# A Level

# Chemistry

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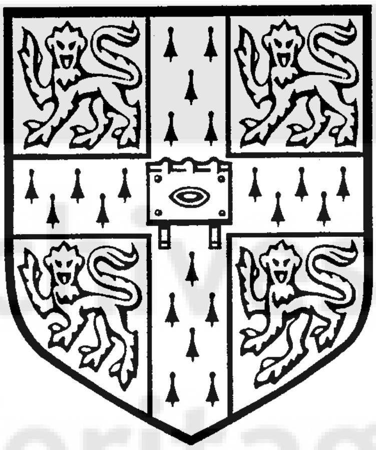


# CHEMISTRY

## Report on the June 1994 Examination

# CHEMISTRY

## ADVANCED LEVEL

## Subject 9250

### *Paper 9250/1 Theory*

*Answers to Numerical Calculations*

2. (b) **A** = $ICl_3$
(c) (ii) 17.1 $cm^3$
3. (c) (i) 0.080 mol $dm^{-3}$
(ii) 7.2 g $dm^{-3}$
(d) $1.26 \times 10^{-4}$ mol $dm^{-3}$
4. (a) (ii) 1.16 V
(b) 5.68 $dm^3$
6. (b) (ii) 22.2 $cm^3$

*General Comments*

The general standard of answers was well up to last year's, with many candidates showing good knowledge over a range of topics. Two questions caused marks to be lost through careless reading: the interpretation of the mass spectrum in *Q.2*, and the description of the chlorides of the elements sodium *to* phosphorus, not sodium *and* phosphorus, in *Q.6*. In addition, candidates' attention is drawn to the distinction between questions that ask for the *identity* of a substance (e.g. name *or* formula, in *Q.7 (a) (i)*) and those that ask specifically for the *name* (*Q.7 (b) (i)*) or the *structural formula* (*Q.10*), or the *displayed formula* (*Q.9 (b)*).

Some candidates also lost marks through a lack of thought about significant figures in final answers to calculations (unless otherwise stated, three figures are invariably sufficient).

*Comments on Specific Questions*

*Q.1* Some candidates had clearly anticipated a question on bonding and were determined to include everything they knew in their answer. The question was well answered on the whole, but some answers were too general and failed to include the interpretation of the data, as the question asked. Common misconceptions were that neon and argon consist of diatomic molecules containing Ne-Ne or Ar-Ar covalent bonds, that the strength of van der Waals' bonding increases with atomic mass (rather than the number of electrons contained in the molecule) and that covalent or ionic bonds in diamond and sodium fluoride were individually weak, only becoming strong in bulk. Few candidates pointed out that the van der Waals' bonding in water would be expected to be about the same as that in neon, due to same number of electrons.

*Q.2* Several candidates did not read the question correctly—if *m/e* 127 is the third peak in the mass spectrum (after *m/e* 35 and 37 as the first two), no peaks due to $Cl_2$ (*m/e* about 70) should have been included in their answers.

In *(b)*, many used 238 as the $M_r$ of $ICl_3$, rather than 233.5.

Several also included $Cl_2$, rather than $KCl$, or $Cl^-$, on the right-hand side of their equations in *(c)* and did not seem to know the stoichiometry of the $I_2/S_2O_3^{2-}$ reaction.

In *(d)*, the dot-and-cross diagram of $ICl_3$ was well drawn, but many suggested a pyramidal shape for the molecule—either Δ-planar or (the correct) T-shaped were accepted for the shape of $ICl_3$.

*Q.3* Graphs were plotted well, with axes correctly labelled, but the lack of smooth curve-drawing, and the mistaken assumption of pH 7 being the end-point, led to many incorrect neutralisation volumes. Comments on shape should have included the relative flatness during the *buffer region*, the sharp increase in pH *through the end point*, and the final flatness as the hydroxide ions predominate in the solution.

Many candidates guessed a correct indicator but did not seem to be aware that phenolphthalein is used for weak acid-strong base titrations because the pH at its changeover is on the alkaline side. Many variants on its spelling were noted, including 'phenol fehlings'!

The calculation in *(c)* was well done—allowance was made for the wrong neutralisation volume on scripts where the logic of the calculation was clear.

Many candidates, however, were stumped by the $K_a$ calculation. This calculation could have used either the fact that the pH at the half neutralisation point (where [lactic acid] = [lactate]) equals the $pK_a$ value, or the fact that the starting pH gives the $[H^+]$ (and hence [lactate]) in 0.080 mol $dm^{-3}$ lactic acid.

*Q.4* A surprisingly large number of candidates suggested an electrolysis circuit for *(a)*, including an external battery and giving the wrong sign for the zinc electrode. Most picked out the correct oxygen half-cell, but some mis-calculated $E_{cell}$ due to confusion over signs. Acceptable electrolytes were any ionic substance that does not react with the $OH^-$ formed, NaOH(aq) being the preferred one.

The calculation in *(b)* was quite taxing, involving the correct use of the 20% efficiency, the $\Delta H_c$, the $M_r$ and the density; nevertheless, it was well done by the majority.

*Q.5* Most candidates correctly outlined the production of chlorine at the anode during the electrolysis of brine. (One candidate suggested bubbling fluorine through brine to displace the chlorine!).

In general, observations were lacking in *(b)*, apart from the production of brown fumes in *(ii)*. In *(i)* and *(ii)*, the green colour of $Cl_2$ would be seen to disappear and, in *(ii)*, an oily liquid would be produced. The descriptions of the reactions were good (disproportionation, redox or displacement, and addition), but the equations were poor—especially in *(i)*, where $HCl$ often appeared on the right-hand side, or the disproportionation was left at the chlorate(I) stage.

*Q.6* Part *(a)* was answered well—a few candidates misread the question and answered about only the two elements Na *and* P, rather than the five from Na *to* P. Several candidates fell into the inevitable trap of writing an equation for the dissolution of sodium chloride in water, including equimolar amounts of NaOH and $HCl$ on the right-hand side. Half of them then went on to state that the resulting solution would be alkaline and the other half said it would be acidic! Many thought that aluminium chloride is ionically bonded and that its hydrolysis goes all the way to $Al(OH)_3$—some even stating that a white precipate would be produced.

Many did not recognise the yellow solid in *(b)* to be sulphur—one suggested it was solid chlorine! Allowance was made in marking the calculation for those candidates who *showed* that they thought $H_2SO_3$ was monobasic, rather than dibasic.

*Q.7* Parts *(a) (i)* and *(ii)* proved fairly straightforward, but some candidates did not know the formula of ammonium chloride ($NH_2Cl$ and $NH_3Cl$ were far too common), and others calculated the oxidation number of N in it as +5. Several failed to deduce that the nitrogen oxide formed in *(iii)* was $N_2O$ — NO was the most popular suggestion.

Part *(b)* was a fairly standard 'recall' type of question, but *names*, not formulae, should have been given in *(i)*. Many did not appreciate the environmental consequences of nitrates in *(iii)*: acid rain and ozone depletion appeared in answers. Those who did mention eutrophication often did not explain the chain of events—needed in an A level answer: over-growth of algae ⇨ cutting out light from bottom-living oxygenating plants ⇨ decomposing dead algae ⇨ increasing b.o.d. ⇨ insufficient oxygen for animal life.

*Q.8* Many candidates suggested $HCl$ rather than $PCl_5$ (or $SOCl_2$) as the reagent needed in *(a)*. The reactions of benzoyl chloride were well known, however.

In *(b)*, electrophilic substitutions were not expected. The final answer in *(b)* should have said that benzoyl chloride is *more reactive* in nucleophilic substitution due to a *more* $\delta+$ carbon atom as a consequence of the *electron-withdrawal* by the $C{=}O$ oxygen atom. There was some confusion between $CH_3\text{-}C_6H_4\text{-}Cl$ and $C_6H_5\text{-}CH_2\text{-}Cl$ for the comparison compound, some candidates thinking that *both* were implied.

*Q.9* Many candidates failed to appreciate the zwitterionic character of phenylalanine in *(a)*. Solubilities were expected to be explained in terms of hydrogen bonding or dipole-ion attractions, and melting points in terms of hydrogen bonding and cation-anion attractions. Several candidates suggested that benzoic acid is only sparingly soluble due to its only ionising to a small extent—only the ions dissolving in water!

In *(b)*, candidates lost marks through not including all bonds in their *displayed* formulae—especially bonds from H to O and N. Several thought $HCl$(aq) gave the acid chloride. The omission of a $CH_2$ group in the structural formula of phenylalanine in the question did not cause any confusion, thankfully. Some tried to make the dipeptide in *(c)* cyclic, whilst others thought a dipeptide had to include *two peptide links*, so ended up with a tripeptide. Others drew the C–N skeleton correctly but failed to show the di-anion that would be formed at pH 12.

*Q.10* Part *(a) (i)* proved straightforward, but few candidates appreciated that the reaction between sodium and hydroxyl groups in *(ii)* is a *redox*, or *reduction*, reaction. The formula of the alkoxide product should have included the ionic charges—several drew a covalent bond between the O and Na. In *(iii)*, either *oxidation* or *iodoform* was accepted for the type of reaction. Although many candidates correctly identified iodoform as one of the products, fewer also included ethanoic acid or its anion.

The reasoning used in *(b)* was, in general, described well: **C**, with two oxygens per molecule, was likely to be a carboxylic acid; **B** had to be a primary alcohol in order to be oxidised to an acid; **D** was obtained from **B** by *dehydration* and had to be a terminal alkene because it lost *one* carbon atom when the C=C bond was *cleaved* by $KMnO_4$. Despite this, however, many candidates did not make the connection between the branched chain 2-methylpropanoic acid and the necessity to include a branched chain in **B**, **C** and **D**.

*Q.11* This popular question was, in general, well answered. There were few candidates who forfeited marks through incorrectly describing other mechanisms like nucleophilic substitution. The most popular examples of electrophilic substitution were the nitration or the bromination of benzene. Most commonly, marks were lost through giving an incorrect or incomplete equation for the formation of the nitryl cation (*two* molecules of $H_2SO_4$ are needed per *one* molecule of $HNO_3$), and through the careless drawing of the cation intermediate—the positive charge should be shown as being associated with the residual π-bond, and not the $sp^3$ carbon atom or the $NO_2$/Br group. Electrophilic addition was usually illustrated by the addition of bromine or HBr to ethane. The mechanism was well known, but the conditions used ($Br_2$ dissolved in an inert solvent, or aqueous; room temperature, *not* in the presence of uv light) were less so.

*Paper 9250/2 Theory*

*Comments on Individual Questions*

*Further Transition Metal Chemistry*

The answers to the questions in this topic were of a rather better standard than in recent papers. However, *Q.2* showed that candidates still have difficulties in coping with redox potentials.

*Q.1* *(a)* *(i)* Candidates frequently answered this part of the question by defining the term empirical formula. A simple definition such as—stoichiometry = relative ratio of ion : ligand would have been acceptable.

*(ii)* This part of the question was generally well answered:

K = 26.8/39 = 0.687/0.2286 = 3(.005)
Fe = 12.8/56 = 0.2286/0.2286 = 1.0
C = 16.5/1 = 1.375/0.2286 = 6(.01)
O = 43.9/16 = 2.744/0.2286 = 12(.00)

Therefore, the overall formula is $K_3FeC_6O_{12}$ and the required stoichiometry is 1 : 3, i.e. $K_3Fe(C_2O_4)_3$.

*(b)* This part was well answered, the majority of candidates scoring full marks.

*(c)* The red colour is $Fe(SCN)^{2+}$; only the best candidates were able to give the correct formula of the complex ion.

The concept of stability was well understood, the decreasing order being $[Fe(CN)_6{}^{3-}] > [Fe(SCN)^{2+}] > [Fe(C_2O_4)_3]^{3-}$.

*Q.2* *(a)* The 3d and 4s orbitals have approximately the same energy; successive ionisation energies are roughly compensated by successive hydration energies: therefore, ions of different oxidation numbers have approximately the same energy.

In other metals, successive IE's are much higher because of breaking into an inner shell.

This part of the question was, generally, not well answered. A few candidates appreciated the first point but made little further progress.

*(b)* *(i)* $\mathrm{MnO_4^-} \longrightarrow \mathrm{Mn^{2+}}$; $E^\ominus = +1.52\ \mathrm{V}$

$\mathrm{Br^-} \longrightarrow \mathrm{Br_2}$; $E^\ominus = +1.07\ \mathrm{V}$

therefore,

$\mathrm{MnO_4^-} \longrightarrow \mathrm{Mn^{2+}}$

$\mathrm{Br^-} \longrightarrow \mathrm{Br_2}$: $E^\ominus_{\mathrm{cell}} = (1.5 - 1.07)\ \mathrm{V} = +0.45\ \mathrm{V}$

Therefore, reaction takes place; Mn goes down 5 in oxidation number (*or* corresponding statements for Mn(VII) to Mn(IV)).

*(ii)* $\mathrm{Fe^{3+}} \longrightarrow \mathrm{Fe^{2+}}$; $E^\ominus = +0.77\ \mathrm{V}$

$Cl_2 \longrightarrow Cl^-$ $E^\ominus = +1.36\ \mathrm{V}$

Both are in fully oxidised states, so no reaction.

*(iii)* $\mathrm{VO_2^+} \longrightarrow \mathrm{VO^{2+}}$; $E^\ominus = +1.00\ \mathrm{V}$

$\mathrm{Sn^{2+}} \longrightarrow \mathrm{Sn^{4+}}$; $E^\ominus = +0.15\ \mathrm{V}$

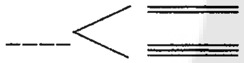
therefore,

$\mathrm{VO_2^+} \longrightarrow \mathrm{VO^{2+}}$

$\mathrm{Sn^{2+}} \longrightarrow \mathrm{Sn^{4+}}$; $E^\ominus_{\mathrm{cell}} = +0.85\ \mathrm{V}$

Reaction takes place; vanadium goes down 1 in oxidation number, (*or* corresponding statement for $\mathrm{VO^{2+}} \rightarrow \mathrm{V^{3+}}$).

Some confusion still exists in candidates' minds with regard to calculating $E^\ominus$ values: for instance, a large number used the correct values in *(b) (ii)* but still got the wrong answer.

*Q.3* *(a)* In $\mathrm{Cr^{3+}(aq)}$, the d orbitals are split (or  )

There are vacancies in the top levels; electrons can jump from bottom to top; by *absorbing* a quantum of *visible* light.

In $Al^{3+}\mathrm{(aq)}$, the energy gap to the lowest unfilled orbital is large, hence absorption is in the uv.

Candidates frequently failed to indicate that there are vacancies in the top levels. Far too often emitting coloured light was given as an explanation, and only the very best candidates were able to explain why $Al^{3+}\mathrm{(aq)}$ ions are colourless.

*(b)* *(i)* **A** would be yellow/orange/red (absorbs blue)
**B** would be blue/green/purple (absorbs yellow/red)

*(ii)* A longer wavelength corresponds to a smaller energy.

Energy gap between the d orbitals is larger in $\mathrm{Cr}L_6^{3+}$ than in $\mathrm{Cr}J_6^{3+}$.

*(iii)* *L* is the stronger ligand because in a 50 : 50 mixture of *L* and *J*, the spectrum more closely resembles that of **A**.

Large numbers of candidates reversed some or all of the above answers.

*Phase Equilibria*

*Q.4* *(a)* Many candidates, having correctly calculated the ratio, called it a 1 : 1 ratio or reversed it to obtain $Ca_4Mg_3$.

*(b)* Generally, the plotting of the graph was satisfactory. However, the following common problems still occurred:

*(i)* bad choice of scale—making the plotting of points difficult, or producing graphs which were far too small and did not use the graph paper to good effect;

*(ii)* some candidates still persist in joining their points with a ruler;

*(iii)* many candidates failed clearly to indicate the various areas of the graph, e.g. lines joining the eutectic compositions were commonly drawn, and many failed to label the areas correctly.

*Q.5* *(a)* Generally, the sketches of the boiling point/composition curve were very satisfactory. The commonest mistakes were as follows:

*(i)* after correctly labelling the axes, candidates then drew the curves the wrong way round;

*(ii)* carelessly drawn curves which had a maximum above the azeotropic mixture.

*(b)* Many candidates did not understand the theory of the sketch they had drawn in *(a)* and stated that nitric acid was the most volatile and would therefore distil off. A number of candidates also failed to mention the significance of the azeotropic mixture.

*(c)* *(i)* Many candidates had learned Raoult's Law thoroughly: however, a number of candidates confused it with Dalton's Law of Partial Pressures.

*(ii)* There was generally a sound understanding of the reasoning behind the deviation.

*Q.6* *(a)* Components travel at different speeds; due to different solubilities in solvent (mobile phase); and different attraction (affinity) for the stationary phase.

Answers to this section were generally very vague, a number mentioned partition coefficients; but very few had a good understanding of solubility *versus* attraction.

*(b)* *(i)* Most candidates were able to draw a satisfactory apparatus, the most common error being the omission of a suitable material to prevent the packing material being washed out of the column.

*(ii)* Suitable mixtures were generally suggested, such as, mixtures of dyes or amino acids. The correct choice of solvent was more problematical, little regard being shown for the solubility of the mixture in the solvent.

A number of candidates had confused column chromatography with fractional distillation and suggested that crude oil was separated by this method, using powdered aluminium in one case!

*Biochemistry*

This continues to be a very popular option and some excellent answers were submitted.

*Q.7* *(a)* The information to answer this question can be found in the *Notes for Guidance.*

Arrangement in DNA should include: base pairing; bases linked by hydrogen bonds; DNA is a double helix.

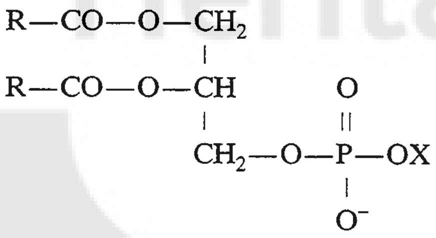
*(b)* The enzyme fits around the DNA at a definite sequence of bases and breaks a particular linkage; hydrolysis; a water molecule required for each break.

A large number of candidates suggested that the splitting of the DNA by the enzyme was at the hydrogen bonds linking the base pairs.

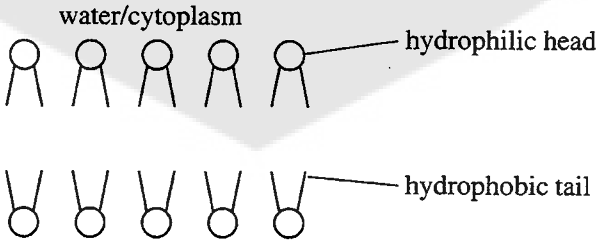
*(c)* Sugars and bases are not charged, only the phosphate which contains P–O$^-$.

*(d)* The size of the fragments; the $M_r$ of each fragment (the smaller fragments move farthest).

*Q.8* The most important class of compound present in membranes is the phospholipid



These molecules form bimolecular layers, which are the basis of membranes



Membranes also contain proteins; both integral and peripheral.

Passage through membrane possible only by very small molecules or ions; by passive transport (no energy expended) or by active transport (energy required); membrane possesses the necessary mechanism to allow passage of molecules or ions.

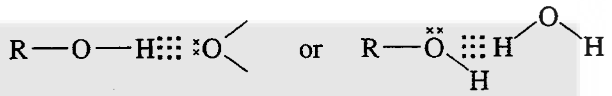
This question scored quite highly but, as is often the case in open-ended questions, the Examiners had to be on the look-out for the marks because the answers were frequently badly organised.

*Q.9* *(a)* The nature of the hydrogen bonding in secondary structures—the α-helix and the β-pleated sheet are fully covered in the *Notes for Guidance.*

*(b)* The Examiners expected to see one of the following given as an instance, together with a correctly drawn hydrogen bond:

$$-CH_2CO_2H, \quad -CH_2NH_2, \quad -CH_2OH, \quad -CH_2C_6H_4OH$$

*(c)* The –OH groups in sugars form H-bonds with water



Monosaccharides dissolve completely; polysaccharides disperse/form colloids (more complex structures); cellulose (fewer OH groups) tends to be insoluble.

Candidates answered *(a)* quite well but, in *(b)*, showed a lack of knowledge of R groups or their interactions in tertiary structures. The solubilities of monosaccharides were well understood; however, polysaccharide solubility was certainly not appreciated, most candidates thinking they were more soluble because they had more –OH groups.

*Food Chemistry*

*Q.7* *(a)* Cadmium—vegetables grown on 'mining waste'/leached from cooking utensils.

Lead—exhaust gases from internal combustion engines.

Mercury—mercury containing fungicides/factory waste discharged into rivers/ timber treatment chemicals entering rivers.

*(b)* **Hydrolytic rancidity** — oxidation of lipid yielding propan-1,2,3-triol and free carboxylic acids.

Prevention—removal of some water and microorganisms which can produce hydrolytic rancidity.

**Oxidative rancidity**—oxidation of lipid giving rise to aldehydes and ketones.

Prevention—removal of material from contact with oxygen/removal of traces of catalytic agents and the use of antioxidants.

Candidates answered *(a)* well: answers to *(b)*, on the other hand, showed much confusion in the minds of candidates and few really good answers were seen.

*Q.8* *(a)* *(i)* fats/lipids/oils

*(ii)* fat soluble vitamins

*(b)* Chromatography—Extract colouring material with suitable solvent; spot on to chromatographic paper; elute with suitable solvent; dry, using hot air; investigate coloured spots produced.

*(c)* Hydrolysis in both cases.

Disaccharides and polysaccharides → monosaccharides

Proteins → amino acids.

This question was the most popular question in this option and was well answered by the majority of candidates who attempted it, although *(c)* proved to be troublesome to the candidates.

*Q.9* *(a)* Protein hydrolysed by heating with 6 mol $dm^{-3}$ $HCl$ for prolonged periods.

Chromatography used to separate the components; spot hydrolysate on to chromatographic paper; suspend paper in solvent for about 2 hours; mark solvent front and dry; spray with locating agent (ninhydrin) and re-dry.

Candidates were generally very unsure of the conditions necessary to bring about the hydrolysis of proteins in the laboratory.

*(b)* Essential amino acids either cannot be synthesised by the human body or the body manufactures them too slowly.

Varied diet essential to ensure that the eight essential amino acids are obtained.

*(c)* Denaturation. Protein unfolds (loss of secondary and tertiary structure) and from hydrogen bonds with adjacent chains bringing about coagulation.

Candidates were often confused as to the reasons for the coagulation of proteins.

*Soil chemistry*

Very few candidates attempted the questions in this option.

*Q.10* *(a)* High charge leads to strong adhesion of the ion.

Small hydrated size allows stronger adhesion ... because ion is able to be closer to the binding charge at the cation exchange site. The dominant factor is the size of the charge: $Ca^{2+}(aq)$ is smaller than $Mg^{2+}(aq)$; it is, therefore, held more strongly. Since $K^{+}(aq)$ has the smaller charge, it binds less strongly than the divalent cations.

*(b)* Since the CEC is 10, 500 g of soil can hold 50 meq of ions:

1 meq of $Mg^{2+}$ is 0.5 mmol ($0.5 \times 10^{-3}$).

Therefore, the soil sample extracts 80% of $50 \times 0.5 \times 10^{-3} = 0.02$ mol

Solution is 0.5 mol $dm^{-3}$ and contains 0.05 mol in 100 $cm^{3}$: hence $(0.05 - 0.02)$ mol = 0.03 mol remains after the exchange sites become occupied. Concentration of the remaining magnesium sulphate is 0.3 mol $dm^{-3}$.

This question was not very popular but some very good answers were seen by the Examiners.

*Q.11* *(a)* Phosphorus is mobile in plants. This means that the phosphorus reaches the growing points of the plants most readily. The older leaves are then left deficient and show this by turning yellow.

*(b)* $H_2PO_4^-$, $HPO_4^{2-}$, $PO_4^{3-}$

$\text{acid} \xrightarrow{\hspace{3cm}} \text{alkali}$

*(c)* **A** would tend to precipitate the phosphorus as iron(III) phosphate or aluminium phosphate.

**B** would tend to precipitate the phosphorus as calcium phosphate.

**C**: although the organic material is likely to contain adequate phosphorus, it must be converted to an inorganic form before utilisation by the plant. This process (mineralisation) is normally slow, restricting phosphorus availability (inorganic material is likely to contain very little phosphorus).

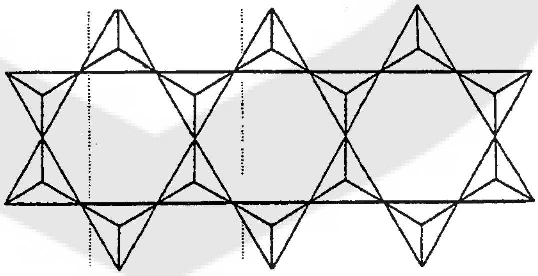
*(d)* A sulphate deficiency would appear on newer leaves since sulphate is not mobile.

Part *(a)* was well answered but the Examiners saw few correct answers to *(b)* and a great deal of confusion was apparent in *(c)* and *(d)*.

*Q.12* *(a)* The ratio mol Si : mol O is 39/28.1 : 61/16
= 1.388 : 3.813
= 1 : 2.75
= 4 : 11

The ion is therefore $Si_4O_{11}^{6-}$

*(b)* It is an amphibole of double chain structure as follows



*(c)* Half of the $SiO_4^{4-}$ units share oxygens at 3 corners and the other half share oxygens at 2 corners.

Therefore, the formula is $SiO_{(1+3*\frac{1}{2})} + SiO_{(2+2*\frac{1}{2})}$.

This is $Si_2O_{5\frac{1}{2}}$ or $Si_4O_{11}^{6-}$.

[Other correct methods of calculation were also credited.]

*(d)* Weathering would be relatively slight.

The majority of candidates who attempted this question made little progress beyond the first line of the calculation.

*Chemical Engineering*

The Examiners saw very few answers from candidates prepared for this option. Candidates obviously not prepared for the option frequently attempted *Qs 13 or 14*, usually very badly. The Examiners expected to see answers as outlined below.

*Q.13* Any 5 from the following:

- Is the raw material available in a pure enough state to be used?

  Purification may add significantly to the cost, particularly if there is a risk of poisoning the catalyst.

- How exothermic is the reaction?

  This may be a benefit in maintaining the reaction temperature, but it could be a problem since increased temperature will favour the back reaction. (Le Chatelier)

- How easy is it to separate the product from the reaction mixture?

  Since the conversion is only 12%, the reactants will need to be recycled.

- Are there any by-products to this reaction, and if so what are they?

  These could be useful if they can be sold, or may cause increased costs if they need to be disposed of.

- Are there cost benefits in this process over other methods of making cyclohexanol?

  In order to justify the construction of a new plant, the process must have financial benefits.

- Is there a sufficient and constant supply of raw material?

  If the process is to be developed, supplies of raw material must be guaranteed in order to re-coup development costs.

- Is there a sufficient market for the product?

  In order to pay for the development and plant, the product must be able to be sold at a sufficient price.

*Q.14* *(a)* The diagrams and descriptions of these pieces of equipment are in the *Notes for Guidance.*

*(b)* The majority of candidates were unable to draw the graph with the information provided.

*(c)* *(i)* Perfumes, flavourings, natural products, pharmaceuticals

*(ii)* Reduces possibility of decomposition of compounds with decomposition temperatures close to their boiling points.

Reducing pressure—reduces boiling point (aids vaporisation)

*Q.15* *(a)* and *(b)* The material required to answer these sections is fully covered in the *Notes for Guidance*.

*(c)* For streamline linear flow, $N_{\text{Re}} = 2000$:

$$2000 = \frac{0.15 \times 880 \times V}{0.0075}$$

$$V = \frac{2000 \times 0.0075}{0.15 \times 880}$$

$$= 0.1134 \text{ m s}^{-1}$$

Flow would become turbulent. Increasing temperature decreases the viscosity more than it decreases the density.

*Polymers*

The standard of answers to questions in the option were of a higher standard than in previous years.

*Q.16* *(a)* *(i)* covalent bonds.

*(ii)* hydrogen bonds; dipole-dipole bonds.

*(iii)* two of melting, dissolving, vaporising, adsorption, deformation or flow.

*(b)* Thermoplastics and thermosets are fully covered in the *Notes for Guidance*.

On the whole, candidates made a sound attempt at this question, with *(a) (ii)* and *(iii)* proving to be the most common cause of difficulty.

*Q.17* *(a)* The functioning of initiators in addition polymerisation can be found in the *Notes for Guidance* in the section on phenylethene.

*(b)* Thermal decomposition of the initiator requires heat.

Addition reactions (e.g. $C = C \rightarrow C - C$) following the initiation are strongly exothermic. Heat must be removed because higher temperatures give relatively low molecular mass polymers.

Stronger candidates produced some very good answers to this question and the overall standard was sound. Part *(b)* is in the *Notes for Guidance* but is obviously not well known.

*Q.18* The information required to answer this question is fully explained in the *Notes for Guidance* under the sections on polysulphide rubbers and silicones.

It is surprising that this question, which, as indicated, is fully covered in the *Notes for Guidance*, produced such relatively poor responses.

*Spectroscopy*

Regrettable printing errors in *Qs 20 and 21* required the Examiners to adjust the mark schemes to ensure that candidates were not adversely affected.

*Q.19* *(a)* From the left in each case

Spectrum 1 1 (singlet)
1 (singlet)

Spectrum 2 1 : 3 : 3 : 1 (quartet)
1 : 2 : 1 (triplet)

Spectrum 3 1 (singlet)
1 : 1 (doublet)
complex
1 : 1 (doublet)

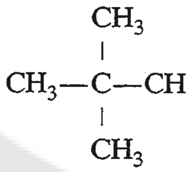
*(b)* Spectrum 1: Isolated single hydrogen; 9 equivalent hydrogens (or three methyl groups).

Spectrum 2: Two $-CH_2$ groups adjacent to two $-CH_3$ groups or two $-C_2H_5$ groups.

Spectrum 3: Isolated single hydrogen, one $-CH_2-$ group, two $-CH_3$ groups.

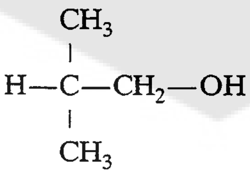
Single hydrogen adjacent to carbon with groups containing many equivalent hydrogens.

*(c)*

Spectrum 1: 

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH$$

Spectrum 2: $C_2H_5-O-C_2H_5$

Spectrum 3: 

$$H-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-OH$$

Some very good answers were seen to this question. Although candidates did not generally set out their answers as indicated above, the points were frequently all present.

*Q.20* *(a)* Use methanol labelled with $^{18}O$; react this with ethanoic acid to give the ester; separate the ester and compare its mass spectrum with that of unlabelled ester; look at relative heights of peaks corresponding to $CH_3O^+$ at *m/e* 31 and 33.

Candidates, in the majority of cases, mentioned only the first two points above. They failed to separate the ester and to compare the mass spectra of labelled and unlabelled esters.

*(b)* *(i)* The unintended omission of the M and (M + 1) values from the spectrum required candidates to use a different method, as indicated

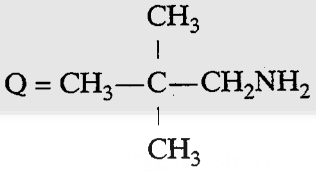
$M_r$ of Q is 87 (from M on spectrum); 87 – $M_r$ of N (14) = 73;

By assuming Q to be saturated, it must then contain 5 carbon atoms; 73 – 60 indicates 13 hydrogen atoms; hence Q = $C_5H_{13}N$

*(ii)* V = (M – $CH_3$) (or $C_4H_{10}N^+$)

U = $^+CH_2NH_2$ (or $^+CH_4N$)

*(iii)*



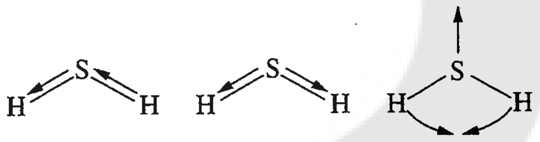
$$Q = CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2NH_2$$

or other acceptable structure.

Many answered this question well. Nevertheless, it was surprising that having correctly answered parts *(i)* and *(ii)* a number of candidates were not able to suggest a displayed formula for Q.

*Q.21* *(a)* Absorption of ir results from quantisation of vibrational energy; corresponds to stretching and bending of bonds; only bonds possessing a dipole which changes during stretching or bending, absorb.

*(b)*



*(c)* During printing, the register of the spectral line was slightly moved relative to the x-axis, suggesting the presence of a C–C*l* bond.

From spectrum, S contains (ignoring C–C*l*)
–C = O absorption at 1725 $cm^{-1}$ (± 25 $cm^{-1}$)
–C–O– absorption at 1275 $cm^{-1}$ (± 25 $cm^{-1}$)

High carbon : hydrogen ratio suggests benzene ring ($C_6H_5$)

Possible structure

$C_4H_6CO_2C_2H_5$

(or isomers but NOT acids)

If the presence of C–C*l* was indicated then credit was given for correct inferences given.

This question was answered well and, with the above adjustments to the mark scheme, candidates did not appear to be inconvenienced by the printing error.

*Paper 9250/3 Structured Questions (Theory)*

*Comments on Individual Questions*

*Q.1* *(a)* The first ionisation energy is the number of kilojoules per mole required for

$$X(g) - e^- \rightarrow X^+(g)$$

The chief error was to omit the state symbol or to refer to the solid state.

The first ionisation energy decreases down a Group because the outermost electron is further from the nucleus despite the shielding effect of the inner electron shells.

*(b)* Most candidates gained the mark for the graph and noted that the two lines cross over. In *(ii)*, Al loses the single, unpaired 3p electron quite easily, leaving the full, paired $3s^2$, which requires more energy to disrupt. Tl has more protons in its nucleus than Ba.

*(c)* To make $Ba^{2+}(g)$ requires 1468 kJ $mol^{-1}$; for $B^{3+}(g)$, 6879 kJ $mol^{-1}$. The question did ask candidates to use these values. The lower value for barium is the reason for the ion formation. It is energetically favourable for boron to share electrons.

*Q.2* *(a)* $K_{sp} = [Ca^{2+}]\,[OH^-]^2$

A common error was to omit the charges on the ions, but this was only penalised if no reference was made to ions in the rest of the question.

*(b)* *(i)* $[OH^-] = 0.046 \text{ mol dm}^{-3}$

*(ii)* pH = 12.7

*(iii)* $[Ca^{2+}] = 0.023 \text{ mol dm}^{-3}$

$K_{sp} = 4.7 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$

The question, as always, was marked taking account of consequential error.

*(c)* Calcium hydroxide is limewater, used as a test for $CO_2$. The major use, which depends on its solubility, is rectifying acidity in soil. Marks were not given for its use in cement, mortar nor as an anti-acid for indigestion.

*Q.3* *(a)* $CCl_4$ is not hydrolysed but $SiCl_4$ is. $PbCl_2$ is an ionic solid which is almost insoluble in water. $CCl_4$ and $SiCl_4$ are both liquids, small molecules, covalently bonded.

*(b)* *(i)* It is easiest to take $CO_2$ here. $SiO_2$ does not react with acids.

*(ii)* It is easiest to take PbO as example.

*(c)* *(i)* Tin

*(ii)* $2\,MnO_4^- + 16H^+ + 5Sn^{2+} \rightarrow 2\,Mn^{2+} + 8H_2O + 5Sn^{4+}$

The following was also considered acceptable

$$2\,MnO_4^- + 8H^+ + 3Sn^{2+} \rightarrow 2\,MnO_2 + 4H_2O + 3Sn^{4+}$$

Common errors were $Sn \rightarrow Sn^{2+}$ and to use the $MnO_4^- \rightarrow MnO_4^{2-}$ change (which is possible only in alkaline solution).

*Q.4* *(a)* Either propanol will give propene on dehydration.

*(b)* The material **X** is a ceramic and answers such as silica, alumina and iron oxide were expected. Carbonates would decompose on heating and could not score. **X** needs to be heated strongly to break the bonds in the propanol vapour. In *(iii)*, the black solid is carbon, always formed when organic molecules are subjected to strong heat. Since there would be little oxygen present, no credit was given for references to combustion. Sucking-back is avoided in *(iv)*.

*(c)* The answers are straightforward here. However, only about half the candidates could accurately give two repeat units of poly(propene).

*Q.5* *(a)* Benzocaine is likely to be oil-soluble: esters are hydrophobic, aryl amines are insoluble, it is a large aromatic molecule and does not form strong hydrogen bonds.

*(b)* *(i)* The preferred reagents and conditions are:-

I Concentrated nitric acid, sulphuric acid below 60 °C.

II Acidic or alkaline manganate(VII) under reflux.

III Ethanol, concentrated sulphuric acid under reflux.

IV Tin and concentrated hydrochloric acid under reflux.

Worthy alternatives also scored the marks.

*(c)* The isomer is 2-nitromethylbenzene.

*Paper 9250/4* *Multiple Choice*

| *Question Number* | *Key* | *Question Number* | *Key* |
|---|---|---|---|
| 1 | C | 21 | D |
| 2 | A | 22 | C |
| 3 | D | 23 | C |
| 4 | A | 24 | B |
| 5 | A | 25 | C |
| 6 | C | 26 | B |
| 7 | A | 27 | C |
| 8 | A | 28 | D |
| 9 | C | 29 | C |
| 10 | B | 30 | D |
| 11 | C | 31 | D |
| 12 | C | 32 | C |
| 13 | D | 33 | B |
| 14 | A | 34 | B |
| 15 | B | 35 | A |
| 16 | C | 36 | B |
| 17 | B | 37 | D |
| 18 | A | 38 | C |
| 19 | C | 39 | B |
| 20 | A | 40 | C |

*General Comments*

For this paper, the mean score was 24.6 (61.5%) and the standard deviation of the scores was 6.71 (16.8%). This was the first time that the paper had been constructed from four-choice questions rather than five and it is significant to note that the increase in facility and the decrease in standard deviation have been only marginal from those of comparable examinations and that these parameters both remain very satisfactory.

The first 30 questions were simple completion items; *Qs 31 to 40* were three-statement multiple completion items.

*Comments on Individual Questions*

*Q.1* This question was intended as an 'easy starter', but there are indications that it did not discriminate well between the more and less able candidates and that many candidates were guessing the answer. These point to a lack familiarity in the interpretation of simple mass spectra.

*Q.4* Many of the more able candidates chose option **C** rather than the key **A**, the mistake being an elementary one of forgetting that water remains a liquid at 27 °C. This was not intended as a 'catch' question, but so it proved to be.

*Q.18* This question had a high facility, indicating that the association of colour with bromine, and of the ready oxidation of the bromide ion by warm concentrated sulphuric acid, are well known.

*Q.19* Whereas candidates were clearly aware that the complex between iron(III) ions and thiocyanate is deep red, they were unsure of the reaction of iron(III) ions with an alkaline ammonium salt solution and thus had difficulty in selecting the key **C** [the formation of $Fe(OH)_3$] from possible complexes with either $NH_3$ or $OH^-$.

*Q.20* In this question, some of the more able candidates chose the distractor **B** rather than the key **A**. Among the structures of the three drugs displayed, there was only one chiral carbon centre (in amphetamine); presumably, some candidates thought there was another within phenobarbital, not appreciating the symmetrical nature of the ring in this molecule.

*Q.33* This question again failed to discriminate between the more and the less able candidates, some of the former choosing option **A** rather than **B**. This implies that statement (3) is correct, that 'increasing the temperature decreases the rate of the forward reaction'. Examiners of other papers still commonly come upon this misconception that an increase of temperature will decrease the rate of an exothermic reaction, and teachers could do well to stress the distinction between the effects of temperature on equilibrium and on reaction rate.

*Q.40* Some 68% of candidates thought that the presence of hydrogen chloride in the products of the chlorination of methane indicates that the mechanism of the reaction is a free-radical one. Notwithstanding the fact that the reaction is a free-radical one, hydrogen chloride could be produced by other mechanisms. This point is perhaps too subtle at this level of examination and caused the question to discriminate badly.

*Qs 34 and 36* Both of these questions involved an appreciation of redox reactions and of oxidation number, an area of confidence for most candidates, leading to slightly high facilities.

*References are given to the Assessment Objectives within each section of the Syllabus*

| *Item Number* | *Assessment Objective* | *Item Number* | *Assessment Objective* |
|---|---|---|---|
| 1 | 1(d) | 21 | 11.2(g) |
| 2 | 1(h) | 22 | 11.3(a), (b) |
| 3 | 2(i) | 23 | 11.4(b); 11.5(e) |
| 4 | 4(b) | 24 | 11.5(d) |
| 5 | 1(h) | 25 | 11.4(c) |
| 6 | 5(i) | 26 | 11.3(b) |
| 7 | 2(j) | 27 | 11.6(h) |
| 8 | 3(b), (d) | 28 | 11.6(a), (h); 11.1(g) |
| 9 | 3(c); 4(e) | 29 | 11.7(g); 11.6(b) |
| 10 | 1(b); 6(d) | 30 | 11.8(c) |
| 11 | 8(a), (h) | 31 | 5(c) |
| 12 | 8(a) | 32 | 6(k) |
| 13 | 9(a), (b) | 33 | 7(b) |
| 14 | 9(j) | 34 | 10(d) |
| 15 | 10.1(c) | 35 | 10.2(f), (e), (c) |
| 16 | 10.1(e); 1(h) | 36 | 10.5(e); 10(d) |
| 17 | 10.3(a) | 37 | 11.2(c); 11.1(g) |
| 18 | 10.4(e), (a) | 38 | 11.5(c), (d), (e) |
| 19 | 10.5(e) | 39 | 11.4(b) |
| 20 | 11.1(g) | 40 | 11.2(b) |

*Paper 9250/5 Practical Test*

*General Comments*

Examiners thank Supervisors for their comments on the paper and for providing results to the experiments in *Qs 1 and 2*.

*Q.1* **FA1** was magnesium sulphate-7-water.

Accuracy marks in this question were awarded by comparing a candidate's (mass loss ÷ mass remaining) with the theoretical value of 1.05, which was almost invariably supported by the Supervisor's results. Full marks were given for ratios within 0.03 of 1.05, falling by stages to nil for ratios that differed by more than 0.15.

Despite the hint from the appearance of the second table of weighings, together with the sentence in bold print below this, fewer than half the candidates reheated their tube and contents to constant mass.

Calculations seemed to pose no problem to the majority of candidates with often an evaluation error in *(d)* being the only fault, almost invariably caused by use of an approximated answer to *(c)*.

*Q.2* This question was not standard textbook material and the Examiners took account of the practical problems associated with it.

In the first titration, full marks for accuracy were awarded for titres within 0.10 $cm^3$ of the Supervisor's, ranging to zero for values differing by more than 2.00 $cm^3$. The accuracy marks thus obtained were on a par with those obtained in this type of question for previous years.

In the second titration, fewer marks were allocated for accuracy, with full marks given for values within 0.20 $cm^3$ of the Supervisor.

Most candidates answered *(a)*, *(b)* and *(c)* correctly but, in plotting the volumes, values such as 20.9 were frequently plotted as 29.0, usually as big crosses made with a blunt pencil that was subsequently used to draw the graph itself. At the other extreme, better candidates plotted their points with a sharp pencil and drew a graph that passed cleanly through the points. About a quarter of the entry could not progress past the graph but the rest correctly read off the value of the intercept with the vertical axis and used this to earn the marks for *(f)* and *(g)*.

*Q.3* **FA5** was an aqueous solution of potassium chromate(VI) and copper(II) nitrate.

A total of 33 mark-earning points were identified, with 25 stipulated as the maximum mark to be awarded: as usual, most of the marks were allocated for accurate observations and the associated correct deductions, with only a token mark given for the final conclusion of ions present.

No test seemed to cause common difficulties, though a minority of candidates failed to find ammonia in *(b)*, often wasting time by finding it present in *(d)*.

Marks obtained in this question were very similar to the totals of last year.

*Paper 9250/9*

*General Comments*

One hundred and thirty Centres used the Internal Assessment of Practical option this year and the moderators were pleased to note the steadily improving variety and quality of the practical work employed. Overall, the mean mark of the candidates initially was just in excess of 37 out of 48 and this was reduced by 0.9 once moderation had been completed. This is very much in line with the experience of previous years.

A welcome feature of this year's practical work was the thoughtful response of Centres to the comments made by the moderators in previous years. Although it is not possible to provide the kind of detailed feedback that some Centres would value, it is always hoped that any observations made (terse though they sometimes are) will aid teachers to understand how the work of their candidates broadly compares with others. Many Centres, however, sent samples of work that seemed ideally suited to the process of assessment and no particular comments were felt to be necessary. It was particularly helpful where information additional to the formal marking schemes was provided in order to allow the moderators to understand the basis on which a particular skill level had been awarded. It is a practice which is to be encouraged since the process of moderation requires a clear understanding of the approach being adopted during assessment. This applies especially to *Skill D* which is normally the most demanding for candidates and where it may be necessary for the teacher to provide some initial aid not strictly in adherence to a pre-determined marking scheme. For this skill, it once again needs emphasising that the initial plan should be submitted to the moderators even though this may be in the form of rough notes.

A general concern which seemed more noticeable this year was the practice adopted by some Centres of doing several of the assessments in one short space of time. Whilst it is recognised that open days, interviews and absences do make planning very difficult, it is the intention that, wherever possible, practical work should be integrated with the theory and that assessments therefore be spread realistically throughout the course. It is also hoped that Centres will be careful to review the demands that a practical is making on their candidates. The change in the nature of GCSE practical work has meant many have found that experiments used in previous years are no longer suitable. It should always be the case that a task has the capacity to distinguish clearly between those of appropriate competence and those whose skill is less.

There are two further points where the help of Centres would be appreciated. If a candidate is given a mark of zero, or if marks on fewer than the required eight occasions are submitted, it would aid the moderators for some explanation to be supplied. Although, of course, it is the Centre's responsibility to ensure that normally the required practical work is completed, some special consideration might be given if this was through no fault of the candidate. All practical work should be annotated on the candidate's script to show how it has been marked. It is not sufficient to provide the work and a separate marking scheme and leave the moderators to deduce how it has been applied.

### *Paper 9250/0 Special Paper*

### *General Comments*

After the first two or three introductory points in each question, it was not immediately easy to score marks on this paper. Each mark had to be earned and all the sections of each question needed to be answered if a good score was to be obtained. As well as having a thorough knowledge of the syllabus, candidates needed to show insight regarding, and extrapolate principles within the core of syllabus to, substances that are less 'mainstream'. In this particular paper, such substances included ozone, hydrogen peroxide, transition metals, fluorine and fluorides, oxides of nitrogen, e.g. $N_2O$.

### *Comments on Individual Questions*

*Q.1* *(a)* The concentration of gases at street level can be taken as 1 mol per 24 $dm^3$. The value here of 22.4 $dm^3$ is just as good.

The mole fraction of oxygen is approximately 0.2.

Hence

*(i)* $[NO] = 8 \times 10^{-8} \times \frac{1}{24} = 3.3 \times 10^{-9}\ \text{mol dm}^{-3}$

$[O_2] = 0.2 \times \frac{1}{24} = 8.3 \times 10^{-3}\ \text{mol dm}^{-3}$

and rate $= 6.5 \times 10^{-16}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

*(ii)* $[NO_2]$ after 3 hours $= 3 \times 3600 \times 6.5 \times 10^{-16}\ \text{mol dm}^{-3}$

$= 7 \times 10^{-12}\ \text{mol dm}^{-3}$

*(b)* *(i)* $[O_3] = 4 \times 10^{-8} \times \frac{1}{24}$ mol dm$^{-3}$ = $1.7 \times 10^{-9}$ mol dm$^{-3}$

and rate = $5.6 \times 10^{-11}$ mol dm$^{-3}$ s$^{-1}$

*(ii)* $[NO_2]$ after 3 hours = $6 \times 10^{-7}$ mol dm$^{-3}$

*(c)* *(i)* Any worthy mechanism which involved two stages gained marks for the $NO + O_2$ reaction. The most popular mechanisms were

$$2NO \rightarrow (NO)_2 \quad \text{or} \quad O{=}N{-}N{=}O$$

then

$$(NO)_2 + O_2 \rightarrow 2NO_2$$

Nearly all the candidates who answered this question had the bimolecular mechanism

$$NO + O_3 \rightarrow NO_2 + O_2$$

which is probably what happens.

*(ii)* The rate of $NO_2$ formation is facilitated by ozone as the concentration data bear out. Also, ozone is hazardous to lungs, organic materials etc.

*(d)* $\Delta H$ for $NO + CO \rightarrow \frac{1}{2} N_2 + CO_2$ is –373 kJ mol$^{-1}$ which is more exothermic, and therefore more likely, than $NO \rightarrow \frac{1}{2} N_2 + \frac{1}{2} O_2$ for which $\Delta H$ is –90 kJ mol$^{-1}$.

*(e)* *(i)* The lower temperature means that less NO is formed; the excess of oxygen leads to less incomplete combustion.

*(ii)* Many answers were accepted here, for example: too much investment in conventional engines; car engines have to work at such high speeds that incomplete combustion is inevitable; car-buying customers do not want to creep along in the inside lane.

*Q.2* *(a)* All these molecules seem to be used as aerosol propellants. Their physical or chemical properties must include: readily liquefiable by pressure (which means the b.p. must not be too low), or readily compressed; non-toxic; odourless; and it is preferable if they are not flammable. Actually, propane and butane seem to be the commonest propellants in hair lacquers with grim warnings to keep away from naked flames. A large proportion of candidates did not mention flammability and the halogenoalkanes would undoubtedly produce toxic gases, if ignited.

*(b)* A mark was allocated for calculating the $M_r$ values. Both alkanes have van der Waals' forces only between the molecules. $CH_3Cl$ has a dipole, as has $N \equiv N \rightarrow O$. $CF_4$ has the lowest b.p. but the highest $M_r$; it is tetrahedral. The low b.p. is due to repulsion between the molecules for F atoms repel those on adjacent molecules.

*Q.3* *(a)* *(i)* The two equilibria are

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \text{ and } HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

*(ii)* $[H^+] = [HSO_4^-] = 10 \text{ mol dm}^{-3}$ from the first stage of ionisation.

*(iii)* $K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$

These early marks were scored by most candidates who answered this question.

*(iv)* Let $[SO_4^{2-}] = x$, then $[H^+] = (10 + x)$ and $[HSO_4^-] = (10 - x)$

so that $1.0 \times 10^{-2} = \frac{(10 + x)\,x}{10 - x}$

$x^2$ will be very small compared to x, giving $x \approx 0.010 \text{ mol dm}^{-3}$

*(v)* $[H^+] = 10.01$, $[HSO_4^-] = 9.99$, $[SO_4^{2-}] = 0.01$ $\text{mol dm}^{-3}$

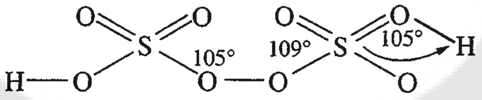
*(vi)* Cathode $2H^+ + 2e^- \rightarrow H_2$

anode $2HSO_4^- - 2e^- \rightarrow H_2S_2O_8$

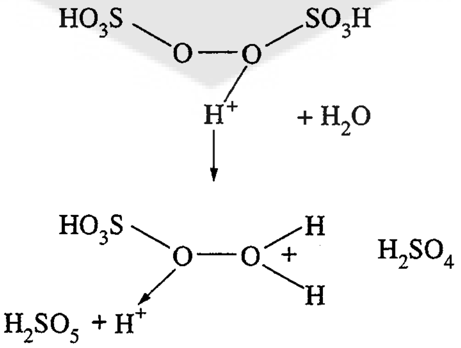
then $H_2S_2O_8 + H_2O \rightarrow H_2O_2 + 2H_2SO_4$

This recycles the sulphuric acid electrolyte.

*(b)* The full displayed formula is



*(c)* $H^+$ is the likely catalyst and it is likely to attack the peroxide linkage.



*Q.4* *(a)* $AlF_3$ is ionic and hence has a high lattice energy and is probably insoluble. $AlCl_3$ is covalent, forms small molecules which are hydrolysed. A mark was allocated for the dimers, correctly described.

*(b)* **A** is CrO. The sky-blue solution is $Cr^{2+}$ which is oxidised by air to $Cr^{3+}$. The half-equations are:

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-; \quad E^{\ominus} = +\,0.40\ V$$

$$Cr^{2+} - e^- \rightarrow Cr^{3+}; \quad E^{\ominus} = -\,0.41\ V$$

**B** and **C** are $Cr(H_2O)_6\ Br_3$, with $M_r = 400$. Hence $10^{-3}$ moles are involved in the calculation:

**B** is $Cr(H_2O)_6{}^{3+}\ 3Br^-$; **C** is $Cr(H_2O)_4Br_2{}^+\ Br^-.\ 2H_2O$

*(c)* **B** gives a green precipitate of $Cr(OH)_3$, which is soluble in an excess of alkali.

Iron(II) sulphate gives a green precipitate of $Fe(OH)_2$, which goes brown due to aerial oxidation.

*Q.5* *(a)* *(i)* Most candidates used discussions of the repulsion of the two electronegative oxygen atoms. However, the bond energies are in the *Data Booklet* and the equation, as written, has a $\Delta H$ of $-20$ kJ $mol^{-1}$.

*(ii)* The equilibria are

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3{}^-(aq)$$

and le Chatelier's principle can be applied for the effect of heat and of adding dilute acid.

*(iii)* These are explained by the bonding and the inability of silicon to form double bonds. In *(iv)*, it is the presence of vacant d-orbitals in Si which allow two $F^-$ to form dative bonds (of appropriate energy level)

**D** is $Si(NH_2)_4$; **E** is $Si_3N_4$

*Q.6* *(a)* The neutralisation is straightforward as is the effect of heat on sodium nitrate. The calculation needs to be completed.

The $E^{\ominus}$ potential to produce $NO_2$ from nitrate ions is

$$HNO_3 + H^+ + e^- \rightarrow H_2O + NO_2; \quad E^{\ominus} = +\,0{\cdot}81\ V$$

A metal having a reduction potential between + 0.81 V and 0.00 V is required: copper would be satisfactory. Other metals would produce hydrogen or reduce the nitrate to other oxidation states, as indicated in the *Data Booklet.* A common error was to use zinc which would be too powerful a reducing agent and produce ammonia (or ammonium nitrate).

*(b)* *(i)* The brown colour is due to $NO_2$. The equation is

$$2HNO_3 \rightarrow H_2O + 2\,NO_2 + \tfrac{1}{2}\,O_2$$

*(ii)* Dehydration by $P_4O_{10}$ gives $N_2O_5$. The ions are $NO_2^+$ and $NO_3^-$.

$NO_2^+$ is involved in nitration, and it is produced thus:

$$N_2O_5 + 3H_2SO_4 \rightarrow 2NO_2^+ + H_3O^+ + 3HSO_4^-$$

*(c)* The equations are:

$$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$$

$$NCl_3 + 3NaOH \rightarrow 3NaClO + NH_3(\mathbf{F})$$

$$3NaClO \rightarrow NaClO_3 + 2NaCl$$

Sodium chlorate(V) will oxidise $Fe^{2+}$

$$ClO_3^- + 6H^+ + 6Fe^{2+} \rightarrow Cl^- + 3H_2O + 6Fe^{3+}$$

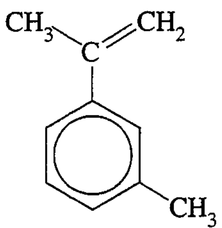
*Q.7* *(a)* *(i)* There are three isomers for dichlorobenzene in the Ladenburg structure, four for the Kekulé and three in fact.

*(ii)* There are the same numbers for each for bromochlorobenzene.

*(iii)* The Ladenburg structure has no double bonds which can be used to explain its behaviour with bromine or reagents for electrophilic addition. However, it will not hydrogenate to $C_6H_{12}$. Other explanations could be equally valid.

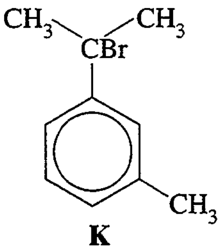
*(b)* *(i)* **J** is $C_5H_6$. **K** is $C_{10}H_{13}Br$. Hence, the molecular formula of **J** is $C_{10}H_{12}$.

Hydrolysis gives AgBr, so the Br must be in a side-chain. One possibility for **J** is



**J**

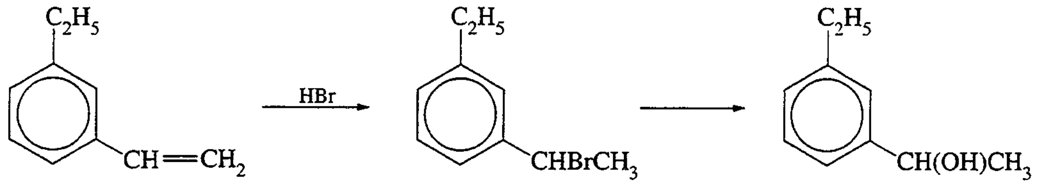
which gives



**K**

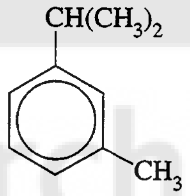
which has no chiral centre. The other reactions follow, including the $CHI_3$ formation.

Other possibilities are not quite so good but would score most of the marks.



The products here do have a chiral carbon atom but will give $CHI_3$ and oxidise to benzene -1,3-dicarboxylic acid.

*(ii)* **L** is



and since there is one major product, this has to be by replacement of the single tertiary hydrogen atom.

*Q.8* Answers to this question tended to score low marks. Explanations are more difficult to get right than intuitive analytical problems included in the other organic questions on this paper.

*(a)* *(i)* This should have been straightforward for candidates but insufficient explanation was often given. The polarisation of the carbonyl group is easily explained by the different numbers of protons on the two atoms. The mechanism is nucleophilic addition and $CN^-$ is the nucleophile. HCN is a weak acid so alkali generates cyanide ions.

*(ii)* This is the reverse mechanism: $OH^-$ removes the H from the OH group of the cyanohydrin.

*(iii)* The acid catalyses the hydrolysis of the nitrite to the ammonium salt of a hydroxycarboxylic acid (which is stronger than ethanoic acid by virtue of the electron-attracting OH group).

*(b)* Ethanol is a weaker acid than water; it is less ionised.

Hence, its conjugate base $C_2H_5O^-$ is a stronger base than $OH^-$.

*(c)* This follows from *(b)*. $C_2H_5O^-$ removes a proton from the secondary alcohol. Since ethanol is a minor product, candidates had to work out a plausible equation, such as

$$CH_3\overset{\overset{\displaystyle O^-}{|}}{C}H.CO_2C_2H_5 + C_2H_5OH \rightarrow CH_3CHO + H.CO_2C_2H_5 + C_2H_5O^-$$

*Q.9* *(a)* The calculation gives $M_r = 41{\cdot}9$. Hence,

$$CH_3COCH_3 \rightarrow CH_4 + CH_2{=}C{=}O$$

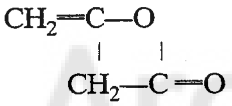
*(i)* Ethanol gives $CH_3CO_2C_2H_5$

*(ii)* Ethanoic acid gives $CH_3CO.O.COCH_3$

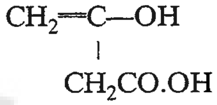
Ketene gives the expected products with hydrogen, bromine, DNP, $CH_3NH_2$, hydrogenation etc.

*(b)* The bond angles are 120° and 180°.

*(c)* The dimer is an ester



which hydrolyses to



$$\begin{array}{l} CH_2{=}C{-}OH \\ \quad\;\, | \\ CH_2CO.OH \end{array}$$

and by enol-keto change gives 3-oxobutanoic acid.

*(d)* Hydrogenation of the dimer gives $CH_3CH(OH)CH_2CH_2OH$ which gives butadiene on dehydration. This can add one or two molecules of bromine.

Isomers include $CH_2{=}C{=}CHCH_3$ and cyclic structures.

## CHEMISTRY 9250

### Component Threshold Marks

| Component | Maximum Mark | A (1, 2) | B (3) | C (4) | D (5) | E (6) | N (7) |
|---|---|---|---|---|---|---|---|
| 1 | 80 | 60 | 51 | 45 | 39 | 34 | 29 |
| 2 | 40 | 29 | 25 | 22 | 19 | 17 | 15 |
| 3 | 40 | 30 | 26 | 22 | 18 | 15 | 12 |
| 4 | 40 | 31 | 27 | 23 | 20 | 17 | 14 |
| 5 | 50 | 41 | 38 | 35 | 32 | 30 | 28 |
| 9 | 48 | 40 | 37 | 34 | 31 | 29 | 27 |

### Special Paper

| | |
|---|---|
| 1 | 59 |
| 2 | 50 |

### Overall Threshold Marks

| Combination | Maximum Mark | A | B | C | D | E | N |
|---|---|---|---|---|---|---|---|
| 1, 2, 3, 4 and 5 | 250 | 185 | 162 | 145 | 129 | 113 | 97 |
| 1, 2, 3, 4 and 9 | 248 | 184 | 160 | 144 | 128 | 112 | 96 |

The percentage of candidates awarded each grade was as follows:

| **GRADE** | A | B | C | D | E | N |
|---|---|---|---|---|---|---|
| **Cumulative %** | 22.7 | 41.9 | 57.5 | 70.4 | 82.5 | 91.2 |

The total candidature was 3197.

These statistics are correct at the time of publication.