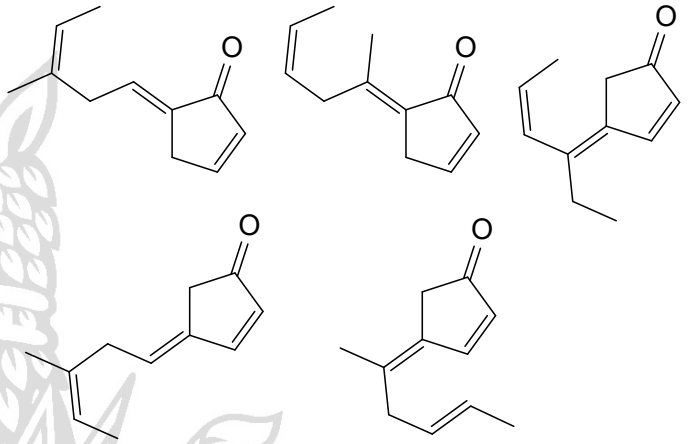


G

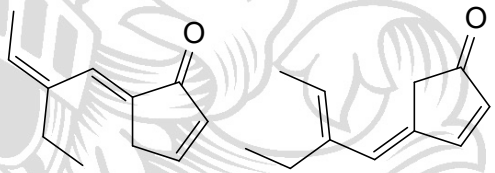


H

Other possible structures of **F** (excluding stereoisomers):



Wrong structures of **F** as they lead to corresponding **G** with only 2 chiral centres:



<u>Question 3</u>

(a)(i) $\Delta H^{\ominus} = 944+436\times3-390\times6 = -88$ kJ mol^{-1}

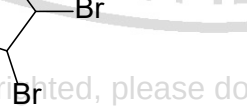
(a)(ii) $\Delta G^{\ominus} = -88-(450+273)(-199/1000)$
$= +55.9$kJ mol^{-1}

(a)(iii) Since $\Delta H^{\ominus} < 0$ and $\Delta S^{\ominus} < 0$, the reaction is spontaneous at low temperatures. Thus, increasing temperature decreases the spontaneity of the formation of ammonia as the $|T\Delta S^{\ominus}|$ increases relative to $|\Delta H^{\ominus}|$, causing $\Delta G^{\ominus}$ to be more positive.

(b)(i) conjugate acid-base pairs:
- NH_3 and NH_4^+
- H_2S and HS^-

(b)(ii) $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$ $\quad pK_a(NH_4^+) = 9.25$
$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$ $\quad pK_a(H_2S) = 6.98$

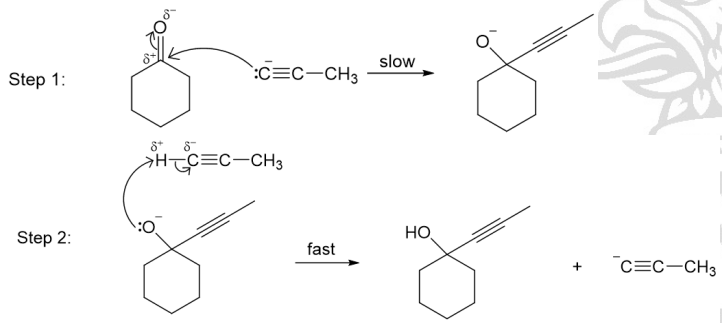
$$K_{eq} = \frac{[NH_4^+][HS^-]}{[NH_3][H_2S]} = \frac{K_a(H_2S)}{K_a(NH_4^+)} = \frac{10^{-6.98}}{10^{-9.25}} = 186$$

(c)  Since NH_2^- has 2 bond pairs of electrons (b.p.) and 2 lone pairs of electrons (l.p.), and the repulsion between

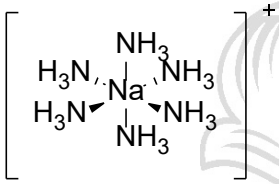
l.p.−l.p. > l.p.−b.p. > b.p.−b.p., to minimise electronic repulsion, the H-N-H bond angle is 104.5°.

(d)(i) Nucleophilic Addition

(d)(ii)



(e)(i)



(e)(ii) In $[Na(NH_3)_6]^+$, the complex contains a central Na^+ ion linked to 6 surrounding NH_3 molecules (called ligands) by co-ordinate bond (or dative covalent bond).

In $[Na(NH_3)_6]^+$, the NH_3 ligand is a molecule which contains one atom bearing a lone pair of electrons which is donated into a low-lying vacant orbital of the central Na^+ ion forming a co-ordinate bond (or dative covalent bond), resulting in the formation of a complex.

Question 4

(a) The first ionisation energies of the elements generally decrease down Group 1. Down a group, the number of electron shells increases, distance between the nucleus and the valence electrons increases and shielding experienced by valence electrons increases. Despite the increasing nuclear charge, electrostatic attraction between the nucleus and the valence electrons decreases, resulting in a decrease in the energy required to remove a valence electron.

(b)(i) $1s^2 2s^2 2p^6 3s^1$

(b)(ii) 2nd, 3rd, 4th, 8th, 10th

(b)(iii) In the successive ionization of Na, the number of protons remain the same and hence the nuclear charge remains the same. The number of electrons decreases, resulting in decreased shielding effect. Hence, the electrostatic attraction between the nucleus and the remaining electrons increases, resulting in an increase in energy required to remove each subsequent electron.

The significant increase in energy from the 1st to 2nd ionisation energy as well as 9th to 10th ionisation energy is due to the 2nd and 10th electrons being removed from an inner shell which is closer to the nucleus, experience less shielding effect and is more strongly attracted to the nucleus. Hence more energy is required to remove the 2nd electron compared to the 1st electron as well as the 10th electron compared to the 9th electron.

(c) $NaCl$ dissolves readily in water.

$NaCl(s) + aq \longrightarrow Na^+(aq) + Cl^-(aq)$

pH = 7

$AlCl_3$ dissolves readily with appreciable hydrolysis.

$AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

pH = 3

$SiCl_4$ hydrolyses to form $HCl(aq)$.

$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq)$

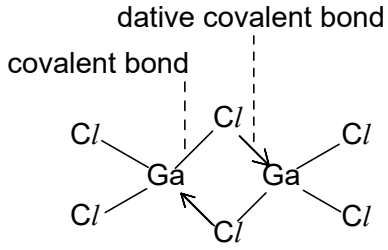
pH = 2

(d)(i) Lewis acid is an electron pair acceptor.

(d)(ii) Lewis acid strength: $BCl_3 > AlCl_3 > GaCl_3$

Both B of BCl_3 and N of NH_3 are in Period 2 and have similar size orbitals for more effective overlap to form a dative bond as compared to Al and Ga from Period 3 and 4 respectively.

(e)



(f) number of moles of $GaCl_3$

$= \frac{0.881}{69.7 + 35.5 \times 3} = 0.005$ mol

	$2GaCl_3(g) \rightleftharpoons Ga_2Cl_6(g)$	
initial / mol	0.005	0
change / mol	−0.3(0.005)	−(0.3/2)(0.005)
eqm / mol	3.5×10^{-3}	7.5×10^{-4}

Eqm partial pressure of $GaCl_3$

$= \frac{3.5 \times 10^{-3}}{3.5 \times 10^{-3} + 7.5 \times 10^{-4}} \times 250 = 205.88$ kPa

Eqm partial pressure of Ga_2Cl_6

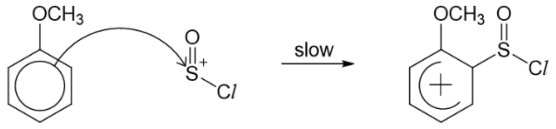
$= \frac{7.5 \times 10^{-4}}{3.5 \times 10^{-3} + 7.5 \times 10^{-4}} \times 250 = 44.12$ kPa

$K_p = \frac{44.12}{205.88} = 1.04 \times 10^{-3}$ kPa^{-1}

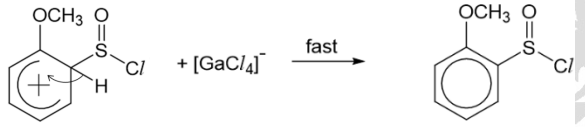
(g)(i) Electrophilic Substitution

$GaCl_3 + SOCl_2 \rightleftharpoons SOCl^+ + [GaCl_4]^-$

Step 1:

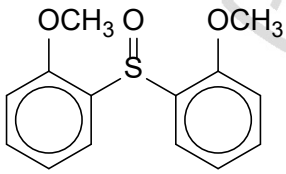


Step 2:



+ HCl + $GaCl_3$ (regenerated)

(g)(ii)



Question 5

(a)(i) This is due to due to the close similarity in energy of the 3d and the 4s electrons, that both the 3d and the 4s electrons are available for bond formation (ionic or covalent).

(a)(ii) Across the first-row transition elements, the number of protons increases, and hence, the nuclear charge increases. As electrons are added to the 3d subshell, the increase in the number of inner 3d electrons provide more shielding between the nucleus and the outer 4s electrons. This increase in shielding effect offsets the increase in nuclear charge considerably. Hence, the electrostatic attraction between the nucleus and outer 4s electrons increases minimally. The atomic radii are relatively similar.

(a)(iii) Both Co and Ca are metals. Co is a transition element and both its 3d and 4s electrons are available for delocalisation into the sea of electrons since the 3d and 4s electrons are close in energy. With a greater number of delocalised electrons and higher charge density of the titanium cations, Co has stronger metallic bonding than Ca, which requires more energy to overcome.

(b)(i) Complex formation

(b)(ii) Carbon monoxide bonds strongly (almost irreversibly), via a dative covalent bond, to the iron in haemoglobin. CO is a stronger ligand than O_2 and its presence destroys the O_2 carrying capacity of haemoglobin. Thus, CO is poisonous.

(c) amount of $S_2O_3^{2-} = \frac{23.80}{1000} \times 0.0450$

$= 0.001071$ mol

amount of $I_2 = \frac{1}{2} \times 0.001071$

$= 0.0005355$ mol

amount of $O_2 = \frac{1}{2} \times 0.0005355$

$= 0.00026775$ mol

mass of $O_2 = 0.00026775 \times 16.0 \times 2$

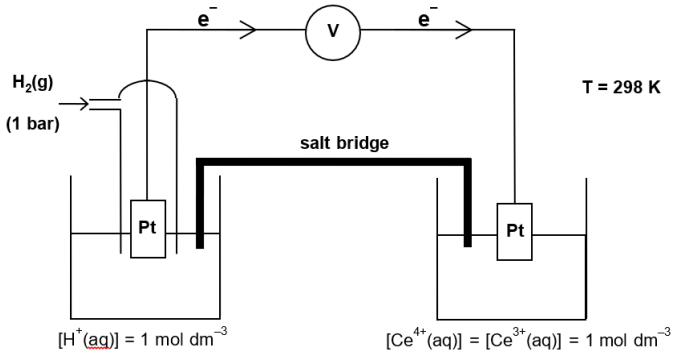
$= 0.008568$ mol

Concentration of dissolved O_2 in g dm^{-3}

$= 0.008568 \div \frac{250}{1000} = 0.0343$ g dm^{-3}

(d)(i) The standard electrode potential of a half–cell is the electromotive force, measured at 298 K, between the half–cell and the standard hydrogen electrode, in which the concentration of any reacting species in solution is 1 mol dm^{-3} and any gaseous species is at a pressure of 1 bar.

(d)(ii)



(d)(iii) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

$-405.3 \times 10^3 = -(3)(96500)E^{\ominus}_{cell}$

$E^{\ominus}_{cell} = \frac{-405.3 \times 10^3}{-(3)(96500)} = +1.40$ V

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = +1.40$ V

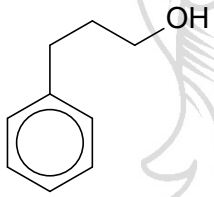
$E^{\ominus}_{anode} = E^{\ominus}_{cathode} - 1.40$

$E^{\ominus}_{(BiO+/Bi)} = E^{\ominus}_{(Ce4+/Ce3+)} - 1.40 = +1.72 - 1.40$

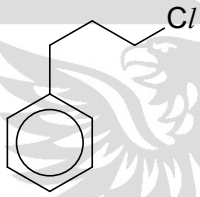
$= +0.32$ V

(e)(i)

N:



O:



(e)(ii) Step 1: $LiAlH_4$ in dry ether

Step 2: anhydrous PCl_3 OR PCl_5 OR $SOCl_2$ OR dry HCl(g), heat

Step 3: anhydrous $AlCl_3$