CHEMISTRY

2005 NATIONAL QUALIFYING EXAMINATION

Time Allowed
Reading Time: 15 minutes
Examination Time: 120 minutes
Total Marks: 120

INSTRUCTIONS

- This paper is in **two** sections and you must answer each section according to the instructions.

Section A:	Answer **ALL** questions — spend no more than 30 minutes on this section. [This section is worth 30 marks.]
Section B:	Apportion your time equally on the questions in this section. Answer **ANY THREE (3)** of Questions 16, 17, 18 or 19 [This section is worth 90 marks.]

- All answers to Section A must be answered, using a 2B pencil, on the Multiple Choice answer sheet.
- All answers to Section B must be written in the space provided.
- Use **blue** or **black** pen to write your answers; pencil is **NOT** acceptable.
- Rough working must be done only on pages 30 and 31 of this booklet.
- You are not permitted to refer to books, periodic tables or written notes.
- The only permitted aid is a non-programmable electronic calculator.
- Relevant data that may be required for a question will be found on page 2.

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DATA

Avogadro constant (N) 6.02×10^{23} mol^{-1}	Velocity of light (c) 2.998×10^{8} m s^{-1}
1 faraday 96,486 coulombs	Density of water at 25°C 0.9971 g cm^{-3}
1 coulomb 1 A s	Acceleration due to gravity 9.81 m s^{-2}
Universal gas constant (R) 8.314 J K^{-1} mol^{-1} 8.206×10^{-2} L atm K^{-1} mol^{-1}	1 newton (N) 1 kg m s^{-1}
Planck's constant (h) 6.626×10^{-34} J s	1 pascal (Pa) 1 N m^{-1}
Standard temperature and pressure (STP) 273 K and 101.3 kPa 0°C and 101.3 kPa 0°C and 1 atm 0°C and 760 mm Hg	$\mathrm{pH} = -\log_{10}[\mathrm{H}^+]$ pH + pOH = 14.00 at 25°C $K_a = [\mathrm{H}^+]\,[\mathrm{A}^-] / [\mathrm{HA}]$ $PV = nRT$ $E = h\nu$ $c = \nu\lambda$
Molar volume of ideal gas at STP 22.4 L	
1 atm = 101.3 kPa	Surface area of sphere $A = 4\pi r^2$

ATOMIC NUMBERS & RELATIVE ATOMIC MASSES*

1	H	1.008	23	V	50.94	45	Rh	102.9	67	Ho	164.9	89	Ac	(227)
2	He	4.003	24	Cr	52.00	46	Pd	106.4	68	Er	167.3	90	Th	232.0
3	Li	6.941	25	Mn	54.94	47	Ag	107.9	69	Tm	168.9	91	Pa	(231)
4	Be	9.012	26	Fe	55.85	48	Cd	112.4	70	Yb	173.0	92	U	238.0
5	B	10.81	27	Co	58.93	49	In	114.8	71	Lu	175.0	93	Np	(237)
6	C	12.01	28	Ni	58.69	50	Sn	118.7	72	Hf	178.5	94	Pu	(244)
7	N	14.01	29	Cu	63.55	51	Sb	121.8	73	Ta	180.9	95	Am	(243)
8	O	16.00	30	Zn	65.38	52	Te	127.6	74	W	183.9	96	Cm	(247)
9	F	19.00	31	Ga	69.72	53	I	126.9	75	Re	186.2	97	Bk	(247)
10	Ne	20.18	32	Ge	72.59	54	Xe	131.3	76	Os	190.2	98	Cf	(251)
11	Na	22.99	33	As	74.92	55	Cs	132.9	77	Ir	192.2	99	Es	(252)
12	Mg	24.31	34	Se	78.96	56	Ba	137.3	78	Pt	195.1	100	Fm	(257)
13	Al	26.98	35	Br	79.90	57	La	138.9	79	Au	197.0	101	Md	(258)
14	Si	28.09	36	Kr	83.80	58	Ce	140.1	80	Hg	200.6	102	No	(259)
15	P	30.97	37	Rb	85.47	59	Pr	140.9	81	Tl	204.4	103	Lw	(260)
16	S	32.07	38	Sr	87.62	60	Nd	144.2	82	Pb	207.2	104	Db	
17	Cl	35.45	39	Y	88.91	61	Pm	(145)	83	Bi	209.0	105	Jt	
18	Ar	39.95	40	Zr	91.22	62	Sm	150.4	84	Po	(209)	106	Rf	
19	K	39.10	41	Nb	92.91	63	Eu	152.0	85	At	(210)	107	Bh	
20	Ca	40.08	42	Mo	95.94	64	Gd	157.3	86	Rn	(222)	108	Hn	
21	Sc	44.96	43	Tc	(98)†	65	Tb	158.9	87	Fr	(223)	109	Mt	
22	Ti	47.88	44	Ru	101.1	66	Dy	162.5	88	Ra	226.0			

* The relative values given here are to four significant figures.

† A value given in parentheses denotes the mass of the longest-lived isotope.

SECTION A

It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section. Each question carries 2 marks. There is no penalty for incorrect answers. Answer the multiple choice questions, using a 2B pencil, on the computer sheet provided. If you make a mistake **make sure that your incorrect answer is completely erased.**

Please note the following:

- **It is recommended that you first record your answer on this question paper by circling ONE of the letters A, B, C, D or E.**
- **Then transfer these answers on to the computer sheet which will be computer marked for assessment.**

1. An electrochemical cell is constructed by putting a copper electrode in a beaker containing 100 mL of 0.1 mol L^{-1} copper(II) sulfate and a zinc electrode in a beaker containing 100 mL of 0.1 mol L^{-1} zinc nitrate. The two beakers are connected with a salt bridge and the potential difference between the electrodes is measured. The cell is then connected to a light bulb and the length of time the bulb continues to glow is noted.

   It is decided to repeat the experiment, this time taking 200 mL of each solution. How do the new results compare with those for the original cell?

   (a) Both the potential difference and the cell lifetime are doubled.
   (b) Neither the potential difference nor the cell lifetime change.
   (c) The potential difference is doubled, but the cell lifetime remains the same.
   (d) The potential difference is doubled, so the cell lifetime is halved.
   (e) The potential difference remains the same, but the cell lifetime is doubled.

2. The solubility product of magnesium hydroxide is 1×10^{-11} $mol^3\ L^{-3}$ at 25°C. What is the solubility of magnesium hydroxide in a solution of pH 11.0?

   (a) 6 g L^{-1}
   (b) 1 g L^{-1}
   (c) 0.1 g L^{-1}
   (d) 0.0006 g L^{-1}
   (e) 6×10^{-7} g L^{-1}

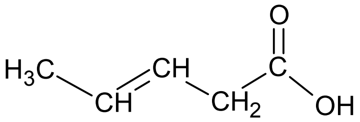
3. An alkane **Y** was mixed with excess oxygen in a rigid (constant-volume) reaction vessel maintained at 200°C in a thermostat bath. The pressure inside the vessel was 1.02 atmospheres. The mixture was ignited with a spark, burning the alkane to form water vapour and carbon dioxide. When the contents of the vessel reverted to the bath temperature of 200°C, the pressure was found to be 1.02 atmospheres. Identify **Y**.

   (a) cyclohexane, C_6H_{12}
   (b) ethane, C_2H_6
   (c) ethanoic acid, $C_2H_4O_2$
   (d) methane, CH_4
   (e) propane, C_3H_8

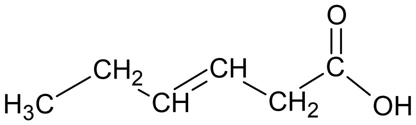
4. Which one of the following compounds, when dissolved in water, would **not** give an acidic solution?

(a) $FeCl_3$
(b) H_3PO_4
(c) KI
(d) NH_4Cl
(e) SO_3

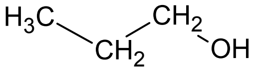
5. An organic chemist analysed an unknown compound. By mass spectrometry, the chemist found that the compound had a molecular mass of 114 g mol^{-1}. An elemental analysis was also performed which showed that the compound contained 63% C, 9% H and 28% O by mass. Which one of the following compounds could it have been?



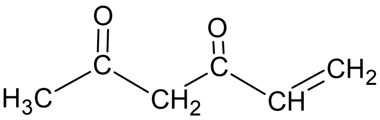
(a)



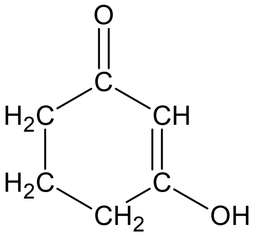
(b)



(c)



(d)



(e)

6. What is the oxidation number (state) of vanadium in ammonium orthovanadate, $(NH_4)_3VO_4$?

(a) I
(b) II
(c) III
(d) IV
(e) V

7. The first four ionisation energies of an element **Q** are, in order, 0.596 1.152, 4.918 and 6.480 MJ mol^{-1}. When **Q** is allowed to react with chlorine gas, what is the formula of the major product formed?

(a) QCl
(b) QCl_2
(c) Q_2Cl
(d) Q_2Cl_3
(e) Q_3Cl_4

8. Approximately how far on average is a molecule of air in the room in which you're sitting this exam from the nearest molecule of air to it?

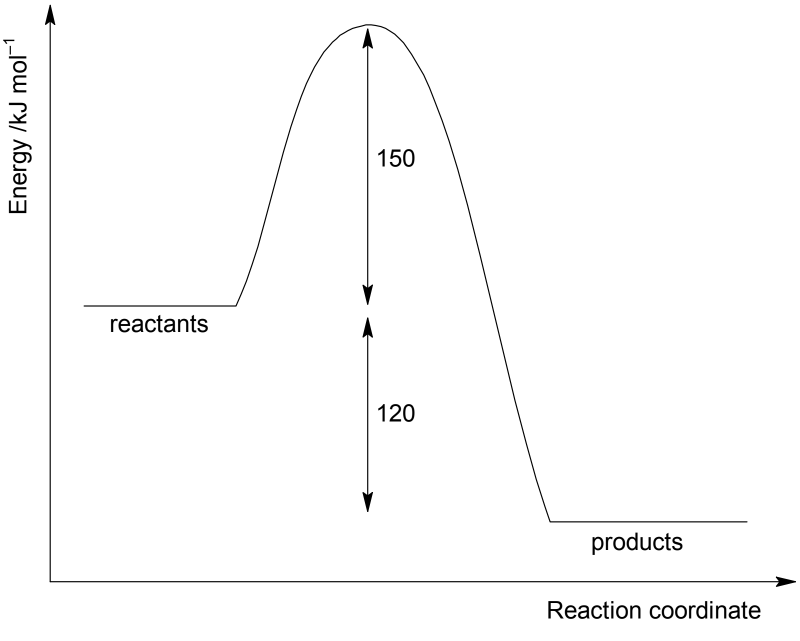
   (*Hint*: You might start by making reasonable assumptions about the pressure and temperature, and assuming that air may be treated as an ideal gas.)

   (a) 3 m
   (b) 3×10^{-3} m
   (c) 3×10^{-6} m
   (d) 3×10^{-9} m
   (e) 3×10^{-12} m

9. Chlorine is a pale yellow-green gas which disproportionates (is both oxidised and reduced) when dissolved in water. Which one of the following describes the resulting aqueous solution?

   (a) It has pH < 7, and is an oxidising agent.
   (b) It has pH < 7, and is a reducing agent.
   (c) It has pH < 7, and exhibits no redox properties.
   (d) It has pH > 7, and is an oxidising agent.
   (e) It is neutral, and is a reducing agent.

10. Consider the following energy profile diagram for a chemical reaction.



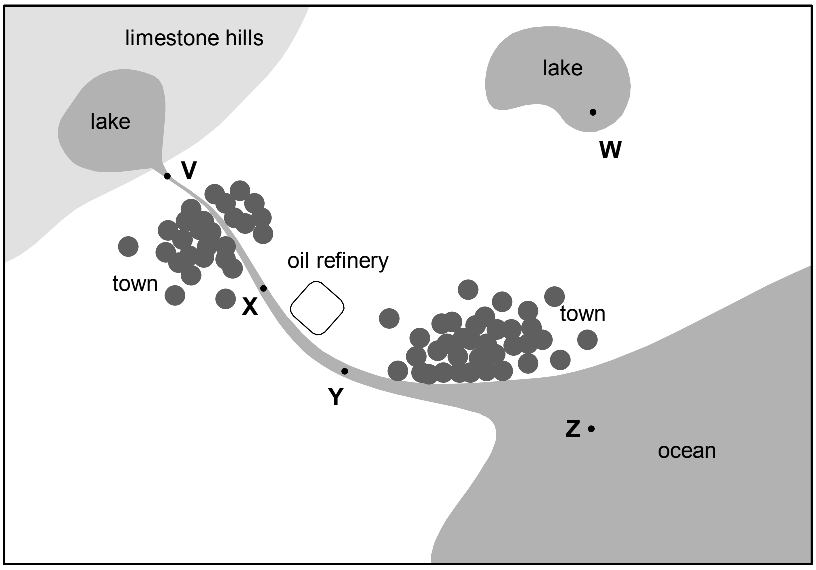
Which one of the following statements about this reaction **must** be correct?

   (a) The activation energy of the forward reaction is 120 kJ mol^{-1}.
   (b) The activation energy of the reverse reaction is 270 kJ mol^{-1}.
   (c) The energy change ΔE of the forward reaction is –30 kJ mol^{-1}.
   (d) The forward reaction is spontaneous.
   (e) The reverse reaction is exothermic.

11. Copper metal reacts with dilute nitric acid to give water, copper(II) nitrate solution and nitrogen monoxide (NO) gas. Determine the mass of copper that would produce 3.74 L of NO at standard temperature and pressure.

(a) 5.01 g
(b) 10.6 g
(c) 15.9 g
(d) 31.8 g
(e) 190.6 g

12. The diagram below is a map of a countryside.



At points **V**, **W**, **X**, **Y** and **Z**, water samples were taken and the concentrations of various analytes determined. The results are shown in the table below.

Sample no.	**1**	**2**	**3**	**4**	**5**
Dissolved oxygen (mg L^{-1})	8.0	7.0	3.0	2.5	8.0
pH	8.0	8.2	7.5	3.5	6.2
Cl^- (mg L^{-1})	0.5	1×10^{-3}	1×10^{-2}	6×10^{-2}	1×10^{-3}
Ca^{2+} (mg L^{-1})	5×10^{-3}	5×10^{-3}	5×10^{-3}	5×10^{-3}	5×10^{-4}
Coliform count (per 100mL)	50	0	5000	4000	0

Which one of the following alternatives correctly matches each sample to the location from which it was taken?

Sample no.	**1**	**2**	**3**	**4**	**5**
(a)	**Z**	**V**	**Y**	**X**	**W**
(b)	**Z**	**W**	**X**	**Y**	**V**
(c)	**W**	**Z**	**Y**	**X**	**V**
(d)	**Z**	**V**	**X**	**Y**	**W**
(e)	**V**	**Z**	**Y**	**W**	**X**

13. At room temperature, fluorine is a gas (boiling point –188°C), while bromine is a liquid (boiling point +59°C). Which one of the following best explains the difference in the physical states of these two halogens?

(a) the covalent bonds in bromine are more polar.
(b) the covalent bonds in bromine are stronger.
(c) the covalent bonds in bromine are weaker.
(d) the intermolecular forces in bromine are stronger.
(e) the intermolecular forces in bromine are weaker.

14. In order to determine the sulfate composition of a fertiliser, a chemist dissolved 2.00 g of fertiliser in 100 mL of water, and added barium nitrate solution. The chemist noticed the formation of a white solid, and kept adding the barium nitrate solution until no more solid formed. The white solid was filtered and, after drying, weighed 1.90 g. What is the percentage by mass of sulfate in the fertiliser?

(a) 95%
(b) 78%
(c) 41%
(d) 39%
(d) 22%

15. A hydrocarbon **X** of molecular formula C_6H_{14} was allowed to react with limited chlorine gas in the presence of light. The resulting mixture contained two products with different boiling points, as well as excess starting material. What is the systematic name of **X**?

(a) 2,2-dimethylbutane
(b) 2,3-dimethylbutane
(c) 2-methylpentane
(d) 3-methylpentane
(e) hexane

SECTION B

Marks will be deducted for incorrect use of significant figures. You are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.

Answer any THREE (3) of the four questions in this section.

Each question is worth 30 marks.

Question 16 [30 marks]

Uranium is commonly alloyed with other metals such as iron, cobalt and niobium. As these metals can undergo the same chemical reactions as uranium the determination of the uranium in the alloys presents a challenge.

One method for the determination of uranium involves the use of a zinc column. The uranium-bearing alloy is dissolved in a mixture of hydrofluoric and sulfuric acids to give uranium(VI) as the UO_2^{2+} ion, and then passed through the column where it is converted into uranium(IV) as U^{4+}, by the zinc, which in turn is converted into Zn^{2+}. An excess of an iron(III) solution is then added converting the uranium(IV) into uranium(VI) and producing iron(II) as Fe^{2+}. The Fe^{2+} ion is titrated with a standardized cerium(IV) solution as Ce^{4+}, giving iron(III) and cerium(III). The solution remains acidic throughout the determination.

(a) Write a half equation for each of the following reactions and indicate whether the reaction is oxidation or reduction.

(i) Zinc metal to zinc(II).

Oxidation or reduction?

(ii) Iron(II) to iron(III).

Oxidation or reduction?

Question 16 continues

(iii) Uranium(IV) to uranium(VI).

Oxidation or reduction?

[6 marks]

(b) Write a balanced equation for each of the following redox reactions used in the determination of uranium. Underline the oxidant in each case.

(i) Uranium metal with dilute strong acid.

(ii) The dissolved uranium with the zinc metal.

(iii) The reduced uranium with iron(III) ion.

(iv) Iron(II) with the standardized cerium(IV) solution.

[8 marks]

Question 16 continues

The uranium in a 1.000 g sample of a uranium alloy was determined using the method described above.

(c) If 20.69 mL of a 0.375 mol L^{-1} standardized Ce^{4+} solution was required for the determination calculate the percentage by mass of uranium in the alloy.

[5 marks]

Unfortunately niobium is always present in the alloy and is involved in the reactions used during the analysis. Niobium becomes niobium(V), Nb^{5+}, upon dissolution and is converted into niobium(III), Nb^{3+}, by zinc metal. It is then allowed to react with the iron(III) ions to give niobium(V) and iron(II).

(d) Is the answer to **(c)** above higher or lower than the actual percentage of uranium in the sample?

[1 mark]

Question 16 continues

With the use of a bismuth (Bi) column, instead of a zinc column, only uranium can convert Bi metal into Bi(III). Bismuth is a less reactive metal than zinc and so does not react with the other metals in the alloy.

Another 1.000 g of the same alloy was determined **now using bismuth in the place of zinc**.

(e) If 18.62 mL of the same standardized Ce^{4+} solution was required, what is the actual percentage mass of uranium in the alloy?

[5 marks]

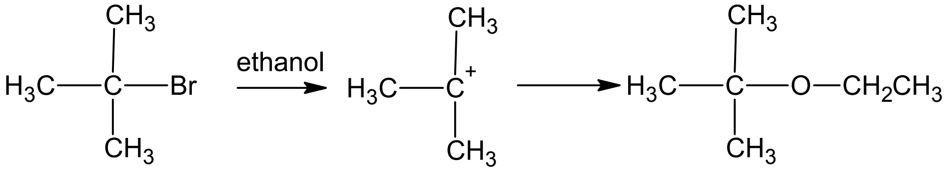
(f) What is the percentage by mass of **niobium** in the alloy?

[5 marks]

Question 17 follows

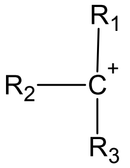
Question 17 [30 marks]

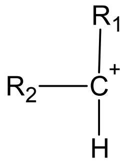
Carbocations are species bearing a formal positive charge on carbon. They are hypovalent species, as they have only three shared pairs of electrons around carbon, instead of the usual four. This incomplete octet around carbon makes carbocations very unstable and very reactive. Nevertheless, carbocations are known to be formed as intermediates in many types of organic reactions. For example, in the reaction of 2-bromo-2-methyl propane with ethanol, the bromide ion is lost, forming a carbocation intermediate, before the ethoxide ion ($CH_3CH_2O^-$) is attached:

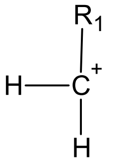


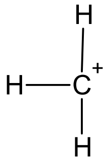
2-bromo-2-methylpropane carbocation intermediate 2-ethoxy-2-methylpropane

There are four possible degrees of alkyl substitution on a carbocation: three attached alkyl groups (referred to as **tertiary**, or 3º, carbocations), two attached groups (**secondary**, or 2º), one attached group (**primary**, or 1º), or no attached alkyl groups (**methyl**). If we let R_1, R_2 and R_3 represent alkyl chains (but not H atoms), we can draw these three classes as follows:


tertiary carbocation

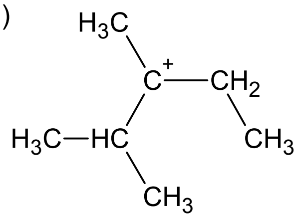

secondary carbocation

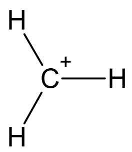

primary carbocation

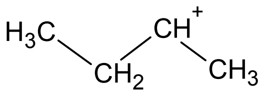

methyl carbocation

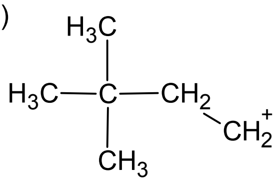
Because alkyl groups are able to share some of the positive charge on the positive carbon, the more substituted the carbocation is (that is, the more alkyl groups attached to the positive carbon), the more stable the carbocation.

(a) Identify the following species as methyl, 1°, 2°, or 3° carbocations. Rank them from most stable to least stable.

(i)


(ii)


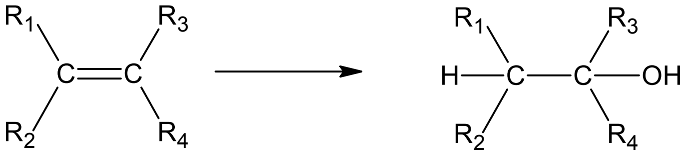
(iii)


(iv)


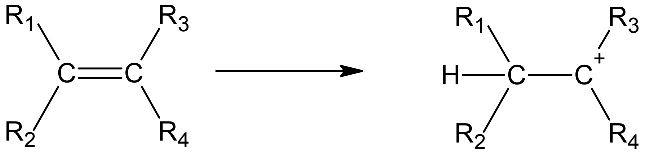
[6 marks]

Question 17 continues

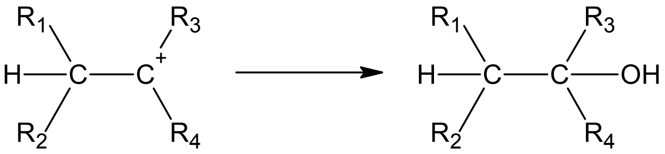
The stability of carbocations influences reactions in which they are intermediates. When water is added to an alkene in the presence of an acid catalyst, an alcohol is formed in such a way that one H^+ from water adds to one end of the double bond while the remaining OH^- adds to the other end, and the double bond itself is broken. This is called **hydration**. The overall reaction is:



But in fact, the process occurs in two steps. First, the H^+ is added to one carbon, causing the double bond to break. A carbocation is then formed at the other end of the double bond:



The OH^- then attaches at the positive carbon:



Of course, in the reaction above, the H^+ could also have added to the other end of the double bond. The carbocation which predominately forms in the first step will be the more stable one.

Question 17 continues

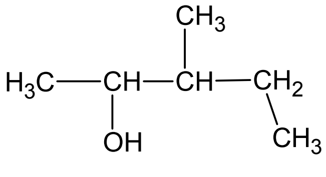
(b) Draw the structure of the expected carbocation intermediate and the major product for hydration (in the presence of sulfuric acid as a catalyst) of:

(i) 1-butene

(ii) 2-methyl-2-butene

[4 marks]

(c) Draw the molecule of the alkene which is hydrated (with catalytic acid) to produce the following alcohol.



[2 marks]

Question 17 continues

(d) Write a general statement to predict to which carbon the H^+ and to which the OH^- will attach in these hydration reactions.

[2 marks]

Just as there are primary, secondary and tertiary carbocations, there are primary, secondary and tertiary alcohols, designating 1, 2 or 3 alkyl chains attached to the carbon bearing the –OH group. One laboratory technique used to distinguish these three classes of alcohols is to use the Lucas reagent (a mixture of $ZnCl_2$ and HCl). Alcohols are classed according to how quickly they react with the reagent to become cloudy owing to the formation of water-immiscible chloroalkane:

- primary alcohols do not react at all, not even on heating
- secondary alcohols react slowly, and usually require heating to induce a reaction
- tertiary alcohols react rapidly

(e) An unknown alkene **A**, which is known to have a molecular formula of C_5H_{10}, is hydrated, with catalytic acid. To the resulting solution, Lucas reagent is added. No change is observed, but when the reaction mixture is heated gently, a cloudy solution is observed. Draw two possible structures of alkene **A**.

[4 marks]

(f) An isomer of alkene **A**, alkene **B**, is treated in the same way, but this time the reaction mixture rapidly turns cloudy. Draw two possible structures of alkene **B**.

[4 marks]

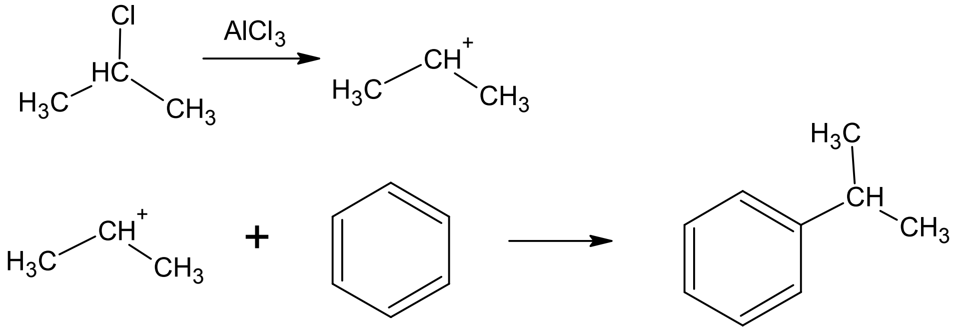
Question 17 continues

After performing these tests, an organic chemist wants to try to synthesise another isomer of **A**, alkene **C**, for which the hydrated product does not react with Lucas reagent, regardless of temperature.

(g) What advice would you give to the chemist? Explain your answer.

[2 marks]

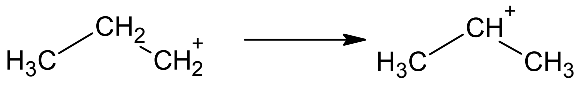
Carbocations also occur in other reactions. When an alkyl chloride is put in the presence of $AlCl_3$, a carbocation is formed. This carbocation then adds to benzene. This is called Friedel-Crafts alkylation. For example:



(h) Draw the structure for the product of the reaction between benzene and 2-chloro-2-methylbutane in the presence of $AlCl_3$.

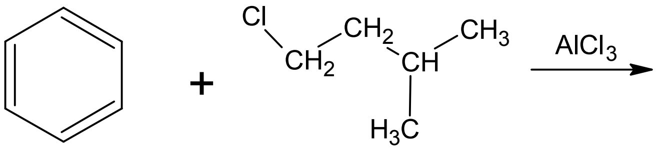
[3 marks]

One issue faced in Friedel-Crafts alkylation is that the carbocation formed can rearrange to form a more stable one. That is, the positive charge can move along the length of the molecule. For example



Question 17 continues

(i) Draw the structure for what you might expect to be the major product of the following reaction.



[3 marks]

Question 18 follows

Question 18 [30 marks]

Acids and bases have been used as laboratory chemicals since the time of alchemists and they remain indispensable, not only in university and industrial laboratories, but in the home as well.

Some acids (for example, citric acid) have a sour taste. In fact, sourness was a defining property since the seventeenth century: an acid was a substance that had a sour taste. In contrast a base was any substance that had a bitter taste and a slippery feel.

Definitions in science, however, evolve because as descriptions become too limited, they must be replaced by broader ones. Although the early definitions of acids and bases described distinctive properties, they inevitably gave way to definitions based on molecular behaviour.

The earliest definition of acids and bases that reflects their molecular nature was suggested by Svante Arrhenius.

- An Arrhenius acid is a substance that has H in its formula and dissociates in water to yield H_3O^+.
- An Arrhenius base is a substance that has OH in its formula and dissociates in water to yield OH^-.

(a) Give one example of an Arrhenius acid and an Arrhenius base.

Acid

Base

[2 marks]

A major shortcoming of the Arrhenius definition is that many substances, such as ammonia and organic amines, that yield OH^- ions when they dissolve in water, do not contain OH in their formulas. Another limitation was that water had to be the solvent for the acid-base reactions.

In the early twentieth century, Brønsted and Lowry suggested definitions that removed these limitations. According to the Brønsted-Lowry acid-base definition:

- An acid is a proton donor.
- A base is a proton acceptor.

(b) Are all Arrhenius acids also Brønsted-Lowry acids?

[1 mark]

(c) What is an essential characteristic of a Brønsted-Lowry base that enables it to bind the H^+ ion?

[1 mark]

Question 18 continues

Acids and bases may be strong or weak depending on the extent to which they ionise in water. Strong acids and bases essentially completely ionise whereas weak acids and bases only partially ionise.

For a weak acid, HA, we write its ionisation as:

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{A^-} + \mathrm{H_3O^+}$$

The equilibrium constant expression for this reaction is:

$$K_c = \frac{[\mathrm{A^-}][\mathrm{H_3O^+}]}{[\mathrm{H_2O}][\mathrm{HA}]}$$

The concentration of water is so large that its concentration changes negligibly during this reaction and we simplify the K_c expression by including the $[H_2O]$ term with the value of K_c.

$$K_c \times [\mathrm{H_2O}] = \frac{[\mathrm{A^-}][\mathrm{H_3O^+}]}{[\mathrm{HA}]} = K_a$$

The acid ionisation constant, K_a, is a specific equilibrium constant used for acid ionisation. The larger the value of K_a the stronger the acid.

Similarly the ionisation constant of water, $K_w = [H_3O^+] [OH^-]$ is experimentally determined to be 1.00×10^{-14} at 25°C.

At 25°C a solution is defined as acidic if $[H_3O^+] > [OH^-]$, basic if $[OH^-] > [H_3O^+]$ and neutral if $[H_3O^+] = [OH^-]$.

The pH scale is a contextual way of defining the acidity of a solution. The pH is a log scale based on 10 where $\mathrm{pH} = -\log_{10} [H_3O^+]$.

(d) Calculate the pH of 1.5×10^{-3} mol L^{-1} HCl at 25°C.

[2 marks]

(e) At 50°C, K_w for water is 5.19×10^{-14}. Calculate the pH of pure water at 50°C.

[2 marks]

Question 18 continues

(f) Is pure water at 50°C acidic, neutral or alkaline? Explain your answer.

[3 marks]

In a Brønsted-Lowry acid-base reaction, when the acid donates a proton, it becomes the conjugate base of the original acid; when a base accepts a proton it becomes the conjugate acid of the original base.

(g) Write the equation showing HCN behaving as a Brønsted-Lowry acid with H_2O.

[2 marks]

(h) Write the K_a expression for the reaction in (g) above.

[1 mark]

(i) Write the equation showing CN^- behaving as a Brønsted-Lowry base with H_2O.

[2 marks]

(j) Write the K_b expression for the reaction in (i) above.

[1 mark]

Question 18 continues

(k) Based on your answers to (h) and (j) above, what is the relationship between K_a of an acid, K_b of its conjugate base, and K_w?

[1 mark]

At the reading of your eccentric great-uncle Balthazar's will, you were shocked to discover that the rather large fortune he made trading rare earth metals is locked inside a safe to which nobody knows the combination. Believing that only a chemist was a worthy recipient of his money, Uncle Balthazar encoded the combination as the pH of solution A, described below, followed by the pH of solution B. (For example: if the pH of solution A is 2.42 and that of solution B is 5.17, then the combination to the safe is 2-42-5-17.) Can you find the combination to the safe using only the information below (all at 25°C)?

Solution A is 50.0 mL of 0.011 mol L^{-1} HNO_3.

Solution B is 0.020 mol L^{-1} of the weak acid CH_3COOH. K_a for CH_3COOH is 1.76×10^{-5}.

(l) What is the combination to the safe?

[6 marks]

Question 18 continues

Another acid-base concept to consider was developed by G N Lewis. Whereas the Brønsted-Lowry concept focuses on the proton in defining a species as an acid or a base, the Lewis theory highlights the roles of the **electron pair**. The Lewis acid-base definition says that:

- An **acid** is any species that **accepts** an electron pair.
- A **base** is any species that **donates** an electron pair.

Many species that do not contain H are Lewis acids. For example, the electron-deficient BF_3 molecule completes its octet by reacting with NH_3 which has a lone pair of electrons. BF_3 is a strong Lewis acid. The hydration of a metal ion, such as Al^{3+}, can also be viewed as a Lewis acid-base reaction. The Al^{3+} ion accepts one electron pair from each of six water molecules to form $[Al(H_2O)_6]^{3+}$.

(m) Can all Brønsted-Lowry bases Lewis bases and can all Lewis bases be Brønsted-Lowry bases? Explain your answer.

[2 marks]

When $FeCl_3$ is dissolved in water giving Fe^{3+}, the solution becomes acidic due to the formation of $[Fe(H_2O)_5(OH)]^{2+}$ and H_3O^+. The overall process involves both Lewis and Brønsted-Lowry acid-base reactions.

(n) Write equations to illustrate this process.

[2 marks]

(o) $FeSO_4$ is similarly dissolved in water giving Fe^{2+}. Which solution (Fe^{2+} or Fe^{3+}) is the more acidic? Explain your answer.

[2 marks]

Question 19 follows

Question 19 [30 marks]

At any given pressure, a pure substance will undergo sharp changes of phase, such as melting or vaporising, at fixed temperatures. This information can be summarised in a *phase diagram*, which shows the phase in which the substance will be found at any pressure and temperature.

Consider the phase diagram for carbon dioxide shown on the following page. (A particularly interesting region has been magnified for clarity.) At a temperature of 240 K and pressure of 4 MPa, for example, we can consult the diagram to find that at these conditions carbon dioxide is a liquid. On the lines separating two phases, both phases can coexist.

(a) A carbon dioxide cylinder at 25°C contains liquid and gaseous CO_2 in equilibrium. What is the pressure inside the cylinder?

P =

[1 mark]

Two important points on the diagram have been marked **A** and **B**. Point **B** (304 K, 7.4 MPa) is called the *critical point*. Beyond this point, there is no distinction between the liquid and gas phases, so no sharp phase change occurs. Point **A** (217 K, 520 kPa) is called the *triple point*.

(b) What is significant about point **A**?

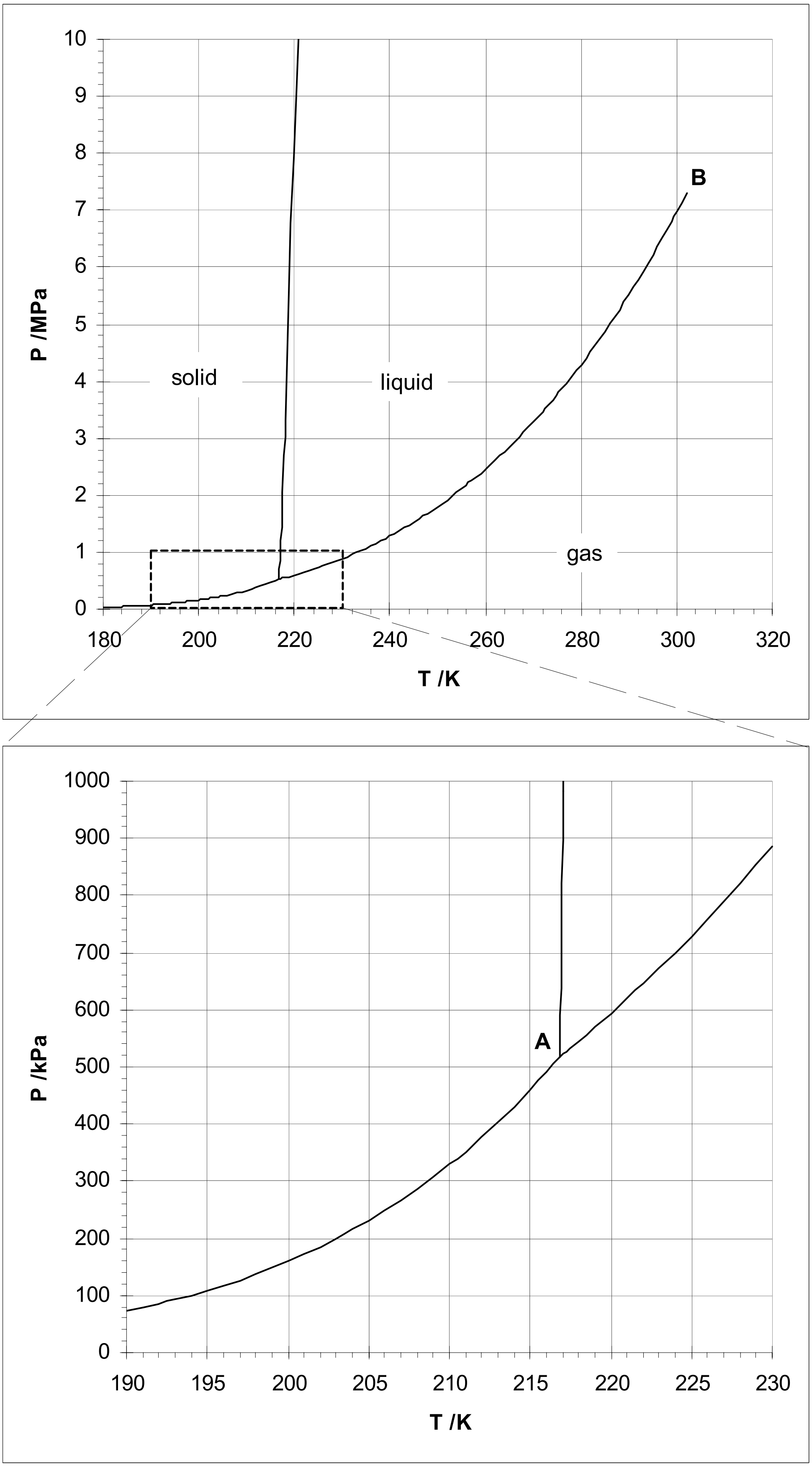
[2 marks]

(c) A sample of solid carbon dioxide ("dry ice") at 190 K and atmospheric pressure (101.3 kPa) is heated to 230 K at constant pressure. Indicate any observable changes, and the temperatures at which they occur, in the following table.

Temperature	**Observation**
K	

[1 mark]

Question 19 continues



Question 19 continues

(d) A sample of solid carbon dioxide at 190 K and 600 kPa is heated to 230 K at constant pressure. Indicate any observable changes, and the temperatures at which they occur, in the table below.

Temperature	Observation
K	
K	

[2 marks]

It can be shown that if (P_1, T_1) and (P_2, T_2) are points on the solid-gas coexistence curve, they are related by

$$\ln\frac{P_2}{P_1} = \frac{\Delta_{sub}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where $\Delta_{sub}H$ is the enthalpy of sublimation of carbon dioxide and R is the ideal gas constant.

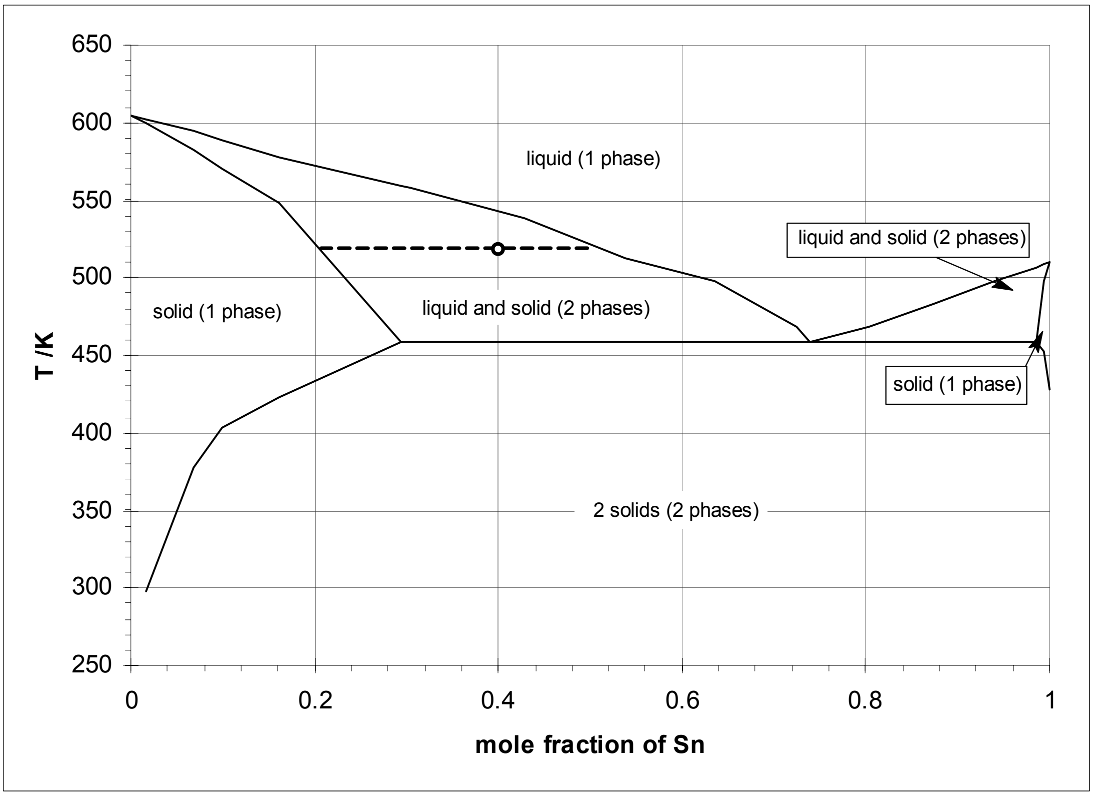
(e) Estimate the enthalpy of sublimation of carbon dioxide.

$\Delta_{sub}H =$ kJ mol^{-1}

[3 marks]

When we're dealing with mixtures instead of pure substances, the situation becomes more complicated. If we fix the pressure, the phases present will depend on both the temperature and on the composition of the mixture. For instance, consider the diagram for lead-tin mixtures at atmospheric pressure:

Question 19 continues



At some temperatures and compositions, only one phase is present. For example, the diagram above shows that at 600 K a mixture containing 40% tin and 60% lead by mole will be liquid. In other regions of the diagram, however, two phases coexist. For example, the same mixture at 520 K is in a region labelled “2 phases”. To find the composition of these phases, we draw a horizontal line (thick and dotted in the diagram) and follow it to the boundaries of the regions corresponding to the two relevant phases. In this example, the solid contains only 20% by mole Sn and the liquid is about 50% by mole Sn.

(f) What percentage (by mole) of this mixture will be solid, and what percentage liquid, at 520 K?

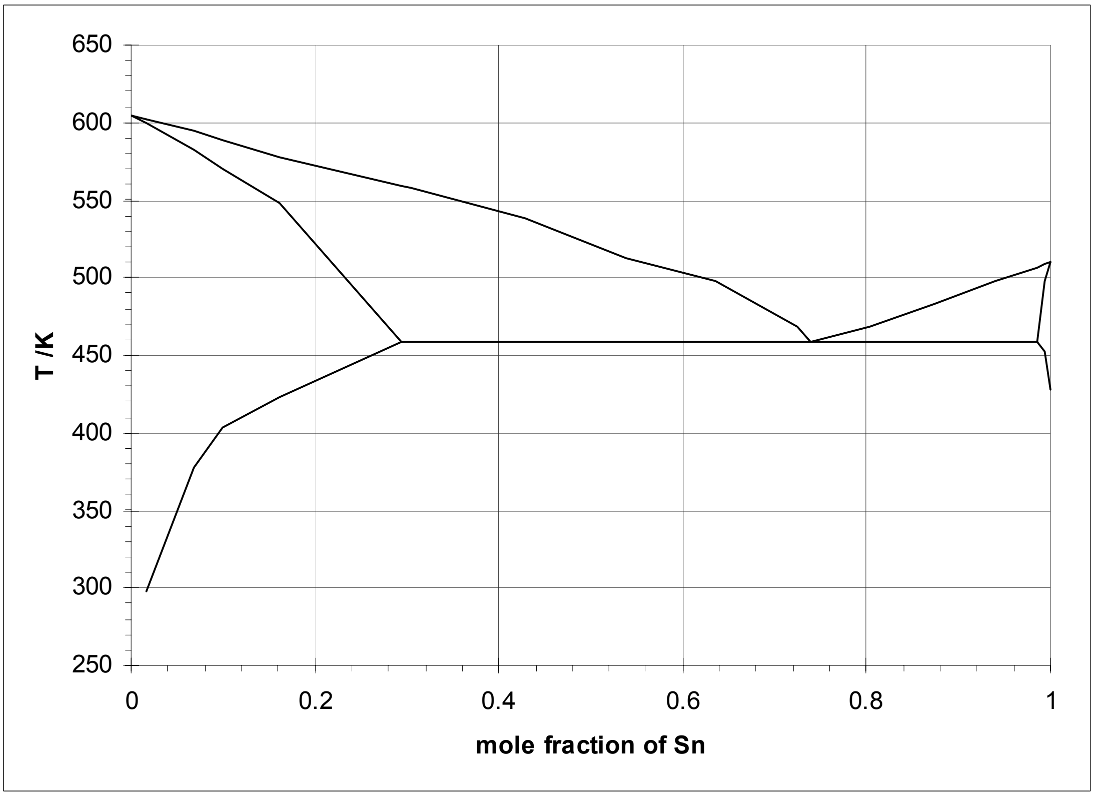
% by mole solid

% by mole liquid

[4 marks]

Question 19 continues

(g) Draw a similar line on the diagram below and hence determine the phases present in a mixture containing 20% Sn at 550 K, and their compositions.



state (solid, liquid, gas)	**% Sn (by mole)**	**% Pb (by mole)**

[3 marks]

(h) The mixture from part (g) is warmed from 450 K to 600 K. Indicate any observable changes, and the temperatures or temperature ranges over which they occur, in the table below.

Temperature	**Observation**
K	
K	
K	

[3 marks]

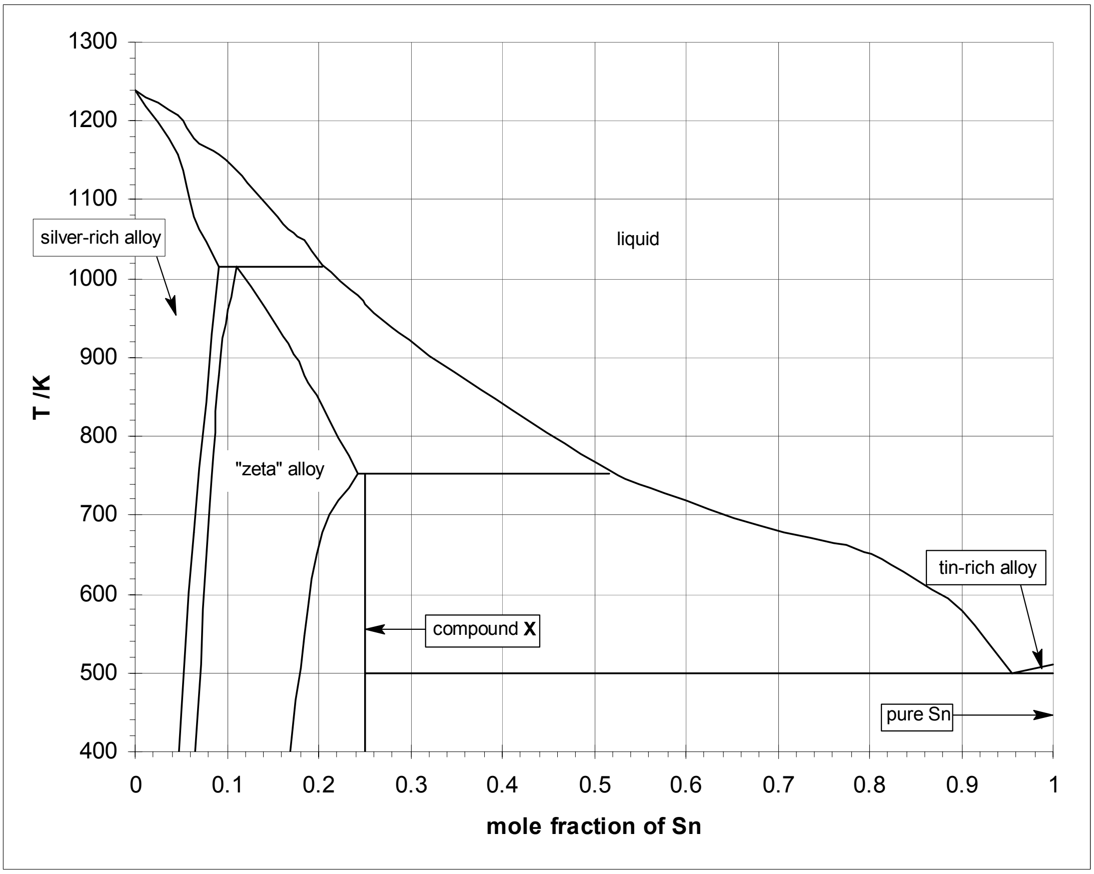
Question 19 continues

(i) Solder is an alloy of tin and lead which is useful for its low melting point. In order to be practical, solid solder must melt at a single temperature, rather than over a large temperature range, without changing its composition. What is the best composition for solder?

% Sn (by mole)	% Pb (by mole)

[1 mark]

Finally, consider the diagram for a silver-tin mixture, which is made more complicated (and interesting) by the fact that silver and tin form a binary compound which we can call **X**.



There are six different phases possible for this mixture: a solid silver-rich alloy (which could indeed be pure silver), a solid “zeta” alloy, a solid tin-rich alloy, pure solid tin, solid **X**, and a liquid. The regions corresponding to these phases have been marked on the diagram; all unmarked regions correspond, as before, to mixtures of these phases.

Question 19 continues

(j) A mixture of 10% by mole Sn and 90% by mole Ag is warmed from 900 K to 1200 K. Indicate any observable changes, and the temperatures or temperature ranges over which they occur, in the table below.

Temperature	**Observation**
K	
K	
K	
K	
K	

[5 marks]

(k) A sample of **X** is warmed from 450 K to 1100 K. Indicate any observable changes, and the temperatures or temperature ranges over which they occur, in the table below.

Temperature	**Observation**
K	
K	
K	

[4 marks]

(l) What is the chemical formula for **X**?

Compound **X** =

[1 mark]

END OF QUESTIONS

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