



CHEMISTRY

2001 NATIONAL QUALIFYING EXAMINATION

Time Allowed

Reading Time: 15 minutes

Examination Time: 120 minutes

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.
Section B: Apportion your time equally on the questions in this section.
Question 16 is **compulsory**
Answer **any two** of Questions 17, 18 or 19
- All answers must be written in the space provided in the answer book.
- Use **blue** or **black** pen to write your answers, pencil is **not** acceptable.
- Rough working must be done only in the indicated areas of the answer book.
- 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.

DATA

Avogadro constant (N)

$6.02 \times 10^{23} \text{ mol}^{-1}$

1 faraday 96,486 coulombs

1 coulomb 1 A s

Universal gas constant (R)

$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$

Planck's constant (h)

$6.626 \times 10^{-34} \text{ J s}$

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

Molar volume of ideal gas at STP

22.4 L

Velocity of light (c)

$2.998 \times 10^8 \text{ m s}^{-1}$

Density of water

1000 kg m^{-3}

Acceleration due to gravity

9.8 m s^{-2}

ATOMIC NUMBERS & RELATIVE ATOMIC MASSES*

1 H	1.008	23 V	50.94	45 Rh	102.9	67 Ho	164.9	9 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	100Fm	(257)
13 Al	26.98	35 Br	79.90	57 La	138.9	79 Au	197.0	101Md	(258)
14 Si	28.09	36 Kr	83.80	58 Ce	140.1	80 Hg	200.6	102No	(259)
15 P	30.97	37 Rb	85.47	59 Pr	140.9	81 Tl	204.4	103Lw	(260)
16 S	32.07	38 Sr	87.62	60 Nd	144.2	82 Pb	207.2	104Db	
17 Cl	35.45	39 Y	88.91	61 Pm	(145)	83 Bi	209.0	105Jt	
18 Ar	39.95	40 Zr	91.22	62 Sm	150.4	84 Po	(209)	106Rf	
19 K	39.10	41 Nb	92.91	63 Eu	152.0	85 At	(210)	107Bh	
20 Ca	40.08	42 Mo	95.94	64 Gd	157.3	86 Rn	(222)	108Hn	
21 Sc	44.96	43 Tc	(98)†	65 Tb	158.9	87 Fr	(223)	109Mt	
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. Only one choice is allowed per question and this should be made by clearly crossing the chosen answer box in **the answer book**. If you make a mistake **correct it clearly** so that the examiners can read your answer.

- Q1** A colourless solution is known to contain one of these ions. Which ion is present if adding dilute HCl produces a white precipitate that dissolves when the solution is warmed?
- A Ag^+
 - B Cu^{2+}
 - C Hg_2^{2+}
 - D Al^{3+}
 - E Pb^{2+}
- Q2** If 1.50 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were heated to drive off the water of hydration, how much anhydrous $\text{H}_2\text{C}_2\text{O}_4$ would remain?
- A 0.34 g
 - B 0.43 g
 - C 0.92 g
 - D 1.07 g
 - E 1.50 g
- Q3** What is the pH of a 0.025 M solution of KOH?
- A 1.60
 - B 3.69
 - C 7.00
 - D 10.31
 - E 12.40
- Q4** What is the conjugate acid of HPO_4^{2-} ?
- A $\text{H}_3\text{PO}_4(\text{aq})$
 - B $\text{H}_2\text{PO}_4^-(\text{aq})$
 - C $\text{H}_3\text{O}^+(\text{aq})$
 - D $\text{H}^+(\text{aq})$
 - E $\text{PO}_4^{3-}(\text{aq})$
- Q5** How many isomers have the formula $\text{C}_3\text{H}_8\text{O}$?
- A 2
 - B 3
 - C 4
 - D 5
 - E 6

- Q6** What is the $[H^+]$ of a 0.075 M solution of the acid HA? Equilibrium Constant, K_a , for HA is 4.8×10^{-8} .
- A $6.1 \times 10^{-4} M$
 - B $2.2 \times 10^{-4} M$
 - C $6.0 \times 10^{-5} M$
 - D $4.8 \times 10^{-8} M$
 - E $3.1 \times 10^{-9} M$
- Q7** A 1.50 g sample of an ore containing silver was dissolved, and all of the Ag^+ was converted to 0.124 g of Ag_2S . What was the percentage of silver in the ore?
- A 14.23%
 - B 10.8%
 - C 8.27%
 - D 7.20%
 - E 6.41%
- Q8** Methyl-t-butyl ether, $C_5H_{12}O$, is added to gasoline to promote cleaner burning. How many moles of oxygen gas, O_2 , are required to burn 1.0 mol of this compound completely to form carbon dioxide and water?
- A 9.5 mol
 - B 8.0 mol
 - C 7.5 mol
 - D 6.0 mol
 - E 4.5 mol
- Q9** What is the Na^+ ion concentration in the solution formed by mixing 20 mL of 0.10 M Na_2SO_4 solution with 50 mL of 0.30 M Na_3PO_4 solution?
- A 0.09 M
 - B 0.15 M
 - C 0.24 M
 - D 0.48 M
 - E 0.70 M
- Q10** What is the total pressure in a 2.00 L container that holds 1.00 g He, 14.0 g CO, and 10.0 g of NO at $27.0^\circ C$?
- A 0.250 atm
 - B 0.310 atm
 - C 1.24 atm
 - D 13.2 atm
 - E 21.6 atm

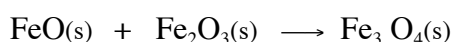
Q11 Consider the following reaction and the associated value for ΔH° :



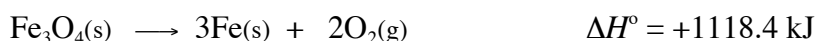
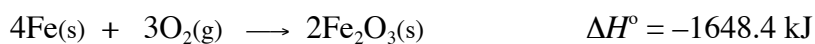
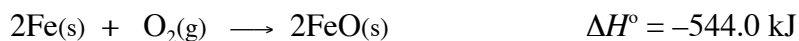
Which statement about this information is *incorrect*?

- A The ΔH° value will be -92.3 kJ if the HCl is produced as a liquid.
- B The four HCl bonds are stronger than the four bonds in H_2 and Cl_2 .
- C If the equation is reversed, the ΔH° value equals $+92.3 \text{ kJ}$.
- D 23.1 kJ of heat will be evolved when 1 mol of $\text{HCl}(\text{g})$ is produced.
- E The reactants are in their standard states.

Q12 Determine the heat of reaction for the following process:



Given information:



- A -1074.0 kJ
- B -422.6 kJ
- C -22.2 kJ
- D $+249.8 \text{ kJ}$
- E $+2214.6 \text{ kJ}$

Q13 If equal volumes of BaCl_2 and NaF solutions are mixed, which of these combinations will not give a precipitate? The solubility product, K_{sp} , for BaF_2 is 1.7×10^{-7} .

- A 0.020 M BaCl_2 and 0.0020 M NaF
- B 0.015 M BaCl_2 and 0.010 M NaF
- C 0.010 M BaCl_2 and 0.015 M NaF
- D 0.0040 M BaCl_2 and 0.020 M NaF
- E None of the combinations give a precipitate.

Q14 Which species has the same shape as the NO_3^- ion?

- A SO_3
- B SO_3^{2-}
- C ClF_3
- D ClO_3^-
- E NH_3

Q15 What takes place when zinc metal is added to an aqueous solution containing magnesium nitrate and silver nitrate?

1. Zn is oxidised.
2. Mg^{2+} is reduced.
3. Ag^+ is reduced.
4. No reaction takes place.

- A** 1 and 2 only
B 1 and 3 only
C 1, 2, and 3 only
D 2 and 3 only
E 4 only

SECTION B

Candidates are advised that the correct use of significant figures will be taken into consideration when marking answers to these problems. Candidates are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.

Question 16 is compulsory. You have a choice of answering any two questions of the remaining three questions.

Compulsory question

Candidates should note that for calculations they are required to give answers both as expressions and as computed results. Failure to provide either of these will result in marks being deducted.

Q16 Whilst redox is an integral part of inorganic chemistry, organic species, such as ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and its related aldehyde, ethanal (CH_3CHO) can also participate in redox reactions. Acidified solutions containing the dichromate anion ($\text{Cr}_2\text{O}_7^{2-}$) can oxidise both ethanol and ethanal to ethanoic acid (CH_3COOH), whilst the dichromate anion is reduced to chromium(III). Aqueous ammonia solutions of silver(I) cations, however, can only oxidise ethanal, leaving ethanol untouched. In this process, the silver(I) ions are reduced to metallic silver.

An eager young chemist is provided with 500.0 mL of an aqueous solution containing unknown amounts of both ethanol and ethanal. In order to determine the amounts of each of these, they decide first to standardise an approximately 0.05 mol L^{-1} acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$ by titrating it with an aqueous iron(II)sulfate solution (the dichromate anion oxidises iron(II) to iron(III)). This iron(II) solution was prepared by dissolving 7.43 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in exactly 100.0 mL of de-ionised water. 25.0 mL of this solution required 23.12 mL of the dichromate solution to reach the equivalence point. In turn, 50.0 mL of the unknown ethanol/ethanal solution required 22.45 mL of the dichromate solution to reach its equivalence point.

Finally, an excess of an aqueous ammonia solution of silver(I) nitrate was added to another 50.0 mL of the unknown ethanol/ethanal solution, and the young chemist found 0.234 g of metallic silver was deposited. She realised now that she had enough information to work out the number of moles of each of ethanol and ethanal in the unknown solution.

- (a) Write suitable balanced half equations for:
- (i) The reduction of $\text{Cr}_2\text{O}_7^{2-}$ (ii) The oxidation of ethanol
- (iii) The oxidation of ethanal (iv) The reduction of Ag^+
- (v) The oxidation of Fe^{2+}
- (b) Using your answers to part (a) above, write balanced ionic equations for the following reactions:
- (i) $\text{Cr}_2\text{O}_7^{2-}$ with ethanol (ii) $\text{Cr}_2\text{O}_7^{2-}$ with ethanal
- (iii) $\text{Cr}_2\text{O}_7^{2-}$ with Fe^{2+} (iv) Ag^+ with ethanal
- (c) Why is it necessary for the dichromate solutions to be acidified?
- (d) Calculate the molarity of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution used in the above analysis.
- (e) Calculate the number of moles of silver(I) nitrate used in the oxidation of ethanal in the ethanol/ethanal solution, and hence the number of moles of ethanal present in 50.0 mL of the unknown solution.
- (f) Using your answer to part (e) above, calculate the number of moles of dichromate anion that

calculate the number of moles of dichromate anion that are used to oxidise just the ethanol in 50.0 mL of the ethanol/ethanal solution.

(g) Calculate the number of moles of

- (i) Ethanol (ii) Ethanal

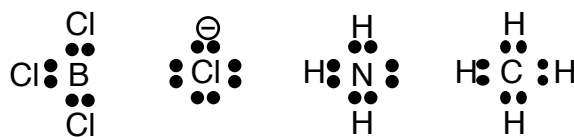
in the entire 500.0 mL of unknown solution presented to the young chemist.

Q17 Central to the art of organic chemistry is the recognition and understanding of the characteristics of organic molecules and the ways in which they interact. One of the core concepts is the identification of reactive sites within the molecule(s) in a given reaction.

A guiding principle in such an analysis is that electron-poor centres tend to react with electron-rich centres. These electron-poor centres are termed 'electron-loving' or electrophilic; the electron-rich centres are referred to as nucleophilic. Electron poor atoms are identified by an incomplete valence shell and electron rich atoms are identified by a full valence shell containing at least one lone pair (unbonded pair) of electrons designated($\bullet\bullet$). Such lone pairs are associated only with one atom as distinct from bonding pairs which are associated with two atoms.

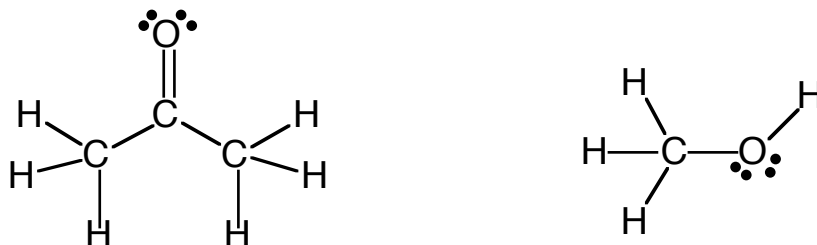
Eg H^+ is electron-poor(electrophilic), $\bullet\bullet\text{H}^-$ is electron-rich (nucleophilic).

(a) Identify the following species as electrophiles or nucleophiles or neither:



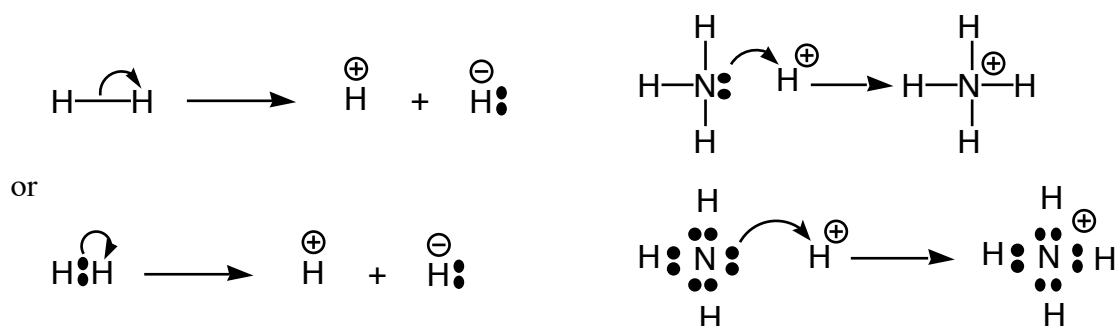
Atoms such as nitrogen, oxygen and halogens are more electronegative than carbon, and so tend to draw electron density towards themselves. This will, therefore, affect the electron distribution on these atoms as well as on the adjacent carbon atoms from which electron density is being withdrawn.

(b) Using this information, label (in your answer book) the nucleophilic (electron-rich) and electrophilic (electron-poor) sites on the following molecules:



Chemical mechanisms in organic chemistry are generally denoted using the so-called 'curly arrow' notation. The movement of a pair of electrons during the reaction is represented by \curvearrowright . For example:

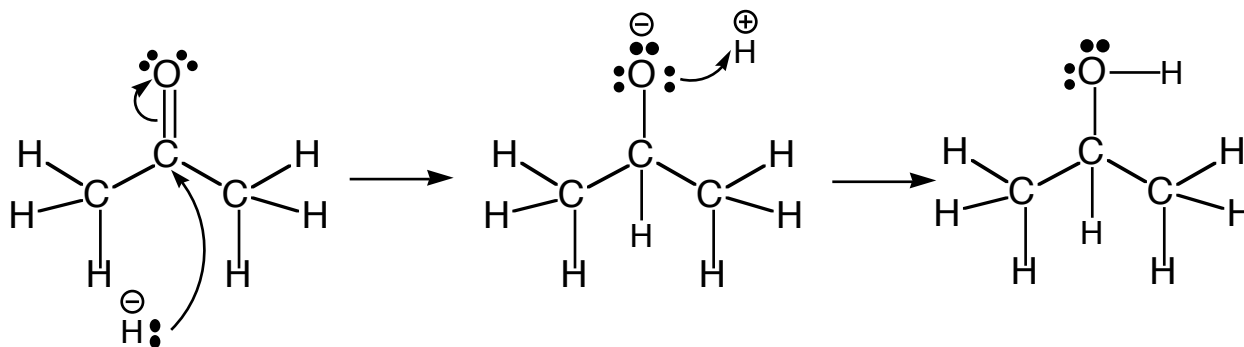
Question 17 continues on the next page.



Note: The two bonding electrons in dihydrogen end up as a lone pair on the hydride (H^-) ion.

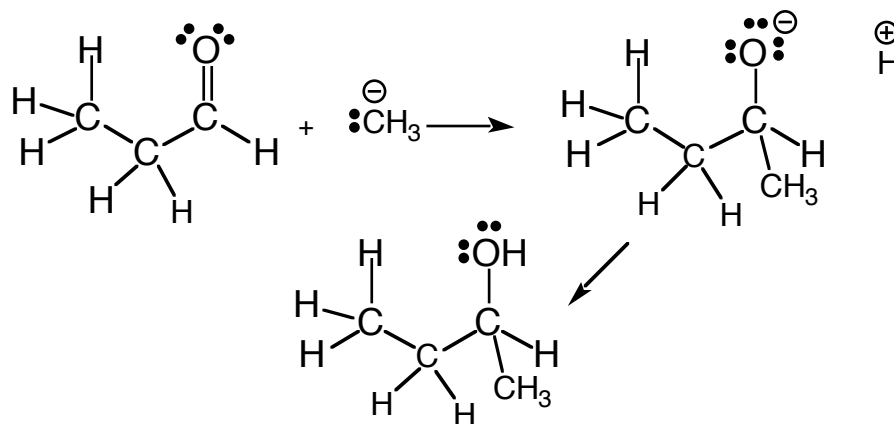
The lone pair of electrons on the nitrogen in ammonia end up as a bonding pair, ie a new single bond in the ammonium ion.

Putting these ideas together the reduction of a ketone can be shown in two steps. Firstly the reaction of a nucleophilic hydride followed by the reaction of the intermediate with an electrophilic proton.

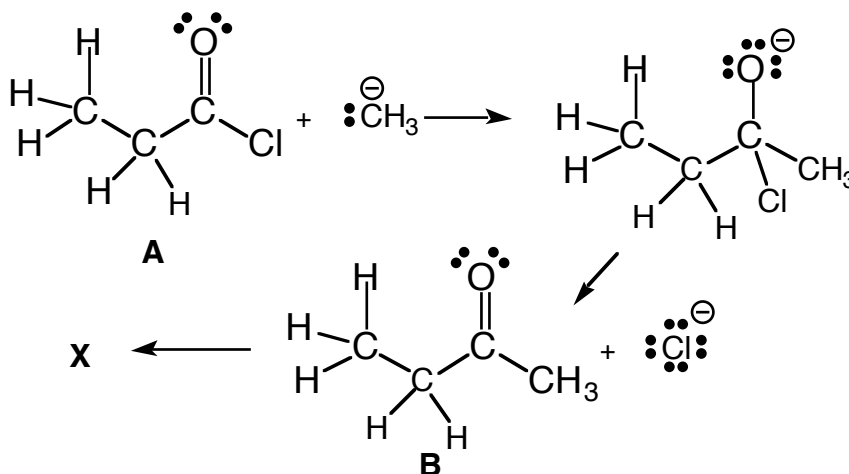


Compounds known as Grignard reagents, such as methyl Grignard (CH_3MgI), are commonly used to convert ketones and aldehydes into more highly substituted alcohols. Their active agent is a nucleophilic carbon centre that can be represented as, for example, :CH_3^- . The reaction is carried out in two distinct steps. Firstly the reaction with the nucleophile and then the reaction with a proton.

- (c) In your answer book complete the mechanism for the reaction of methyl Grignard with propanal by adding the appropriate curly arrows



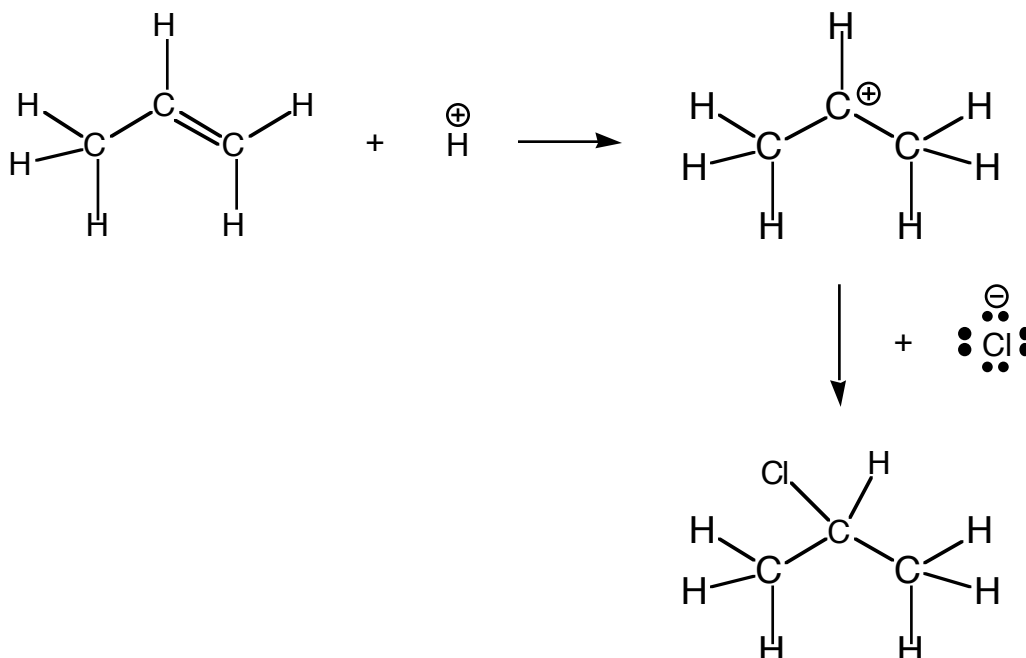
If methyl Grignard is allowed to react with propanoyl chloride (**A**), compound **B** is initially obtained.



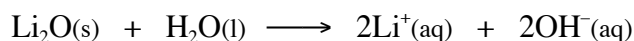
- (d) In your answer book add the curly arrows that explain the formation of **B**.
- (e) If an excess of the Grignard reagent is used another compound, **X**, forms and can be isolated after adding acid to the solution. Draw the structure of compound **X**.
- (f) A young and rather rash young chemist was asked to go into the laboratory and conduct the reaction of methyl Grignard with propanone. In something of a hurry our young friend decided to combine steps 1 and 2 in order to save time. Sadly the outcome of adding the Grignard reagent and the acid simultaneously was a violent fizzing and the evolution of a lot of gas! Draw the structure of the gas evolved in this misconceived experiment.

Carbon to carbon double bonds are relatively weak and are easily broken by the reaction with electrophiles. The following reaction scheme outlines the key steps in the addition of hydrogen chloride to propene

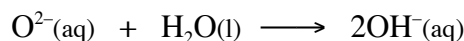
- (g) In your answer book draw the mechanism for the following reaction, using curly arrows:



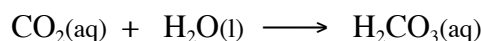
Q18 Oxides can be classified as basic, acidic or amphoteric. Ionic metal oxides are basic, they react with water to give a basic solution, e.g. Li_2O :



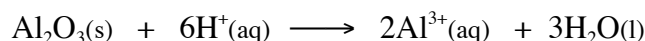
This is due to the high basicity of the oxide ion, O^{2-} , and its virtual complete hydrolysis to the OH^- ion:



Oxides of non-metals are typically acidic, e.g. CO_2 :



Oxides containing elements with intermediate electronegativities are often amphoteric, they display both acidic and basic properties, e.g. Al_2O_3 :



- Write balanced equations for the reaction with water of the basic oxides barium oxide and indium(III) oxide.
- Sulfur dioxide and sulfur trioxide are acidic oxides. Write balanced equations for the reaction with water of these two oxides.
- Which of the two oxides in (b) forms the stronger acid? Can you give a rationale for this behaviour?
- Arrange the following oxyacids of chlorine in order of increasing acid strength: HClO_3 , HClO , HClO_4 and HClO_2 .
- Which of the two oxides SnO and SnO_2 would be the more basic? Explain your answer.
- Beryllium oxide and arsenic(III) oxide are both considered to be amphoteric. Write balanced equations to illustrate the acidic and basic properties of these two oxides.

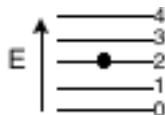
Ionic metal peroxides, superoxides and nitrides similarly display basic properties when they react with water; a soluble metal hydroxide is typically formed in each case. They contain the peroxide, O_2^{2-} , superoxide, O_2^- , and nitride, N^{3-} , ions, respectively. Hydrogen peroxide, H_2O_2 , is also produced in the reaction of an ionic metal peroxide or superoxide with water. In the latter case O_2 is also liberated.

- Write balanced equations for the reaction of barium peroxide and potassium superoxide with water.
- What is the N-containing species produced in the reaction of an ionic metal nitride with water? Write a balanced equation for the reaction of magnesium nitride with water.
- What is the P-containing species produced when sodium phosphide, Na_3P , reacts with water? Write a balanced equation for the reaction.

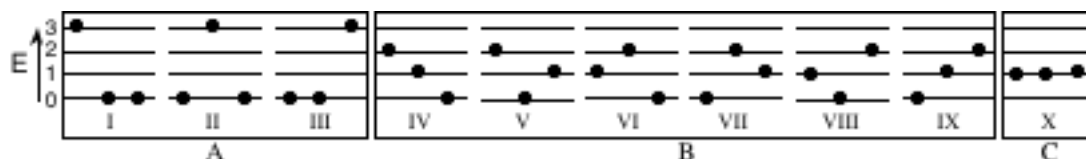
- (j) Which compound is expected to be the stronger base, the N-containing compound produced in (h) or the P-containing species in (i)? Explain your answer.

Q19 Quantum mechanics tells us that a molecule can only have certain allowed, discrete energies. Each energy is associated with a kind of motion, or degree of freedom. For a particular molecule we can specify how much energy is associated with each degree of freedom, but we cannot determine this for a collection of molecules, especially if we have 10^{20} of them! What we can do is specify the number of molecules and their total energy and work out what is likely to be the case.

Consider an hypothetical molecule with only 1 degree of freedom which has energy levels starting from 0, spaced the hypothetical unit of 1 "quantum" apart, so if we have 1 molecule with 2 quanta of energy, it would be represented as



Define N = number and E = total energy of those molecules. So for $N = 3$ and $E = 3$, we have



Each dot represents a molecule, so in IV, the molecule on the left has 2 quanta of energy, the one in the middle has 1 quantum and the molecule on the right has no quanta of energy. Each of I - X is called a microstate (= a different possible distribution of energy). We can group similar microstates together, I, II and III all have 1 molecule with 3 quanta of energy and 2 with none; each similar group of microstates is called a configuration.

(a) Consider the case where $N = 4$ and $E = 2$. On the grid in your answer book draw out a representation similar to the one above of the possible distributions of energy for this system. Appropriately label the following in similar fashion to the example:

- the energy levels
- the different microstates I, II, III, etc
- the different configurations with the letters A, B, C, ... etc. (Note: Label these sequentially with A having the most molecules in higher energy states, as in the example).

(b)(i) How many possible microstates are there?

(ii) How many different configurations are there?

We can simplify all this (and save ourselves from drawing out energy level diagrams all the time) by introducing the concept of occupation numbers. n_i is the number of molecules in a particular energy state i . So for I, II and III above in configuration A, $n_0 = 2$, $n_1 = 0$, $n_2 = 0$ and $n_3 = 1$. We usually leave out energy levels with an occupation number of 0, so this simplifies to $n_0 = 2$, $n_3 = 1$. Note that all microstates in the same configuration have the same occupation numbers.

(c) Using the concept of occupation numbers complete the tables in your answer book for the following.

(i) For $N = 3$, $E = 3$. (ii) For $N = 4$, $E = 2$.

We can also simplify the process of calculating the number of microstates (denoted by W for a particular configuration) by using the formula

$$W = \frac{N!}{\prod_i n_i!} \left(= \frac{N!}{n_0! \times n_1! \times n_2! \times \dots} \right) \quad \text{where} \quad N! = N \times (N-1) \times \dots \times 2 \times 1 \quad (\text{Note } 0! = 1)$$

Another assumption we can make is that every allowed microstate of a system will occur with equal probability, (Equal Probability Assumption).

(d) Using these further assumptions:

- (i) Verify that the above formula works by calculating the number of microstates (W), for both configurations A and B, for the $N = 4, E = 2$ case.
- (ii) For the listed configurations, complete the occupation numbers for $N = 10, E = 5$ that have been left blank in the answer table.
- (iii) Calculate the number of microstates (W) for the $N = 10, E = 5$ case by considering W for each configuration. Do your calculations on the Rough Working page at the left and then enter your answer in the appropriate column in the answer book table.
- (iv) State the occupation numbers of the most probable configuration and calculate the probability that it will occur.

As you can see, even for the $N = 10, E = 5$ case, the probability of the system adopting the most probable configuration is quite high. This effect increases as N and E increase, so that for large N and E , the probability of the system adopting the most probable configuration approaches 1. This means that for N and E large enough, we can "cheat" by ignoring all other configurations and only consider the most probable one.

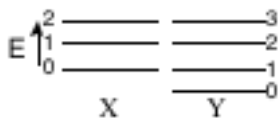
Still considering the $N = 10, E = 5$ case, we can model a simple isomerisation reaction $X \rightleftharpoons Y$. If we just have X molecules the most probable configuration is given by the answer to (d) (ii) above. If X and Y are now allowed to interconvert, we can use the same logic applied above to find out that (one of) the most probable configurations is:

$$n_0^X = 3, n_1^Y = 3, n_1^X = 2, n_1^Y = 1, n_2^Y = 1 \quad \text{or} \quad \begin{array}{c} E \uparrow \\ \begin{array}{c} 2 \text{ --- } \bullet \\ 1 \text{ --- } \bullet \bullet \\ 0 \text{ --- } \bullet \bullet \bullet \end{array} \quad \begin{array}{c} \text{--- } \bullet \\ \text{--- } \bullet \\ \text{--- } \bullet \bullet \bullet \end{array} \\ \text{X} \quad \quad \quad \text{Y} \end{array} \quad \begin{array}{l} \text{This is one possible} \\ \text{microstate from} \\ \text{this configuration.} \end{array}$$

(e)(i) Calculate W (number of microstates) for the above configuration (the formula above still applies).

(ii) How many molecules of X and Y respectively do we have?

Now consider the case where Y is lower in energy than X , such that the lowest energy level of X is now equal in energy to the second lowest of Y , ie:



Note that the n^{th} energy level of X now has an energy of $(n + 1)$ quanta.

Again using the same logic as before, (one of) the most probable configurations is

$$n_0^X = 2, n_0^Y = 6, n_1^Y = 1, n_1^X = 1$$

(f) (i) Calculate W for the above configuration.

(ii) Is this what you expected? How many molecules of X and Y respectively are there now? Which are there more of, and is this what you expected? Rationalise this observation.

This page is intentionally left blank.

This page is intentionally left blank.

This page is intentionally left blank.