

A competition to select the team to represent the

UNITED KINGDOM

at the

**XXXVIth INTERNATIONAL CHEMISTRY
OLYMPIAD**

STUDENT QUESTION BOOKLET

Round I - 2004

* * * * *

- The time allowed is 2 hours.
- Attempt all 7 questions.
- Write your answers in the special answer booklet.
- In your calculations, please write only the essential steps in the answer booklet.
- Always give the appropriate units and number of significant figures.
- You are provided with a copy of the Periodic Table.
- Do *NOT* write anything in the right hand margin of the answer booklet.

Some of the questions will contain material you will not be familiar with. However, by logically applying the skills you have learnt as a chemist, you should be able to work through the problems. There are different ways to approach the tasks – even if you cannot complete certain parts of a question, you may still find subsequent parts straightforward.

H 1 1.008																	He 2 4.003			
Li 3 6.94	Be 4 9.01	<table border="1"> <tr> <td>symbol</td> </tr> <tr> <td>atomic number</td> </tr> <tr> <td>mean atomic mass</td> </tr> </table>										symbol	atomic number	mean atomic mass	B 5 10.81	C 6 12.01	N 7 14.01	O 8 16.00	F 9 19.00	Ne 10 20.18
symbol																				
atomic number																				
mean atomic mass																				
Na 11 22.99	Mg 12 24.31											Al 13 26.98	Si 14 28.09	P 15 30.97	S 16 32.06	Cl 17 35.45	Ar 18 39.95			
K 19 39.102	Ca 20 40.08	Sc 21 44.96	Ti 22 47.90	V 23 50.94	Cr 24 52.00	Mn 25 54.94	Fe 26 55.85	Co 27 58.93	Ni 28 58.71	Cu 29 63.55	Zn 30 65.37	Ga 31 69.72	Ge 32 72.59	As 33 74.92	Se 34 78.96	Br 35 79.904	Kr 36 83.80			
Rb 37 85.47	Sr 38 87.62	Y 39 88.91	Zr 40 91.22	Nb 41 92.91	Mo 42 95.94	Tc 43	Ru 44 101.07	Rh 45 102.91	Pd 46 106.4	Ag 47 107.87	Cd 48 112.40	In 49 114.82	Sn 50 118.69	Sb 51 121.75	Te 52 127.60	I 53 126.90	Xe 54 131.30			
Cs 55 132.91	Ba 56 137.34	La* 57 138.91	Hf 72 178.49	Ta 73 180.95	W 74 183.85	Re 75 186.2	Os 76 190.2	Ir 77 192.2	Pt 78 195.09	Au 79 196.97	Hg 80 200.59	Tl 81 204.37	Pb 82 207.2	Bi 83 208.98	Po 84	At 85	Rn 86			
Fr 87	Ra 88	Ac⁺ 89																		

*Lanthanides	Ce 58 140.12	Pr 59 140.91	Nd 60 144.24	Pm 61	Sm 62 150.4	Eu 63 151.96	Gd 64 157.25	Tb 65 158.93	Dy 66 162.50	Ho 67 164.93	Er 68 167.26	Tm 69 168.93	Yb 70 173.04	Lu 71 174.97
+Actinides	Th 90 232.01	Pa 91	U 92 238.03	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

1. This question is about redox reactions

Give half-equations for the following reactions in aqueous acid solution. In each case, indicate whether the reaction is an oxidation or a reduction by ticking the appropriate box in the answer booklet.

- (a) FeCl_3 to FeCl_2
- (b) HCl to H_2
- (c) K_2MnO_4 to KMnO_4
- (d) SO_4^{2-} to $\text{S}_2\text{O}_8^{2-}$
- (e) NO_3^- to NO_2
- (f) H_2O_2 to O_2
- (g) $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+}

Redox

[f. RED(UCTION + OX(IDATION).]

A reversible reaction in which one species is oxidized and another reduced; usu. *attrib.*, indicating (some connection with) such a reaction, or a simultaneous oxidation and reduction, as *redox couple*, *electrode*, *indicator*, *potential*, *reaction*, etc.

Oxford English Dictionary

2. This question is about pollution and the Taj Mahal



You should need to refer to the following solubility data to help answer this question.

Substance	CaCO ₃	CaSO ₄	BaCO ₃	BaSO ₄
Solubility in water / mol dm ⁻³	1.3 x 10 ⁻⁴	4.5 x 10 ⁻²	9.1 x 10 ⁻⁵	9.4 x 10 ⁻⁶

Although calcium carbonate is effectively insoluble in pure water, it reacts with acidic rainwater, thereby accelerating the erosion of marble and limestone monuments.

- (a) Give the equation for the reaction between calcium carbonate and carbonic acid, H₂CO₃(aq).

In addition to this reaction, the pollutant SO₂ forms SO₃ in the atmosphere, which then dissolves in rainwater forming sulfuric acid. This slowly converts calcium carbonate into solid calcium sulfate.

- (b) i) Write the equation for the reaction between calcium carbonate and sulfuric acid.
- ii) Why does the conversion of calcium carbonate into calcium sulfate accelerate the erosion of marble and limestone?

The life of monuments like the Taj Mahal is now being extended by treatment with an aqueous mixture of barium hydroxide, Ba(OH)₂ and urea, CO(NH₂)₂. As this solution soaks into the porous marble / limestone, the urea slowly hydrolyses forming ammonia and carbon dioxide. The carbon dioxide released reacts with the barium hydroxide forming barium carbonate.

- (c) Write the equation for the hydrolysis of urea.
- (d) i) Write the equation for the reaction between barium hydroxide and carbon dioxide.
- ii) Why does the formation of barium carbonate slow down the rate of erosion of the monument?

Finally, surface barium carbonate on the treated monument can react with sulfur dioxide in the air, forming a layer of barium sulfate, and carbon dioxide.

- (e) i) Give the equation for the reaction between barium carbonate and sulfur dioxide, in the presence of oxygen.
- ii) Will this secondary reaction speed up or slow down the erosion process? Explain briefly.

3. This question is about dissolved oxygen in water

Aquatic life can only survive because of the oxygen gas dissolved in the water; without it, the water rapidly becomes toxic due to decaying organic matter.

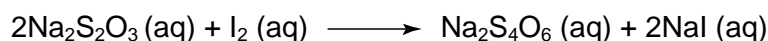
Hence it is important to monitor the dissolved oxygen concentration (DOC) in rivers and lakes – if this falls below 5 mg dm^{-3} , most species of fish cannot survive.



One of the most accurate methods for measuring the DOC in water is the *Winkler method*. Under alkaline conditions Mn^{2+} is rapidly oxidised to Mn^{3+} by dissolved oxygen, producing a pale brown precipitate of $\text{Mn}(\text{OH})_3$. A sample of river water is shaken with excess alkaline Mn^{2+} , and the resulting pale brown precipitate is then reacted with an excess of potassium iodide, which it oxidises to iodine. The iodine is then determined by a titration with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution of known concentration.

- (a) Write balanced symbol equations for:
- the oxidation of $\text{Mn}(\text{OH})_2$ to $\text{Mn}(\text{OH})_3$ by aqueous oxygen,
 - the oxidation of KI by $\text{Mn}(\text{OH})_3$,

The equation for the reaction between sodium thiosulfate and iodine is:



- (b) Suggest an indicator for the iodine-thiosulfate titration.

25.0 cm^3 of a sample of river water treated in this way required 25.0 cm^3 of $0.00100 \text{ mol dm}^{-3}$ sodium thiosulfate solution.

- (c) Calculate the concentration of the dissolved oxygen in mg dm^{-3} .

Nitrate(III) ions are found to interfere with this method since they too can oxidise iodide ions to iodine. During the reaction, a colourless gas is given off, which instantly turns brown on exposure to the air.

- (d) What is the colourless gas? Give a balanced equation for its reaction in air.
- (e) Write a balanced equation for the oxidation of iodide ions by nitrate(III) ions.

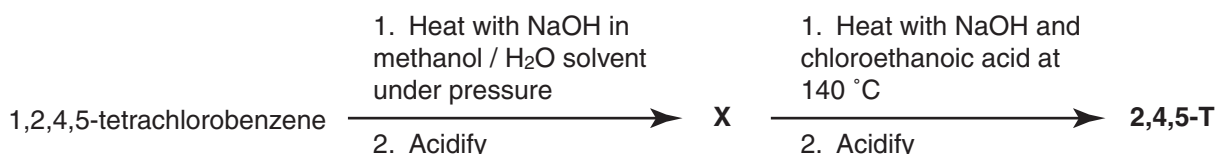
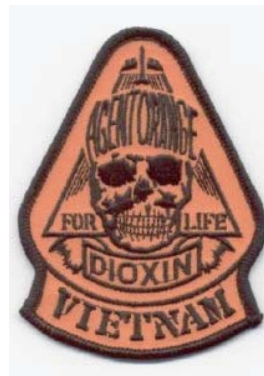
In a modification of the Winkler method to prevent the interference by nitrate(III) ions, a solution of sodium azide, NaN_3 , is added to the river water. During this reaction, two gases are evolved: nitrogen and N_2O .

- (f) Write a balanced equation for the reaction between nitrate(III) ions and azide ions in aqueous acid.

4. This question is about Agent Orange

Agent Orange was the name given to the powerful defoliant used during the Vietnam War. It consisted of a 1:1 mixture of two herbicides, '2,4-D' and '2,4,5-T'.

Shown below is a route for synthesising 2,4,5-T.



The proton NMR spectra for the starting material, 1,2,4,5-tetrachlorobenzene, the intermediate **X**, and 2,4,5-T are shown over the page.

After the first step in the synthesis, if the reaction mixture is acidified not with normal acid, H_3O^+ , but with deuterated acid, D_3O^+ , then the signal at 5.8 ppm in the ^1H NMR spectrum of **X** disappears. [Deuterium, D, is the ^2H isotope of hydrogen.]

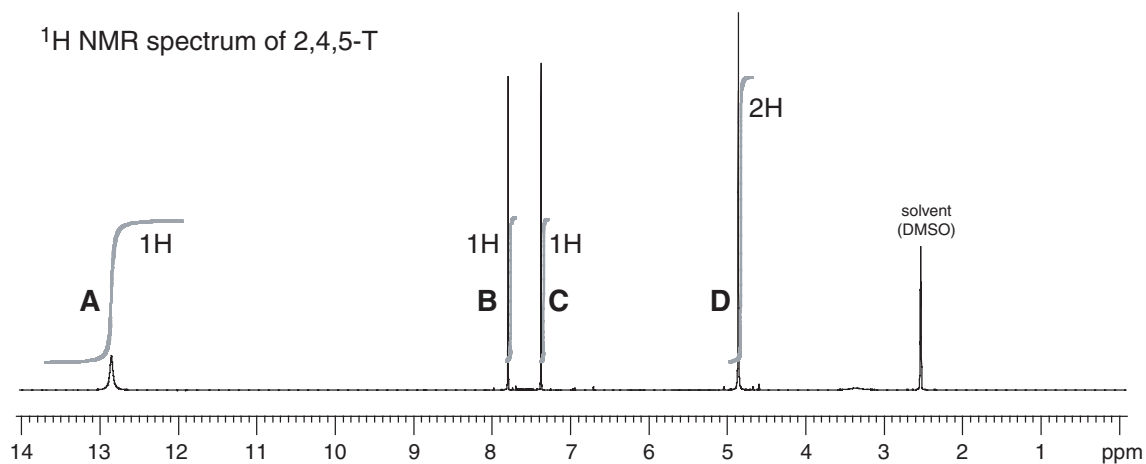
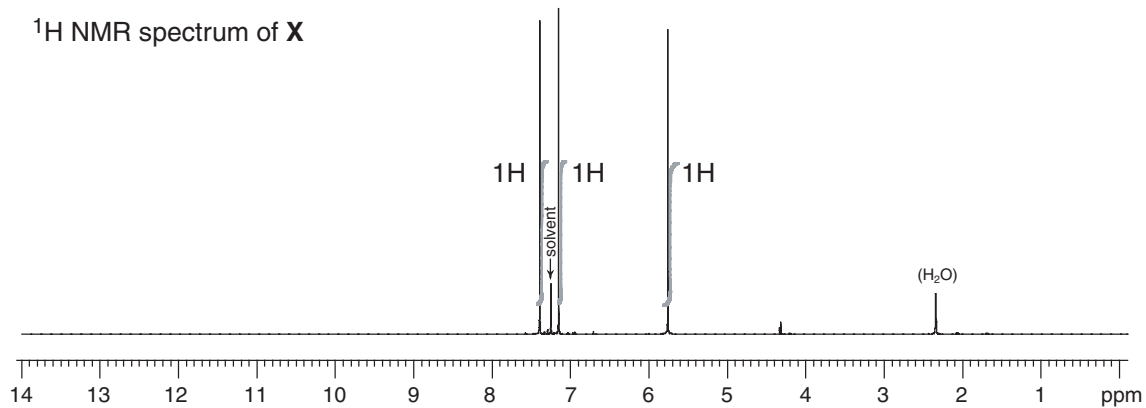
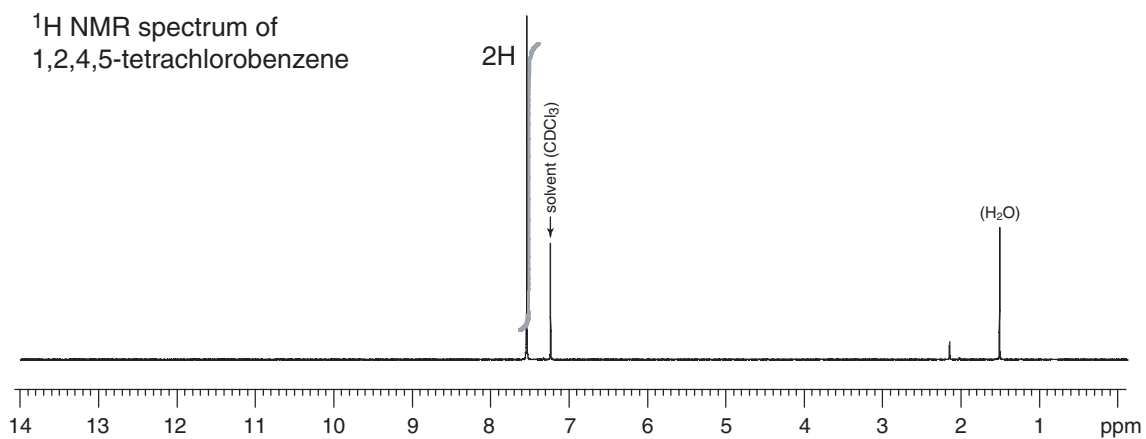
- Draw the structure of 1,2,4,5-tetrachlorobenzene.
- Suggest a structure for the intermediate **X**.
- Give the systematic name for intermediate **X**.
- Draw the structure for **X** if the reaction mixture had been acidified with D_3O^+ instead of H_3O^+ .
- Draw the structure of chloroethanoic acid.
- Suggest a structure for 2,4,5-T.
- On your structure, indicate as far as you are able which hydrogens correspond to which signals (**A**, **B**, **C** or **D**) in the ^1H NMR spectrum of 2,4,5-T.

Whilst 2,4,5-T is a highly effective herbicide, its commercial use has been discontinued due to the presence of an incredibly toxic impurity called Dioxin which may be formed from intermediate **X** during the synthesis of 2,4,5-T.



The ^1H NMR spectrum of Dioxin shows just a single peak at 7.2 ppm.

- Suggest a structure for Dioxin.



[The faint lines are the integrals used in working out the relative numbers of hydrogens.]

5. This question is about tin pest

Tin can exist as two stable allotropes: β -tin or white tin, which is metallic, and α -tin or grey tin, which is a non-metal. The conversion from one form to the other occurs at a critical temperature, T_c . The conversion from the metallic form to the powdery non-metallic form is known as *tin pest* or *tin disease*, partly because the accompanying change in density may cause 'warts' to form on the surface.



The organ at the Royal Albert Hall contains 150 tonnes of tin!

Tin pest has been suggested as the cause of organ pipes disintegrating in certain cold churches (previously thought to be the work of the devil), and even as a possible reason for the failure of Captain Scott's expedition to the South Pole, when the tin solder used in the fuel cans deteriorated.

The question refers to the change: white tin \longrightarrow grey tin

You should use the following data.

	$\Delta_f H^\ominus$ / kJ mol ⁻¹	S^\ominus / J K ⁻¹ mol ⁻¹	density / g cm ⁻³	atomic distance to nearest neighbour / pm
white tin	0	51.4	7.31	302
grey tin	-2.09	44.1	5.75	280

(a) Calculate the standard enthalpy change, $\Delta_r H^\ominus$, for the change.

It is possible to calculate the standard entropy change, $\Delta_r S^\ominus$, for this reaction in a similar way to the above using the standard entropy values, S^\ominus , given in the table.

(b) Calculate $\Delta_r S^\ominus$ for this reaction.

The feasibility of any chemical process at an absolute temperature T can be determined by calculating the change in the Gibbs energy, $\Delta_r G$, for the process at that temperature, where

$$\Delta_r G = \Delta_r H - T \Delta_r S .$$

If $\Delta_r G$ is less than zero, the process can take place; if it is greater than zero, it cannot.

(c) Calculate $\Delta_r G$ for the change white tin \longrightarrow grey tin at room temperature, 25 °C.

(d) Which allotrope of tin is stable at room temperature? Justify your answer.

(e) Calculate the temperature, T_c , at which both allotropes are in equilibrium.

(f) Calculate the percentage increase in volume as white tin converts to grey tin.

(g) Which allotrope possesses the greater coordination number? Justify your answer.

6. This question is about a supernova

The electronic ground state (*i.e.* the lowest electronic state) of a hydrogen atom may be written $1s^1$ indicating that the single electron resides in the $1s$ orbital. If sufficient energy is given to the atom, the electron may be promoted from the $1s$ orbital to a higher energy orbital, such as the $2p$ orbital or the $3p$ orbital.

The energy of an electron in a hydrogen atom (or any ionized atom with nuclear charge Z and with just one electron remaining) is given by the following equation:

$$E_n = -R_H \frac{Z^2}{n^2}$$

The energy of a free, ionized electron is zero; electrons in the atom have lower energy, hence the minus sign.

In the equation, Z is the number of protons in the nucleus ($Z = 1$ for hydrogen); n is the principal quantum number ($n = 1$ for the $1s$ orbital, 2 for the $2s$ and $2p$ orbitals, 3 for the $3s$, $3p$ and $3d$ orbitals, *etc.*); R_H is the *Rydberg constant* equal to the ionization energy of a hydrogen atom ($R_H = 2.179 \times 10^{-18}$ J).

- Calculate the energy of an electron in a $2p$ orbital in an excited hydrogen atom.
- Calculate the energy needed to promote the electron in a hydrogen atom from the $1s$ orbital to the $2p$ orbital.
- Calculate the ionization energy of a helium ion, He^+ .

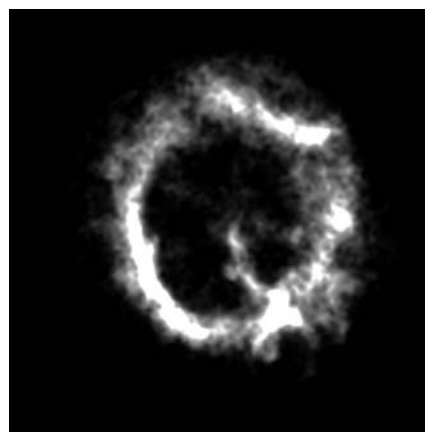
When an electron returns from a higher energy orbital to a lower one, energy is given out as light (the cause of the familiar flame colours). The frequency of the light, f , (in Hz) is related to the energy of the transition, ΔE , by the equation:

$$\Delta E = hf \quad (\text{where } h \text{ is Planck's constant} = 6.626 \times 10^{-34} \text{ J s}).$$

- Calculate the frequency of light for the electronic transition in a hydrogen atom from a $2p$ orbital to the $1s$ orbital (the so-called Hydrogen Lyman- α line).

Supernova remnant E0102-72, located some 200,000 light years away, has been found to contain more than a billion times the amount of oxygen contained in the Earth's oceans and atmosphere. At the incredibly high temperatures in the supernova (many millions of Kelvin), the oxygen atoms are multiply ionized to single electron species, O^{7+} . The oxygen was detected by the specific frequency of its Lyman- α line (the transition $n = 2$ to $n = 1$).

- Calculate the frequency of the O^{7+} Lyman- α line.
- Another element present in large quantities has its Lyman- α line at 2.471×10^{17} Hz. What element is this?



Supernova remnant E0102-72 as photographed by the UV / x-ray telescope *Chandra*.

7. This question is about 'asparagus-pee'

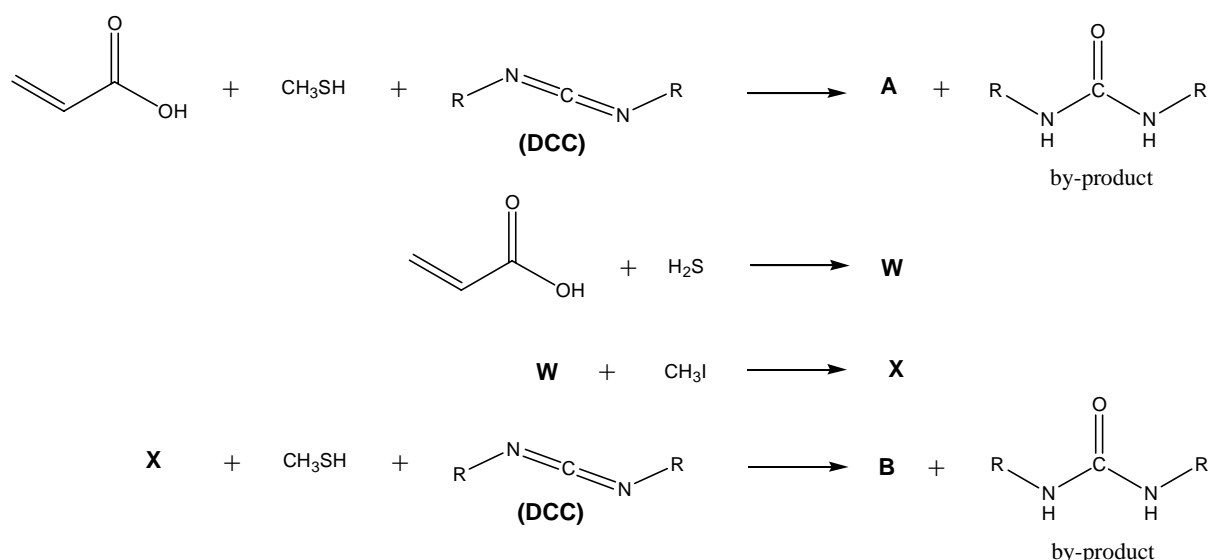
It has long been known that after eating asparagus, many people can detect an odd odour in their urine. (Whether or not a person can actually smell it is apparently genetic.)

In the 19th century it was thought that the compound responsible for the smell in so-called 'asparagus-pee' was methanethiol, CH₃SH.

In a more recent study, no methanethiol was detected in the vapour from asparagus-pee but two other sulfur-containing compounds, **A** and **B**, were identified by mass spectrometry. The M⁺ ion for compound **A** is at $m/e = 102$; for compound **B**, $m/e = 150$.



For comparative purposes, compounds **A** and **B** were also prepared in the laboratory from propenoic acid by the following routes.



Compound **A** reacts with HBr to give **Y** and with Br₂ to give two isomers, **Z1** and **Z2**.

Y is not optically active and has two peaks for its M⁺ ion at $m/e = 182$ and 184 (1:1 ratio).

Z1 and **Z2** are enantiomers (optical isomers) and their M⁺ ions have $m/e = 260$, 262 , and 264 (ratio 1:2:1).

- (a) State the role of the reagent 'DCC': **i)** catalyst; **ii)** hydrating agent; **iii)** dehydrating agent; **iv)** hydrogenating agent or **v)** dehydrogenating agent.
- (b) Suggest structures for compounds **A**, **B**, **W**, **X**, **Y**, **Z1**, and **Z2**.
- (c) Both **A** and **B** may be hydrolysed in water, releasing methanethiol, (hence the earlier suspicion of this compound). Write balanced equations for the hydrolysis reactions of both **A** and **B**.

[Naturally occurring bromine is a 1:1 mixture of ⁷⁹Br and ⁸¹Br]