



CHEMISTRY

2004 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.
Answer **any three** of Questions 16, 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)	$6.02 \times 10^{23} \text{ mol}^{-1}$	Velocity of light (c)	$2.998 \times 10^8 \text{ m s}^{-1}$
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)	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$	1 newton (N)	1 kg m s^{-1}
Planck's constant (h)	$6.626 \times 10^{-34} \text{ J s}$	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	pH = $-\log_{10}[\text{H}^+]$ pH + pOH = 14 $K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$ PV = nRT E = hv	
Molar volume of ideal gas at STP	22.4 L	c = $v\lambda$ Q = It	
Dissociation constants	$\text{NH}_3 - K_b = 1.79 \times 10^{-5}$ $\text{CH}_3\text{COOH} - K_a = 1.76 \times 10^{-5}$	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	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.

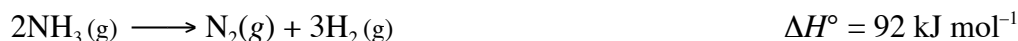
SECTION A

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.

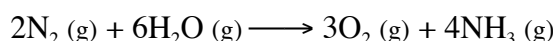
- Q1** An 0.5000 g sample of magnetite ore (impure Fe_3O_4) is treated so that the iron is precipitated as iron(III) hydroxide. The precipitate is heated and converted to 0.4980 g Fe_2O_3 . What is the percentage of Fe_3O_4 in the ore?
- A 69.0%
B 96.3%
C 99.6%
D 35.0%
E 48.1%
- Q2** Quinaldine red is a useful acid-base indicator which is red in solutions of pH greater than 3.5, but colourless below pH 1.5. Which of the following solutions would turn red if a few drops of quinaldine red were added?
- 0.1 mol L^{-1} HCl
 - 0.05 mol L^{-1} NH_3
 - 0.0005 mol L^{-1} CH_3COOH
- A 1 and 2 only
B 1 and 3 only
C 2 and 3 only
D 2 only
E 3 only
- Q3** Which one of the following atoms has the largest radius?
- A As
B Br
C P
D S
E Se
- Q4** Element **X**, a grey solid, reacts with element **Z**, a colourless gas, to form a compound in which there are twice as many atoms of **X** as there are of **Z**. Which of the following statements about the ground-state electron configurations of these atoms is most likely to be true?
- A **X** has one valence electron and **Z** has six.
B **X** has one valence electron and **Z** has five.
C **X** has two valence electrons and **Z** has one.
D **X** has two valence electrons and **Z** has five.
E **X** has seven valence electrons and **Z** has six.

- Q5** Around service stations there is often a distinct smell of petrol, indicating the presence of gaseous petrol molecules in the air. Interestingly, although the air also contains oxygen, the petrol does not seem to have reacted. Which of the following is the best explanation for this observation?
- A The petrol and the oxygen are in equilibrium and will not react further.
 - B Safety laws require that petrol contain an additive to prevent it from reacting with oxygen.
 - C The petrol and the oxygen have already reacted, and it is the products of this reaction which we smell.
 - D At room temperature and pressure, petrol is a liquid, so the amount in the gaseous phase is negligible.
 - E At room temperature, most petrol and oxygen molecules do not have sufficient kinetic energy to react.

- Q6** Given the following enthalpy changes:



calculate the enthalpy change for the reaction



- A -576 kJ mol^{-1}
 - B -392 kJ mol^{-1}
 - C 392 kJ mol^{-1}
 - D 1268 kJ mol^{-1}
 - E 1636 kJ mol^{-1}
- Q7** The standard reduction potentials of silver and nickel are $E^\circ(\text{Ag}^+, \text{Ag}) = +0.80 \text{ V}$ and $E^\circ(\text{Ni}^{2+}, \text{Ni}) = -0.23 \text{ V}$. Which of the following statements is true?
- A Ag^+ is an oxidizing agent but Ni^{2+} is a reducing agent.
 - B Ag^+ is a better oxidizing agent than Ni^{2+} and Ag is a better reducing agent than Ni .
 - C Ni^{2+} can be reduced by silver metal.
 - D Ag^+ is a better oxidizing agent than Ni^{2+} and Ni is a better reducing agent than Ag .
 - E Ni^{2+} is a better oxidizing agent than Ag^+ and Ag is a better reducing agent than Ni .
- Q8** A container of 250 mL capacity contains 0.374 g of a particular gas at a temperature of 22.5 °C and pressure of 1.00 atm. The gas could be:
- A H_2
 - B He
 - C CH_4
 - D H_2S
 - E HCl

- Q9** In the early years of the nineteenth century, John Dalton published a list of atomic masses. One experiment on which it was based involved measuring the composition by mass of ammonia. By assigning hydrogen a mass of 1 unit and using the chemical formula for ammonia, he could deduce the atomic mass of nitrogen.

Unfortunately, he incorrectly believed that the formula for ammonia was NH. What atomic mass did he propose for nitrogen on the basis of this formula?

- A 2
- B 5
- C 14
- D 16
- E 42

- Q10** A brown-black compound of thallium was found to contain 89.5% Tl and 10.5% O. What is the oxidation number of thallium in this compound?

- A 0
- B I
- C II
- D III
- E IV

- Q11** A sample of phosphorus pentachloride is placed in a sealed container, where it decomposes into phosphorus trichloride and chlorine gas according to



Once the mixture is at equilibrium, a small quantity of helium gas is added, at constant pressure and temperature, and the mixture is allowed to return to equilibrium. Which of the following best describes the second equilibrium position with respect to the first?

- A The second equilibrium position is the same as the first, because helium is much lighter than any of the other molecules in the container and will have a negligible effect on the reaction.
- B The second equilibrium position is the same as the first, because helium does not react with any of the other molecules in the container.
- C The second equilibrium position has more PCl_3 than the first.
- D The second equilibrium position has more PCl_5 than the first.
- E It is impossible to tell what will happen without knowing the equilibrium constant for this reaction.

- Q12** Which of the following substances has the lowest normal boiling point?

- A NH_3
- B H_2O
- C C_3H_8
- D $(\text{CH}_3)_2\text{O}$
- E CH_4

- Q13** In a properly functioning automobile engine, the two principal products of the combustion of the petrol are:
- A CO and H₂O
 - B CO₂ and H₂O
 - C H₂O and NO
 - D CO and NO
 - E CO₂ and NO
- Q14** An unknown compound was discovered to have molecular formula C₁₀H₂₀O₂. To which of the following classes of compounds could this unknown **not** belong?
- A alkynes
 - B alkenes
 - C alcohols
 - D esters
 - E ethers
- Q15** Bob dissolved 4.021 g of NaOH in water and made up the solution to 1 litre with water. He then pipetted 10.00 mL of this solution into a flask and titrated it with 0.050 M HCl solution from a burette. A volume of 20.32 mL of acid had been used at the endpoint. Bob's teacher deduced that:
- A the analysis is as accurate as can be expected using this apparatus
 - B the NaOH absorbed H₂O from the air after its mass was measured
 - C the burette was rinsed with water instead of HCl
 - D the flask was rinsed with HCl instead of water
 - E the pipette was rinsed with water instead of NaOH

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 of the four questions in this section.

Q16

For aerobic organisms, oxygen is a vital element for it acts as an electron acceptor in the biochemical reactions that generate the energy required to survive.

- (a) (i) Write a balanced equation for the reaction of a carbohydrate ($C_6H_{12}O_6$) with oxygen and clearly identify the oxidant and reductant.
- (ii) Write a balanced equation for the reaction of palmitic acid (a component of fat, $C_{16}H_{32}O_2$) with oxygen.

Whilst terrestrial life-forms have an abundant supply of oxygen in the atmosphere, aquatic life-forms have special evolutionary adaptations designed to extract the trace amounts of oxygen in water, in which it is poorly soluble. Certain agricultural contaminants such as phosphate can promote “algal blooms” which speeds up the consumption of dissolved oxygen, thus depriving fish its supply.

A sample of water from an agricultural runoff is assessed for its oxygen content by employing the Winkler method. After removal of contaminants that might interfere with the analysis, manganese(II) sulfate is added to the sample of water followed by the addition of excess potassium iodide dissolved in aqueous sodium hydroxide. Under these conditions, oxygen oxidises the manganese(II) ion to manganese(III) hydroxide.

- (b) Using half equations write a balanced equation for the reaction between Mn^{2+} and O_2 and clearly show the oxidation number of each atom in the balanced equation.
- (c) Approximately 1 mL of sulfuric acid is added to the mixture to render the solution acidic and dissolve the precipitate of $Mn(OH)_3$. Under these conditions, manganese(II) is regenerated and the solution now has a slightly brown tinge. Note that in acidic conditions, $Mn(OH)_3$ dissolves to give free Mn^{3+} ions.
- (i) Using half equations write a balanced equation for the reaction between Mn^{3+} and I^- .
- (ii) What causes the brown colour in the solution?

The solution is now shaken with carbon tetrachloride (CCl_4), in which the brown colour is observed to be transferred to the latter. The carbon tetrachloride is separated from the water sample and shaken with an aqueous solution of hydrogen peroxide (H_2O_2). Iodate ions (IO_3^-) are found in the aqueous phase of this reaction and H_2O_2 is reduced to water.

- (d) Using half equations write a balanced equation for the reaction between the brown substance and H_2O_2 and clearly show the oxidation number of each atom in the balanced equation.

The remaining hydrogen peroxide is decomposed by boiling the solution. In this reaction H_2O_2 is simultaneously oxidised and reduced, one of the products being a colourless gas which supports combustion. An excess of potassium iodide is then added. The brown tinge observed in the reaction in (c) is regenerated.

- (e) (i) Using half equations write a balanced equation for the decomposition of the hydrogen peroxide.
- (ii) Using half equations write a balanced equation for the reaction that produces the observed brown tinge.
- (iii) How much more of the brown substance does one now have compared to (c)?

This final solution is titrated with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). However, as sodium thiosulfate is not a primary standard it has to be standardised with potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). 5.000 g of solid potassium dichromate is dissolved in a 500.0 mL volumetric flask and made up to the mark. 25.00 mL of this solution is pipetted into a 250.0 mL volumetric flask and again made up to the mark. 20.00 mL of this diluted solution is acidified and required 16.75 mL of thiosulfate to reach endpoint (using starch indicator). The thiosulfate ion is oxidised to tetrathionate ($\text{S}_4\text{O}_6^{2-}$) whilst dichromate is reduced to chromium(III).

- (f) (i) Using half equations write a balanced equation for the reaction between dichromate and thiosulfate.
- (ii) Calculate the concentration of the thiosulfate solution from the results of the standardisation.

The thiosulfate solution is subsequently used to titrate the brown substance liberated in 250.0 mL aliquots of the agricultural runoff. On average it takes 23.69 mL of thiosulfate solution to reach the endpoint, again using starch indicator.

- (g) Using half equations write a balanced equation for the reaction between thiosulfate and the brown substance.
- (h) Calculate the amount of oxygen in the original water sample expressed in parts per million (1 ppm = 1 mg/L).
- (i) Fish need more than 5.0 ppm of oxygen to survive. Can this sample support fish?

After preparing buffer solutions last year, our young chemist Bob now turns toward honing his titration skills for the school's titration team. He was successful, making it to the national finals. The Winkler titration was part of the Redox Titration Final Qualifiers competition. Deciding to save time, Bob carries out all the preliminary steps but lets his conical flasks containing his aliquots to stand uncovered on the bench as he performs the final titrations. Disaster struck: all of his titres were lower than expected and the precision was poor.

- (j) What happened?

Q17

Ammonium nitrate is widely used as a fertilizer and as an explosive in the mining industry. It is prepared commercially by passing ammonia gas through a solution of nitric acid.

- (a) Write a balanced equation for the reaction.

Ammonium nitrate decomposes explosively above about 300 °C to give N₂, O₂ and H₂O.

- (b) Write a balanced equation for the reaction.

Indeed, most compounds of nitrogen are thermodynamically less stable than N₂ and decompose exothermically to it. Ammonia is an exception.

Careful heating of NH₄NO₃ to about 250 °C gives nitrous oxide, N₂O, and water.

- (c) Write a balanced equation for the reaction.

Nitrous oxide is one of seven known molecular oxides of nitrogen. It is used as a mild anaesthetic (often referred to as 'laughing gas') and as a propellant for whipped cream (due to its high solubility in fats).

Nitric oxide can be formed by the direct combination of N₂ and O₂ at elevated temperatures or by the action of dilute nitric acid on copper or iron. Commercially it is prepared by reacting ammonia with O₂ at *ca* 850 °C in the presence of a catalyst (to give NO and water).

- (d) Write a balanced equation for the reaction.

In the absence of the catalyst no nitric oxide is formed.

- (e) Name the product(s) formed. Write a balanced equation for the reaction.

Nitric oxide is prepared commercially for use in the production of nitric acid (known as the Ostwald process). It is also of biological significance as it is a common neurotransmitter in the brain that plays an important role in muscle relaxation. It readily reacts with O₂ to give nitrogen dioxide.

- (f) Write a balanced equation for the reaction.

The reaction is exothermic and in the commercial process (the second step of the Ostwald process) is cooled to 25 °C using water because the rate of the reaction **decreases** with increasing temperature. The reaction is believed to proceed *via* the coupling of two molecules of NO to form an unstable oxide of nitrogen, N₂O₂ (NO and N₂O₂ are presumed to exist in equilibrium) followed by reaction of the latter with O₂ to give two equivalents of nitrogen dioxide.

- (g) Using this information, provide an explanation as to why the rate of the reaction decreases with increasing temperature.

Nitrogen dioxide, like NO, is an odd electron molecule that is known to exist in equilibrium with its dimer, N₂O₄.

- (h) Sketch the molecular structures of N₂O, NO₂, N₂O₂ and N₂O₄.

Nitrogen dioxide is an acidic oxide, it reacts with water to form an acid, nitric acid. This is the final step in the Ostwald process. Nitric oxide is also produced in the reaction and recycled in the process.

- (i) Write a balanced equation for the reaction of NO_2 with water. Clearly show the oxidation number of each atom in the equation.

The reaction of NO_2 with water is an example of a disproportionation reaction.

- (j) Explain what is meant by this term and why the reaction of NO_2 with water is an example of such a reaction?

Nitric acid is a strong acid and a powerful oxidizing agent that is primarily used in the production of ammonium nitrate. It is photochemically sensitive slowly decomposing to NO_2 , O_2 and water in the presence of sunlight.

- (k) Write a balanced equation for the reaction.

Two other unstable oxides of nitrogen are also known, N_2O_3 and N_2O_5 . The former can be prepared by condensing equimolar quantities of NO with NO_2 at $-20\text{ }^\circ\text{C}$ and the latter by the dehydration of nitric acid.

- (l) Sketch the molecular structures of N_2O_3 and N_2O_5 .

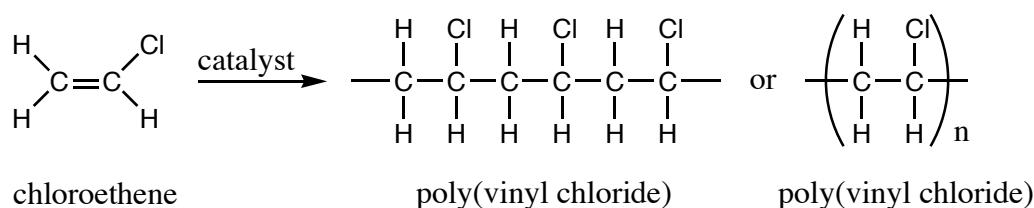
Q18

Polymers

Polymers are a general class of compounds made from one or more 'monomer' units linked together in a chain. Sometimes the chains are branched or cross-linked too, changing the polymer's properties. Many materials that we use every day are polymers; let's investigate some of them.

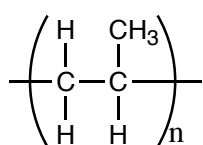
Polymers can be categorised as addition or condensation polymers, depending on how the monomer units are linked together. We'll look at addition polymers first: in these the monomer units are linked together by rearranging the electronic structure of the monomers (which are often alkenes).

One polymer you will no doubt have come across is the plastic poly(vinyl chloride), or PVC, which is manufactured by polymerising chloroethene (vinyl chloride is an old name for chloroethene). The reaction is as follows:



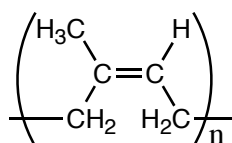
A long chain of monomer units bonded together is produced; for simplicity we can abbreviate its structure by showing just the repeating unit (as seen on the far right).

- (a) Another everyday polymer is poly(tetrafluoroethene) (PTFE), marketed as Teflon[®] by DuPont. It is primarily used to make non-stick surfaces. PTFE is made by polymerising tetrafluoroethene. Draw the structure of PTFE in the abbreviated form shown above.
- (b) Polypropylene, used in dishwasher-safe plastic containers has the structure below. Draw the monomer from which polypropylene is formed.



polypropylene

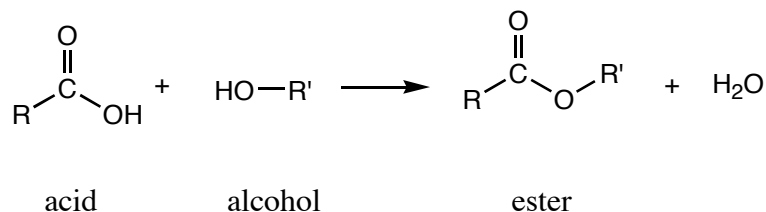
- (c) Natural rubber has the polymeric structure below. Draw the monomer from which natural rubber is formed.



Q18 continues on the next page

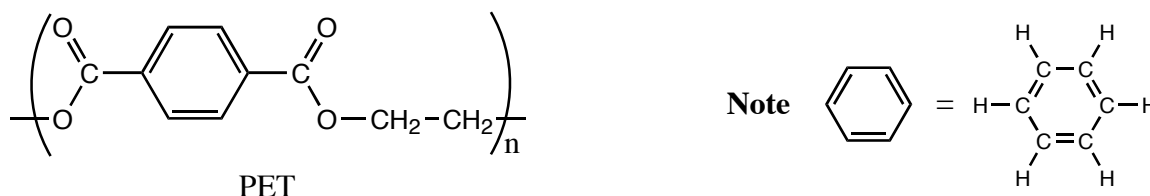
Condensation polymers

Many of you will have met esters before, yes, those pleasant and often fruity-smelling compounds. Esters are formed in a condensation reaction between an acid and an alcohol (R and R' denote general alkyl groups, e.g. $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$ etc):



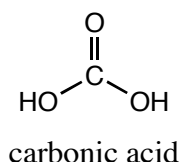
If however, we have a dicarboxylic acid and a dialcohol, we can form long chains of the monomer units bound together using ester linkages. These are so-called polyesters, which have uses as varied as groovy '70s clothing and soft drink bottles.

- (d) Poly(ethylene terephthalate), thankfully shortened to PET, is the polymer used in plastic drink bottles. Its structure is shown below (the ring structure is called a benzene ring; don't worry if you haven't seen them before). Draw the monomer unit(s) used to make PET.

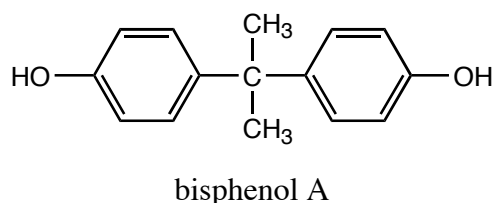


- (e) If a typical PET chain is made up of 100 repeating units, what mass of water (to the nearest gram) is formed when 1000 g of PET is produced?

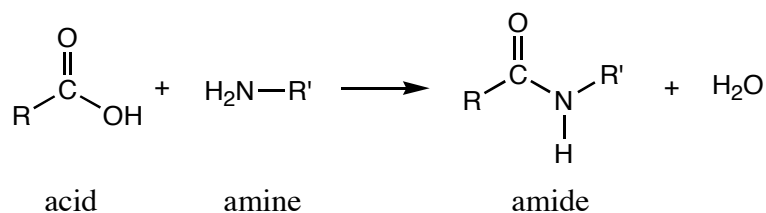
Polycarbonates are rather similar to polyesters, in that they are polyesters of carbonic acid, structure below.



- (f) The polycarbonate of bisphenol A is marketed under the trade name Lexan[®], and is used in shatterproof windows and lightweight eyeglass lenses. The structure of bisphenol A is given below. Using the repeating unit notation, draw the structure of Lexan[®].

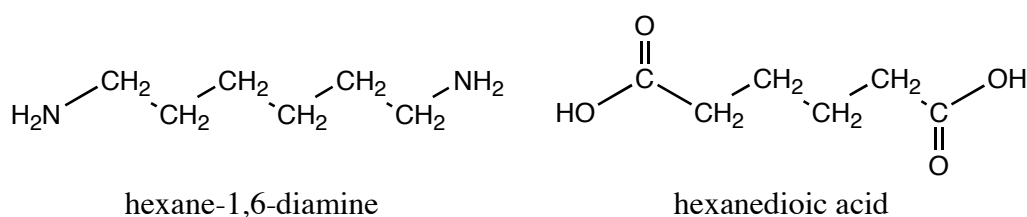


The product of the reaction between an acid and an amine (analogous to ester formation) is called an amide. For example:



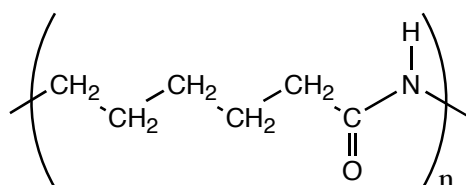
Nylons are similar to polyesters, but use amide instead of ester linkages between the monomer units.

- (g) Nylon (6,6), used in stockings, toothbrush bristles, rope and parachutes, is formed when hexanedioic acid reacts with hexane-1,6-diamine, structures given below. Using the repeating unit notation, draw the structure of nylon (6,6).

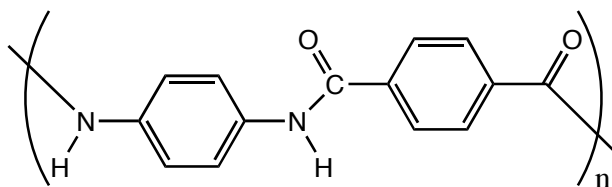


DuPont patented nylon (6,6) soon after they discovered it, so rival companies quickly developed the very similar nylon 6 to get into the nylon industry.

- (h) The structure of nylon 6 is given below. Give the structure of the monomer(s) used to make nylon 6.



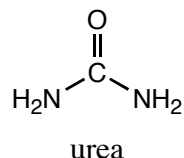
Kevlar[®] is a type of nylon used to make such products as bullet proof vests, puncture-proof bicycle tyres and presumably bullet proof bicycle tyres should such a market develop. Kevlar[®] has the following structure:



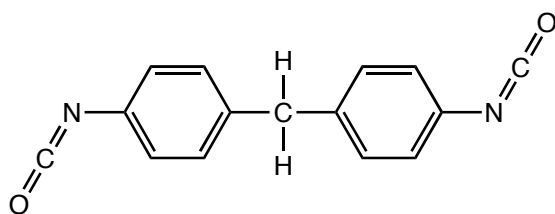
Kevlar[®]

- (i) Draw the monomer(s) from which Kevlar[®] is manufactured.

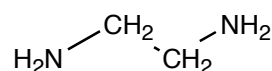
Polyureas are polymers whose monomer units are joined together by means of a substituted urea linkage. In fact they are often referred to as ‘polyurethanes’ even though they are not (see paragraph before (k)), due to negative associations with the word urea. Polyurethanes and polyureas are extremely versatile, and are used in anything from foam to paints, and fibres to adhesives. The structure of urea is shown below:



- (j) Using the repeating unit notation, draw the structure of the polyurea formed from bis(4-isocyanatophenyl)methane and ethane-1,2-diamine (structures below):



bis(4-isocyanatophenyl)methane

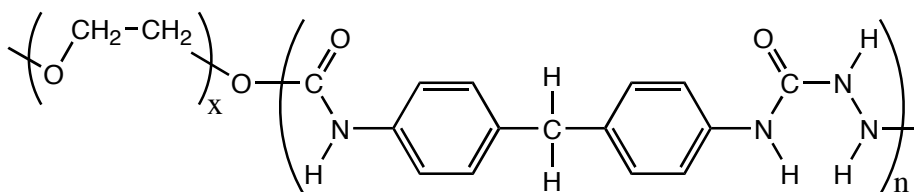


ethane-1,2-diamine

True polyurethanes (monomer units joined with urethane links rather than urea links) are formed similarly to polyureas, but using dialcohols instead of diamines.

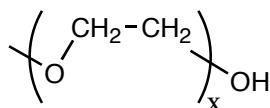
- (k) Using the repeating unit notation, draw the structure of the polyurethane formed from bis(4-isocyanatophenyl)methane (structure in (j)) and ethane-1,2-diol.

Lycra is also polymeric; it has the following structure:



where $x \approx 40$ and n is arbitrary.

- (l) Apart from the compound below, what other starting materials would be used?

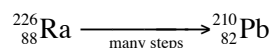


Q19

The mole was a useful concept long before Avogadro's number was actually measurable. This problem is about the calculation of Avogadro's number using two different experimental methods. The two parts of the problem are independent, so if you get stuck on one, try the other!

1st PART

One method of calculating Avogadro's number is by measuring **radioactive decay**. Radium-226 decays to lead-210 via several intermediates:



The first step in this chain occurs very slowly (over thousands of years), while the rest occur in a matter of days. In fact, the lead-210 is itself unstable, but decays over a period of years, far longer than the duration of our experiment, so we can treat it as stable for our purposes.

The decay chain from radium-226 to lead-210 involves only α -decays, where a ${}^4_2\text{He}$ nucleus escapes from the atom's nucleus, and β^- -decays, where a neutron converts to a proton and emits an electron at high speed.

- (a) How many of each type of decay occur in this chain?

The experiment involves leaving a radium-226 sample for several months and measuring the volume of helium gas generated by the α -particles (which quickly attract electrons to become helium atoms). The first step is to measure the rate of decay of radium.

- (b) It is found that when a 6.3×10^{-5} g sample of radium-226 is placed in a vacuum and exposed to a screen of area 1.0 mm^2 placed 1.5 m away from the sample, an average of 46 α -particles hit the screen in 10.0 minutes. During this short time we can assume that only the first step in the decay chain occurs. Calculate the total number of decays per gram of radium-226 per second.
- (c) Briefly explain why it is necessary to place the sample in a vacuum to make this measurement.

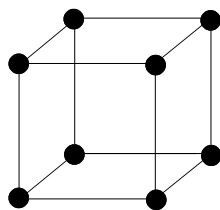
An experiment by Ernest Rutherford early last century showed that a sample of 192 mg of radium-226 left for 83 days produced 6.83 mm^3 of helium gas, measured at 0°C and 1 atm.

- (d) Calculate the number of moles of helium produced.
- (e) Using your answer from (a) and (b), calculate the number of helium atoms produced.
- (f) Hence calculate Avogadro's number.

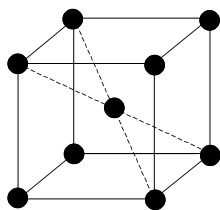
Q19 continues on the next page

2nd PART

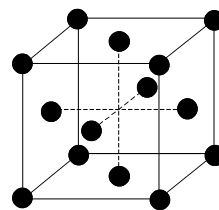
Another modern method of evaluating this constant is to use **X-ray diffraction** from metals. Three possible metallic structures are shown below. (The pictures show the *unit cells*, which you have to imagine repeating over and over in all three dimensions.)



simple cubic



body-centred cubic



face-centred cubic

The simplest structure is called *simple cubic*, and has an atom at each corner of the cubic unit cell. You get a *body-centred cubic* cell by adding an atom to the very centre of the simple cubic cell. Similarly, you get a *face-centred cubic* cell by adding an atom to the middle of each face of a simple cubic cell.

In visualising these structures we have to remember that some of the atoms belong to more than one unit cell when the pattern is repeated in 3D. For instance, although there appear to be eight atoms in the simple cubic unit cell, each of these atoms is shared between eight unit cells, so on average there is only really one atom in each simple cubic unit cell.

- (g) In the same way, count the net number of atoms in the body-centred cubic and face-centred cubic unit cells.

X-ray diffraction can be used to determine the side length of the unit cell. In this case it can be shown that

$$\lambda = \frac{2}{\sqrt{3}} d \sin \theta$$

where λ is the wavelength of X-ray used, d is the side length of the unit cell, and θ is the angle at which the so-called *first-order diffraction peak* occurs.

- (h) The diffraction pattern of a sample of copper was measured using X-rays of wavelength 1.54×10^{-10} m, and the first-order diffraction peak was measured at an angle of 21.68° . Calculate the side length of the copper unit cell.
- (i) Another copper sample of mass 10.7522 g was dropped into a measuring cylinder containing 5.0 mL of water. The total volume was read as 6.4 mL. Calculate the density of copper.
- (j) By careful analysis of the X-ray diffraction pattern it was established that copper crystallises in a face-centred cubic structure. Use this information together with your previous results to calculate Avogadro's number.
- (k) Which step is the main source of error in this experiment? *Briefly* describe a way of improving the precision of this step.

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