ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2002

These answers are designed to help students who are preparing to take the Canadian National High School Chemistry Examination in 2003 or subsequent years. Note that information given here will generally not include material from the 2001 answers, so that students should go through the 2001 questions and answers before attempting the 2002 examination.

Students should attempt to do the questions in Part A of the 2002 Examination on their own, and then compare their answers with the solutions given below. Students should not be put off by the length of the explanations, which do not reflect the length of time needed to think out answers to the questions. Rather, these notes are designed as a teaching aid, and they discuss subjects arising from the questions, as well as how to work out the answers. They also contain tips about how to set about doing a multiple choice examination in general.

These notes have been prepared in order give students (and teachers) some indication of the sort of things that the National Examiner expects high school students to know - and what topics might appear on future exams. Note that, unless otherwise stated, the multiple choice part of the National High School Chemistry Examination is based on the requirements of the Pan-Canadian Protocol for Collaboration on School Curriculum - Common Framework of Science Learning Outcomes, see http://www.cmec.ca/science/framework/Pages/english/11-12%20chemistry.html.

It is strongly recommended that students read these explanations in conjunction with a text book, and try to draw their own diagrams, where appropriate, in order to gain a thorough understanding of the verbal explanations.

These solutions have been prepared by the National Examiner, Leslie Barton. Please direct any comments or queries to her at bartonl@sympatico.ca or lesliebarton@hotmail.com.

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1. Safety is a new topic for the National High School Chemistry Examination, however, I expected that this would have been covered by all teachers very early on in any chemistry course. It was therefore surprising to me that very few first year university students could answer this question correctly in trials. Nevertheless I chose to leave it on the exam because I felt that it involved such a simple idea with important everyday applications. The point is that whenever a chemical is spilled on the **skin** the immediate first aid treatment is always to apply copious amounts of water, irrespective of the nature of the chemical. So the answer is **B**.

The most popular answer was D (baking soda, $NaHCO_3$), with a few students choosing E (washing soda, Na_2CO_3). Clearly the students who chose these options thought that it would be best to try to neutralize the battery acid (H_2SO_4), however this neutralization should never be attempted on the skin. This is because (1) the reaction will generate heat, which might result in burns, and (2) a residual excess of the neutralizing agent could be left on the skin which would then have to be removed. (Alkalis are themselves caustic and are particularly dangerous to the eyes.) Even though battery acid generates heat when mixed with water, it will not be as great as the heat generated by reaction with alkali, and an excess of water will ensure that the skin is cooled without further damage.

In the case of acids spilled on **benches or the floor**, it **is** appropriate to use a neutralizing agent such as sodium hydrogen carbonate. The excess solid can be swept up, and any further residue can be dissolved in water and mopped up. Proprietary neutralization packs are also available, and are, in fact, recommended for these situations.

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2. After last year's question on the pH of solutions of nitrogen compounds (2001, Q.14), it was, perhaps, a little tough to include this question. For an oxide of nitrogen we said that the greater the proportion of oxygen the more acidic the solution of the oxide would be. This holds true for the oxides of a particular non-metal, but metallic

oxides behave differently. The oxides of metals are generally basic and the oxides of Group I metals dissolve to form alkaline solutions (which is why they are called the alkali metals of course). Note that when a basic oxide dissolves in water it **never** gives oxide ions in solution, instead the oxide ions immediately react with water to form hydroxide ions.

Lithium oxide is a typical example of a basic oxide. In the solid state it contains lithium ions (Li^+) and oxide ions (O^{2-}) in a regular crystalline array. When it dissolves the water molecules rip the ions apart and react with the oxide ions. This can be shown as:

$$(Li^+)_2 0^{2-}(s) + H_2O(l) \rightarrow 2Li^+(aq) + 2OH^-(aq)$$

This is more usually written as:

$$Li_2O(s) + H_2O(l) \rightarrow 2LiOH(aq)$$

Other Group I metal oxides with this stoichiometry (metal:oxygen = 2:1) behave similarly. Where the stoichiometry differs it is because the oxygen is present in another kind of ion, for example the peroxide ion (O_2^{2-}) or the superoxide ion (O_2^-). Like O^{2-} ions, these are also unstable in water. Further discussion of these fascinating ions is really beyond the scope of high school chemistry, but suffice it to say that sodium peroxide (Na_2O_2) is, in fact, the compound formed when sodium and oxygen react, whilst potassium superoxide (KO_2) is formed when potassium and oxygen react. These substances react with water as follows:

$$Na_2O_2\,(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2O_2(aq)$$

$$2KO_2(s) + 2H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq) + H_2O_2(aq) + O_2(g)$$

In both cases the solutions are strongly alkaline, with the presence of hydrogen peroxide making very little difference to the pH.

Last year we said that nitrogen hydride (a.k.a. ammonia, NH_3) gives an alkaline solution. This is because it reacts as a Bronsted-Lowry base with water. Other non-metal hydrides (e.g. HCl) can behave as Bronsted-Lowry acids, or they may be amphiprotic (i.e. able to behave as either a Bronsted-Lowry acid or a Bronsted-Lowry base) as is H_2O itself, or they may be unreactive with water (e.g. methane, CH_4).

The acidity of the hydrides of elements in Group 16 of the Periodic table increases as the group is descended due to the bond energy of the covalent bond (in the undissolved, molecular, form of the acid) becoming weaker as it gets longer. Thus if we compare aqueous solutions of equal concentrations we find that the pH decreases in the series $H_2S > H_2Se > H_2Te$. This is largely due to the fact that the atoms become larger down the group so that the bonds with hydrogen become weaker. A similar effect might be expected in Group 17 with the acids HCl, HBr and HI, however these are all such strong acids that their pH values in aqueous solutions of the same concentration are virtually identical (i.e. there is a levelling effect). (HF is, in fact, a weak acid because the covalent bonds in its molecules are so strong that they do not dissociate very much when the acid dissolves in water.)

The Group 17 hydrides are more acidic than Group 16 hydrides largely because the electronegativity value of each Group 17 element is greater than that of the Group 16 element in the same period. The “pull” of a more electronegative element weakens the bond with hydrogen, allowing it to be more easily released into solution.

Since S is in Group 16 and I is Group 17, H_2S is likely to be less acidic than HI, and this is reinforced by the fact that S is in a higher position in its group than I is. The answer to question 2 is therefore **E**.

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3. The best way of tackling this question is to start with the name of the compound, ammonium metavanadate, which tells you that you have a compound containing ammonium ions and metavanadate ions (even though the term "metavanadate" is a trivial name, which may not mean much to you). You can therefore write the formula as $(NH_4^+)(VO_3^-)$, and, if you wish, you can forget about the ammonium ion, and simply concentrate on the metavanadate ion in order to work out the oxidation number of vanadium.

Now it is simply a question of applying the rules for finding oxidation numbers (given at the end of the solutions to the 2001 NHSCE). The rules that are relevant to this question are:

- *In any substance, the more electronegative atom has the negative oxidation number, and the less electronegative atom(s) has the positive oxidation number. (Remember that the elements in simple formulae are usually written in order of increasing electronegativity.)*

  Here vanadium has the positive oxidation number.

- *The oxidation number of oxygen is always –2 (except in peroxides when it is –1, and in* OF_2 *when it is +2).*

  Peroxides and OF_2 do not apply here. We have three "regular" oxygens in the metavanadate ion so they contribute 3 x –2 = –6.

- *In ions, the algebraic sum of the oxidation numbers equals the charge on the ion.*

  Here the charge on the ion is –1. Thus vanadium must have an oxidation number of +5.
  (Check: +5 – 6 = –1, the overall charge on the ion.)

The answer to this question is therefore **D**.

Note that, because the oxidation state of vanadium in the anion is 5, the systematic (IUPAC) name for ammonium metavanadate is ammonium vanadate(V). Note also that +5 is the maximum oxidation number for vanadium, which is in Group 5 (new IUPAC system) or Group 5A (old IUPAC system) of the periodic table[1].

You can work out the oxidation number of nitrogen in the ammonium ion using a similar method, but here you should note that the formula of the ion is generally written with the more electronegative element, nitrogen, first, thus (NH_4^+). Now you need to apply the rule:

- *The oxidation number of hydrogen in all its compounds, except metal hydrides, is +1. (In metal hydrides it is –1.)*

  We are not looking at a metal hydride here, so we are looking at four "regular" hydrogens in the ion, which contribute 4 x +1 = +4.

  Then, as before, we apply

- *In ions, the algebraic sum of the oxidation numbers equals the charge on the ion.*

  Here the charge on the ion is +1. Thus the nitrogen must have an oxidation number of –3. (Check: –3 + 4 = +1, the overall charge on the ion.)

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[1] Note that there has been considerable confusion about naming the groups of the periodic table over the years. What is now Group 5 in the new IUPAC system used to be Group 5A in the old IUPAC/European system, and Group VB in th old Chemical Abstracts/US system.

Note that I shall be continuing to ask questions that involve a knowledge of oxidation numbers on the exam, even though some teachers have indicated that they may not have taught it by the exam date. It is an important concept and it is on the Pan-Canadian protocol. If you feel that you need more practice exercises these can be found in most Canadian textbooks.

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4. I thought that this was the easiest question on the exam, and, from the scripts I saw, most students found it so. Like the beginnings of questions 1 and 3 last in year's exam you need to start by calculating the amount of substance n, using:

$n = m/M$ Where n is the amount of substance (chemical amount) in mol
m is the mass (usually in g)
M is the molar mass (usually in $g{\cdot}mol^{-1}$)

You are given M_r for $CuSO_4{\cdot}5H_2O = 249.7$. M_r stands for ***relative*** molar mass, which is the mass of one mole relative to one-twelfth the mass of one mole of carbon-12 atoms. As it is calculated from one mass divided by another it has **no units**. However, you need units for the molar mass value that you use in the above formula, or your chemical amount will not come out in the correct units (moles). This is no problem since the two values are numerically the same, i.e. M for $CuSO_4{\cdot}5H_2O = 249.7$ $\mathbf{g{\cdot}mol^{-1}}$. Thus:

The chemical amount of $CuSO_4{\cdot}5H_2O$ dissolved = 62.425 g/249.7 $g{\cdot}mol^{-1}$ = 0.2500 mol.

Note that each mole of $CuSO_4{\cdot}5H_2O$ contains one mole of $CuSO_4$, and that, once the solid is dissolved, the water of crystallization simply joins the water in the solution, so that the solution contains 0.2500 mol of $CuSO_4$. This amount is assumed to be evenly distributed throughout the solution. This is initially contained in a 250.00 mL of solution, but an aliquot of only 25.00 mL is taken, so that only

0.2500 mol x 25.00 mL/250.00 mL = 0.02500 mol are taken.

The answer is therefore **C**. Incorrect answers involve calculation errors, or assume that M_r must be that of $CuSO_4$ rather than the one that was given for $CuSO_4{\cdot}5H_2O$.

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5. This is another question on redox, which students may only just be beginning to study at the time of the exam. It does not, however, require an in-depth knowledge of the topic, and can be done whether you have started by learning electrolysis or electrochemical cells first. In either kind of cell it is important to know the following two rules:

1) **OIL RIG** i.e. **O**xidation **I**s **L**oss (of electrons) and **R**eduction **I**s **G**ain

2) **O**xidation takes place at the **A**node and **R**eduction takes place at the **C**athode
(One way of remembering this is to think of O for Oxidation and A for Anode as being vowels, and R for reduction and C for Cathode as being consonants.)

Knowing the second rule means that you can immediately eliminate answers C and E, which state that reduction is taking place at the anode.

The next thing to work out is which electrode is positive and which is negative in the two different kinds of cell. If you consider an electrochemical cell (i.e. one in which a chemical reaction takes place spontaneously, giving out energy) then the oxidation reaction taking place at the anode will produce electrons, making the anode negative. This does not correspond to any of the keys: furthermore answer D can be eliminated because it has the anode of an electrochemical cell being positive.

In an electrolytic cell, electrons are pushed round the circuit by a (direct current) power source in such a way as to force a reaction to occur that would not normally happen spontaneously. The anode is forced to be positive and this attracts the negative ions (anions) in the electrolyte. The negative ions are forced to give up their electrons, i.e. they are oxidized at the anode. The correct answer is therefore **A**.

In a nutshell we can say that:

Oxidation occurs at the anode in both electrochemical and electrolytic cells: the difference is that in electrochemical cells it is spontaneous and in electrolytic cells it is not.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAM 2002 continued

6. The Pan-Canadian protocol is not very clear about the depth to which organic chemistry should be studied at high school, and different provinces appear to have interpreted this aspect of the protocol in different ways. It is, however, quite clear that students should be able to recognize some of the more common functional groups.

This question requires students to recognize an alcohol group. This can be defined as a hydroxy (-O-H) group that is attached to a carbon in an alkyl group of an organic compound. Note that if the carbon to which the hydroxy group is attached is part of an aromatic ring then it behaves differently, and the compound is called a phenol, however a hydroxy group that is on an alkyl chain coming off a ring is an alcohol. Thus CH_3OH is an alcohol and C_6H_5OH is a phenol, but $C_6H_5CH_2OH$ is an alcohol. None of the compounds shown in the this question has a C_6H_5- group in it, so all you need to look out for is the functional group:

Consider each of the keys in turn:

A. CH_3CHO contains the -CHO group, which shows that it is an aldehyde. It is, in fact, ethanal (the trivial - or common - name for which is acetaldehyde).

B. C_2H_5COOH contains the -COOH group (sometimes written as -CO_2H), which shows that it is a carboxylic acid. It is, in fact, propanoic acid (previously known as propionic acid).

C. $(CH_3)_2O$ can also be written as CH_3-O-CH_3, which makes it clearer to see that it has -O- as a functional group. This is the ether group. The name of this compound is methoxymethane (previously known as dimethyl ether).

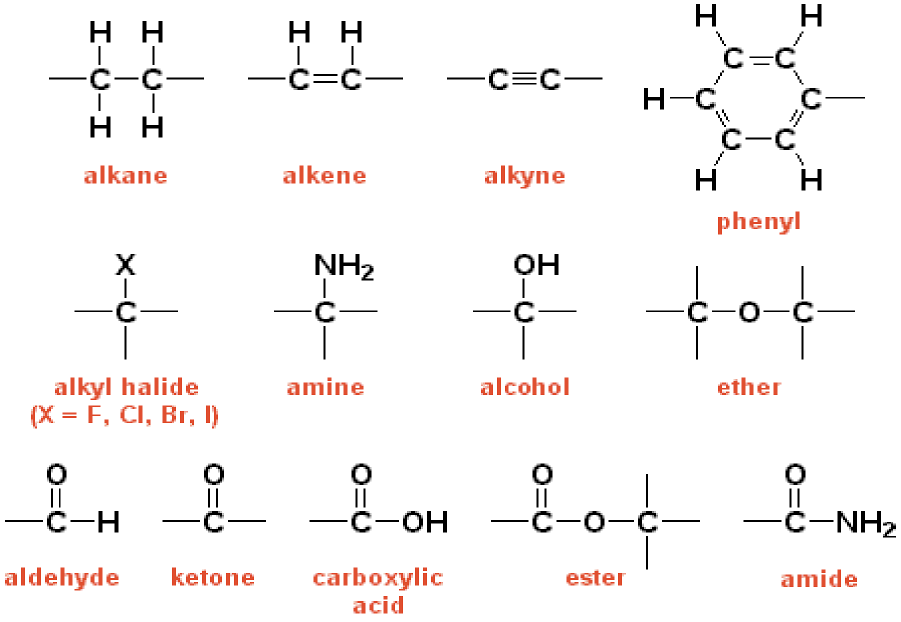
Note that, for every ether there is an alcohol that is isomeric with it. These kind of isomers are compounds that have the same molecular formulae but different structural formulae or “connectivity”. These isomers are called **constitutional isomers** (their former name was structural isomers). The molecular formula of $(CH_3)_2O$ is C_2H_6O, and the alcohol with this molecular formula is C_2H_5OH. (The formula CH_3-O-CH_3 is an alternative structural formula for the ether, which shows the way the atoms are connected somewhat better than the condensed version, $(CH_3)_2O$.) As you can see, molecular formulae are of very limited use in organic chemistry, as they tell you so little about the properites of compounds.

D. $(CH_3)_2CO$ can also be written as CH_3-CO-CH_3, which shows the -CO- or ketone functional group. The name of the compound is propanone (common name: acetone).

Note that ketones and aldehydes both contain the >C=O group, but that in a ketone the carbon of the carbonyl group is attached to two alkyl (or aryl) groups, whereas the carbon of the carbonyl group in an aldehyde is attached to one alkyl group and one hydrogen (-CHO). Many ketones have an isomer that is an aldehyde, thus $(CH_3)_2CO$ has an isomer that is C_2H_5CHO (they both have the molecular formula C_3H_6O).

E. This final key is the correct one. $(CH_3)_3COH$ has the hydroxy (-OH) group on a tetrahedral (sp^3-hybridized) carbon atom, which means it is an alcohol. In fact the “key” carbon is connected to three alkyl groups (three -CH_3 groups here), which makes it a ***tertiary*** alcohol. If it were connected to two alkyl groups (and one hydrogen) it would be a ***secondary*** alcohol, and if it were connected to just one alkyl group (and two hydrogens) it would be a ***primary*** alcohol.

Some common functional groups that it would be useful for you to know are given below:

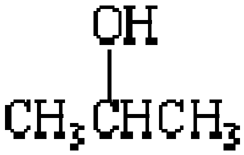


The difference between primary (p), secondary (2^o) and tertiary alcohols (3^o)are shown in the examples given below:

CH_3CH_2OH

p

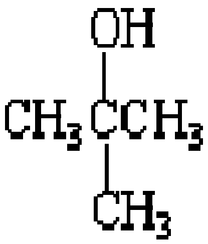
Ethanol



$CH_3CH(OH)CH_3$

2^o

Propan-2-ol



$CH_3C(OH)(CH_3)CH_3$

3^o

2-methylpropan-2-ol

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7. This is like last year's Question 16, but it asks for a conjugate base rather than a conjugate acid. You need the definitions:

The Brønsted-Lowry definition of an acid is a substance that can donate a proton: a base is a substance that accepts a proton. If an acid-base reaction is considered to be an equilibrium, system then a generalized equation can be written, thus:

$$HA + B^- \rightarrow HB + A^-$$

Acid 1 + Base 2   Acid 2 + Base 1

Base 1 is called the conjugate base of Acid 1, because it can be converted back to Acid 1 by the addition of a proton (H^+). Acid 2 is called the conjugate acid of Base 2, because it can be converted back to Base 2 by the removal of a proton (H^+).

HPO_4^{2-} (the hydrogen phosphate ion) is an **amphiprotic** substance, which means that it can act as either a

Brønsted-Lowry acid or a Brønsted-Lowry base. When it acts as an acid it gives away a proton to become PO_4^{3-} (the phosphate ion), which is its conjugate base, so the correct key is **D**.

When HPO_4^{2-} acts as a base it gains a proton and becomes the $H_2PO_4^-$ (dihyrogen phosphate) ion, which is the conjugate acid of HPO_4^{2-} . Note that the dihyrogen phosphate ion is itself amphiprotic. You may like to try writing out its conjugate acid and base forms.

Note also that polyprotic acids all form amphiprotic anions, but phosphoric acid is somewhat unusual being triprotic, so that it forms two amphiprotic anions. For example, carbonic acid, H_2CO_3 is a diprotic acid, and forms the amphiprotic hydrogen carbonate anion HCO_3^- (see NHSCE 2000, Question 22). This ion is very important in controlling the pH of blood, i.e. it is a buffer (as are most of these amphiprotic anions).

8. The octet rule is often found in elementary textbooks, which use it to help explain how bonding works in simple compounds. Note that bonding is extensively covered in the answer to Question 9 in the NHSCE 2001.[1] Suffice it to say here that ionic bonding can be expected between a metal and a non-metal, whilst covalent bonding occurs between a non-metal and a non-metal. (Metallic bonding occurs between a metal and a metal.) However, because the difference between metals and non-metals are not clear-cut, it needs to be understood that there is considerable blurring in the distinctions between the three main types of bonding.

The **octet rule** states that, when atoms are involved in bonding, they tend to be so in such a way as to achieve an octet of electrons (i.e. eight electrons) in their outermost (valency) shell. This octet corresponds to the stable electron arrangement found in the noble gases. Thus a sodium atom tends to lose an electron to form a Na^+ ion, which has the same electronic configuration as a neon atom. On the other hand a sulfur atom tends to gain two electrons to become an S^{2-} ion, which has the same electronic configuration as an argon atom. Covalent bonding can also help an atom to achieve an octet configuration by allowing the atom to share electrons with another atom. For example, in methane (CH_4), the carbon atom, which normally has only four electrons, can share the electrons from four hydrogen atoms to achieve an octet. In this particular compound, however, it can be seen that the octet rule breaks down, because each of the hydrogen atoms only achieves a total of two electrons (a duet) in their shell. This duet is nevertheless stable, because it is has the same electronic configuration as the helium atom.

Many compounds do not obey the octet rule and this question focusses on several different examples of them. Let us consider each of these in turn:

A. NaH (sodium hydride). Sodium is a metal and hydrogen is a non-metal, so this is an ionic compound comprising Na^+ ions and H^- ions. The sodium ion has an octet of elections (see above) but the hydrogen ion has only a duet, so it does not obey the octet rule. (If you are surprised that hydrogen forms negative ions, you should read the answer to NHSCE 2001, Question 10, which discusses some of the different kinds of bonding that hydrogen can be involved in.)

B. BF_3 (boron trifluoride). This is a covalent compound. Boron is classified as a non-metal although it is very close to the zig-zag line which is often shown on periodic tables as the divide between the metals and non-metals. It is in Group 3, and, as it has very small atoms, the valency shell is quite close to the positive nucleus. It is therefore very difficult for all three valency electrons to be removed from a boron atom to form a B^{3+} ion, and it would be even more difficult to create a B^{5-} ion, as this would involve pushing five extra electrons very close to each other. A fluorine atom can get an octet by gaining or by sharing an electron, so the electrons from three fluorine atoms can share their electrons with the three electrons of boron, but that only gives the boron a total of six electrons in its valency shell. Boron trifluoride does not, therefore, obey the octet rule.

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[1] Any student who had studied the solutions to the 2001 exam should have found the essay question on bonding, which was in Part B of the 2002 exam, very easy! It is the examiner's intention that these solutions should help with future essay questions, as well as multiple choice questions.

Note that BF_3 combines very easily with other species if these have a lone pair of electrons that can be used to complete boron's octet. In other words, BF_3 , is a Lewis acid, and will combine with species such as H_2O or alcohols, which behave as Lewis bases. The addition compounds so formed have a dative covalent (coordinate) bond between the Lewis base and BF_3 .

C. PbI_2 (lead(II) iodide). This is a compound between a metal and a non-metal, and it is ionic. An iodine atom gains an electron when it becomes an iodide ion, and thus obeys the octet rule. A lead atom loses two electrons when it becomes Pb^{2+} , which has the electron configuration of $[Xe]4f^{14}5d^{10}6s^2$ (the atom has lost its $6p^2$ electrons). This is not a noble gas structure (which requires a full p orbital i.e. a p^6 configuration) but it does have a kind of stability which is associated with a complete d orbital (d^{10}) and is known as a "quasi noble gas" configuration. There is also a complete s orbital, containing two electrons, which are sometimes called an "inert pair" because they are so stable.

Note that lead, which is in Group 14 (new IUPAC system)[2], has a valency of 4 as well as 2. In its 4-valent state lead usually forms predominately covalent compounds, in which octet stability is achieved by sharing electrons. This is because it is extremely difficult for any atom to lose four electrons - even an atom that is as big as lead.

D. $TiCl_4$ (usually called titanium tetrachloride). This is a metal/non-metal compound so ionic bonding might be expected, however we have just stated that it is very difficult for an atom to lose four electrons, and, in fact it displays covalent properties. There is no problem with the chlorine atoms, each of which achieves an octet whether it shares an electron with another atom or forms a Cl^- ion. If the titanium loses four electrons it would become the Ti^{4+} ion, which has the same electronic configuration as argon, i.e. it obeys the octet rule. If the titanium is involved in covalent bonding, sharing 4 electrons with 4 electrons from other atoms, then it would have 8 electrons in its outer shell. It looks as though the correct answer could be D, but you should check out E to be sure.

E. XeO_3 (xenon trioxide). Xenon is a noble gas, and noble gases were formerly known as "inert" gases because it was thought that they never formed compounds. The fact that it is a noble gas, which has a stable octet to begin with, is an indication that it must break the octet rule if it is to form any kind of compound.

The best answer to this question is therefore **D**.

Note that a number of xenon compounds have been isolated, however, as well as some less stable krypton and radon species. (The problem with radon compounds lies more in the instability of the nucleus than in the electronic stability.) All the xenon compounds known to date involve covalent bonds with oxygen or fluorine, which are sufficiently electronegative to pull electrons away from the xenon atom, thus relieving the atom from the stress of having excess electrons around it. In xenon trioxide each oxygen atom achieves stability by sharing two xenon electrons, which together with their own 6 electrons gives them octets like neon. The xenon, however, has to accommodate a total of 6 electrons from the 3 oxygen atoms, which means it has far more than an octet.

9. This question is very similar to Question 18 in 2000 and Question 18 in 2001, in that they all relate to an industrial process that is based on an equilibrium reaction. However in this year's question you are being asked to consider the **rate** of the reaction rather than the yield. The rate of a reaction can be increased by (i) increasing the temperature, (ii) increasing the concentration of a reactant (or its partial pressure if the reactant is a gas), (iii) using a catalyst and/or (iv) increasing the surface area of a reactant or catalyst if the system is heterogenous. Here the system is heterogeneous, in that the catalyst is a solid whilst the reactants and product are all gases, but changing the surface area of the catalyst is not one of the options offered.

For the next step you need to consider the equilibrium in terms of Le Châtelier's principle. The reaction is:

$$2\ SO_2(g) + O_2(g) <\!\!===\!\!> 2\ SO_3(g);\ \bullet\, H = -\ 197\ \text{kJ·mol}^{-1}$$

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[2] What is now Group 14 in the new IUPAC system used to be Group 4B in the old IUPAC/European system, and Group IVA in the old Chemical Abstracts/US system.

Which, since it has a negative delta H value, can be written with heat shown as a product, thus:

$$2\ SO_2(g) + O_2(g) <\!\!==\!\!> 2\ SO_3(g) + \text{heat}$$

All the options could, in fact, increase the rate, although if the overall pressure of the mixture was increased (as in C) by increasing the partial pressure of the product, (unlikely in an industrial process) then it would reduce the amount of product produced. Heating the mixture will "swing" the reaction back towards the reactants and reduce the amount of product for sure, so the best answer is **A**.

Note that in an industrial process the rate is very important. The reaction must proceed quickly enough for the product to be produced in a reasonable amount of time, but it must not go out of control! Industrial processes are almost always run continuously, in a steady state, rather than being allowed to go to equilibrium. This helps to maintain a good rate - remember that the rate of a reaction slows down as equilibrium is approached, until equilibrium is reached when the rates of the forward and reverse reactions become equal.

In practice the contact process is run at a moderately high temperature (about 450°C), so that a good rate is maintained, even though this reduces the yield somewhat. Vanadium pentoxide (V_2O_5) is used as a catalyst and the amount of oxygen fed into the reactor is increased relative to the sulfur dioxide in order to optimize the amount of sulfur dioxide converted into sulfur trioxide. (It is usual to use an excess of the less expensive reactant in this way.) The overall pressure used is only slightly above atmospheric pressure - just sufficient to push the reactants through the system - because the product yield is easily maintained at 97% or more under these conditions, so the expense of high pressure equipment is not justified.

If you consider this question interesting, then you might like to consider becoming a chemical engineer and running a chemical plant like this. (There are, however, a lot of other career opportunities for chemical engineers other than producing chemicals.)

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10. This question requires you to know that ionic compounds conduct electricity in the liquid state, but not in the solid state. This is because, in ionic compounds, electric current is maintained in a circuit by means of reactions occurring at the electrodes. Even if the current is alternating rather than direct, ions will be attracted to the electrodes, tending to give up electrons or attract them. The ions, however, must be able to move to and from the electrodes in order for this to happen, and the ions can only move in the liquid state (or in solution). The ions are still there in the solid state, but they cannot move around (they can only "jiggle").

You also need to know that, even though you may have learned that "like dissolves like", not all ionic compounds dissolve in water. This is because, in some ionic compounds, the bonds holding the solid together are considerably stronger than any forces of attraction between the ions and the water molecules [3].

Now let us consider each of the keys in turn.

A. Ca. Calcium is a metal, and metals and alloys (which are both held together by metallic bonding) conduct electricity in the solid state as well as the liquid state, so the key cannot be A. A second reason that the answer cannot be A is that calcium dissolves in water, even though it is a metal, because it reacts with water, thus:

$$2Ca(s) + 2H_2O(l) \rightarrow 2Ca(OH)_2(aq) + H_2(g)$$

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[3] Water molecules are polar, that is to say they have one end (the oxygen end) that is slightly negative, and the other end (the hydrogens) that are slightly positive. Neither the positive nor the negative charges amount to a whole electron's worth of charge - water is a molecule, not an ionic compound after all - but the partial charges are enough to make us consider water to be "like" an ionic compound. And the partial negative charge will attract positive ions, whilst the partial positive charge will attract negative ions to some extent. It is these forces of attraction that tend to pull the solid apart when it dissolves.

(Calcium is a fairly reactive metal, and it is significantly more reactive than hydrogen, so it can displace hydrogen from water [4]. However, unlike very reactive metals such as sodium and potassium, the reaction is not violent at room temperature.)

Note that the aqueous solution of calcium hydroxide formed contains Ca^{2+} ions and OH^{-} ions, and these allow the solution to conduct electricity.

B. Cu. Copper is a metal, which means that it can conduct electricity in both the liquid and the solid state, so the key cannot be B. It should be noted, however, that copper does not dissolve in water because it is less reactive than hydrogen. (The green colour that copper becomes when it is exposes to the atmosphere for a long period of time - as in copper roofs - is due to a more complicated redox reaction than simple displacement of hydrogen.)

C. CuI. Copper(I) iodide is a metal/non-metal compound, and is therefore ionic. It therefore conducts electricity in the liquid state, but not in the solid state. Do you know whether it is water-soluble or not? If you don't know for certain, continue to consider Keys D and E.

D. Cl_3CCOOH. Even if you cannot identify this as trichloroethanoic acid, you should at least be able to tell that it is a covalent compound, because it contains only non-metal atoms. So it cannot be ionic, and it cannot conduct electricity in the solid or liquid state. (It is, however, an acid - quite a strong one in fact - and it dissolves in water by reacting and forming ions in solution. So it does conduct electricity in aqueous solution.)

E. $C_6H_{12}O_6$. This is glucose (or another hexose). Again it contains only non-metal atoms so you can see it is a covalent compound, and it does not conduct electricity in either the solid or liquid state. Its molecules are somewhat polar, so it does dissolve in water (it does not ionize, however, and therefore it does not conduct electricity in aqueous solution).

---

[4] Note that you are expected to have some idea of the reactivity (activity) series of the metals even without being given a list of redox potentials. The list (with the more reactive metals first) is usually given as:

Potassium, sodium, calcium, magnesium, aluminium, zinc, iron, lead, copper, silver, gold.

The reactivity series relates the order of the ease with which the metals can be obtained from their oxides, and may be slightly different from the order of the redox potentials, which refer to obtaining the metals from solutions of their salts.

Hydrogen is often included in the reactivity series, where it comes between lead and copper, because it can be displaced from water, steam or hydrochloric acid, by metals that are more reactive than it. Potassium easily reacts with water, but calcium only does so slowly. These metals react violently with steam or acids. Lead will only give hydrogen on boiling with hydrochloric acid, and, although it reacts with water containing oxygen or with oxidizing acids such as HNO_3 or H_2SO_4, it does not give hydrogen as a product in these reactions. In fact this is the only reaction that lead does that qualifies as being more reactive than hydrogen, as lead oxides can be reduced by hydrogen (like oxides of unreactive metals)!

The only possible answer to this question is **C**, because it is the only option given that fulfils the conductivity requirements of the question. CuI **is** water insoluble, as are all simple salts of copper(I) [5].

This information in this question was originally written in tabular form, as it might have appeared as data in an experiment. You are not told what the substances are, only the properties. The group of students who tried this out for me did very poorly on this question in the tabular format, so it was changed. How would you have done?

Original question

Some properties of five pure substances are given in the table below. They are all solids at room temperature and pressure. Which is most likely to have ionic bonding?

	Electrical conductivity		
		Liquid	When dissolved in water
A	Conducts	Conducts	Conducts
B	Conducts	Conducts	Does not dissolve
C	Does not conduct	Conducts	Does not dissolve
D	Does not conduct	Does not conduct	Conducts
E	Does not conduct	Does not conduct	Does not conduct

A, B, C, D and E could be exactly the same substances as in the modified question, so the answer is still **C**.

Note that in future exams we are proposing to improve the appearance of the question papers, as well as increasing the relevance of the questions, by including more material in the form of data tables, diagrams, graphs etc.

---

[5] The +1 oxidation state of copper is less common than the +2 state, and most copper(I) compounds exist only in the solid state. This is because copper(I) ions disproportionate in aqueous solution, thus:

$$2Cu^{+}(aq) \rightarrow Cu^{0}(s) + Cu^{2+}(aq)$$

Disproportionation is a reaction in which a species undergoes simultaneous oxidation and reduction, one atom (or ion) being oxidised while another atom (or ion) is reduced. If a copper (I) compound begins to dissolve then Cu^{+} is oxidised to Cu^{2+} while another is reduced to Cu^{0} (elemental copper). Note, however, that it is possible to stabilise Cu^{+} ions in solution if they are complexed, for example they are, for a little while, stabilised by citrate ions in a Benedict's test reaction or tartrate ions in a Fehling's test reaction.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAM 2002 continued

11. Here is a good example of a reaction that shows that zinc is more reactive than hydrogen, because it displaces hydrogen from hydrochloric acid, thus:

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

As this experiment can be performed in various ways, with either excess zinc or excess acid, we should really consider which of the reactants is the limiting reagent[1], which means that we have to calculate the chemical amount of each reactant.

Let us first consider the zinc:

Using:

$n = m/M$ Where n is the amount of substance (chemical amount) in mol
m is the mass (usually in g)
M is the molar mass (usually in $g{\cdot}mol^{-1}$)

The chemical amount of zinc is therefore = $5.0\ g / 65.4\ g{\cdot}mol^{-1} = 0.0765$ mol

Now for hydrochloric acid:

Using:

$n = cV$ Where n is the chemical amount in mol
c is the concentration (usually in $mol{\cdot}L^{-1}$), and
V is the volume of solution (usually in L)
and remembering that there are 1000 mL in one L.

The chemical amount of hydrochloric acid is therefore

$$= 1.0\ mol{\cdot}L^{-1} \times 100\ mL/1000\ mL{\cdot}L^{-1} = 0.10\ mol$$

Bearing in mind that, according to the equation, 2 moles of HCl are required to react with one mole of Zn, it can be seen that 2 x 0.0765 mol = 0.154 mol of HCl would be required to react with all the zinc, so that in this experiment zinc is in excess and hydrochloric acid is the limiting reagent.

It is also important to realise that the essential reaction is between the zinc and the hydrogen ions, with chloride ions being "spectators". This means that the equation can be considered to be:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Note that this does not change the fact that zinc is in excess (because each mole of HCl gives a mole of H^+).

Now that you understand the system, you can consider each of the factors that might alter the rate of reaction (or not):

---

[1] It should be noted, however, that, in this particular question, the limiting reagent does not really affect the logic of determining the answer.

A. Warming the HCl before adding the zinc. Increasing temperature increases the rate of reaction, so the key cannot be A.

B. Using zinc powder instead of zinc granules. Powder particles are smaller than granules, so they will have a larger surface area for a given mass. The reaction between zinc metal and hydrogen ions takes place at the surface of the zinc, so that using powder instead of granules will increase the rate of reaction. Note that the assumption here is that **all** the surface of the zinc will be in contact with the acid: I have seen this reaction performed with zinc granules that are sticking up out of the acid solution, but this just slows the reaction down even more in comparison with the powder. (It is bad experimental practice, of course, because not all the surface of the zinc comes in contact with the acid at the beginning of the reaction.)

C. Using 50 mL of 2.0 M HCl, means that exactly the same chemical amount of acid is used but the concentration of acid is greater. This means that, providing there is sufficient acid to cover the zinc, more hydrogen ions will be in contact with the zinc at the beginning of the reaction, so that the rate of reaction will be greater than with 1.0 M acid.

D. Using 200 mL of 1.0 M HCl means that there are now 0.2 mol of acid available, and zinc is now the limiting reagent. However, assuming that the zinc is covered in both cases, then the **initial** rate of reaction will be the same, although the reaction will take longer to finish completely.

E. Using 100 mL of 1.0 M H_2SO_4 instead of 1.0 M HCl means that the concentration of hydrogen ions is doubled (because there are **two** moles of hydrogen ions released from each mole of H_2SO_4). This significantly increases the rate of reaction.

The best answer to this question is therefore **D**, because, in the determination of rates, it is the rate of reaction at a particular time (normally the initial rate) that is important. In D, the length of time for the reaction to finish completely has changed simply because the reacting amounts have changed. The slope of the concentration/time graphs (from which rates are determined) will be the same for any particular concentration of acid, gradually decreasing until one or other of the reagents is depleted, when the rate becomes zero. (Try drawing sketches of HCl versus time graphs on the same axes if you can't visualise them in your head. The two graphs are parallel but meet the concentration = 0 axis at different times.)

---

12. This question is about the equilibrium reaction:

$$CaCO_3(s) \Longleftrightarrow CaO(s) + CO_2(g)$$

The equilibrium constant, K_c for this reaction could be written as:

$$\frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

where the square brackets [ ] indicate the **equilibrium concentration** (never the intial concentration) of the substance shown between the brackets.

The concentration of a pure solid or a pure liquid, however, equals its density, which does not vary. Thus, providing that there is some of the pure solid (or liquid) present, and the temperature is constant, then a modified equilibrium constant can be written:

$$K_{c1} = [CO_2(g)]$$

This indicates that the equilibrium constant depends on the concentration of carbon dioxide at equilibrium, and since the concentration is equal to the amount divided by the volume, and the system is enclosed, then the equilibrium constant depends on the equilibrium amount of $CO_2(g)$. So the correct key is **C**.

Note that similar considerations apply to equilibrium constants that are expressed in terms of partial pressures (K_p values), so that it can be shown that this equilibrium depends on the partial pressure of $CO_2(g)$ in the enclosed system.

Also note that this is the reaction used in the manufacture of quick lime (CaO) from limestone ($CaCO_3$). The limestone is heated in a kiln, which, however, is not an enclosed system. The carbon dioxide is allowed to escape from the kiln, so that the reaction is never allowed to achieve equilibrium, instead it continues until all the limestone has been converted to quick lime. Simple lime kilns use a batch process, in which the kiln has to be cooled down and the quick lime raked out before the kiln is reacharged. This process has been used since Roman times, and is still used today for the production of small amounts of quicklime. On a large scale, however, the limestone is fed into the top of the kiln, and the quicklime removed from the bottom, in a continuous process.

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13. The Pan-Canadian protocol indicates that isomers should be on the high school chemistry curriculum, but it does not specify which ones. I intend to include consititutional iomers - both chain-branch and positional - and geometric isomers - both diastereomers (cis/trans isomers) and enantiomers (also called mirror image or optical isomers).

A pair of enantiomers are mirror images in the same way as a left hand and a right hand are. In organic chemistry the essential requirement for the existence of enantiomers is that the molecule contains a carbon atom connected to four different groups. This is difficult to draw in two dimensions, but can easily be seen if you make up molecular models. The carbon atom that has four different groups on it is called the stereocentre (or asymmetric carbon atom) and it is often indicated in formulae by an asterisk.[2]

Let us consider each of the keys in turn (note that we shall be counting carbon atoms from left to right):

A. H_2NCH_2COOH. This is aminoethanoic acid (also known as glycine). The first carbon atom is attached to one amino group, two hydrogen atoms and one carbon, so it is not asymmetric. The second carbon (part of a carbonyl group) is attached to one carbon, one oxygen in a double bond and one oxygen in a hydroxyl group, so it is not asymmetric. Note that any time a carbon is multiply bonded to another atom it is precluded from being asymmetric.

B. $H_2NCH(CH_3)COOH$. This is 2-aminopropanoic acid (also known as alanine). The first carbon is attached to one amino group, one hydrogen atom, one methyl group and one carboxyl group, i.e. it is attached to four different things, so it is asymmetric and can exist as enantiomers. The compound may be written as $H_2NC^*H(CH_3)COOH$, indicating the stereocentre carbon with an asterisk. The answer to this question is therefore **B**.

You may like to check for yourself that the other compounds given are not asymmetric. They are:

C. $H_2NCH_2CH_2COOH$ (3-amino propanoic acid)

D. $H_2NCH_2COOCH_3$ (the methyl ester of aminoethanoic acid)

E. $(CH_3)_2CHCOOH$ (2-methyl propanoic acid)

---

[2] The stereocentre is sometimes referred to as the "chiral carbon" or "chiral centre", but these terms are confusing, because chirality is a property of a molecule. A stereocentre is not essential for the existence of enantiomers, but it is the "usual" situation. Enantiomers can exist where no stereocentre is present (e.g. in compounds with restricted rotation around a sigma bond due to bulky substituent groups).

14. The bond angle in a molecule is the angle formed between three atoms that are connected to each other in a line with one of the atoms between the other two. The angle occurs at the middle atom of the three.

In simple molecules, such as the ones given in this question, it is usually fairly easy to establish which is the central atom. Hydrogen will always be an outer atom, because it only has one valency electron with which to bond. The central atom is generally the more electropositive of the atoms, with more electronegative elements, such as oxygen, at the "ends" of the angle.[3] Sometimes oxygen (which forms two bonds) will come between a central atom and hydrogen (as in H_2SO_4 and other oxo-acids).

Once you have established which atom is the central atom, you then need to draw a Lewis "dot-and-cross" diagram showing the valency electrons of the atoms in the molecule - particularly those around the central atom. Bear in mind that the electrons may be bonding pairs or non-bonding (lone) pairs, and, where they are bonded they may be involved in single or double bonds or in coordinate bonds (formerly called dative covalent bonds). This last kind of bond is where both the electrons in the bond are considered to have come from the same atom.[4]

Now let us consider the bonding in each of the options that you are given. If you draw the Lewis diagrams for these it will help you to understand what is happening. You can then use VSEPR theory to work out the shape[5].

A. CH_4 This is methane. The carbon (Group 14) is the central atom in the molecule, and its 4 valency electrons are each shared with one electron from each of the hydrogen atoms. The 4 pairs of electrons are arranged around the carbon in the classic tetrahedral shape, so the H-C-H bond angle is the tetrahedral bond angle of 109.5^o.

B. NH_3 This is ammonia. The nitrogen (Group 15) is the central atom in the molecule, and its 5 valency electrons are arranged in such a way that three are shared each with one electron from each of the hydrogen atoms, and the remaining two are a lone pair. This gives four pairs of electrons around the nitrogen in what is essentially a tetrahedral arrangement, however there is some distortion of the shape due to the fact that the lone pair repels the bonding pairs more strongly than bonding pairs repel each other. This means that the H-N-H angle is slightly less than the ideal tetrahedral angle of 109.5^o (in fact the angle in ammonia is about 107^o).

Note that the shape of the molecule is no longer described as tetrahedral when one (or more) of the four electron pair positions is taken by a lone pair. The shape of a molecule is given by the positions of the outermost atoms, so that the ammonia molecule is, in fact, a "flattened" tetrahedral shape known as trigonal pyramidal.

C. H_2O is water of course. Oxygen (Group 16) is the central atom here, and its 6 electrons are arranged in such a way that two of its electrons are each shared with an electron from each ot the two hydrogens, and there are two lone pairs. This gives four pairs of electrons around the oxygen in what is essentially a tetrahedral arrangement, however there is considerable distortion of the shape since two lone pairs repel the bonding pairs even more than a single lone pair. This means that the H-O-H angle is 104.5^o (i.e. considerably less than the tetrahedral angle). The shape of this molecule is just known as bent or V-shaped.

---

[3] Bear in mind, however, that some electronegative elements (e.g. N, P, S, Cl, Br and I) have multiple oxidation states, and that, when they are in higher oxidation states, they are more likely to be "central" atoms.

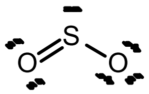
[4] Dot-and-cross diagrams are a useful way of keeping track of the numbers of electrons on particular atoms, and how they might be distributed within a bonded species. You should, however, be aware that, once a covalent bond has been formed, there is no way of distiguishing between the electrons in the bonding pair, or from where those electrons might have originated. In particular, in a coordinate bond, there is no way of telling which atom has "donated" the bonding pair - both electrons in the bond behave in a similar manner.

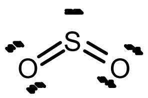
[5] VSEPR stands for Valence Shell Electron Pair Repulsion. VSEPR is a bonding model that is used for predicting geometry. It was developed by Canadian chemist, Ronald Gillespie, and states that **pairs of electrons that surround the central atom of a molecule repel each other and arrange themselves in space in such a way that they are as far apart as possible.**

D. SO_2 Sulfur dioxide, which is also known as sulfur(IV) oxide. If is important to realise that sulfur is in the +4 oxidation state here (each oxygen is in its customary -2 state), because this tells you that four of the sulfur's valency electrons are involved in bonding.

Sulfur (Group 16) has 6 valency electrons, of which four are involved in bonding. If you apply the octet rule then you need to consider that two of the four bonding electrons are involved in a double bond with one of the oxygens, and the other two electrons form a single (coordinate) bond with the other oxygen atom. This leaves a lone pair of electrons on the sulfur's valency shell, causing the molecule to be bent-shaped.

An alternative way of looking at the bonding in sulfur dioxide is to consider expanding the octet. (This is possible in sulfur because it has empty 3d orbitals into which electrons can go once the 3s and 3p orbitals are full.) Instead of using two of the four valency electrons to form a coordinate bond with the second oxygen they could be used to form another double bond. Each double bond would consist of two electrons that come from the sulfur and two that come from the oxygen. Note that this still allows the oxygen atoms to achieve an octet.





Of the two alternative ways of representing the SO_2 molecule, neither one can really be considered more likely than the other. The molecule can best be considered as a "resonance hybrid" in which the bonds end up by being somewhere between double and single bonds. Experimental data supports this theory as the S-O bond in sulfur dioxide is shorter than S-O bonds in other compounds, and its strength is greater. The molecule is bent with an O-S-O bond angle close to 120^{o}.

E. CO_2 Carbon dioxide. Carbon (Group 14) has four valency electrons, and uses them to form a double bond with each of the oxygens. The two double bonds are furthest apart when they are on opposite sides of the carbon atom, so a linear molecule O=C=O is formed, and the angle is 180^{o}. This is by far the largest of the angles, and so the correct key is **E**.

Note that this question can be solved simply by considering the simple VSEPR model, without the refinement of lone pairs repelling bonding pairs more than bonding pairs repelling each other. Analysis of student results, however, indicated that many students forgot about the lone pairs altogether, and keys C and D were often chosen as answers to this question.

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15. Dipole moments and related issues are discussed in the solutions to Question 11 and 12 of the 2001 NHSCE. Essentially a dipole moment is set up between a positive and a negative charge. If the centre of these charges are at points X and Y, which are a distance d apart, and the size of the charge is q, thus:

← d →
X --------- Y
(+q)   (-q)

then the size of the **dipole moment = d x q** (irrespective of whether the charge is considered to be positive or negative).

In this year's question, the molecules are all diatomic, so that the centre points of the charges can be taken as the centres of the two atoms, and the symmetry of the molecules does not have to be considered. The size of the dipole moment will depend, to a certain extent, on the interatomic distance (d), but to a much greater extent on the electronegativity difference between the two atoms which influences the size of q.

You have not been given any electronegativity values, but you should nevertheless be able to work out relative values for the molecules that are given. All the molecules involve hydrogen, and the first molecule H_2 can only have a dipole moment of zero because the two atoms are the same and so there is no electronegativity difference between them (the covalent bond between the two atoms involves equal sharing of electrons). In all the other molecules hydrogen is combined with a halogen atom, and you should be aware that fluorine has the greatest electronegativity of all atoms (Pauling gave it an electronegativity of 4, and made it the standard from which all his other electronegativity values were calculated). You should also be aware that electronegativities decrease down any particular group of the periodic table, so none of the other halogens can possibly have as high a value as fluorine. Of all the molecules given in this question the one with the greatest dipole moment is HF, and the correct key is therefore **B**.

You may be interested to see the original version of this question, which is given in the answer to Question 16 in the next set of answers to the NHSCE 2002..

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAM 2002 continued

16. This question is like question 11 in the 2000 NHSCE and question 11 of the 2001 NHSCE, and a full discussion of the factors affecting boiling point is given in the answers to the 2001 exam. Essentially a high boiling point is an indication of strong intermolecular forces. In the league of intermolecular forces (given molecules of comparable sizes), hydrogen bonds are usually stronger than permanent dipole-dipole interactions, which, in turn are generally stonger than temporary dipole-dipole interactions. Hydrogen bonding is not applicable here, as it only really occurs in molecules containing nitrogen, oxygen or fluorine (but see question 25 on this year's exam for a noteworthy exception). In the present question we are looking at temporary dipole-dipole interations in the symmetrical molecules (CH_4 and CCl_4), and at permanent dipole-dipole interactions in the other three molecules. At first glance, one of the three molecules with dipole-dipole interactions might be expected to have the strongest intermolecular forces, and therefore the highest boiling point. However, there is another effect that must be considered, and that is the molar mass of the molecules.

Molecules with higher molar masses have more electrons, and so their dipole moments are often higher than those of smaller molecules. This molar mass effect is significant, even where only temporary dipoles are possible, and where molar masses are very different it can mean that molecules with temporary dipole-dipole interactions can have stronger intermolecular forces between them than molecules with permanent dipole-dipole interactions. This is the case here, where the relative molar masses (M_r) are:

A. CH_4, $M_r = 16.0$: B. CH_3Cl, $M_r = 50.5$: C. CH_2Cl_2, $M_r = 84.9$: D. $CHCl_3$, $M_r = 84.9$ E. CCl_4, $M_r = 153.8$

The substance with the strongest intermolecular forces is therefore CCl_4 and the correct key is **E**.

(The boiling points in ^oC are: A. CH_4, -163.9^oC: B. CH_3Cl, -24.1^oC: C. CH_2Cl_2, $+ 40.1^oC$: D. $CHCl_3$, $+ 61.8^oC$: E. CCl_4, $+76.6^oC$)

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17. This question involves being able to predict the products of double displacement reactions (also called double decomposition or metathesis reactions), in which solutions of two ionic compounds are mixed and give a precipitate (or are otherwise removed from the solution). In this type of reaction the anions and cations in the original solutions "swap partners".

There was a howl of protest from teachers over this question because the solubilities of the relevant salts were not given, however I do expect students to know some of the common solubility rules. (Yes, I know that it involves memory work, but we are talking about some very common substances here.) These rules are given overleaf and apply to room temperature.

The Solubility Rules

1. All **nitrates** are soluble in water
2. All the common **chlorides** are soluble, except for those of silver, lead(II) and mercury(I).
3. All the common **sulphates** are soluble, except those of barium and lead. Calcium and silver sulphates are slightly soluble.
4. All common salts of **Group 1 metals** (sodium, potassium etc.) and **ammonium** are soluble.
5. All the common **carbonates** are insoluble, except those of Group 1 metals (sodium, potassium etc.) and ammonium.
6. Group 1 hydroxides are soluble, some of the Group 2 hydroxides are slightly soluble, and all other **metal hydroxides** are insoluble.
7. **Lead nitrate and lead ethanoate** (acetate) are the only common soluble lead salts.

Knowledge of some of the common tests for specific ions could also have helped in this question.

Let us consider each pair of reagents in turn (note that where reactions can occur, the precipitating substances are all sufficiently insoluble as to appear as solids at the concentration given):

A. $HCl + AgNO_3$. These react as follows:

$$HCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + HNO_3(aq)$$

Silver chloride is an insoluble chloride as noted in the solubility rules above. Note that silver nitrate, in the presence of acid (usually nitric acid) is used as a test reagent for chloride ions in solution, the curdled, white precipitate of silver chloride, which darkens in light, being a very clear indication that chloride ions are present in the solution being tested.

B. $NaOH + CuSO_4$. These react as follows:

$$2NaOH(aq) + CuSO_4(aq) \rightarrow Na_2SO_4(aq) + Cu(OH)_2(s)$$

As copper is not in Group 1 or Group 2 of the Periodic Table (it is in Group11), its hydroxide is not water soluble. It forms a characteristic gelatinous (jelly-like) bluish-white precipitate, which, on a warm day, decomposes to give black copper(II) oxide.

C. $CaCl_2 + Na_2CO_3$. These react as follows:

$$CaCl_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaCl(aq)$$

The precipitate of calcium carbonate forms very slowly giving first a colourless gel, which eventually settles to give a powdery white solid. This reaction is not really suitable, therefore, for use as an identification test.

D. $H_2SO_4 + Ba(OH)_2$. These react as follows:

$$H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow BaSO_4(s) + 2H_2O(l)$$

Barium is in Group 2 of the Periodic Table, and its hydroxide is the most soluble hydroxide one in this group, giving a solution about 0.1 $mol{\cdot}L^{-1}$ if it is pure. Barium sulfate is extremely insoluble, and a solution of barium ions (usually as barium chloride in the presence of hydrochloric acid) is used as the standard test for sulphate ions in solution. The precipitate formed is white.

The reaction between sulfuric acid and barium hydroxide solution is often used in demonstrations of conductimetric titrations. At the endpoint of the titration there are virtually no ions in solution (barium ions and sulfate ions being locked in the insoluble lattice of $BaSO_4$, whilst hydrogen ions and hydroxide have reacted to form molecules of water). The lack of ions in the solution means that the conductivity of the solution is virtually zero.

E. $NH_4NO_3 + K_2CrO_4$. These do not react. As all salts of potassium and ammonium ions (and nitrate ions) are water soluble, there is no possible combination of anions and cations that can give a precipitate. The correct answer is therefore **E**. And the only solubility rule that you really needed to know was the one about Group I metals and ammonium salts being soluble. Not so difficult after all!

18. This is quite a long question, because you have to first find the concentration of the benzoic acid in a saturated solution in $mol{\cdot}L^{-1}$ (having been given it as the solubility in $g{\cdot}L^{-1}$), then you have to find the hydrogen ion concentration using the K_a value that you are given, and finally you have to calculate the pH. This is how it goes:

1) Note that converting a value from $g{\cdot}L^{-1}$ to $mol{\cdot}L^{-1}$ is done just as though the conversion is from grams to moles, because we are thinking of the solute being dissolved in one litre of solvent in each case.

We can therefore use: $n = m/M$

Where n is the amount of substance (chemical amount) in mol
m is the mass (usually in g)
M is the molar mass (usually in $g{\cdot}mol^{-1}$)

Then the **concentration** of the benzoic acid in a saturated solution is therefore:

$= 3.4\ g{\cdot}L^{-1} / 122.12\ g{\cdot}mol^{-1}$

$= 0.0278\ mol{\cdot}L^{-1} = 2.78 \times 10^{-2}\ mol{\cdot}L^{-1}$ (Check that the units work out.)

2) The formula of benzoic acid (benzene carboxylic acid) is C_6H_5COOH, but you don't actually have to know this. Let's just call it HA. Now we can set up a simple equilibrium equation, with the equilibrium concentrations of the acid and its ions underneath. Let the concentration $[H^+] = [A^-] = x$ (see footnote [1]) with all concentrations being in $mol{\cdot}L^{-1}$.

$$HA \Longleftrightarrow H^+ + A^-$$

or

$$\begin{array}{cccc} HA & + H_2O & \Longleftrightarrow & H_3O^+ + A^- \\ (2.78 \times 10^{-2} - x) & & & x \qquad x \end{array}$$

The equilibrium constant expression, $K_a = [H^+][A^-]/[HA]$ or $[H_3O^+][A^-]/[HA]$ (see footnote [2])

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[1] Alternatively we could consider the reaction in terms of hydroxonium ions (also known as hydronium ion or oxonium ions) replacing H^+ with H_3O^+ throughout.

[2] The concentration of undissociated water is not usually considered in the equilibrium constant expression, because its concentration is so very much larger than the concentration of the H^+ (or H_3O^+) ions that any changes due to dissociation are negligible. By the same token, the concentration of H^+ (or H_3O^+) ions that are contributed to the solution by the dissociation of water rather than acid are not usually considered because they are extremely low (being suppressed in fact by the presence of the acid).

Substituting the values given under the reaction equation above gives:

$$K_a = x^2/(2.78 \times 10^{-2} - x)$$

However, as $K_a = 6.40 \times 10^{-5}$, which is three orders of magnitude smaller than the concentration, the expression can be approximated to:

$$K_a = x^2/(2.78 \times 10^{-2})$$

Note that some books give units of $\text{mol}\cdot\text{L}^{-1}$ to the equilibrium constant, which would help you to get the correct units of concentration for the hydrogen ion, thus:

Then the hydrogen ion concentration (x) = $\sqrt{(2.78 \times 10^{-2}\ \text{mol}\cdot\text{L}^{-1} \times 6.40 \times 10^{-5}\ \text{mol}\cdot\text{L}^{-1})}$

$= 1.33 \times 10^{-3}\ \text{mol}\cdot\text{L}^{-1}$ but see footnote [3]

3) pH = $-\log[H^+]$ or $-\log[H_3O^+]$

The pH of the benzoic acid solution = $-\log(1.33 \times 10^{-3}\ \text{mol}\cdot\text{L}^{-1}) = 2.87$ (note that there are no units here because pH is essentially a log value) [4]

The correct key to this question is therefore **B** (pH = 2.9)

Some reviewers of the exam expressed concern over the approximation of the pH value. Although most high schools don't have the apparatus to measure pH values any better than this, there is considerable error associated with using pH values that are only given to two figures [5]. (You can check this for yourself by working back from pH = 2.9 to concentration.) On the other hand the assumptions made in the calculation also introduce errors. And the data book value for the pH of a saturated solution of benzoic acid is only given to two figures (it is given as 2.8).

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19. This is another question that caused an howl of protest from teachers, who thought that K_a values would be needed to solve it. However, I was hoping that it would be solved at a simpler level. It is also, in a sense, a follow-on question from Question 2 of the NHSCE 2001, so that any student that had prepared for the 2002 exam, by reading the full solutions to the 2001 exam should have had a good idea of how to set about it.

You do need to be aware that sodium carbonate is the salt of a weak acid (carbonic acid), and, as such, will give an alkaline reaction in solution. This solution is in the flask so it is the starting point for the titration. As hydrochloric acid is added to the sodium carbonate, "acid competition" will occur in which the stronger acid displaces the weaker acid from its salt.

Also, as carbonic acid is a diprotic acid it forms two different salts. Sodium carbonate, Na_2CO_3, is the normal salt, but there is also an acid salt, sodium hydrogencarbonate (sodium bicarbonate) $NaHCO_3$. The reaction between

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[3] Note that the use of units in equilibrium constants of any kind is not considered acceptable in advanced work, where activities rather than concentrations are substituted into the equilihrium constant expression. Activities do not have units, so that any equilibrium constant derived from them will not have units.

[4] Strictly speaking the pH expression should be written as pH = $-\log[H_3O^+]/(\text{mol}\cdot\text{L}^{-1})$ so that units are eliminated before the log calculation is performed.

[5] It should be noted that the value 2.9, whilst having two figures, is only accurate to ***one** significant **figure***. As it is a logarithm, the number in front of the decimal point only indicates the ***magnitude*** of the answer.

sodium carbonate and hydrochloric acid therefore goes through two stages:

$HCl(aq) + Na_2CO_3(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$ .... (1)

Followed by $HCl(aq) + NaHCO_3(aq) \rightarrow NaCl(aq) + H_2CO_3(aq)$... (2)

(Note that if the concentration is high enough, so that H_2CO_3 breaks down to give H_2O and CO_2, but this does not usually occur when 0.1 M solutions react.)

Each of these stages corresponds to the endpoint of a titration, and can be detected using a suitable indicator. At the endpoint of a titration the pH of the solution corresponds to the pH of the products of the titration reaction, and around this point the pH changes very rapidly. The indicator needs to have a pK_{In} value that is approximately the same as the pH of the endpoint solution, and, in addition it needs to be sensitive enough to give a sharp colour change within the region of rapid pH change.

It helps if you have some idea of the characteristics of the substances used in this question, all of which can be found around the house. It is particularly useful to know about "the sodas": these are sodium hydroxide (caustic soda) strongly alkaline, sodium carbonate (washing soda) moderately alkaline, and sodium hydrogen carbonate (baking soda) very slightly alkaline. In addition there are sodium chloride (common salt) neutral, carbonic acid (natural rain) very slightly acidic, and hydrochloric acid (muriatic acid) strongly acidic.

This information can be summarized as follows:

$$\begin{array}{ccccccccccc} NaOH & \rightarrow & Na_2CO_3 & \rightarrow & NaHCO_3 & \rightarrow & NaCl & \rightarrow & H_2CO_3 & \rightarrow & HCl \\ \text{High pH} & & & & & & \text{pH} = 7 & & & & \text{Low pH} \end{array}$$

Remember that the solutions being used are 0.1 mol•L^{-1}. Thus the pH of the alkaline solutions are lower than they would be at 1.0 mol•L^{-1} (e.g. pH 13 instead of pH 14 for NaOH) whilst the pH of acidic solutions are higher (e.g. pH 1 instead of pH 0). The pH of neutral solutions such as NaCl, or water itself, remains at pH 7. (Assuming in all cases that the temperature remains at 25^{o}C.)

In the first stage of the titration the solution is going to go from moderately alkaline through to very slightly alkaline (going on to being slightly acidic as the endpoint is just exceeded), so that thymol blue (base) with a pK_{In} of 8.9 is the most suitable indicator given (Key **D** is correct). Alizarin yellow R ($pK_{In} = 12.5$) has a colour change in the strongly alkaline to moderately alkaline range, so it would be in the middle of its colour change at the beginning of the titration, and there would be no clear endpoint.

Note that even if you were not sure about the pH of sodium hydrogen carbonate, and thought that an indicator in the neutral region would be more appropriate, azolitmin (litmus) would not be the correct choice. This is because it is a mixed indicator (which is why it does not have a pK_{In} value quoted) and its colour change is only very gradual, so a clear endpoint cannot be obtained with it. An indicator used for a titration should change colour with the addition of just ***one drop*** of acid to base (or vice versa). Litmus is a good reagent for indicating whether a solution is acidic or alkaline, but it should never be used for titrations.

If you were to continue to the second stage of the titration, then you would find that the solution turns from being mildly alkaline, through a very slightly acidic endpoint, changing shortly after the endpoint to a strongly acidic solution. The appropriate choice of indicator for this part of the titration would be bromophenol blue, with a pK_{In} of 4.0, although to get good results you would really need to boil the solution to remove carbon dioxide thus:

$$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2\,(g)$$

This ensures that the titration reaction quickly goes to completion.

A final point that you need to consider in a double indicator titration is the colour of the indicator remaining in the solution after the first endpoint. Thymol blue is yellow in acid solution, and this colour will still be there when the second indicator is added. Bromophenol blue would normally change colour from yellow to blue, but in the presence of thymol blue the solution just after the endpoint will probably appear green. However, there is also another factor to be considered with thymol blue, namely that it has a second colour change in the acid region - it turns from yellow to red between pH 2.8 and 1.2, so perhaps the final solution would appear purple. Phenolphthalein, which is the usual indicator used for the first part of this titration, is a much better choice, because it is colourless in acid solution and so it does not interfere with the second colour change. Phenolphthalein was not, however, an option in this question.

In order to visualize what is happening in this titration it is recommended that you check in a textbook for a titration curve (i.e. a graph showing pH versus volume of titrant added) which also shows indicator ranges on it or go to http://www.chemguide.co.uk/physical/acidbaseeqia/phcurves.html (see footnote [6]).

Do you still want to know the relevant pK_a values? These are 6.4 for carbonic acid and 10.3 for the hydrogen carbonate ion. The indicator for the first endpoint should have a pK_{In} halfway between these two values, and the second indicator should have a pKI_n that is 2 to 3 units lower than the carbonic acid value.

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20. Plaster of Paris is the hemihydrate of calcium sulfate, when water is added, it sets to give the dihydrate, gypsum. The equation for this reaction is:

$$CaSO_4{\cdot}0.5H_2O(s) + 1\,\tfrac{1}{2}\,H_2O(l) \rightarrow 2CaSO_4.{\cdot}H_2O(s)$$

This question involves a simple equation calculation in which you need to find the chemical amount of $CaSO_4{\cdot}0.5\ H_2O$ from the mass you are given, then calculate the chemical amount of water you will need, finally converting back to the mass of water.

The formula you need for the calculation is: $n = m/M$

Where n is the amount of substance (chemical amount) in mol
m is the mass (usually in g)
M is the molar mass in (usually in $g{\cdot}mol^{-1}$)

For $CaSO_4{\cdot}0.5H_2O$, $M_r = 145.1$ (given) and the mass is 0.500 kg. Note that you will need to convert the mass into g.

Thus the chemical amount = $0.500\ kg \times 1000\ g{\cdot}kg^{-1}/145.1\ g{\cdot}mol^{-1} = 3.446\ mol$

The equation shows that 1.5 mol of water are used for each mole of $CaSO_4{\cdot}0.5H_2O$

Therefore, for water the chemical amount = 3.446 mol x 1.5mol/1mol = 5.169 mol

Then manipulating the formula for the calculation to $m = nM$, the mass of water = $5.169\ mol \times 18.0\ g{\cdot}mol^{-1} = 93.0\ g$

This is close enough to key **B** (93.1g) for it to be the answer. (The difference can be attributed to minor differences in rounding.)

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[6] Note that this web page leads you to a page on indicators and it even has the titration curve for a double indicator titration involving carbonate, however in this case the more usual indicators are used. These are phenolphthalein for the alkaline endpoint and methyl orange for the acid endpoint. The pH changes for these indicators are: phenolphthalein - red in alkali to colourless in acid, changing over a pH range of 10.0 to 8.2, and methyl orange - yellow in alkali and red in acid, changing over a pH range of 4.4 to 3.2.

21. This question uses the same equation and amounts of substance as Question 20 (this is designed to help speed up the exam).

Consider the equation again:

$$CaSO_4{\cdot}0.5H_2O(s) + 1\tfrac{1}{2}\,H_2O(l) \rightarrow CaSO_4{\cdot}2H_2O(s)$$

And bearing in mind that the enthalpy change of a reaction per mole of equation is given by the sum of the enthalpy changes of formation of the products minus the sum of the enthalpy changes of formation of the reactants, then:

The enthalpy change of hydration of $CaSO_4{\cdot}0.5H_2O$ per mole of equation is therefore:

$$\Delta H_f\{CaSO_4{\cdot}2H_2O\} - [\Delta H_f\{CaSO_4{\cdot}0.5H_2O\} + 1\tfrac{1}{2}\,\Delta H_f\{H_2O(l)\}]$$

substituting numerical values gives:

$$-2023 - [-1577 + 1.5 \text{ x} - 285.8]\ \text{kJ}{\cdot}\text{mol}^{-1} = -17.3\ \text{kJ}{\cdot}\text{mol}^{-1}$$

This is the enthalpy change **per mole of equation**. It is also the enthalpy change per mole of $CaSO_4{\cdot}0.5H_2O$ as there is one mole of $CaSO_4{\cdot}0.5H_2O$ in one mole of equation. However, the question is not yet finished, because you do not have one mole of $CaSO_4{\cdot}0.5H_2O$, you have 0.500 kg, i.e. 3.446 mol (as calculated in question 20), so the enthalpy change associated with the hydration of 0.500 kg is

$$-17.3\ \text{kJ}{\cdot}\text{mol}^{-1} \text{ x } 3.446\ \text{mol} = -59.6\ \text{kJ}$$

The negative sign indicates that the reaction is exothermic, i.e that heat is evolved in the reaction, so it can be said that + 59.6 kJ of heat is evolved, i.e. the correct key to this question is **B**. If you have ever had a broken limb set with plaster you will probably have noticed that it heats up as it sets. Bond forming is exothermic, and this reaction is exothermic due to the bonds that are being formed between water and the calcium and sulphate ions.

Note that $\Delta H_f\{CaSO_4\}$, which is given in the data for this question, is not needed in the calculation. It is a red herring.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAM 2002 continued

22. This question boils down to a standard solubility calculation, although you must remember that two moles of fluoride ions are obtained per mole of calcium fluoride. This is shown in the equation:

$$CaF_2(s) <====> Ca^{2+}(aq) + 2F^{-}(aq)$$

This is written as an equilibrium equation because, in a saturated solution, an equilibrium exists between the dissolved and the undissolved solid. Note that ions exist both in the solid and in the solution, even though they are not generally shown in the formula for the solid.

The solubility product constant is a special concentration equilibrium constant, that does not include the concentration of the solid CaF_2 because this is constant (compare this with question 12 in this year's exam). Only the equilibrium concentrations of the ions in solution are used in the solubility constant expression, thus:

$$K_{SP} = [Ca^{2+}(aq)]\,[F^{-}(aq)]^2$$

If the concentration of calcium fluoride in the saturated solution is *s* mol•L^{-1}, then the concentration of the calcium ions is s mol•L^{-1}, and the concentration of fluoride ions is **2***s* mol•L^{-1}, and the solubility product constant expression becomes:

$$K_{SP} = \{s \text{ mol}\cdot\text{L}^{-1}\}\{\mathbf{2}s \text{ mol}\cdot\text{L}^{-1}\}^2$$
$$= 4s(\text{mol}\cdot\text{L}^{-1})^3$$

Note that in the first K_{SP} expression the concentration is given as $[F^{-}(aq)]$: this is the **total** fluoride ion concentration in the saturated solution at equilibrium. This is substituted by **2***s* mol•L^{-1} in the second version of the expression, because this total fluoride concentration is twice the calcium ion concentration. [1]

The next step in this question is to find a value for "*s*". This is done by rearranging the K_{SP} expression to give:

$$s = {}^{3}\sqrt{(K_{SP}/4)}$$

then substituting for K_{SP}, gives $s = {}^{3}\sqrt{(4.0 \times 10^{-11}/4)} = {}^{3}\sqrt{(10^{-11})} = 2.15 \times 10^{-4}$ (mol•L^{-1})

Do not now be led astray by the fact that this is one of the answers proffered (key A)! Remember that *s* mol•L^{-1} is the concentration of **calcium** ions: the concentration of **fluoride** ions is twice this, thus:

$[F^{-}(aq)] = 2 \times 2.15 \times 10^{-4}$ (mol•L^{-1}) = 4 .30 x 10^{-4} (mol•L^{-1}), i.e the correct key is **C**.

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[1] Note also that, although the solubility product constant is given without units in the question, we have ended up with units because we have substituted concentrations into the solubility product expression. Strictly speaking we should substitute activities, not concentrations, into equilibrium constant expressions. Activities take into the account the fact that solutions do not behave ideally (for example ions in concentrated solutions tend to "pair up", so that their concentrations appear less they really are). A full discussion of activities is beyond the scope of these solutions, but suffice it to say that they are ratios, so they do not have units. Also, in dilute solutions such as those involved in saturated solutions of barely soluble solids, numerical values of concentrations and activities are effectively the same.

Note that the concentration of fluoride in this solution is equivalent to about 8.2 mg•L^{-1} (or 8.2 ppm), so if you depend on water from a source embedded in fluorspar rock you could easily be drinking much more than the maximum daily limit of 1.5 mg of fluoride per day. Above this level you are at risk of contracting fluorosis (a disease that causes muscular and skeletal weakness and urinary tract problems) and possibly cancer.

Having said all this, I am reliably informed that the simple solubility expression that we have used in this question would not work very well. This is because HF is a weak acid, and so there are several equilibria involved in the solution, viz:

$$H_2O(l) + H_2O(l) \leftrightarrow H_3O^+(aq) + OH^-(aq) \qquad K_w$$

$$CaF_2(s) \leftrightarrow Ca^{2+}(aq) + 2F^-(aq) \qquad K_{sp}$$

$$F^-(aq) + H_2O(l) \leftrightarrow HF(aq) + OH^-(aq) \qquad K_b$$

{And also probably $Ca^{2+}(aq) + OH^-(aq) \leftrightarrow CaOH^+(aq)$}

You might like to reflect on what effect this combination of equilibria could have on the quality of drinking water.

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23. In order to determine the approximate enthalpy change of combustion for methoxymethane (dimethyl ether) from bond enthalpy terms, you need first of all to write the equation for the combustion reaction and then consider exactly which bonds are broken and which are formed as the reaction takes place. Bearing in mind that the standard enthalpy change of combustion is the enthalpy change that occurs when one mole of substance is completely burned under standard conditions, then the equation for the combustion of methoxymethane is:

$$CH_3\text{-}O\text{-}CH_3(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

Note that state symbols are not really required for doing the calculation, but you should be aware that the enthalpy change would be affected if the water were in the gas state, and that the enthalpy change required to vaporise the combusted substance would need to be considered if it were in the solid or liquid state.

Note also that, when balancing the equation, one mole of oxygen atoms is present within the mole of CH_3-O-CH_3, and this must be counted as part of the oxygen used in the combustion. In this equation a whole number of moles of oxygen molecules is required, but, in some cases half moles might be required for the equation to balance. If this happens then you should leave the equation balanced this way - don't double the whole equation in order to keep all the stoichiometric coefficients as integers. This is because the definition of the enthalpy change of combustion refers to burning one mole of compound: burning two moles would give double the enthalpy change.

The next step is to determine which bonds are broken and which are formed. It is assumed that all the reactant molecules are broken up into atoms, and then the atoms are reassembled forming new bonds. The bond breaking process is endothermic (energy is used in pulling bonds apart) and so the bond breaking enthalpies are positive. As bond enthalpy terms are defined [2] in terms of bond breaking they are also positive. The bond forming process is

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[2] The bond enthalpy term is defined as the enthalpy increase that accompanies the homolytic fission of one mole of bonds in a covalently bonded species, to give individual atoms and/or radicals, with both the original species and the resulting fragments being in their standard states, and at standard temperature and pressure. The bond enthalpy is the average value of the bond dissociation enthalpy for the same kinds of bonds, but in a number of different compounds. The bond enthalpy is also referred to as the bond energy term or bond energy.

The bond dissociation enthalpy is similarly defined but refers to a specific bond in a specific compounds.

exothermic (energy is released when bonds are formed) and so bond forming enthalpies are negative. Each bond forming enthalpy is numerically the same as the equivalent bond energy term, but carries a negative sign. The approximate enthalpy change for the whole reaction is the sum of the bond breaking (positive) enthalpies and the bond forming (negative) enthalpies.

Now it is simply a question of counting the bonds (if you have trouble visualising this, draw out the molecules so that you can see all the bonds), thus:

<u>Bonds broken</u> (positive)

For CH_3-O-CH_3 6 x C-H + 2 x C-O

For $3O_2$ 3 x O=O

<u>Bonds formed</u> (negative)

For $2CO_2$ 2 x 2 x C=O

For $3H_2O$ 3 x 2 x O-H

The expression for calculating the approximate enthalpy change of combustion from bond enthalpy terms (E values [3]) therefore becomes:

$$6 \text{ x } E(\text{C-H}) + 2 \text{ x } E(\text{C-O}) + 3 \text{ x } E(\text{O=O}) - 6 \text{ x } E(\text{O-H}) - 4 \text{ x } E(\text{C=O})$$

Therefore the correct answer to this question is **C**.

We could, if we wished, continue the calculation to find a numerical value for the enthalpy change. Looking at data book tables of bond enthalpy terms we find that

E(C-H) average = 413 kJ•mol^{-1}, E(C-O) average = 358 kJ•mol^{-1} , E(O=O) as in O_2 = kJ•mol^{-1},
E(O-H) as in H_2O = 464 kJ•mol^{-1} and E(C=O) as in CO_2 = 805 kJ•mol^{-1}

Substituting these values into the expression given above, gives the enthalpy change of combustion of methoxymethane

$$= (6 \text{ x } 413) + (2 \text{ x } 358) + (3 \text{ x } 498) - (6 \text{ x } 464) - (4 \text{ x } 805) \text{ kJ•mol}^{-1}$$

$$= -\ 1316 \text{ kJ•mol}^{-1}$$

Note that this is a large negative value. All combustion reactions are exothermic, so enthalpy changes of combustion are always negative. Values of enthalpy changes of combustion are generally large, typically in the thousands of kJ•mol^{-1}, which is why the reaction can continue once it has been initiated. Initiation (for example by sparking) allows the activation energy to be overcome for a few molecules, then, when they have reacted, they give out sufficient energy to provide the activation energy for further molecules to react. Combustion reactions are oxidation reactions that are self-sustaining once they have been initiated.

The data book value for the enthalpy change of combustion of methoxymethane is –1460 kJ•mol^{-1}, which is slightly

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[3] I have been told that, strictly speaking, E or *E* should not be used for bond enthalpy terms as E is the symbol for energy. In future I shall use the symbol *D* for dissociation enthalpy and $\overline{D}$ or <*D*> for bond enthalpy term (in accordance with the provisional recommendations of the IUPAC advisory committee for thermochemical symbols and nomenclature.

different from the value calculated from the bond enthalpy terms. This is because the bond enthalpy terms for C-H and C-O bonds are average values, and can be expected to be not quite the same as the bond dissociation enthalpies for these bonds in a specific compound.

You might like to try calculating this enthalpy change of combustion from enthalpy changes of formation. Using the values in my data book this method gives $-1460\ \text{kJ·mol}^{-1}$, which is exactly the same value as that quoted above (which will have been determined experimentally). The bond enthalpy term method of calculating enthalpy changes of reaction is usually only used where neither the experimental value nor one or more of the enthalpy changes of formation are not available.

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24. This is a follow-up question to NHSCE 2001 Question 6, and the theory of addition and condensation polymers are discussed in the solutions to that question.

First some definitions:

A **polymer** is a substance that is composed of macromolecules. Macromolecules are formed when molecules of one or more simple compounds join together to give a new compound (the polymer). These simple compounds are called monomers.

A **monomer** is a substance that consists of simple molecules that are capable of joining up with others to formthe essential structure of a polymer. Many monomer molecules (often hundreds or thousands) are usually needed to create a polymer.

An **addition polymer** is formed by the addition of monomer molecules to one another. Such a polymer contains *all* of the atoms from the original monomer molecules. An addition polymer is usually derived from just one particular monomer, and has the same empirical formula as the original compound, but a much higher molar mass. The monomers from which addition polymers are derived are usually unsaturated compounds, that is they contain a double bond (or sometimes a triple bond). A double bond "opens up" and becomes a single bond when the monomers join together.

A **condensation polymer** (also known as an addition-elimination polymer) is formed when two monomers with different functional groups combine releasing small molecules (such as water, ammonia, hydrogen chloride or hydrogen bromide) as they react. Two different molecules are usually involved in making a condensation polymer, although it is possible for a condensation polymer to form from just one type of molecule providing that that molecule has two different functional groups that can react. Examples of functional groups that can react to form linkages in condensation polymers are alcohol and acid groups (that can react to form ester linkages, eliminating water as they do so) or amine and acid groups (that can react to form amide linkages, again eliminating water).

In order to recognise whether a polymer is an addition polymer or a condensation polymer, you need to look at the links in the repeat unit of the chain, known as the **mer** unit. The mer unit is shown in the formula of the polymer with brackets around it and is repeated n times, where n is a very large number (alternatively the number may be specified).

An addition polymer will be characterised by chains of carbon in the mer unit, e.g. $\text{-(-C-C-)}_n\text{-}$ Other atoms and groups may be joined to these carbons. A condensation polymer is likely to have a link containing atoms other than carbon, e.g. an ester link -COOC- or an amide link -NHCO- in the chain.

Note that it is very important to distinguish between esters and amides that might be attached to a carbon chain in an addition polymer, and ester and amides that are part of a chain in a condensation polymer. It is a good idea to try drawing out the structures so that you can clearly distinguish the two sorts of polymers.

Now let us consider each of the suggested answer keys in turn:

A. - (-CH(C_6H_5)-CH_2-$)_n$- (This could also be written as - (-C(C_6H_5)H-CH_2-$)_n$-). It has a carbon chain and is therefore an addition polymer. The mer unit in this compound has two carbons in it, one of which has a phenyl group attached. The monomer is phenylethene (CH(C_6H_5)=CH_2 or C(C_6H_5)H=CH_2)and the polymer is called polyphenylethene (more commonly known as polystyrene, which is used in styrofoam cups etc.)

B. - (-CH_2-CH=CCl-CH_2-$)_n$- Do not be fooled by the fact that there is a double bond in the middle of the mer unit of this compound, it still has a carbon chain, and is therefore an addition polymer. The mer chain has four carbons in it this time, with a chlorine on one of the ones involved in the central double bond. The starting monomer for this polymer has two double bonds in it, which are effectively shuffled around in the polymerisation process, so one is “opened up” and the other moves to the centre of the mer unit. The monomer is 2-chlorobuta-1,3-diene (CH_2=CH-CCl=CH_2) and the polymer is known as Neoprene rubber. It is a strong synthetic rubber which is resistant to oils and organic solvents, and is used to make hoses and gaskets.

C. - (-C(CH_3)($COOCH_3$)-CH_2-$)_n$- Be careful with this one - there is an ester group in it. It is, however, an addition polymer with a carbon chain. There are two “chain carbons” in the mer unit, the first one has a (CH_3) group and a ($COOCH_3$) group on it, whilst the second one just has two hydrogen atoms on it. The monomer is methyl 2-methylpropenoate (CH_2=C(CH_3)($COOCH_3$)) and the polymer is used for lucite (costume jewellery) and Plexiglas or Perspex (a transparent plastic, glass substitute).

D. - (-CH_2-C(CN)H-CH_2-CH(CN)-$)_n$- You have actually been given a double mer unit here. The polymer could just as well have been written as - (-CH_2-C(CN)H-$)_n$- (with n in this second formula being twice as large as in the first case) [4]. Either way it has a carbon chain and is an addition polymer. The monomer is propenenitrile (CH_2=C(CN)H), also known as acrylonitrile, and the polymer is a fibre known as Orlon or just “acrylic” and is used for making clothes.

E. - (-NH-(C_6H_4)-NH-CO-(C_6H_4)-CO-$)_n$- Well now you have got to key **E**, so it must be the correct key! But the real giveaway is that this compound has the characteristic amide (-NH-CO-) group in the middle (and also -NH- at one end of the chain and -CO- at the other end) which tells you that it must be a condensation polymer. The two monomers that are used to form it are NH_2-(C_6H_4)-NH_2 (1,4-benzene diamine also known as *p*-phenylene diamine) and ClOC-(C_6H_4)-COCl (1,4-benzenedicarboxylic acid dichloride also known as *p*-terephthaloyl chloride) - although you can’t tell from the formulae that you have been given exactly where the functional groups are placed on the benzene rings. When the two monomers combine, the small molecule that is eliminated is HCl. Note that the acid chloride is used for the reaction because it is more reactive than the acid itself. The polymer is called Kevlar and is used for bullet proof vests and tear-proof envelopes.

Note that all the compounds referred to in this question are synthetic (man-made) polymers, but there are many similar compounds that occur in nature. In proteins for example, amino acids are joined together by -NH-CO- links, which are known in biochemistry as peptide links rather than amide links. In nature, however, the processes in which large molecules are formed are usually very different from the processes described here, even though the macromolecular compounds may appear quite alike.

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25. This question is concerned with calculating the strength of a hydrogen bond. You need to be aware right from the start that the strength of a bond means its bond dissociation enthalpy (see question 23 above). In the present question you are given all the data needed for determining the enthalpy change of reaction for the formation of one

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[4] The polymer could also be written as - (-CH_2-CH(CN)-CH_2-CH(CN)-$)_n$- the simpler version of which is - (-CH_2 -CH(CN)-$)_n$.

mole of hydrogen bonds in the particular system described. The bond dissociation enthalpy will be numerically equal to this, but with the opposite sign (i.e. positive instead of negative).

The particular hydrogen bond being investigated is between trichloromethane ($CHCl_3$) and methyl ethanoate (CH_3COOCH_3). The first thing that might worry you here is exactly how these two molecules bond together. If you draw the molecules out you will be able to see that neither of the oxygen atoms in CH_3COOCH_3 are connected to a hydrogen in this molecule, so that in both the molecules all the hydrogens are connected directly to carbon atoms. You should know that hydrogen bonds are usually only formed when a hydrogen atom can come between small electronegative atoms, and the only atoms that normally fit the bill are nitrogen, oxygen and fluorine [5]. Carbon might be small enough to get involved in hydrogen bonds but it is not electronegative enough. Chlorine is electronegative enough, but not small enough. So it doesn't look at first sight as though a hydrogen bond can exist here. In fact what appears to happen in $CHCl_3$ is that the three chlorine atoms on the central carbon make the carbon behave as though it is more electronegative than it really is. The hydrogen on this molecule can therefore make a bridge between the "souped up" carbon, and one of the oxygens on the CH_3COOCH_3 molecule. It is not necessary to know which of the oxygens is going to be involved - it would be possible for either of them, or even both of them to be used, and this has been taken into consideration in this very elegant little experiment [6].

You are told in the question that only one hydrogen bond is in fact involved between the two molecules. This has been assured by making the amount of $CHCl_3$ used (0.01 mol) very much less than the amount of CH_3COOCH_3 (0.05 mol). This means that every single molecule $CHCl_3$ is involved in the hydrogen bonding, and that there are plenty of CH_3COOCH_3 molecules left over. The limiting reagent is thus $CHCl_3$, and the amount of substance used for the calculation of $kJ.mol^{-1}$ must be the amount of $CHCl_3$.

The next curiosity is the fact that an insulated glass beaker is used as a container for the reaction. You are probably used to performing enthalpy change experiments with aqueous solutions. For such experiments we often use styrofoam cups as containers, because they are good insulators and also extremely light, which means that they do not abstract very much heat from the reaction mixture. Their mass is usually considered negligible and their heat capacity is ignored in the enthalpy calculation.

Unfortunately the two reagents used in this experiment dissolve styrofoam [7], so a glass container must be used instead. This leads to two complications. First, the heat capacities of each of the liquids need to be considered for the calculation - these are determined from the mass of each liquid multiplied by its specific heat capacity. Note that the specific heat capacity of water, which is used for calculations involving aqueous solutions is **not** appropriate here. Secondly, glass is not such a good insulator as styrofoam so the beaker has to be insulated, for example by placing it in a larger beaker, with a layer of cotton between the two beakers. Note that the heat capacity of only the first beaker has been considered in this experiment, but that of the insulating material has not. The heat absorbed by

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[5] Some researchers are presently looking into interactions that they refer to as "weak hydrogen bonds", which involve other atoms, but these are not generally considered to be strong enough to be referred to as bonds. They are really little more than permanent dipole-dipole interactions that happen to involve hydrogen. We need to remember that in chemistry we tend to learn about clear-cut examples of particular phenomena, when, in fact, most examples lie somewhere in between the various extremes. This is like there being many more "shades of grey" than perfect black or white.

[6] In fact it is likely that it is the carbonyl oxygen in methyl ethanoate that is involved in the hydrogen bond. This is because it is known that when ester hydrolysis occurs under acidic conditions, the first step in the mechanism is protonation of the carbonyl oxygen.

[7] The two reagents used dissolve styrofoam because "like dissolves like". The solvents CH_3COOCH_3 and $CHCl_3$ are relatively non-polar and the styrofoam is a non-polar polymeric solute.

The effect of this is quite dramatic. You can observe something similar by pouring nail varnish remover (either the acetone or the ethyl ethanoate kind) into a styrofoam cup. Note that it is best done in a disposable aluminium baking tray if you don't want to make a mess!

each of the materials (CH_3COOCH_3, $CHCl_3$ and the glass of the beaker) is determined by multiplying the heat capacity by the temperature rise (0.75°C i.e. 0.75 K), and the total heat energy is the sum of the values obtained. This is shown in the table below:

	Mass, g	Specific heat capacity, $J{\cdot}g^{-1}{\cdot}K^{-1}$	Heat capacity, $J{\cdot}K^{-1}$	Heat absorbed, J
CH_3COOCH_3	3.71	1.97	3.71 x 1.97 = 7.31	7.31 x 0.75 = 5.48
$CHCl_3$	1.19	0.96	1.14	0.86
Beaker	60	0.67	40.2	30.15
			TOTAL	36.49

All the heat absorbed by these materials has been generated by the enthalpy change of the hydrogen bond formation. So, assuming that all of the 0.01mol of $CHCl_3$ were used, we can say that 0.01 mol of hydrogen bonds are formed, therefore:

the heat generated by the reaction is 36.49J/0.01mol = 3649 $J{\cdot}mol^{-1}$ = 3.6 $kJ{\cdot}mol^{-1}$

the enthalpy change of bond formation is = – 3.6 $kJ{\cdot}mol^{-1}$ (negative because heat is given out)

and the bond energy (bond strength) is = + 3.6 $kJ{\cdot}mol^{-1}$ (positive because bonds are broken not formed for bond energies)

The correct key is therefore **B**.

Note what a huge effect the mass of the glass beaker has on this calculation, even though its specific heat capacity is low relative to the two liquids. There is no way the mass of the container could be ignored in this experiment if you wanted to obtain a reasonable result.

Note also the order of magnitude of the bond strength. Hydrogen bond strengths vary considerably depending on the environment they are in, but they are typically between 10 and 40 $kJ{\cdot}mol^{-1}$. (The hydrogen bond investigated in the experiment is a very weak one, but then it involves carbon rather than the more usual nitrogen, oxygen or fluorine atoms.) Strengths of covalent bonds are usually in the "hundreds" of $kJ{\cdot}mol^{-1}$ (cf. Question 23 above), whilst ionic and metallic bonds tend to be somewhat weaker, being in the "tens" of $kJ{\cdot}mol^{-1}$ in weakly bonded metal such as Na-Na.