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.

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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.
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*Lanthanides: Ce 58, Pr 59, Nd 60, Pm 61, Sm 62, Eu 63, Gd 64, Tb 65, Dy 66, Ho 67, Er 68, Tm 69, Yb 70, Lu 71

*Actinides: Th 90, Pa 91, U 92, Np 93, Pu 94, Am 95, Cm 96, Bk 97, Cf 98, Es 99, Fm 100, Md 101, No 102, Lr 103

\[ N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \]
1. This question is about the chemistry of touchscreens

In recent years there has been a surge in demand for indium for touchscreen and display equipment. The element is quite rare so its price has rocketed. There are worries that the global supply of the element could run out. Its major use is the electrically conducting transparent glass ITO, indium tin oxide.

(a) Indium(III) oxide can be obtained by heating indium(III) hydroxide. Write an equation for this reaction.

ITO glass is 90% indium(III) oxide, 10% tin(IV) oxide, by mass. The iPad shown above contains about 27 mg of ITO glass in its touchscreen.

(b) (i) Calculate the mass of indium present in the ITO glass of the iPad touchscreen.

(ii) The indium content of ITO glass in touchscreens is taken to be about 700 mg per square metre. Given that the density of ITO glass is about 7.15 g/cm³, calculate the thickness of the ITO glass in the touchscreen.

Indium(III) oxide can take the cubic bixbyite crystal structure. The position of the indium ions approximates to the face-centred cubic (FCC) unit cell shown in the illustration above. A unit cell is the simplest repeat unit that contains all the symmetry of the crystal. In the FCC structure the ions are centred on the corners of the cube and the centres of the faces.

(c) Calculate how many indium ions are actually inside the cube. You will need to consider the fractional occupancy of each ion in the cube.

(d) The oxide ions occupy positions that are wholly inside the cube. Deduce how many oxide ions are present in the cubic cell shown.

(e) When indium(III) oxide is heated to 700 °C in air, its mass decreases by 11.5%. Work out the formula of the compound produced.

(f) When indium(III) oxide is heated with ammonia at 630 °C, the products are water and a semiconductor. Suggest the formula of the semiconductor.
2. This question is about detecting molecules in space

In September 2014, the BBC announced that radio-astronomers had discovered the ‘most complex molecule’ to date in space. Found in ‘Sagittarius-B2(N)’ – the largest star-forming region in our Galaxy – this is the first molecule detected with a branched carbon chain. The systematic name for the molecule is 2-methylpropanenitrile. It was found to be approximately 0.4 times as abundant as its straight-chained isomer.

The molecule was detected from the radio signals given out as it dropped from an excited energy level to a lower one.

A nitrile is a molecule in which one of the carbons has a triple bond to nitrogen.

(a) (i) Draw the structure of 2-methylpropanenitrile.

(ii) Draw the structure and give the systematic name of another nitrile isomeric with 2-methylpropanenitrile.

Astronomers are now looking for the next series of nitriles with the formula C₅H₉N.

(b) Draw all the isomeric nitriles with the formula C₅H₉N.

Most of the molecules detected by radio-astronomers in less active regions of space tend to have linear structures. The largest so far detected has the unlikely-looking formula HC₁₁N.

(c) Draw the structure of the linear molecule with the formula HC₁₁N.

The signals detected in the radio wave region of the electromagnetic spectrum are due to transitions between rotational energy levels, each of which has a particular energy. Molecules have many rotational energy levels available to them, each level with a different energy being specified by the so-called rotational quantum number, \( J \), which takes integer values from 0 upwards.

The energy (in joules) of the \( J^{th} \) rotational energy level, \( E_J \), is given by the formula:

\[
E_J = h \times B \times J (J+1)
\]

where \( B = \) the rotational constant of the molecule (in Hz)  
\( h = \) Planck’s constant = \( 6.626 \times 10^{-34} \) J s.  
and light of frequency \( f \) (Hz) has energy \( h \times f \) (joules)

Two signals have been detected due to HC₁₁N. One is due to the transition from rotational energy level \( (J = 39) \) to \( (J = 38) \), the other due to the transition from level \( (J = 38) \) to \( (J = 37) \).

(d) Given the signal from \( (J = 39) \) to \( (J = 38) \) was observed at 13186.853 MHz, calculate:

(i) the rotational constant, \( B \), for HC₁₁N (in MHz).

(ii) the frequency (in MHz) for the transition from level \( (J = 38) \) to \( (J = 37) \).
One of the most abundant heteronuclear diatomic molecules detected in space is carbon monoxide formed from $^{12}$C and $^{16}$O.

(e) Given the masses of $^{12}$C and $^{16}$O are 12.00 g mol$^{-1}$ and 16.00 g mol$^{-1}$ respectively, calculate the mass (in kg) of a single atom of each of these elements.

When taking both masses of atoms into account in a diatomic molecule, we use the so-called reduced mass, $\mu$. For a diatomic molecule with masses $m_1$ and $m_2$,

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

(f) Calculate the reduced mass of a molecule of $^{12}$C$^{16}$O.

For a diatomic molecule, the rotational constant (in Hz) is given by the expression:

$$B = \frac{h}{8\pi^2 \mu r^2}$$

where $r$ is the bond length.

(g) (i) Given the signal from ($J = 1$) to ($J = 0$) for $^{12}$C$^{16}$O was observed at 115271.204 MHz, calculate the bond length.

(ii) A signal thought to be due to $^{12}$C$^{16}$O was observed at 806651.719 MHz. Given that rotational transitions only take place between adjacent energy levels, determine the transition in $^{12}$C$^{16}$O consistent with this observation.
3. This question is about the performance-enhancing drug Ritalin®

The drug Ritalin® has long been used as a treatment for attention-deficit hyperactivity disorder (ADHD). More recently it has been in the news as a possible performance-enhancing drug taken by students studying for exams. The structure of Ritalin is shown below, where R represents a hydrocarbon group.

Ritalin is synthesised according to the scheme below. Some of the characteristic IR stretching frequencies of the intermediates are shown.

(a) The synthesis begins with the reaction of benzyl chloride and sodium cyanide to form Compound A. Draw the structure of Compound A.

(b) Compound A is then deprotonated to form Anion B⁻. Draw the structure of Anion B⁻.

(c) Draw the structures of Compounds C, D, E and F. For Compound F you do not need to worry about the specific identity of R.
Ritalin is present in the tablets as the hydrochloride salt.

(d) On the structure of Ritalin in the answer booklet, circle the atom that is protonated in the hydrochloride salt (the HCl salt).

(e) (i) The tablets contain 10.00 mg of the hydrochloride salt which corresponds to 8.647 mg of Ritalin. Using this information calculate the molar mass of Ritalin (include your working).

(ii) Hence suggest an identity for the hydrocarbon group R.

(f) For each of the following IR stretching frequencies from this scheme, draw the functional group responsible and indicate with an arrow which of the bonds are vibrating.

(i) 1655 cm\(^{-1}\)  (ii) 1715 cm\(^{-1}\)  (iii) 1740 cm\(^{-1}\)  (iv) 2260 cm\(^{-1}\)

(v) 3000 cm\(^{-1}\) (very broad)  (vi) 3180 and 3390 cm\(^{-1}\) (sharp)

Stereoisomers of a molecule are isomers that have the same connectivity between the atoms but a different three-dimensional arrangement in space. The effectiveness of a drug depends on its three-dimensional shape.

This synthesis leads to the production of a mixture of four stereoisomers of Ritalin, shown below. Some of these isomers are more effective than others.

![Diagram of stereoisomers](image)

(g) By ticking the appropriate box or boxes in the answer booklet, indicate which of these isomers are enantiomers (non-superimposable mirror images).

Some of the less effective stereoisomers can be converted into the more effective ones by deprotonation of Ritalin with the alkoxide base –OR to give Anion G\(^{-}\) as shown below. Upon reprotonation a different stereoisomer can be formed.

![Diagram of deprotonation reaction](image)

(h) Draw the structure of Anion G\(^{-}\).

(i) By ticking the appropriate box or boxes in the answer booklet, indicate which of these isomers could be interconverted via the intermediary of Anion G\(^{-}\).
4. This question is about hangovers

After the consumption of too much alcoholic beverage, people sometimes experience a hangover the following day. There are a variety of causes of a hangover, one of these is the accumulation of the toxic metabolites of ethanol in the body.

In the body, ethanol is first converted into acetaldehyde by the enzyme alcohol dehydrogenase and then into acetic acid by the enzyme acetaldehyde dehydrogenase.

\[
\text{Ethanol} \xrightarrow{\text{Alcohol Dehydrogenase}} \text{Acetaldehyde} \xrightarrow{\text{Acetaldehyde Dehydrogenase}} \text{Acetic Acid}
\]

In the first step, ethanol reacts with nicotinamide adenine dinucleotide (NAD+) to form acetaldehyde, a compound called NADH and H⁺.

(a) What happens to the NAD⁺ in this reaction? Circle the correct answer.

- it is oxidised
- it is reduced
- it is hydrolysed
- it is isomerised
- it remains chemically unchanged

In most parts of the UK, the legal drink drive limit is 80 mg of ethanol per 100 ml of blood.

(b) What concentration of ethanol does this correspond to (in mol dm⁻³)? (1 ml = 1 cm³)

After drinking it is not permitted to drive until the concentration of ethanol has fallen below this level. The reaction to remove ethanol involves the initial combination of the ethanol and the alcohol dehydrogenase to form an enzyme-substrate complex, followed by the conversion of this complex into products. The rate of this reaction (the rate of production of acetaldehyde) has a complicated rate law (as shown below).

\[
\text{rate} = \frac{k_{cat}[\text{AD}][\text{C}_2\text{H}_5\text{OH}]}{K_M + [\text{C}_2\text{H}_5\text{OH}]}
\]

where

- [AD] is the concentration of the alcohol dehydrogenase enzyme
- \(k_{cat} = 1.33 \text{ s}^{-1}\) and is the rate constant for the conversion of the enzyme substrate complex to products
- \(K_M = 1.00 \times 10^{-3} \text{ mol dm}^{-3}\) and is a measure of the ease of dissociation of the enzyme substrate complex back to reactants. It has the units of concentration.
It is often the case that the rate law above simplifies to a much simpler form.

(c) (i) Write down the simplified form of this rate law when the concentration of ethanol is very much larger than the value of $K_M$.

(ii) Write down the simplified form of this rate law when the concentration of ethanol is very much smaller than the value of $K_M$.

(d) Hence, or otherwise, write down the order of this reaction with respect to ethanol at around or above the UK drink drive limit.

The graph shows how the blood ethanol concentration of someone who has drunk a lot of alcohol varies over time.

(e) For the majority of the time that this person is sobering up, what is the rate of loss of ethanol?

(i) In $\text{mg} / 100 \text{ ml} \ h^{-1}$

(ii) In $\text{mol dm}^{-3} \ s^{-1}$

(f) What concentration of alcohol dehydrogenase enzyme does this person have?

(g) The half-life of this reaction is the time taken for the concentration of ethanol to fall to half of its initial value. From the graph, how does the half-life vary over the majority of the period this person is sobering up?

   - It increases
   - It is constant
   - It decreases
   - It is impossible to determine from the graph

(h) As well as ethanol, alcohol dehydrogenase will also metabolise other alcohols. The following metabolites are highly toxic. For each of these suggest which highly poisonous alcohol they came from.

(i) [Formic Acid]

(ii) [Oxalic Acid]

(i) For one of these poisonous alcohols, alcohol dehydrogenase has a $k_{cat} = 1.10 \text{ s}^{-1}$ and a $K_M = 3.2 \times 10^{-2} \text{ mol dm}^{-3}$. What can be concluded about the metabolism of this alcohol? Tick all that apply.

   - The maximum rate of metabolism is faster for ethanol
   - The maximum rate of metabolism is faster for the poisonous alcohol
   - The maximum rate of metabolism is the same for both
   - A higher concentration of ethanol is needed for the reaction to proceed at half of its maximum rate
   - A higher concentration of the poisonous alcohol is needed for the reaction to proceed at half of its maximum rate
   - The same concentration of ethanol and the poisonous alcohol are needed for the reactions to proceed at half of their maximum rate
   - The metabolism of the poisonous alcohol follows a rate law different from that of ethanol
5. This question is about making “green” jet fuel

“Solar-Jet” is a project designed to make aviation fuel from carbon dioxide and water using sunlight as the source of energy. The key to the project is the conversion of carbon dioxide and steam into syngas (a mixture of CO and H₂) with the removal of O₂ as a byproduct. This is achieved using the energy from a solar reactor which focuses and concentrates sunlight.

[In the following question assume the molar volume of a gas is 24.0 dm³ mol⁻¹ at RTP, room temperature and pressure.]

(a) Write a chemical equation to represent the process of carbon dioxide and steam forming syngas and oxygen.

Syngas can then be used to produce hydrocarbon fuels in a procedure called the Fischer-Tropsch process. In this process the carbon monoxide and hydrogen are catalytically converted into alkanes and water.

(b) (i) Give the formula for an alkane with \( n \) carbon atoms and use this to write a general equation for the Fischer-Tropsch process.

(ii) Calculate the ideal ratio of carbon monoxide to hydrogen in order to form dodecane \((n = 12)\), a major component of jet-fuel.

Solar-Jet uses the following procedure to manufacture syngas and oxygen.

Step 1. Cerium(IV) oxide is heated to very high temperatures in the solar reactor which reduces it non-stoichiometrically as shown below:

\[
\text{CeO}_2(s) \rightarrow \text{CeO}_{2-\delta}(s) + \frac{\delta}{2} \text{O}_2(g)
\]

where \( \delta \) is a number much smaller than 1 and represents the number of moles of O atoms that are lost to form oxygen molecules.

Step 2. The temperature in the solar reactor is lowered, steam and carbon dioxide are passed into the solar reactor and are reduced to syngas. During this process the \( \text{CeO}_{2-\delta} \) is oxidised back to \( \text{CeO}_2 \).

(c) (i) Give the overall chemical equation for the reduction of carbon dioxide to carbon monoxide with \( \text{CeO}_{2-\delta} \).

(ii) Give the overall chemical equation for the reduction of steam to hydrogen with \( \text{CeO}_{2-\delta} \).
A laboratory prototype was set up containing 127 g of CeO₂. The prototype was then run under the following experimental conditions:

**Step 1.**
- Run time: 26 minutes
- Power of the solar radiation: 3.60 kW.
- Total volume of oxygen evolved: 367 cm³ at RTP.

**Step 2.**
- Run time: 34 minutes
- Power of the solar radiation: 0.80 kW.

(d) (i) Using the information from **Step 1**, calculate the value of δ.

(ii) Predict the volume (at RTP) of syngas produced in **Step 2**.

Under the conditions of the experiment, the actual volume of syngas produced was found to be 747 cm³ at RTP with a H₂ : CO ratio of 1.70:1.

(e) (i) Calculate the amount (in moles) of hydrogen produced in the experiment.

(ii) Calculate the amount (in moles) of carbon monoxide produced in the experiment.

The crucial factor in deciding whether the process is economically viable, is how efficiently the solar energy is converted into ‘usable energy’. This may be defined as:

\[
\text{efficiency} = \frac{\text{usable energy of syngas produced}}{\text{total solar energy used}}
\]

(f) Calculate the total amount of solar energy used to produce the syngas.

[ Remember 1 W = 1 J s⁻¹. ]

The ‘usable energy’ may be taken to be the energy released when the syngas undergoes complete combustion to form carbon dioxide and water at room temperature and pressure. The standard enthalpy changes of combustion for H₂ and CO are given below.

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(g) (i) Calculate the energy released (the standard enthalpy change) when the sample of syngas produced from the experiment undergoes complete combustion.

(ii) Calculate the efficiency of the solar-jet reactor for this run.

Petrol typically has lighter alkanes than jet-fuel. The average number of carbon atoms in the petrol is \( n = 8 \) whereas in jet-fuel it is \( n = 12 \).

(h) (i) Given the standard enthalpy changes of combustion (Δ_H^c) for heptane (\( n = 7 \)) and octane (\( n = 8 \)) are −4816 and −5470 kJ mol⁻¹ respectively, calculate Δ_H^c of dodecane (\( n = 12 \)).

(ii) By constructing an appropriate Hess’ cycle, calculate the standard enthalpy change for the production of dodecane from syngas.
Acknowledgements & References

References for questions

Q1
The image is from the Royal Society of Chemistry

Q2
The image is from © Shutterstock.

Detection of a branched alkyl molecule in the interstellar medium: iso-propyl cyanide

Detection of HC$_{11}$N in the cold dust cloud TMC-1

Microwave Spectra of Molecules of Astrophysical Interest VII

Q3
The image is from Wikipedia.

Q4
The image is from © Shutterstock.

Evidence-based survey of the elimination rates of ethanol from blood with applications in forensic casework

Kinetic Properties of Human Liver Alcohol Dehydrogenase: Oxidation of Alcohols by Class I Isoenzymes

Q5
The image is from © ETH Zurich.

Syngas production by simultaneous splitting of water and carbon dioxide via ceria redox reactions in a high-temperature solar reactor

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