Raffles Institution Preliminary Examination 2019 H2 Chemistry Paper 2 (Suggested Answers and Comments)

16 Sep 2019

Q1 (a) Assume 100 g of X.

	Si	Ν	Н
Mass / g	48.3	48.1	3.6
Amount / mol	$\frac{48.3}{28.1}$ = 1.72	$\frac{48.1}{14.0} = 3.44$	$\frac{3.6}{1.0} = 3.60$
Molar ratio	1	2	2

Empirical formula of X is SiN₂H₂.

Comm	nents		
• Ge	enerally well done.		

Q1 (b) The first ionisation energy of P is higher than that of Si.

P has one more proton and hence a higher nuclear charge than Si. Though P also has one more electron than Si, the increase in shielding effect is minimal since this additional electron occupies the outermost shell. Consequently, the valence electrons in P experience a higher effective nuclear charge and are more strongly attracted by the nucleus.

Comments

- Most students were able to describe the trend across the period well. The key ideas of increased nuclear charge, relatively similar shielding effect and increased effective nuclear charge were all stated.
- Students should be more concise. For ionization energy, the key consideration should be simply, i) nuclear charge, ii) shielding effect, hence, iii) effective nuclear charge, and attraction for valence electrons.

Q1 (c)
$$Al_2O_3(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O(l)$$

Or $Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O(l)$

 $\begin{array}{l} Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq) \\ Or \ Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \longrightarrow 2[Al(OH)_4]^-(aq) \end{array}$

 $SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l)$ Or $SiO_2(s) + 2OH^-(aq) \rightarrow SiO_3^{2-}(aq) + H_2O(l)$

- Students are reminded to be familiar with all chemical reactions of the Period 3 oxides and chlorides.
- This question was poorly answered. Students need to manage the knowledge of inorganic chemistry with understanding and technique, not just rote, as poor recall means inability to answer these standard questions.
- Firstly, the acid base properties of oxides across period tends from basic to acidic (correlating to structures: ionic to covalent). Thus, Al₂O₃, which has ionic with covalent character, is amphoteric.
- Secondly, basic oxides neutralise acids. Acidic oxides neutralise bases. Amphoteric oxide neutralizes both acids and bases.
- Thirdly, writing equations involve the following technique:
 - i) The formula of the "salt" needs to be recalled.
 - ii) Balance non-H and non-O atoms first (eg, Na, Al, P, SI)

- iii) Balance charges with H⁺ or OH[−] if ionic equation is written
- iv) Always balance the H and O atoms last using H₂O

Rather than memorise and recall equations (with so many coefficients to note), it is better to know the type of reaction, the expected products, and balance with proper technique.

Following steps above				
i)	Identify salts:	Al_2O_3	->	Na[Al(OH)4]
ii)	Balance Na, A <i>l</i> :	$Al_2O_3 + 2NaOH$	->	2Na[A <i>l</i> (OH) ₄]
iii)	No need.			
iv)	Balance H and O with H ₂ O	$Al_2O_3 + 2NaOH + 3H$	I ₂ O -	> 2Na[Al(OH) ₄]

Q1 (d) P₄O₁₀ has a simple molecular structure with weak instantaneous dipole-induced dipole (id-id) interactions between its molecules.

SiO₂ has a giant molecular structure with strong Si–O covalent bonds.

Much less energy is required to overcome the id-id interactions compared to breaking the stronger Si–O covalent bonds during melting.

Hence, P_4O_{10} has a much lower melting point than SiO₂.

Comments

- Be precise in describing structure and bonding, especially of the respective forces between particles covalent bonds between Si and O **atoms**, id-id interactions between P₄O₁₀ **molecules**.
- When answering questions related to structure and bonding, students must state the *type* of intermolecular forces between molecules.

Q2 (a)

	xC(g) ਵ	≐ yA(g)	+ B(g)
initial amount/mol	1.80	0.40	0.40
change in amount/mol	-0.40	+0.40	+0.20
equilibrium amount/mol	1.40	0.80	0.60

From the change in amount, molar ratio of C : A : B = 2 : 2 : 1Hence x = 2 and y = 2

- Many students used the equilibrium amounts of A, B and C at time t_3 . Since some amount of C was added at time t_1 , the stoichiometric coefficients are valid only if you used the "initial" amounts at time t_2 .
- Other common mistakes include misreading the graph.
- Quite a number of students do not realize that the stoichiometric coefficient ratio (the numbers in the equation) correspond to the ratios of the numbers in the "C" row of the ICE table, not I and not E. C (change) represents the amounts of species reacted and produced in the chemical reaction, according to the stoichiometry of the equation.

(b) Immediately before time t_1 ,

$$\mathcal{K}_{\rm c} = \frac{[{\rm A}]^2 [{\rm B}]}{[{\rm C}]^2} = \frac{\left(\frac{0.80}{2}\right)^2 \left(\frac{0.60}{2}\right)}{\left(\frac{1.40}{2}\right)^2} = 0.09796 = 0.0980 \text{ mol dm}^{-3}$$

Comments

- Most students who were able to obtain the correct stoichiometric coefficients from part (a) were able to calculate K_c correctly.
- A common mistake was forgetting to convert the amount values to concentration values.
- (c) $\Delta G^{\ominus} > 0$

Comments

- Very poorly done!
- When K > 1, a reaction is "product-favoured" and hence spontaneous, i.e. ∆G[⊕] is negative.
- Conversely, when K < 1, the reaction is non-spontaneous i.e. ΔG^{\ominus} is positive.
- Students who prefer mathematical equations may find the following equation useful: $\Delta G^{\ominus} = -RT \ln K$. However, this equation is not in syllabus and you will not be asked to recall this.
- (d) The temperature of the system was increased.

Comments

• A common wrong answer was a change in pressure of the system. Increasing the pressure of the system by decreasing the volume of the container would cause the position of equilibrium to shift left (less moles of gas), increasing the amount of C.



Comments

 Very poorly done! Adding an inert gas to the system would increase the total pressure of the system, but have no effect on the partial pressures of each gas since the mole fraction of each gas would decrease proportionally. Hence, there will be no change in the position of equilibrium.

Q3 (a) 4 isomers





Comments

- Students are reminded to label the slow/fast steps of the mechanism.
- Each step of the mechanism must be balanced. Many students forgot to include Br⁻ as a product of the first step.
- Students need to be precise in their arrow pushing e.g. draw arrow originating from the C=C **bond** and not the C atom.

δ+ δ-Br Correct: ⁶

Incorrect:

(c) Carbocation leading to the formation of X

CommentsGenerally well done

(d) (i) (1) Compound X

The intermediate is a <u>primary carbocation which is very unstable</u> since there is only one electron-donating alkyl group bonded to the positively charged carbon present to disperse the positive charge. Hence this carbocation does not form and the yield for X is zero at the stated temperature.

- Students need to answer the question and explain why carbocation X is NOT formed, instead of explaining why carbocation Y is formed.
- Students should understand that a carbocation is an ionic <u>species</u> with a positively charged carbon (e.g. // is a carbocation), a carbocation is <u>not</u> THE positively charged carbon.

(2) Compound Z

In the carbocation, the <u> π -electron cloud</u> (or <u>p-orbitals</u>) of the C=C bond overlap with the empty p-orbital of the carbon with the positive charge.

Hence, the π electrons can delocalise into the empty p-orbital (or carbon with positive charge), dispersing the positive charge, thus stabilising the carbocation.

Hence the percentage yield of Z is high.

Comments

- The key idea here is that despite the fact that the carbocation formed is primary, it is resonance-stabilised. Students need to explain how the carbocation is able to exhibit resonance stabilisation.
- The key ideas to mention would be the
 - o overlapping of the appropriately described p-orbitals, leading to
 - o delocalisation of positive charge or appropriate pi electrons.
- The use of correct terminology has been addressed in both CT1 and CT2. It is clear that some students are not learning from their past experience.
 - The electrons / charge is delocalised, not the orbitals.
 - The orbitals overlap, not the electrons.



The following should be clearly demonstrated

- Both graphs should have two peaks, with 2nd E_a smaller than 1st E_a.
- Both X and Y lower in energy than 1,3-butadiene.
- The intermediate forming Y is lower in energy than that forming X
- Energy of X is higher than Y
- Species correctly and clearly labelled.

- Since this reaction involves a two-step mechanism, both diagrams are to have two peaks, with 2nd E_a lower than 1st E_a (since the 1st step is the slow step). Many students drew diagrams with one peak and mistakenly labelled the peak as the intermediate. The peak, which is a point of maximum potential energy, corresponds to the transition state.
- Since this is an exothermic reaction, as mentioned in the question stem of Q3 on page 6, products X and Y are lower in energy than the reactant, 1,3-butadiene.
- A handful of students did not demonstrate understanding that a more stable product/intermediate is at a lower energy level compared to a less stable product/intermediate.
- Although not asked to label the respective *E*_a's on the diagrams, some students did so incorrectly, especially *E*_a for the 2nd step. See below for correct labelling of *E*_a.



(e)

Comments

ÒН

Br

- Students should notice from table 3.1 that the product of 1,4-addition has the greatest yield. Therefore, atoms are added to carbons 1 and 4 to give the major product (note that the transformation involved when 1,3-butadiene undergoes 1,2- and 1,4-addition is described in the question stem of Q3 on page 6).
- Since 1,3-butadiene reacts with an **equimolar** amount of Br₂(aq), and considering how alkene reacts with Br₂(aq) to form a halohydrin major product, –Br and –OH are to be added to carbons 1 and 4.
- A handful of students were careless and had missing carbon(s), particularly in students who used skeletal formula. Students need to be mindful to check their structures for such common mistakes.

Intermediate compound:

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Step 1: NaOH(aq), heat Step 2: K₂Cr₂O₇, dilute H₂SO₄, heat

Comments

- Since there is no increase in carbon atoms converting Z to W, students should not consider introducing a –CN group.
- Step 1: Aqueous medium must be used to ensure that nucleophilic substitution reaction occurs. Hence the state symbol for NaOH must be stated explicitly. Should ethanolic medium be used, elimination reaction will take place preferentially.
- Step 2:
 - KMnO₄ cannot be used as the oxidising agent as the alkene will undergo oxidative cleavage and not yield W.
 - $\circ~$ Acidic medium must be provided for oxidation with $K_2Cr_2O_7$ and the choice of acid must be specified.
- (ii) Test: Add aqueous Na₂CO₃ to each sample in a test-tube.

Observations:

For **W**, effervescence of CO_2 gas which gives a white precipitate with limewater. For 1,3-butadiene, there is no effervescence of CO_2 gas.

OR

Test: Add Na to each sample in a test-tube.

For **W**, effervescence of H_2 gas which gives a 'pop' sound with a lighted splint. For 1,3-butadiene, there is no effervescence of H_2 gas.

Comments

- Other sensible and well-described answers involving SOCl₂ and PCl₅ were accepted.
- Strong oxidation with KMnO₄ is not a suitable distinguishing test as **both** 1,3-butadiene and W will react to produce CO₂.



further oxidised to CO₂ and H₂O by KMnO₄

- Aqueous Na₂CO₃ should be used instead of solid Na₂CO₃. The aqueous medium is necessary for the carboxylic acid to dissociate to produce H⁺ to react with the carbonate ions.
- Effervescence (learn to spell it correctly!) and description of gas test were often left out in students' observations. These must be included.
- Many students did not get full credit because they did not provide a negative intended observation for 1,3-butadiene.
 Accept: no effervescence, no gas evolved.
 - Reject: no observation, no observation change, no reaction.

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(f) (i)

Q4 (a) (i) reduction reactions: (I) and (II)

Comments

• Generally well done.

(ii) For reaction (I), the C of the C=O group loses a bond to a S atom and gains a new bond to a H atom. OR For reaction (II), the C of the C=O group loses a bond to the O atom and gains a new bond to a H atom.

Comments

- The question required students to "explain, in terms of the bonds lost and gained by the relevant carbon atoms", therefore answers must provide two points – specifically the bonds lost (or broken) and the bonds gained (or formed)
- Answers which described reduction by formation of alcohols from aldehydes for reaction (II) were not accepted.
- Stating of specific bonds lost (or gained) is necessary. Answers which are generic such as "*the* carbon lost a C-S bond and gained a C-H bond" were not accepted.
- A handful of student described the reduction process for reaction (I) as "C of C=O group lost a C-S bond and gained a *hydrogen bond*". Please note that this terminology is used wrongly as a hydrogen bond is specific to the intermolecular forces of attraction between molecules, and not to be used in a covalent bond.

(ii) $CH_3CH_2N(CH_3)_2$



Comments

 Generally well done by students. Many students were able to utilise information provided to provide an answer based on novel chemistry.



- Same as in 4(c)(ii), generally well done.
- A significant number of students submitted answers with errant and problematic structures. Please take a look at some of the common structures given and the remarks for each of them.



(c) (i) As the number of C atoms increases, there is an increase in the total number of electrons in the molecule. The electron cloud becomes increasingly larger and more polarisable. This means the strength of instantaneous-dipole induced-dipole interactions increases.

Hence, as the intermolecular forces of attraction become increasingly stronger, there will be increasingly fewer particles in the vapour phase that is in equilibrium with the liquid phase. This results in a lowering of the vapour pressure.

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- Many students do not read the question in context. This is clear as many seemingly plausible and logical, but incorrect explanations were given by students to explain vapour pressure. Some of these include:
 - 1) bigger size of ketones, leading to reduced molecular speeds of gaseous molecules and reduced vapour pressure
 - 2) heavier mass of ketones, leading to reduced molecular speeds of gaseous molecules and reduced vapour pressure
 - higher intermolecular forces of attraction, leading to deviation from ideal gas behaviour for gaseous molecules and thus reduced pressure on the walls of the container

While these explanations are plausible, in reality they do not explain vapour pressure. The question provided boiling point data, and that was the clue that students should have used to decipher that vapour pressure is dependent on intermolecular forces and boiling point.

• In many cases, students' answers lack the high level of specificity in the terms used that is expected of them at this stage. Some of the examples include:

	Generic answer	Expected answer	
1	"weak intermolecular forces of	"weak instantaneous dipole –	
	attractions"	induced dipole interactions"	
2	"the molecular mass of ketones	"the number of electrons of	
	increase leading to increase in	ketones increase leading to	
	id-id interactions"	increase in id-id interactions"	
3	"the electron cloud increase"	"the electron cloud size increase"	

Students risk using generic terms or incorrect terms at the peril of their own marks.

(ii) $\frac{5.20 - 35.8}{144 - 102} = \frac{5.20 - P}{144 - 130}$

P = 15.4 mm Hg

- Not very well done. Many students simply provided an estimation of the value without calculating, failing to answer the question.
- Similarly there are a number of students who simply stated the correct value of 15.4 mm Hg without providing any calculations. They have failed to fulfil the requirements set out by the question and were not awarded the marks.

Q5 (a) Acid strength: ethanol < water < ethanoic acid < tartaric acid

In the ethoxide ion (CH₃CH₂O⁻), the <u>electron-donating alkyl group intensifies the</u> <u>negative charge on O atom</u>. The charge on CH₃CH₂O⁻ remains localised on the O atom. Therefore, CH₃CH₂O⁻ is the least stable. Ethanol is the weakest acid as compared to water, ethanoic acid and tartaric acid.

In the hydrogen tartrate ion and ethanoate ion, the <u>negative charge on oxygen is</u> dispersed over the two highly electronegative oxygen atoms resulting in two equivalent resonance structures. Hence, both ions are <u>stabilised to a larger extent</u> than the hydroxide/ethoxide ions.

Hydrogen tartrate has <u>2 electron-withdrawing –OH groups and 1 electron-withdrawing</u> <u>–COOH group, which helps to disperse the negative charge on oxygen of –COO⁻ group.</u> Hence hydrogen tartrate is more stable than ethanoate and tartartic acid is stronger than ethanoic acid. <u>Intramolecular hydrogen bonding</u> can exist (shown below) and hence further stabilises the anion.



Comments

- Students must use scientific terminologies to compare the acidities of compounds clearly and accurately. The use of terms which caused confusion in answers and answers with contradictory terms were not given credit.
- For the ethoxide ion, rather than referring to the entire ethoxide ion, students need to state that the negative charge on the oxygen is intensified (<u>not</u> increased). In fact, the charge on the ion remains unchanged at -1.
- For the hydrogen tartrate ion and the ethanoate ion, the answer given should clearly indicate or imply resonance stabilisation. Descriptions using the term delocalisation, or dispersion of charge resulting in resonance structure/resonance stabilisation were also accepted. Dispersion of charge on its own was insufficient.
- Note that negative charge on hydrogen tartrate ion cannot be delocalise on all the -OH and COOH due to the presence of sp³ hybridised carbon atoms.
- (b) (i) Amount of OH⁻ used in titration = $(30.00/1000)(0.100) = 3.00 \times 10^{-3}$ mol Amount of T²⁻ formed = $(\frac{1}{2})(3.00\times 10^{-3}) = 1.50 \times 10^{-3}$ mol Total volume of solution = 0.0250 + 0.0300 = 0.0550 dm³ [T²⁻] = $1.50 \times 10^{-3}/0.0550 = 0.02727 = 0.0273$ mol dm⁻³

- Mostly well done.
- Students need to remember to calculate new total volume of solution.

(ii) T²⁻ undergoes hydrolysis to give an alkaline solution.

$$T^{2-} + H_2O \implies HT^- + OH^-$$

$$K_b \text{ of } T^{2-} = \frac{[HT^-][OH^-]}{[T^{2-}]} = 10^{-(14 - 4.34)} = 10^{-9.66} = 2.188 \text{ x } 10^{-10} \text{ mol } dm^{-3}$$

At equilibrium, $[HT^-] = [OH^-]$. Since T^{2-} is a weak base with a small K_b , assume at equilibrium, $[T^{2-}] = initial [T^{2-}] = 0.02727 \text{ mol dm}^{-3}$

$$\mathcal{K}_{\rm b}$$
 of $T^{2-} = \frac{[{\rm H}T^-][{\rm O}H^-]}{[T^{2-}]} = \frac{[{\rm O}H^-]^2}{0.02727} = 2.188 \text{ x } 10^{-10} \text{ mol dm}^{-3}$

 $[OH^{-}] = \sqrt{2.188 \times 10^{-10} \times 0.0272} = 2.443 \times 10^{-6} \text{ mol dm}^{-3}$ pOH= - log $[OH^{-}] = -\log 2.443 \times 10^{-6} = 5.61$ pH = 14 - pOH = 14 - 5.61 = <u>8.39</u>

Comments

• The equation given in the question indicates that base hydrolysis of T²⁻ occurs in solution. OH⁻ is formed. Hence, K_b expression should be used for calculations. Many students mistakenly used the K_a expression in their calculations.

(c) (i) Amount of NaOH = $(\frac{20.00}{1000})$ (0.0400) = 8.00 x 10⁻⁴ mol dm⁻³ Amount of NaOH in (c)(i) = 8.00 x 10⁻⁴ mol_= amount of HT⁻ present [HT⁻] = solubility of KHT = $\frac{8.00 \times 10^{-4}}{25.0/1000}$ = 0.0320 mol dm⁻³

Comments

 Students need to be able to understand that a saturated solution of KHT is formed at equilibrium, and that at saturation, [HT⁻] = solubility of KHT.

(ii) $[HT^{-}] = 0.0320 \text{ mol } dm^{-3}$

Concentration/mol dm ⁻³	$KHT(s) \ \rightleftharpoons \ K^{+}(aq) +$	HT⁻ (aq)
Initial	x	-
Change	+0.0320	+0.0320
Equilibrium	x + 0.0320	0.0320

 $K_{sp} = [K^+] [HT^-] = (\mathbf{x} + 0.0320)(0.0320) = 2.11 \times 10^{-3}$

 $x = 0.0339 \text{ mol dm}^{-3}$

- Students need to take note that there are 2 sources of K⁺, from potassium nitrate and KHT. Since the solution is saturated, the ionic product of KHT equals that of the K_{sp} expression.
- Studuent need to know that concentration terms, not amount, is used in the $K_{\rm sp}$ expression.



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At low pH, [H⁺] is high, hence equilibrium position of (1) lies to the left.

As pH increases i.e. $[H^+]$ falls, forward reaction of (1) is favoured and position of equilibrium shifts to the right which increases $[HT^-]$.

However as [H⁺] continues to falls, the position of equilibrium of (2) shifts to the right and [HT⁻] falls, hence explaining the presence of a maximal point.

Comments

- Students must <u>explain</u> the <u>shape</u> of the graph drawn.
- Students are expected to explain how a change in the pH of the solution affects the [HT⁻]. A change in pH affects [H⁺]. Thus, with reference to the equations given, students have to discuss how a change in [H⁺] will shift the positions of equilibrium of (1) and (2) which in turn affects the [HT⁻].
- Students must demonstrate understanding that the [HT⁻] peaks at pH 3.7.

(e) Organic product from step 2:



Step 1 : $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat with immediate distillation Step 2 : HCN with trace NaCN (or HCN with trace NaOH)

Comments

• Step 1:

If the stronger oxidising agent KMnO₄ is mistakenly used, ethanedioic acid is formed which will further oxidised to carbon dioxide and water. For this transformation, heating with immediate distillation is necessary to prevent formation of ethanedioic acid

 Step 2: To obtain the products, this reaction has to be carried out in cold condition or room temperature. **Q6 (a) (i)** An aqueous solution of $CoCl_2$ is coloured because it contains the octahedral $[Co(H_2O)_6]^{2+}$ ions.

The presence of the H_2O ligands causes the five originally degenerate 3d orbitals in the Co^{2+} ion to split into two sets of slightly different energy levels.

Since the 3d subshell of Co^{2+} is partially filled, the electrons from the lower-energy d orbitals can absorb energy corresponding to a certain wavelength of light from the visible spectrum and get promoted to the higher-energy d orbitals.

Such d-d transitions are responsible for the colour observed for $CoCl_2(aq)$. The colour observed is the complement of the colour absorbed.

Examiners' Comments

- Many students did not provide the hexaaquacobalt(II) complex formula to illustrate the understanding that the colour of the solution is due to <u>Co²⁺ ion</u> bonded to <u>6 water ligands</u>.
- Many students incorrectly identified the ligands as Cl⁻ instead of H₂O.
- Many students wasted time in explaining the splitting of the d-orbitals when it was not required.
- Students need to show that they understand what they are writing because certain words or phrasing used may actually mean something else or something incorrect. For example:
 - "absorb energy corresponding to visible spectrum" means to absorb the energy corresponding to the entire spectrum, and not just a specific wavelength.
 - o "complementary" is not the same as "complimentary".
 - "frequency" should not be used in place of "wavelength" even though they are related, they are not the same thing.
 - "CO" is not the same as "Co" (legible handwriting, please).
 - "visual light" = ???
 - "orbitals absorb energy" and "orbitals are promoted to higher subshell" it is the electrons which absorb energy and promoted to a higher-energy d orbital.
 - "photons" can come from the non-visible spectrum so do not use this term to simply and conveniently replace the phrase "energy corresponding to a certain wavelength of light from the visible spectrum".
 - "d-d transitions" cannot be used to replace the absorption of energy and promotion of the electrons.
 - "Co²⁺ has *half*-filled 3d orbitals" could be taken to mean Co²⁺ having just a configuration with "3d⁵" i.e. the description is ambiguous.
 - "colour reflected" does not mean "colour observed", as the term "reflection" has an idea of light being reflected from a surface or boundary, and an angle of reflection is actually associated with such a phenomenon. However, this is not the scenario we are describing here.
- Students should hence be careful not to mis-use terms learned from other disciplines because the context may not be the same.
- (ii) The two aqueous solutions have different colours because the Co²⁺ ions in these solutions are bonded to <u>different ligands</u> (H₂O and NH₃). The different ligands split the 3d orbitals into two sets of different energy levels to <u>different extents</u>.

Hence the two solutions absorb energies corresponding to different wavelengths of light from the visible spectrum and consequently different complementary colours are observed.

Examiners' Comments

- Generally well done. Many students displayed understanding that different ligands will result in the splitting of the 3d-orbitals in Co²⁺ to different extent, resulting in different energy gaps between the two sets of d orbitals.
- (b) (i) Step 1: I₂(aq), NaOH(aq), heat Step 2: CH₃OH, conc. H₂SO₄, heat

Examiners' Comments

- Well done for step 1.
- No credit is given if <u>heating</u> or the <u>use of concentrated sulfuric acid</u> is absent in step 2.
- (ii) H₂N–OH or hydroxylamine

Examiners' CommentsA large number of students were able to get this answer.

(iii) Ammonia acts as a base (or Bronsted-Lowry base) in the reaction and accepts a proton from dimethylglyoxime to generate the $C_4H_7N_2O_2^-$ ligand for complexation with the Ni²⁺ ion.

Examiners Comments

- Many students did not realise there were two parts to the question; **state** and **explain**.
- Most students could identify that ammonia acts as a base, but did not highlight that it accepts a proton from dimethylglyoxime to generate the ligand.

(iv)

Examiners' Comments

- Generally well-done. Some mistakes include giving two –OH or two –O⁻ in the structure. Students should be able to deduce the charge of the ligand from Ni(C₄H₇N₂O₂)₂.
- Many students drew a structure of the complex instead. Please read the question carefully.

(v)







Examiners' Comments

- The intramolecular hydrogen bond in the Ni(C₄H₇N₂O₂)₂ complex should be formed between the –OH group of one ligand, and the –O⁻ of the other ligand.
- Many students incorrectly drew the intramolecular hydrogen bond *within* each ligand.
- Several students failed to follow the instruction to **label** the hydrogen bond.
- There is no necessity to draw the dative covalent bond as ": → ". The arrow alone already represents the two electrons used for this bond.
- Some students need to revise the criteria for hydrogen bond formation because they drew it between an O and the H of the nearby –CH₃.
- (vi) The highest energy 3d orbital is $3d_{x^2-v^2}$.

This orbital has its <u>electron density concentrated along the x and y axes</u>. Hence the electrons in this orbital point directly towards the lone pairs of electrons of the donor atoms of the ligands and they experience the <u>greatest repulsion</u> when compared to the electrons in the other 3d orbitals. Consequently, the potential energy of the $3d_{x^2-y^2}$ orbital is raised the highest.

Examiners' Comments

- Students should know how to name the 3d orbitals correctly. In this case, names such as $3d_{(x-y)^2}$, $3d_{x^2+y^2}$ and $(x^2 y^2)$ orbital are incorrect.
- Please phrase properly it is the lobes of this orbital that lies along the x and y axes, not "the *orbital* lies along the x and y axes".
- The names of the axes i.e. x and y, should be clearly stated as there are three axes possible (x, y, or z).



Examiners CommentsGenerally well done.

(c) (i) $CO + NO \longrightarrow CO_2 + \frac{1}{2}N_2$ Or $2CO + 2NO \longrightarrow 2CO_2 + N_2$

Examiners Comments

 Common mistakes include adding oxygen to the reactants and failing to balance the equation. (ii) Rhodium is able to act as a heterogeneous catalyst because the rhodium atoms have partially filled 4d subshell which allow them to form weak bonds with reactant molecules.

Description of how the Rh catalyst speeds up the reaction

Through the formation of weak bonds, the gaseous CO and NO molecules adsorb onto the active sites at the surface of Rh.

This adsorption increases the reaction rate because the covalent bonds within the reactant molecules are weakened, thus reducing the activation energy for the reaction.

In addition, the adsorption increases the concentration of CO and NO molecules on the Rh surface and allows these molecules to come into close contact with proper orientation for reaction to form new bonds.

After reaction, the product molecules (CO_2 and N_2) desorb from the active sites on the Rh surface and diffuse away, allowing the active sites to be reused.

Examiners' Comments

- A number of students interpreted the question incorrectly and went on to explain about Boltzmann's distribution curve and activation energy.
- Students should realise that "increasing the concentration of reactant molecules" and "reactants coming into close contact" is not the same.
- Please get the spelling of these terms correct adsorb / adsorption and desorb / desorption.
- Also, it is the reactant molecules which adsorb onto Rh, not the other way around i.e. Rh **does not** "adsorb" onto the reactant molecules.
- Some students incorrectly described the bonds within the reactants as "C–O" and "N–O" bonds. Note that these bonds in CO and NO are not all single bonds. In this case, students should just leave the description as shown in the answer.
- It is also the bonds "within" the molecules which are weakened, not "between".
- Many students liked to use the phrase "*vacant*, low-lying orbitals". Since the energetically accessible orbitals here are the 4d (not 3d!) orbitals which do contain electrons, the description of "vacant", or "empty", is incorrect.
- Some students described the meaning of "heterogeneous" (in terms of phase) instead of answering the question.

(iii) $CH_3OH + CO \longrightarrow CH_3COOH$

Examiners' Comments

• Generally well-done, except that a number of students still incorrectly left common species on both sides of the reaction equation.