RAFFLES INSTITUTION
2014 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9647/02

Paper 2 Structured Questions **17 September 2014**
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces provided at the top of this page.
Write in dark blue or black pen in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ **12**
2	/ **10**
3	/ **12**
4	/ **14**
5	/ **24**

This document consists of **19** printed pages.

For Examiner's Use

1 Planning

You are to plan an experiment to investigate how the rate of the reaction between propanone and iodine, catalysed by dilute sulfuric acid, depends on temperature and to calculate the activation energy, E_a, for the reaction.

When excess propanone and iodine react in the presence of dilute sulfuric acid, iodine is decolourised and the brown solution becomes colourless when iodine is used up. In the reaction, one of the hydrogen atoms in propanone is replaced by an iodine atom and hydroiodic acid is produced.

(a) Construct a balanced chemical equation for the reaction.

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[1]

A teacher demonstrates this experiment as follows.

She prepares two separate solutions, **X** and **Y**.

Solution **X** contains 5.00 g dm^{-3} iodine solution.

Solution **Y** is a mixture of 500 cm^3 of 1.0 mol dm^{-3} propanone and 500 cm^3 of 1.0 mol dm^{-3} dilute sulfuric acid.

She mixes **10 cm^3** of solution **X** with **10 cm^3** of solution **Y** at **35 ^oC** and, after **40 seconds**, the mixture decolourises.

(b) Consider the description of the experiment given above.

The dependence of the reaction rate on temperature may be determined by performing a number of experiments at different temperatures. You may find it useful to use **1/t** to represent the reaction rate, where **t** is the time taken for the reaction mixture to decolourise.

(i) Draw a labelled diagram of the experimental setup you would use to carry out this experiment. You should use only standard apparatus found in a school laboratory and show clearly the following:

- the apparatus used as the reaction vessel
- how the thermometer will be positioned in order to measure the temperature of the solution as accurately as possible
- how the temperature can be controlled

For Examiner's Use

(ii) Write a plan for such a series of experiments. In your plan, you should use the same volumes of solution **X** and solution **Y** described on **page 2**.

Your plan should ensure that at least one of your experiments would be expected to take **more than 40 seconds**.

You may assume that you are provided with the following:

- solution **X** containing 5.00 g of iodine in 1.0 dm^3 of water
- 1.0 mol dm^{-3} dilute sulfuric acid
- 5.0 mol dm^{-3} propanone solution
- deionised water
- the apparatus normally found in a school laboratory

Your plan should contain the following:

- details for the preparation of 1.0 mol dm^{-3} propanone solution from the propanone solution provided
- details for the preparation of solution **Y**
- the number of experiments you would carry out
- the range of temperatures at which the experiments would be carried out
- what temperature measurements you would make
- all essential experimental details

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For Examiner's Use

[8]

For Examiner's Use

(c) Identify one potential safety hazard in this experiment and state how you would minimise this risk.

[1]

(d) The Arrhenius equation is $k = Ae^{-\frac{E_a}{RT}}$, where k is the rate constant, A is the Arrhenius constant, E_a is the activation energy, R is the molar gas constant, and T is the thermodynamic temperature in Kelvins.

The Arrhenius equation may also be expressed in the following linear form:

$$\ln k = \ln A - \frac{E_a}{RT}$$

(i) State the relationship between k and **t**, the time taken for the reaction mixture to decolourise.

(ii) In the axes below, draw a suitable straight-line graph using only the data collected in your experiment and show how E_a can be found. Label the axes of your graph clearly.

[2]

[Total: 12]

For Examiner's Use

2 Halogens form many interhalogen compounds and ions, in which a halogen atom lower down in the group is surrounded by atoms of halogens higher in the group.

Iodine forms three diatomic interhalogen compounds: IF, IC*l* and IBr.

Species	Bond energy / kJ mol^{-1}
I–F	277
I–C*l*	208
I–Br	175

(a) On heating, iodine monobromide decomposes to give iodine and bromine.

$$IBr(g) \rightarrow \tfrac{1}{2}\, I_2(g) + \tfrac{1}{2}\, Br_2(g)$$

(i) Using bond energies in the *Data Booklet* and in the table, calculate the enthalpy change, ΔH_r, of the above reaction.

(ii) Describe and explain how the thermal stability of the diatomic interhalogen compounds formed by iodine varies down Group VII.

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[5]

For Examiner's Use

(b) When phosphorus(V) chloride dissolves in liquid iodine monochloride, the resulting solution conducts electricity. This is due to the presence of the two ions $[PCl_4]^+$ and $[ICl_2]^-$.

(i) Draw a structure to show the shape of $[PCl_4]^+$ and state the C*l*–P–C*l* bond angle.

(ii) Draw a dot-and-cross diagram for $[ICl_2]^-$ and state the shape of the ion.

[4]

(c) Some halogens dissolve in strongly oxidising solvents to form cations.
For instance, I_2 dissolves in oleum to form the bright-blue I_2^+ ion.

Molecule	Ionisation energy / kJ mol^{-1}
Cl_2	1110
Br_2	1014
I_2	900

Suggest a reason why the ionisation energy of the halogen molecules decreases down Group VII.

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[1]

[Total: 10]

For Examiner's Use

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

(a) Copper is a widely used material in a multitude of products from statues to watches. As the metal is exposed to water and air, it undergoes corrosion and forms a dull green coating known as patina, which contains copper(II) hydroxide as one of its key components. While this green layer is unsightly on statues, it is highly sought after by watch collectors.

(i) Write the overall balanced equation for the corrosion of copper. By calculating $E^{\ominus}_{cell}$, show that the corrosion of copper occurs spontaneously.

(ii) To prevent the corrosion of copper, super-hydrophobic layers can be applied onto the surface of copper.

Suggest how these super-hydrophobic layers help to prevent corrosion.

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(iii) Another method of preventing corrosion is by cathodic protection, where the metal is coated with a thin layer of zinc.

Explain, with the help of suitable equations from the *Data Booklet,* how cathodic protection helps to prevent the corrosion of copper.

[4]

For Examiner's Use

(b) In a lead-acid car battery, Pb and PbO_2 electrodes are dipped into dilute H_2SO_4. The reaction during the discharge process may be represented by the equation:

$$PbO_2(s) + Pb(s) + 2HSO_4^-(aq) + 2H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

(i) Such car batteries tend to malfunction prematurely as a white powder starts to coat the electrode. When hot water is poured over the electrodes to dissolve the white powder, the battery starts to function again.

Explain why such batteries tend to suffer from premature malfunction.

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(ii) 0.33 g of Pb was consumed when a current of 100 A was drawn from the battery for 3.1 s. By calculating the total number of electrons transferred, determine a value for the Avogadro's constant.

(iii) During the charging phase, the used car battery is connected to an external power source to reverse the electrode reactions.

Sketch a simple diagram for the charging process and indicate the following clearly in your diagram.

- polarity of each electrode
- the cathode and the anode
- the electrode at which PbO_2 will be formed

[8]

[Total: 12]

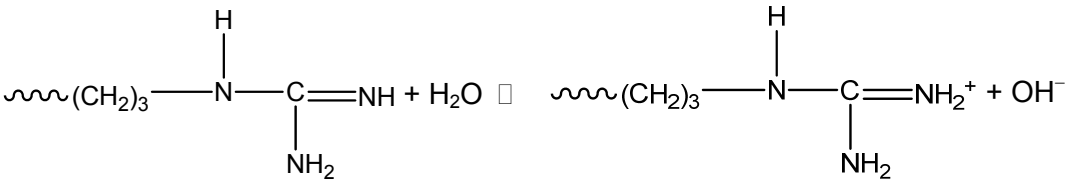
For Examiner's Use

4 Eggs are a good source of proteins.

(a) Egg yolks are used in the making of mayonnaise.
The following amino acids are found in large quantities in egg yolk.

Amino acid	Formula of side chain (R in $RCH(NH_2)CO_2H$)	pK_b of R group
lysine	$-(CH_2)_4NH_2$	3.47
arginine	$-(CH_2)_3NHC(NH_2)=NH$	1.52

(i) Given that the R group in arginine ionises in water as shown in the equation below,



explain why the R group in arginine has a smaller pK_b than the R group in lysine.

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(ii) Suggest a reason why the R group in arginine will **not** undergo a second ionisation in water.

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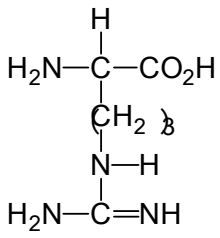
For Examiner's Use

(iii) The structure of arginine is shown on the right.



When arginine is completely protonated, it has three ionisable hydrogen atoms.

Three pK_a values are associated with arginine: 2.17, 9.04 and 12.48.

Make use of these pK_a values to suggest the structures of the two species present in an aqueous solution of arginine at pH 3.

(iv) Write an equation to show how arginine maintains the pH when a small amount of H^+ is added to an aqueous solution of arginine at pH 3.

(v) Similar to all naturally occurring amino acids, the solubility of arginine is lowest at its isoelectric point. Explain why that is so.

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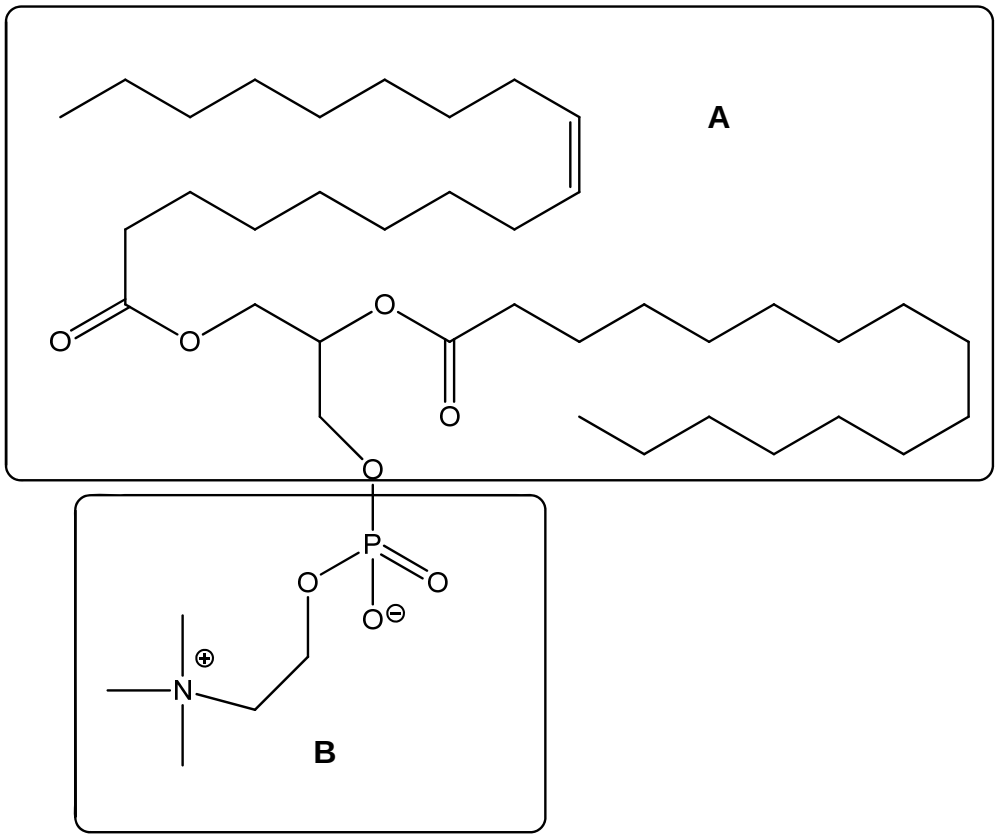
[7]

For Examiner's Use

(b) Mayonnaise is an oil-in-water emulsion in which droplets of oil are dispersed in water through the addition of emulsifiers.

Emulsifiers are compounds that contain both a polar, hydrophilic group, which is attracted to water, and a hydrophobic group, which is attracted to non-polar solvents such as oil. Lecithin is an important emulsifier found in egg yolk.

In the structure of lecithin given below, two groups, **A** and **B**, are enclosed separately in rounded rectangles.



Use the information given above to complete the following table.

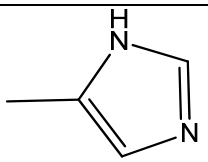
Solvent	Group which interacts with solvent	Type of interactions between group and solvent
Oil		
Water		

[2]

For Examiner's Use

(c) A meringue, which is a dessert, is made by whipping egg whites and sugar to form egg foam that is stiff and firm.

The following amino acids are found in large quantities in egg white.

Amino acid	Formula of side chain (R in $RCH(NH_2)CO_2H$)
aspartic acid	$-CH_2CO_2H$
glutamic acid	$-CH_2CH_2CO_2H$
lysine	$-(CH_2)_4NH_2$
arginine	$-(CH_2)_3NHC(NH_2)=NH$
histidine	

(i) The mechanical force from whipping introduces pockets of air into egg white. Explain how this mechanical force results in the stiff consistency of egg foam needed for making meringues.

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The common problem with egg foam is the inability to hold its shape due to the reforming of R group interactions.

(ii) Lemon juice is often added to egg white to enhance the stiff consistency needed for making meringues.

By considering its interaction with the R groups present in egg white, suggest how lemon juice stabilises the egg foam.

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[3]

(d) Poached eggs are made when the pH of ovalbumin in egg is decreased by the addition of vinegar in boiling water.

Explain why this process will result in the coagulation of egg white only, but is unable to break ovalbumin into its constituent amino acids.

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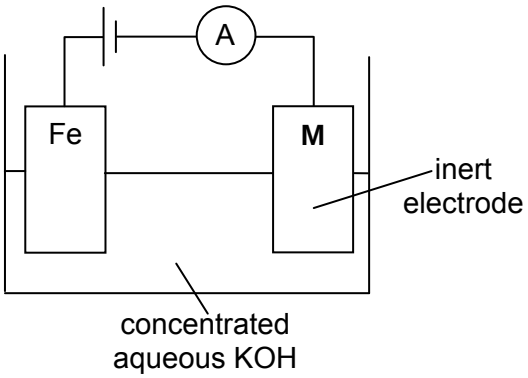
[2]

[Total: 14]

For Examiner's Use

5 This question deals with the chemistry of iron and its compounds.

(a) The diagram below shows an electrolytic cell which is used to prepare potassium ferrate(VI), K_2FeO_4, a powerful oxidising agent.



(i) State the electronic configuration of iron in the anion of K_2FeO_4.

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(ii) *Use of the Data Booklet is relevant to this question*.

During the reaction, the iron electrode is oxidised to ferrate(VI) ion while hydrogen gas is evolved at electrode **M**.

Construct an equation for the overall reaction occurring in the electrolytic cell.

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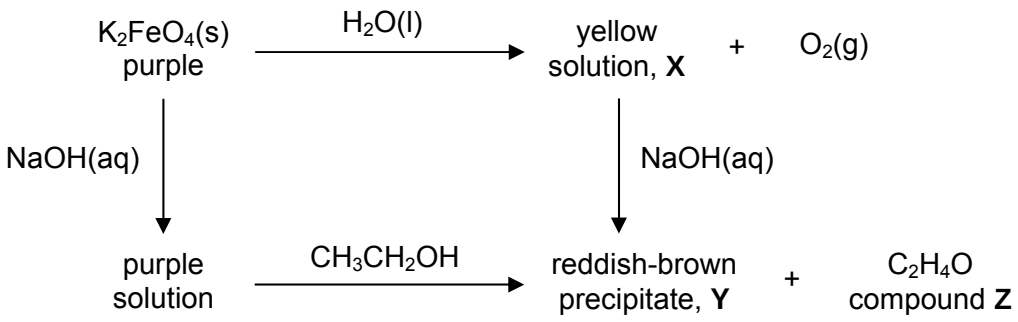
(b) The following scheme shows some reactions involving potassium ferrate(VI).



The complex ion in solution **X** and precipitate **Y** contain iron, oxygen and hydrogen. The oxidation number of iron in **X** is the same as that in **Y**.

(i) Suggest the formula of the complex ion in solution **X**.

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(ii) Write an ionic equation for the conversion of the complex ion in solution **X** into precipitate **Y**.

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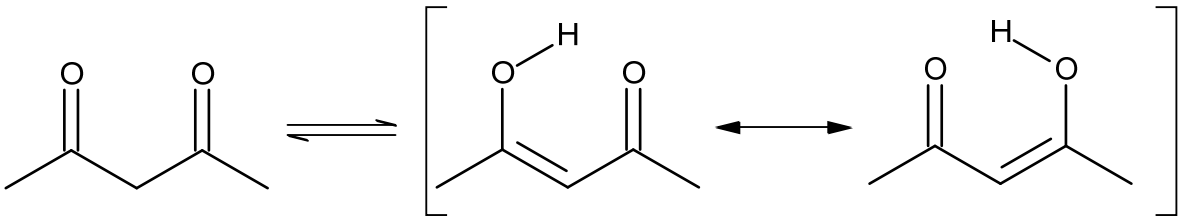
For Examiner's Use

(iii) Compound **Z**, C_2H_4O, reacts with Tollens' reagent to give a silver mirror. Draw the displayed formula of **Z**.

[3]

(c) The following equilibrium exists in gaseous pentane-2,4-dione.



keto enol

(i) What type of isomers are the keto and enol forms of pentane-2,4-dione?

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At 298 K, pentane-2,4-dione ionises in aqueous solution according to the equation

$$CH_3COCH_2COCH_3(aq) + H_2O(l) \rightleftharpoons [CH_3COCHCOCH_3]^-(aq) + H_3O^+(aq)$$

(ii) Suggest a reason why a hydrogen atom on the third carbon atom in pentane-2,4-dione is more acidic than a hydrogen atom on a terminal carbon atom in the same molecule.

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[2]

For Examiner's Use

(d) The pentane-2,4-dionate ion, $[CH_3COCHCOCH_3]^-$, is a *bidentate ligand* and is commonly known as acetylacetonate ($acac^-$).

(i) Explain the meaning of the term *bidentate ligand*.

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Pentane-2,4-dione**,** also known as acetylacetone (acacH), reacts with iron(III) chloride to give a dark red complex, $[Fe(acac)_3]$.

$$FeCl_3.6H_2O(s) + 3acacH(aq) \rightarrow [Fe(acac)_3](s) + 3H_2O(l) + 3H_3O^+(aq) + 3Cl^-(aq)$$

(ii) Explain how the addition of aqueous CH_3COONa to the mixture of iron(III) chloride and acetylacetone will increase the yield of $[Fe(acac)_3]$.

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(iii) There are six iron-oxygen coordinate bonds in the complex.
Suggest the shape of $[Fe(acac)_3]$.

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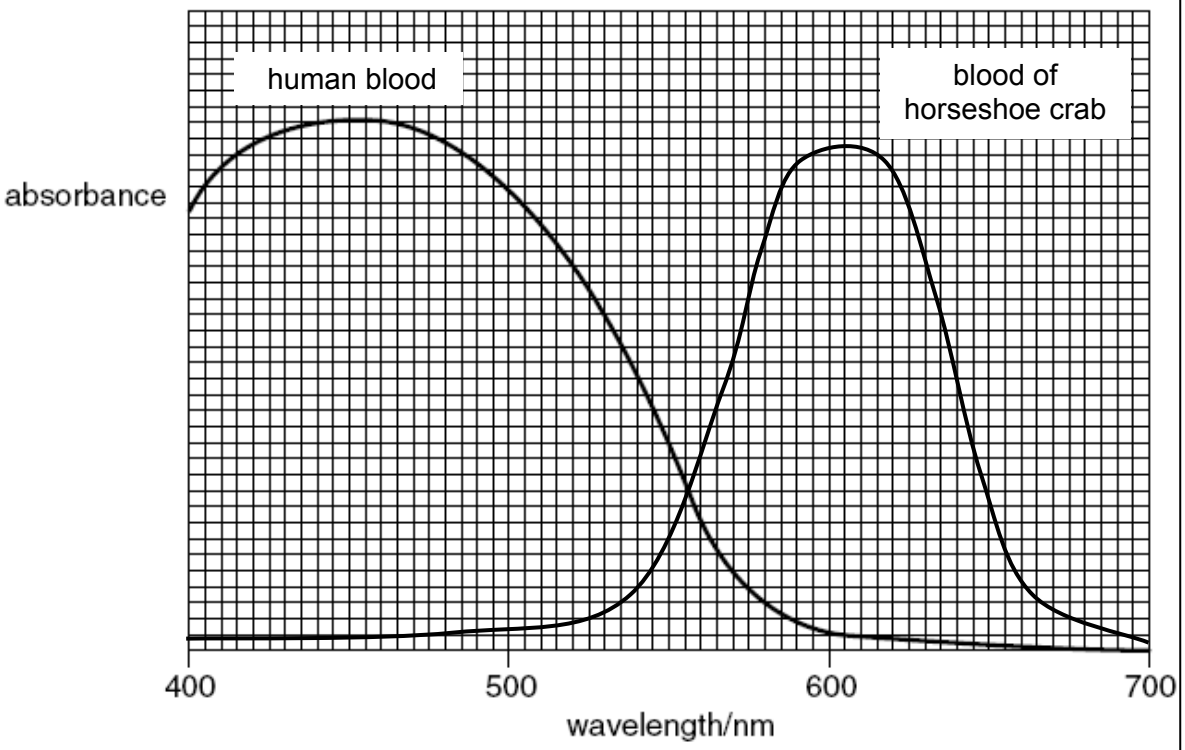
(iv) $[Fe(acac)_3]$ is a chiral compound and it exists as a pair of optical isomers.
Draw 3-D representations of the two isomers of $[Fe(acac)_3]$.

[6]

For Examiner's Use

A spectrometer is a machine which measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. The amount of light absorbed is expressed as an absorbance value. The higher the absorbance, the more of a particular wavelength is being absorbed.

The spectrum below shows the major absorption peak for human blood and for the blood of horseshoe crab.



The wavelengths associated with each colour of visible light are given in the table.

colour	wavelength / nm
violet	400 – 430
blue	430 – 490
green	490 – 570
yellow	570 – 590
orange	590 – 620
red	620 – 750

(e) **(i)** The colour of human blood is red.
State the colour of the blood of horseshoe crab.

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(ii) The blood of sea squirts is green.
On the spectrum above, draw and label the absorption peak for the blood of sea squirts.

For Examiner's Use

(iii) The colour of blood is due to oxygen-carrying proteins which consist of organic groups surrounding a transition metal ion. In humans, this transition metal ion is iron.

Explain why oxygen-carrying proteins in humans are coloured.

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In humans, haemoglobin (Hb) transports oxygen from the lungs to other parts of the body. One molecule of haemoglobin can bind up to four molecules of oxygen.

$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$$

(iv) Explain why a human who is trapped in an enclosed environment containing a high concentration of carbon monoxide may die of a lack of oxygen.

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[6]

For Examiner's Use

(f) Many transition metals and their compounds are useful catalysts.

For instance, iron acts as a heterogeneous catalyst in the Haber process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) What feature of transition metals such as iron makes them suitable as heterogeneous catalysts in chemical reactions?

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(ii) State the three stages of a typical reaction involving a heterogeneous catalyst.

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(iii) An example of homogeneous catalysis is the use of iron(II) or iron(III) ions to catalyse the reaction between iodide ions, I^-, and peroxodisulfate ions, $S_2O_8^{2-}$.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

Write **two** equations to show how iron(III) ions catalyse the reaction between iodide and peroxodisulfate ions. Explain why this reaction can also be catalysed by iron(II) ions.

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[Total: 24]

– END OF PAPER –