RSC | Advancing the Chemical Sciences

INEOS

I Ch O UK

45th INTERNATIONAL

CHEMISTRY OLYMPIAD

2013

UK Round One

STUDENT QUESTION BOOKLET

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- **The time allowed is 2 hours.**
- **Attempt all 5 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.**
- **The marks available for each question are shown below; this may be helpful when dividing your time between questions.**

Question	1	2	3	4	5	Total
Marks Available	9	13	9	15	17	63

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.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 1 1.008																	**He** 2 4.003
Li 3 6.94	**Be** 4 9.01											**B** 5 10.81	**C** 6 12.01	**N** 7 14.01	**O** 8 16.00	**F** 9 19.00	**Ne** 10 20.18
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															

symbol
atomic number
relative atomic mass

***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 rocket fuels

The Mars Curiosity rover's landing in August 2012 was achieved using variable thrust mono propellant hydrazine rocket thrusters. Hydrazine, N_2H_4, is popular with NASA as it produces no carbon dioxide.

The hydrazine is passed over a suitable catalyst and decomposes to its elements. The rapid production of the hot gaseous elements is what provides the thrust. Ammonia can be formed as an intermediate during the decomposition.

(a) Write a balanced equation for hydrazine decomposing to ammonia and nitrogen gas.

(b) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide.

$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l)$ $\quad\quad \Delta_rH^\ominus = -241.0 \text{ kJ mol}^{-1}$

Work out the standard enthalpy change for the decomposition of hydrazine to its elements.
The standard enthalpy changes of formation in kJ mol^{-1} are:

NH_3: −46.1; H_2O_2: −187.8; H_2O: −285.8

(c) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol mixture, known as 'C-Stoff', and hydrogen peroxide ('T-Stoff').

(i) Hydrogen peroxide reacts with the hydrazine as shown in the equation.

$N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$

State the oxidation number of nitrogen and oxygen in the reactants and products.

(ii) Hydrogen peroxide oxidises the methanol to carbon dioxide and water.
Write a balanced equation for this reaction.

(iii) The fighter plane would hold 225 litres of hydrazine and 862 litres of methanol. Use the following standard enthalpy changes and densities to calculate the heat energy evolved under standard conditions for the combustion of this quantity of rocket fuel. Assume that all the hydrazine and methanol are fully combusted.

$\Delta_cH^\ominus (N_2H_4) = -622.2 \text{ kJ mol}^{-1}$ $\quad\quad$ Density of N_2H_4 = 1.021 g cm^{-3}
$\Delta_cH^\ominus (CH_3OH) = -726.0 \text{ kJ mol}^{-1}$ $\quad\quad$ Density of CH_3OH = 0.7918 g cm^{-3}

(d) Hydrazine is also commonly combined with dinitrogen tetroxide, N_2O_4, in rocket fuels. This forms a hypergolic mixture, i.e. the reactants ignite spontaneously on contact. NASA used N_2H_4 / N_2O_4 in many space vehicles and it is likely to be used in next-generation vehicles.

(i) Reactions used in rocketry produce chemically stable products (making the reaction exothermic) that are formed as gases (which provide thrust). Suggest the reaction products that are formed in the reaction between N_2H_4 and N_2O_4.

(ii) Pure N_2O_4, when warmed, initially decomposes not into its elements but instead forms a brown gas. Suggest the identity of this brown gas.

(e) A derivative of hydrazine with formula $C_2H_8N_2$ was used in rocket fuels in the Apollo missions. It has two nitrogen atoms that are in different chemical environments and two carbon atoms that are in the same chemical environment. Draw the structure of $C_2H_8N_2$.

2. This question is about Great Britain being better than any other country at cycling

One of the most successful British sports at the London 2012 Olympics was cycling. British cyclists won eight gold, two silver and two bronze medals. In addition, Bradley Wiggins became the first ever Briton to win the Tour de France.

(a) Bronze medals contain copper. A 0.800 g sample of a bronze medal was dissolved in hot concentrated nitric acid. After cooling and dilution, an excess of potassium iodide solution was added and the solution was made up to 250.0 cm^3. A 25.00 cm^3 aliquot of this solution required 12.20 cm^3 of 0.100 mol dm^{-3} sodium thiosulfate solution in the presence of starch indicator.

Calculate the percentage by mass of copper in the bronze medal.

$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

(b) All medals that were won at London 2012 had a diameter of 85 mm and were 7 mm thick. The silver medal was made up of 92.5% silver and 7.5% copper, by mass.

Calculate the mass of a silver medal. Assume that the density of the alloy varies proportionally to its composition by mass.

Densities in g cm^{-3}: Ag, 10.49; Cu, 8.96

(c) Gold medals are made of gold, silver and copper. A 5.000 g sample of a gold medal was warmed with excess concentrated nitric acid. An undissolved residue was separated by filtration, washed, dried and weighed. Its mass was 0.067 g. Then an excess of dilute hydrochloric acid was added to the solution in nitric acid. The precipitate formed was separated by filtration, washed, dried and weighed. Its mass was 6.144 g.

Calculate the percentage by mass of gold, silver and copper in the gold medal.

The GB cyclists have individually designed bikes, which have to cope with the demands placed on them whilst being as light as possible. One way a light bike could be achieved is by altering the gas used to inflate the bike tyres.

You may assume that for the remainder of this question that gases behave as ideal gases and that they follow the ideal gas law:

$$pV = nRT$$

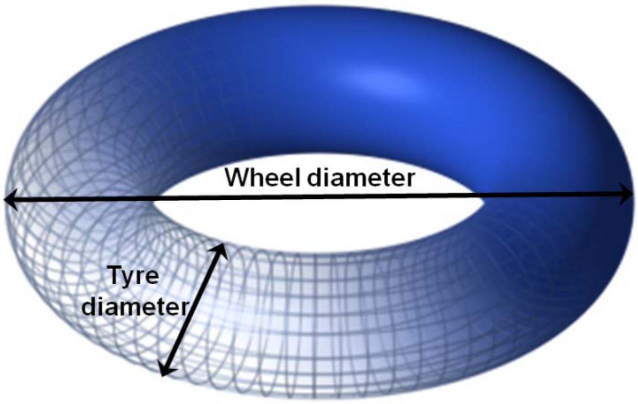
where p = pressure in Pa
V = volume in m^3
n = number of moles
R (the gas constant) = 8.31 J K^{-1} mol^{-1}
T = temperature in Kelvin

The tyres on a bike are approximately the shape of a torus. The equation for the volume of a torus, V, is given below.

$$V = \frac{\pi^2 r d^2}{2}$$

r = distance from centre of torus to **centre** of tyre tube

d = diameter of tyre tube



(d) A typical bike may have a wheel diameter of 66 cm and a tyre diameter of 23 mm.

Calculate the volume of a tyre, in m^3.

If you are unable to calculate the volume of a tyre, you may use the value of 0.001 m^3 in the subsequent parts of this question.

(e) **(i)** The air pressure used in the tyres is typically 120 psi, much higher than atmospheric pressure.

1 psi = 6895 Pa.

Calculate the number of moles of gas in a tyre, at 25 °C.

(ii) Assuming air is a mixture of 80 % nitrogen gas and 20 % oxygen gas, calculate the total mass of air in **both** tyres on a bike.

(iii) In cycling the smallest of changes can make the difference between winning and losing. The small reduction in mass upon inflating tyres with helium instead of air would be worth considering if it was not for that fact that the very small helium atoms escape through the rubber of tyres much more rapidly.

Calculate the reduction in mass of the bike if both tyres were inflated with helium instead of air.

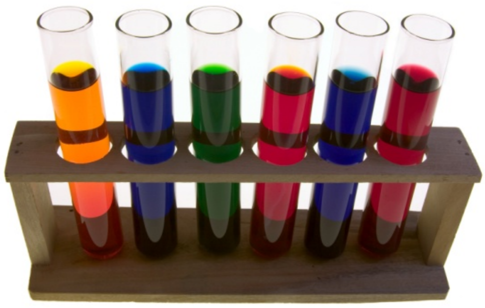
(iv) SF_6 is one of the densest substances that would still remain in the gas phase at this pressure.

What would be the increase in mass if the bike tyres were filled with SF_6?

3. This question is about chemistry general knowledge based on coloured compounds

Chemists recognise many substances by their colour.

This question tests your knowledge about the colour of a range of chemicals that you will have come across as part of your studies of chemistry.



(a) In the answer booklet, a number of colours are listed. For each colour, if one of the substances below is that colour, give its letter. If that colour cannot be made using a single substance, give the letters of two substances that will produce this colour when mixed. A substance may be used more than once.

Choose from

A = $CaCl_2(s)$
B = $CuO(s)$
C = $Cu_2O(s)$
D = $CuSO_4(s)$
E = $Al_2O_3(s)$
F = $FeSO_4.7H_2O(s)$
G = $K_2Cr_2O_7(s)$
H = $NaOH(aq)$
I = $VSO_4.7H_2O(s)$
J = $ZnCl_2(s)$

(b) A student was provided with 7 unknown aqueous solutions. Each solution contained only one substance and all solutions were different.

The student mixed pairs of solutions in an attempt to identify each of the substances. The results from these tests are shown below. A blank cell shows where no observable results were obtained.

Analyse the results and assign the following substances as solutions **T-Z**.

barium chloride   dissolved chlorine gas (i.e. chlorine water)   iron(II) sulfate   lead(II) nitrate

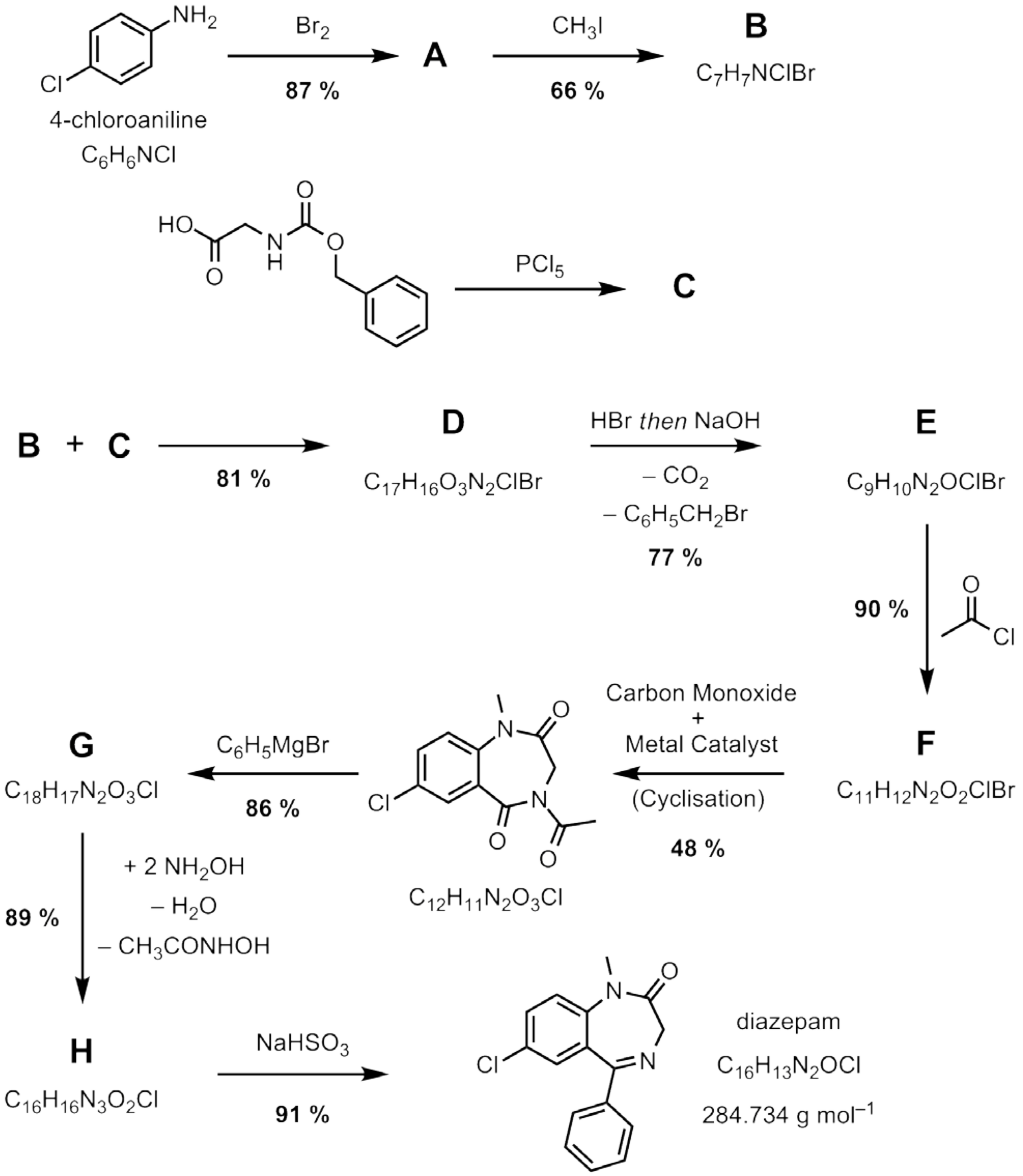
silver nitrate   sodium carbonate   sodium iodide

	T	U	V	W	X	Y	Z
T		Bright yellow precipitate formed	White precipitate formed	–	White precipitate formed	White precipitate formed	White precipitate formed
U	Bright yellow precipitate formed		–	Yellow precipitate formed	–	–	Brown solution
V	White precipitate formed	–		White precipitate formed (darkened in daylight)	White precipitate formed	White precipitate formed	–
W	–	Yellow precipitate formed	White precipitate formed (darkened in daylight)		Off-white precipitate formed	White precipitate formed	White precipitate formed (darkened in daylight)
X	White precipitate formed	–	White precipitate formed	Off-white precipitate formed		Dirty green precipitate formed (turned brown on standing)	–
Y	White precipitate formed	–	White precipitate formed	White precipitate formed	Dirty green precipitate formed (turned brown on standing)		Pale yellow solution
Z	White precipitate formed	Brown solution	–	White precipitate formed (darkened in daylight)	–	Pale yellow solution	

4. This question is about GPs giving out too many drugs

The drugs diazepam (Valium®) and alprazolam (Xanax®) belong to a family of compounds called benzodiazepines which were once hailed as the answer to many ailments. In 1988, The Committee on Safety of Medicines advised GPs to limit their prescriptions of these drugs due to their overuse; however, in England in 2010 more than 6.6 million benzodiazepine prescriptions for anxiety were dispensed. Heath Ledger, Michael Jackson and Whitney Houston are among some of the many people that are believed to have died from drug overdoses that involved benzodiazepines.

The synthesis of diazepam from 4-chloroaniline is shown below. The percentage yield for each step is also shown. By-products are not always shown.



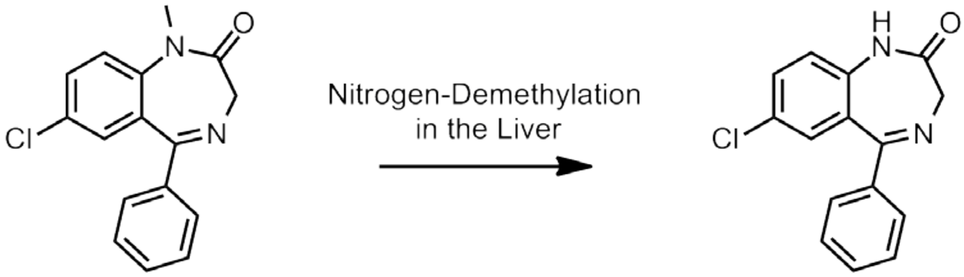
(a) (i) Calculate the overall percentage yield for the conversion of 4-chloroaniline to diazepam.

(ii) A patient was prescribed diazepam for three years at a dose of 5 mg, four times a day.

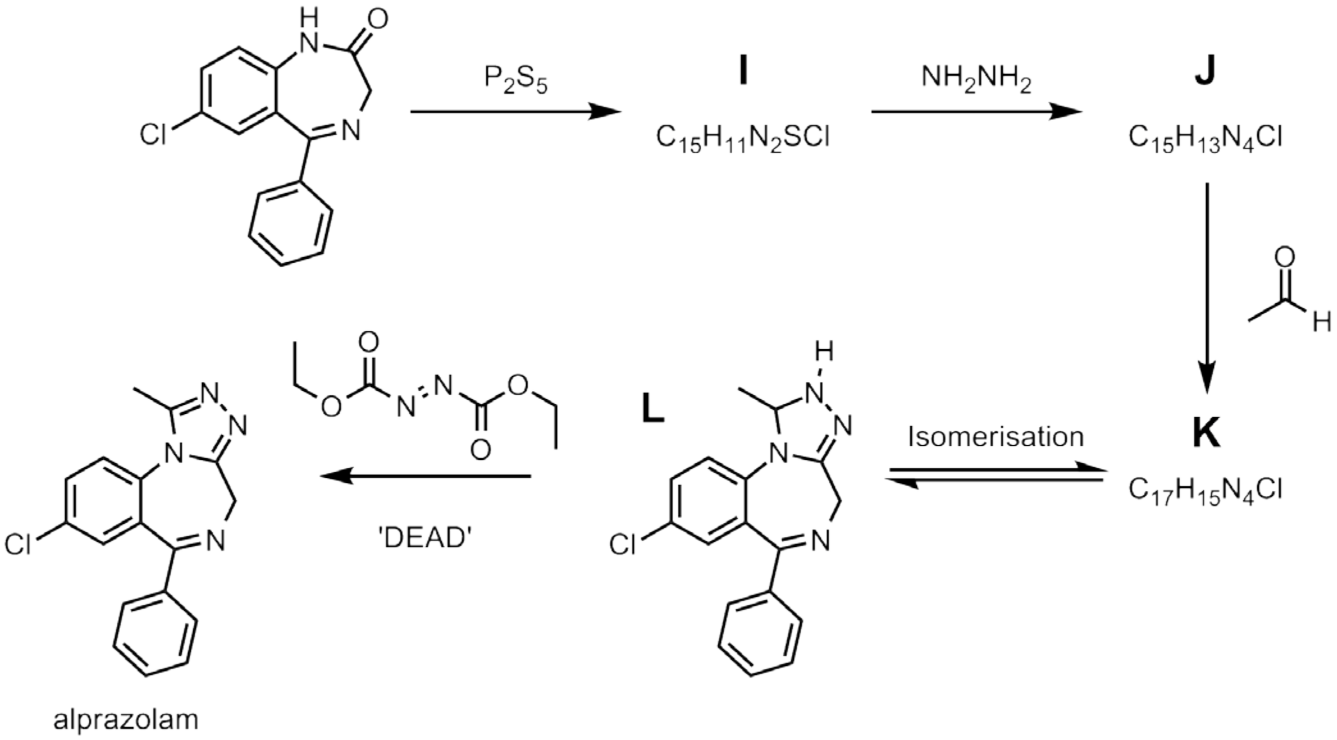
Calculate the mass of diazepam this was, and hence the mass of 4-chloroaniline needed to make the drug for this patient.

(b) Draw the structures of intermediates **A** – **H** in the synthesis of diazepam.

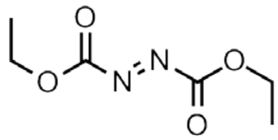
In the liver it was found that diazepam underwent a demethylation reaction. The product of this demethylation reaction was used as inspiration for the synthesis of the drug alprazolam.



(c) The synthesis of alprazolam is shown below. Draw the structures of intermediates **I**, **J** and **K**



(d) In the final stage of the synthesis, compound **L** is treated with a chemical called 'DEAD' to convert it into alprazolam. DEAD stands for diethyl azodicarboxylate.



'DEAD'

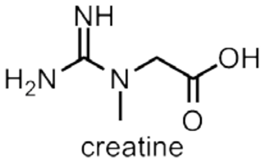
How would you classify the reaction of **L** to alprazolam using one of the terms below?

Tick the correct answer in your answer booklet.

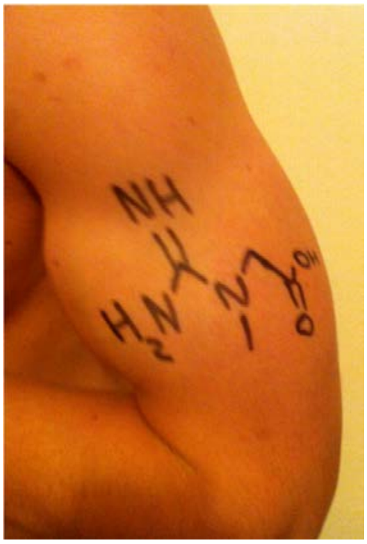
Isomerisation	Hydrolysis	Condensation	Oxidation	Reduction

5. This question is about getting big muscles

Creatine has recently become one of the most widely used nutritional supplements among athletes. Although there is much debate about which of the advertised beneficial effects of creatine are actually true, the use of creatine is generally believed to lead to a short-term gain in body mass/muscle size. The structure of creatine is shown below.



creatine

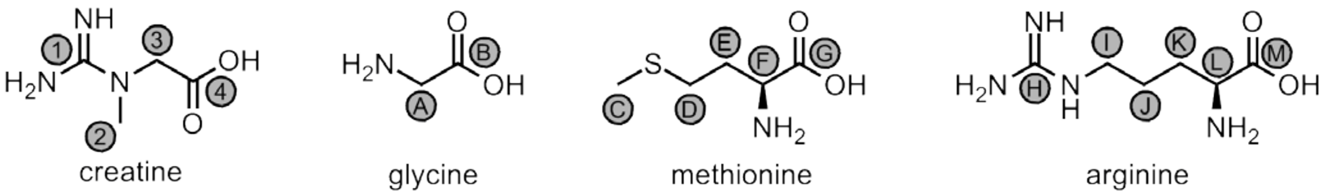


In the body, creatine is converted into phosphocreatine which is used as an energy reserve in the muscles that can be rapidly mobilised to convert adenosine diphosphate (ADP) back into adenosine triphosphate (ATP) – the body's energy currency – in times of need.

(a) Creatine is often sold in capsules labelled as 'Pure Creatine Monohydrate'. Write the molecular formula of creatine monohydrate.

(b) Creatine is synthesised naturally in organisms from three amino acids: glycine, methionine and arginine.

In your answer booklet, for each of the carbon atoms in creatine (labelled as **1-4**), suggest which carbon atom of the three amino acids it came from (labelled as **A-M**)



(c) Like amino acids, creatine exists in different ionised forms depending on the pH of the solution it is in. This causes the overall charge on the molecule to vary. Draw the most common form of creatine at each of the following pHs (the overall charge on the molecule at each pH is given).

(i) pH 1 (overall charge = + 1)

(ii) pH 7 (overall charge = neutral)

(iii) pH 12 (overall charge = − 1)

The chemical structure of creatine and these amino acids can be analysed by ^{1}H NMR.

As these are polar molecules, the NMR spectra are run in D_2O solvent. In D_2O, protons attached to nitrogen or oxygen atoms undergo rapid exchange with deuteriums from the solvent. This means that by the time the NMR is run, all N-H bonds have been replaced by N-D bonds and all O-H bonds by O-D bonds. As signals from deuterium atoms are not observed in ^{1}H NMR spectra, no signals from N-H or O-H groups in the molecule are seen in the spectrum.

The number of signals observed depends on the symmetry of the molecule. Each hydrogen atom in a unique environment gives rise to a signal at a different chemical shift in the spectrum. Occasionally, signals from two different environments can appear on top of one another when the difference in chemical shifts between the environments is very small.

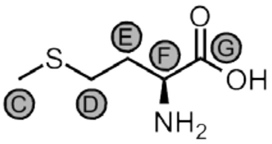
The area under each signal is proportional to the number of protons in that environment. This is shown by an integral trace (the stepped line on the spectrum). The height of each step is proportional to the area under that signal.

The appearance of the signals can be complicated by coupling. If the hydrogen atom(s) are within three bonds of another hydrogen which is in a different environment, instead of appearing as a single peak, its signal is split into a number of peaks. If the hydrogen under consideration is within three bonds of **n** hydrogens in a different environment from itself, it will be split into **(n + 1) equally spaced** peaks. The ratio of the area under the peaks is given by the number in Pascal's triangle (shown on the right). Due to rapid exchange of any protons/deuteriums bonded to oxygen or nitrogen atoms with the solvent, no coupling is seen to protons/deuteriums bonded to oxygen or nitrogen atoms.

n	**Intensities of peaks**
0	1
1	1 : 1
2	1 : 2 : 1
3	1 : 3 : 3 : 1
4	1 : 4 : 6 : 4 : 1

(d) Consider the amino acid methionine.

Complete the table in the answer booklet for carbons **C**, **D** and **F** in methionine to suggest the appearance of the overall signal from the protons bonded to that carbon atom.



methionine

(e) Usually all protons attached to the same carbon atom are in the same chemical environment; however, this is not always the case. Two protons on the same carbon atom that are in different chemical environments are called diastereotopic protons.

These are most often observed where the carbon under consideration is bonded to an asymmetric carbon atom. An asymmetric carbon atom has four different chemical groups attached to it.

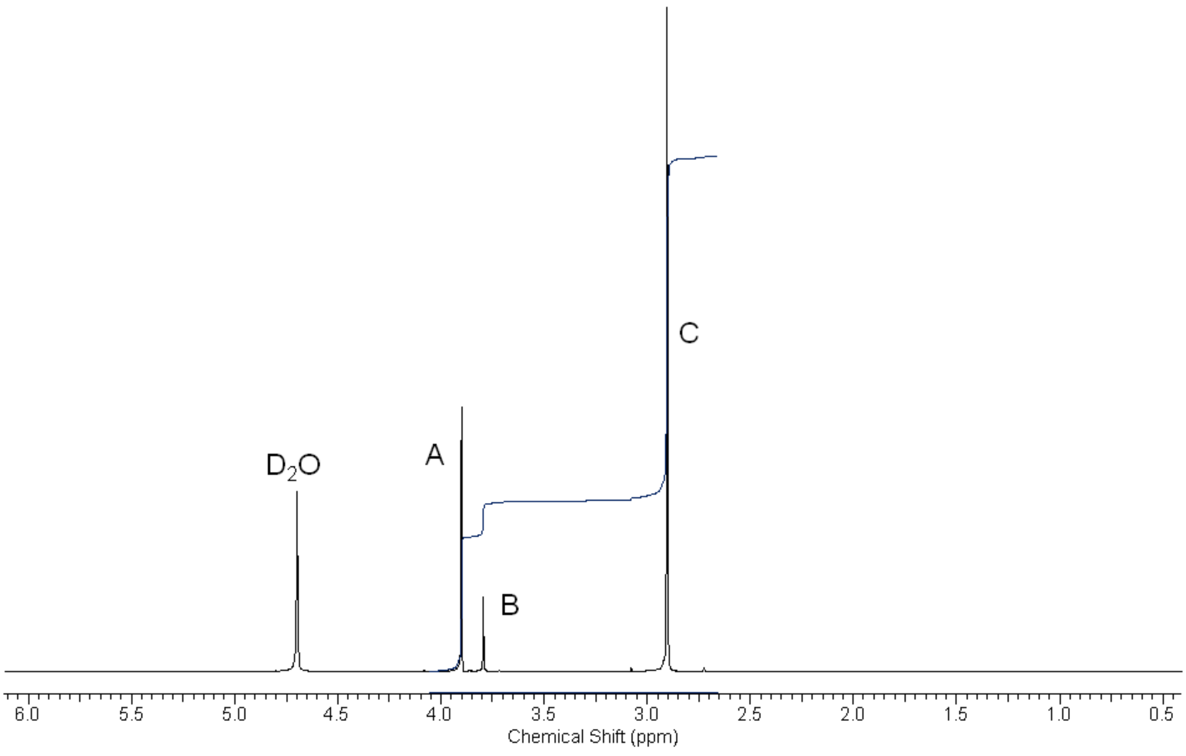
Consider glycine, methionine and arginine. In these three amino acids, write the letters of all such carbons whose diastereotopic protons would be observed as different signals in their spectra.

In the body, creatine is in equilibrium with a cyclic molecule called creatinine, by the following equation. The position of equilibrium varies with pH.

$$\text{creatine} \overset{K}{\rightleftharpoons} \text{creatinine} + H_2O$$

Creatinine is a metabolic waste product that is not used by the body. It is filtered out in the kidneys.

The ^{1}H NMR spectrum in D_2O of a creatine/creatinine solution is shown below. Three signals are observed. Creatinine gives rise to signal A. Creatine gives rise to signal B. Both creatine and creatinine give rise to signal C.



(f) Suggest a structure for creatinine.

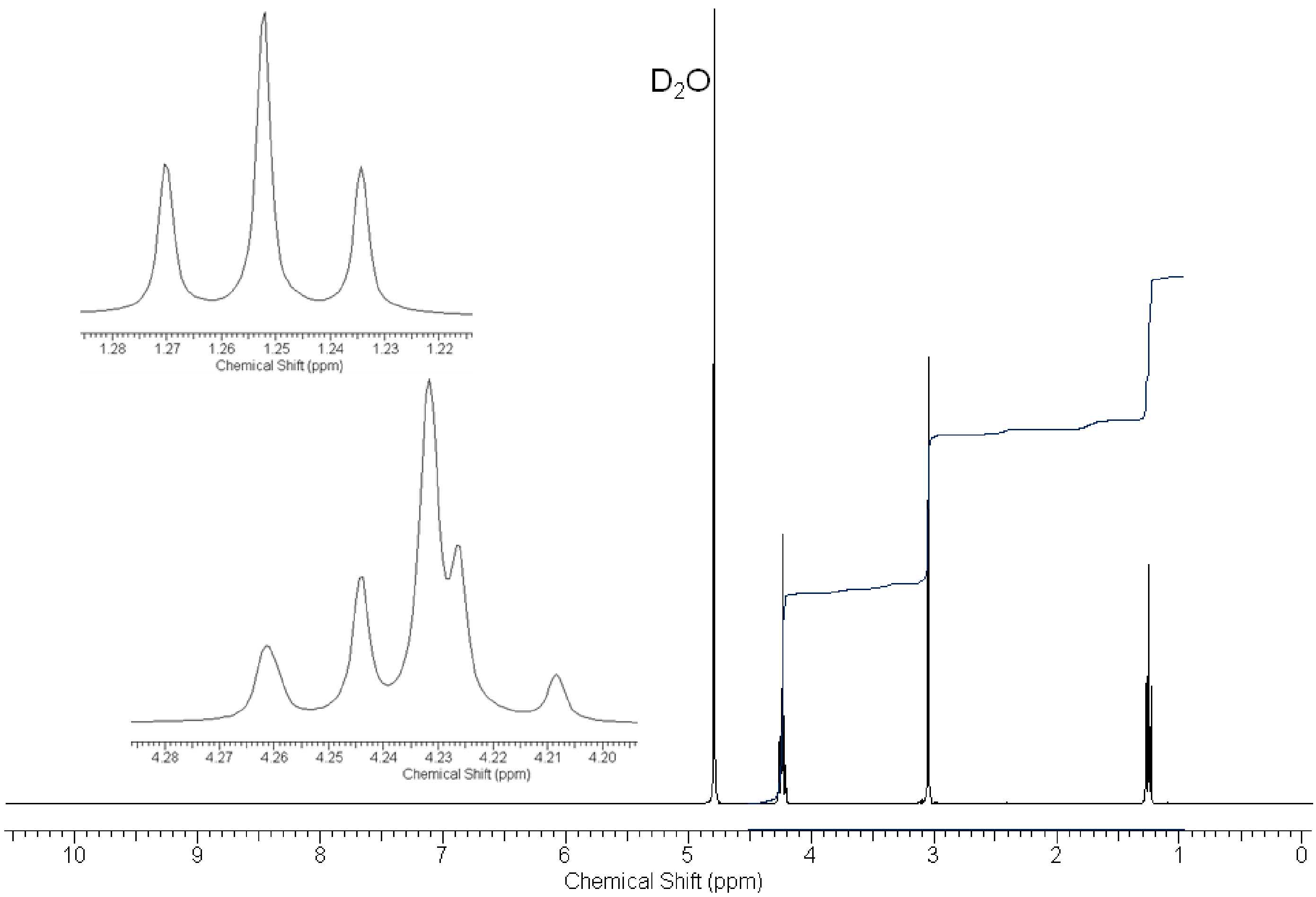
(g) Assuming this sample has reached equilibrium, calculate a value for the equilibrium constant, *K*, at this pH and temperature. Show clearly how you worked this out. You may ignore the concentration of water in your calculation.

(h) A problem with creatine supplementation is that a lot of the creatine taken does not get absorbed by the body. Recently, supplements containing derivatives of creatine have been marketed. These are usually more lipophilic (dissolve more easily in fats) in an effort to improve uptake into the body.

The ^{1}H NMR spectrum in D_2O of one of these supplements is shown below. Some regions of the spectrum have been expanded on the left hand side of the figure to help with your analysis.

This supplement exists in an ionised form at pH 1 but does not exist in an ionised form at pH 12.

Suggest a structure for this supplement.



Acknowledgements & References

Q1

The Curiosity Mars rover image is courtesy of NASA.

Q2

Information on the composition of the medals was taken from www.london2012.com.

The Bradley Wiggins image is courtesy of Getty Images.

Q3

The image of the test tubes is courtesy of iStockphoto.

Q4

The Independent **Thursday 29th December 2011** Doctors sued for creating 'Valium addicts' *Nina Lakhani*

The image of diazepam is courtesy of Paul Brown and Alamy.

Heterocycles **1981** *16* 1491-1494

Journal of Medicinal Chemistry **1977** *20* 1694-1697

Journal of Medicinal Chemistry **1979** *22* 1-7

Journal of Organic Chemistry **1980** *45* 1675-1681

Tetrahedron Letters **1971** *12* 1609-1612

Q5

John Gallacher is thanked for providing an image of his arm.

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The creatine supplements analysed were from Precision Engineered Ltd.

Biochemical Journal **1928** *22* 920-929

Journal of the Chemical Society, Perkin Transactions II **1985** 1465-1467

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