ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2005

These answers are designed to help students who are preparing to take the Canadian National High School Chemistry Examination in 2006 or subsequent years. Note that information given here will generally not include material from answers given for previous years' exams, so that students should go through the 2001 to 2004 exams (questions and answers) before attempting the 2005 examination.

Students should attempt to do the questions in Part A of the 2005 Examination on their own, and then compare their answers with the solutions given below. They 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. 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.

The notes have been prepared in order to 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. Unless otherwise stated, 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.

The people involved in preparing the NHSCE very much appreciate all the comments and feedback that we get from teachers. This year we have tried to incorporate some of these comments in with the solutions. We have also tried to give a little more information about how students did in particular questions. This is based on the papers from 317 students and 64 teachers that found their way back to the National Examiner (not, unfortunately, all the material sent in). It should be pointed out, however, that students in different parts of the country perform very differently in the examination. We feel that this is, in part at least, because the provincial curricula do not necessarily follow the Pan-Canadian protocol, or, if they do, then they empahasize different aspects of the curriculum.

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

1. This is the third year that the National High School Chemistry Exam (NHSCE) has had a question on it that relates to WHMIS (Workplace Hazardous Materials Information System), so I was somewhat disappointed that it was very poorly done. About three-quarters of the teachers thought it was appropriate, 10% thought it was too difficult and 12% thought it was not on the curriculum. Only about 16% of the students gave the correct answer – a lower percentage than would have been obtained if everyone had simply guessed!

   The symbol shown in this question was:

   This is the symbol for an **oxidising material**. Student responses indicated that they had probably confused it with the symbol for a **flammable or combustible material**, which is:

   The difference can easily be remembered if you look at the "O" (for oxidising) which is shown below the flame. The reason that both symbols have a flame in them is because that both contribute to a fire hazard – you need both a flammable material and an oxidising material (as well as a source of heat) for a fire to occur. This subject was discussed in the solution to Question 1 of the 2004 NHSCE, and a knowledge of it was also tested in Part B of the 2005 exam, which had "Fire" as one of the essay choices.

   Descriptions of WHMIS symbols can be found on a number of reliable websites: the Ontario Ministry of Labour wbesite at http://www.gov.on.ca/LAB/english/hs/whmis/whmis_appa.html is a good example.

   Having decided what the WHMIS symbol means, the next step is to decide which one of the substances given in the list of possible answers could be an oxidising agent. There are various ways of doing this, depending on your level of knowledge. Certainly substances that you know to be fuels can be eliminated, because these are combustible material and **need** an oxidising material to give a fire, as discussed above. A better way of deciding would be to consider what you know about reducing materials and oxidising materials.

   If you have learnt anything about oxidation states (oxidation numbers)[1], then you will know that compounds that contain an element in a high oxidation state will be good oxidising agents, whilst those involving low oxidation states tend to be reducing agents.

   If you haven't "done" oxidation states, then you should know that, of the elements, hydrogen is a reducing agent and oxygen is an oxidising agent. Following on from that, as a rule of thumb, compounds containing a high proportion of hydrogen are likely to be reducing agents, whilst compounds containing a high proportion of oxygen are likely to be oxidising agents.

   Now consider each of the options you are given in turn:

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[1] The rules for assigning oxidation numbers are given in the Appendix to at the end of the solutions to Questions 21 to 25 of the NHSCE 2001.

A. Ammonia, NH_3

In ammonia nitrogen has an oxidation number of –3, and hydrogen has an oxidation number of +1. (Notice how the formula is written with the more electronegative element first, whereas most other formulae are written with the less electronegative element first). The oxidation number of –3 is very low for nitrogen, which can have a variety of oxidation numbers from –3 to +5. Also ammonia contains three atoms of hydrogen per molecule, so that it is likely to be reducing rather than oxidising. In fact, this is indeed the case. For example, ammonia will reduce gently heated lead(II) oxide, thus:

$$3PbO(s) + 2NH_3(g) \rightarrow 3Pb(s) + N_2(g) + 3H_2O(g)$$

The answer to this question cannot therefore be A.

B. Hydrogen, H_2

Hydrogen, being in its elemental state, has an oxidation number of 0. Its range of oxidation numbers is from –1 to +1, so it really cannot be considered to be in a high oxidation state. It is a fuel, and, as we have stated above, it is a good reducing agent, (not oxidising), so the answer cannot be B.

C. Octane, C_8H_{18}

Octane is a member of the hydrocarbon series of organic compounds, and these are a class of compounds the formulae of which are written with the more electronegative element first. In octane hydrogen has an oxidation state of +1 and carbon has one of –2.25 (i.e. –18/8) . The range of oxidation numbers for carbon is between –4 and +4, so –2.25 is somewhat low. In fact hydrocarbons are all fuels, reacting with oxygen when they burn. So the answer cannot be C.

D. Potassium nitrate, $K^+(NO_3)^-$

Note, first of all, that potassium nitrate contains 3 moles of oxygen per mole of entity (KNO_3), so that it is in the running for being a good oxidising agent. In this compound potassium in its maximum oxidation state of +1, nitrogen is in the +5 state and oxygen is in the –2 state. The +5 state is the maximum oxidation state for nitrogen, which makes it a very good oxidising agent. The answer is therefore very likely to be D, but let us just check up on the last option to make sure that we have made the right choice.

E. Sodium nitride, $(Na^+)_3N^{3-}$

This is an unusual compound that was only synthesized for the first time in 2002. It contains no hydrogen or oxygen to help you to decide whether it is a reducing agent or an oxidising agent, but it contains sodium in the +1 state and nitrogen in the –3 state. With nitrogen in its lowest oxidation state it cannot be an oxidising agent, and so the answer cannot be E.

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

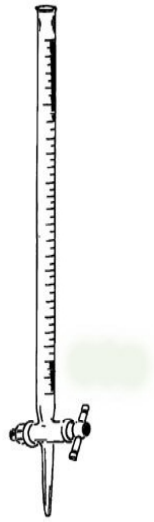
All inorganic nitrates are good oxidising agents, and, indeed, may contribute to explosive reactions. The most famous of these reactions is probably the one used in gunpowder (blackpowder) in which potassium nitrate (saltpetre) is mixed with carbon (charcoal) and sulfur. On ignition the mixture reacts as follows:

$$2KNO_3(s) + S(s) + 3C(s) \rightarrow K_2S(s) + N_2(g) + 3CO_2(g)$$

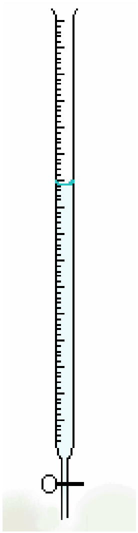
Potassium nitrate provides the oxygen for the reaction, and the propellant effect is created by the gases (nitrogen and carbon dioxide) produced.

2. This question is designed to test the ability of students to read a burette, which is a graduated glass tube used for measuring volume of liquid. Almost a quarter of the teachers thought this question was too easy, although a handful thought that the topic was not on the curriculum. About three-quarters of the candidates got the correct answer.

   The diagram shows a cross-sectional (2-dimensional) diagram of a burette rather than a "pictorial" (3-dimensional) representation. Nowadays most textbooks use pictorial diagrams, because these look more like what a student actually sees, but many scientists still use cross-sectional representations in their notebooks because they are easier to draw. There are a number of conventions governing the drawing of cross-sectional diagrams, including, for example, having no line across the top of the openings of glassware, which makes it easier to see that the vessel is, in fact, open. Examples of the two different kinds of diagram are given below.

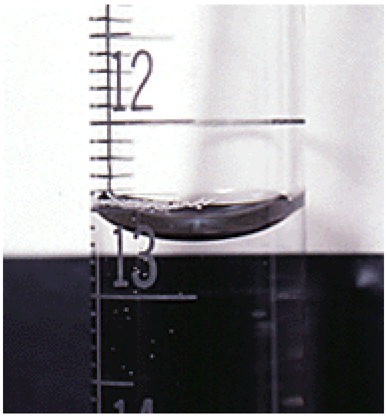


3-dimensional representation of a burette



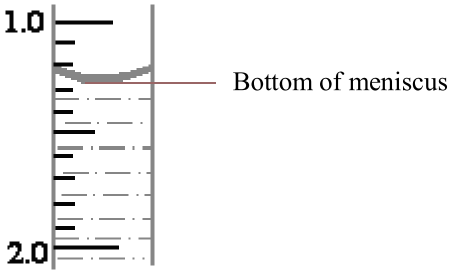
Cross-sectional diagram of a burette

When the stopcock at the bottom of the burette is closed, and the burette contains some liquid, the top of the liquid usually appears as a thick, slightly curving line, called the meniscus. The curved effect is due to the surface tension of the liquid which causes is to be attracted to the walls of the burette. This can be seen in the following photograph:



In cases like this where it is not clear exactly where the surface of the liquid is, it is the convention to take the reading at the bottom of the meniscus[2], largely because it is easier to see than the top for most aqueous solutions. It is essentially your knowledge of this convention that is being tested in this question.

The diagram that you are given shows the meniscus as a thick curved line, so you are expected to take the reading from the bottom of the line as shown. You also need to bear in mind that burettes are usually set up with the zero mark at the top, and this is confirmed by the two numbered calibration marks, which have the smaller number (1.0) above the larger one (2.0). (The units are mL although these are not indicated on the diagram itself.)



Counting the marks on the left hand side of the burette it can be seen that the meniscus lies somewhere between 1.2 and 1.3 mL. The second decimal place is hard to see on the diagram, as it is in the actual apparatus. Some teachers would accept a value of 1.25 ± 0.05 mL, but it is usually possible to do better than that. Here it is clear that the bottom of the meniscus is slightly below the level of 1.25 mL, whilst the top is slightly above this level. The only possible value amongst those given as options is thus 1.26 mL, and the correct answer is therefore **C**. If you had taken the reading at the upper part of the meniscus, you would have picked B as the answer, whereas you would have chosen key D or E chosen if you had been counting from the bottom of the scale rather than the top. Note that it should be possible, with practice, to achieve a precision of ± 0.01 mL on burette readings.

3. Most teachers (about 85%) felt that this question was fair, with a few of them feeling that it was too easy, however only about 56% of students got the correct answer.

The question is concerned with the polarity of **bonds** in different covalent molecules. Students are, perhaps, more accustomed to being asked about the polarity of the molecules themselves, but determining the polarity of a molecule starts with looking at whether the bonds are polar or not, before going on to consider the geometry of the molecule.

A covalent bond involves two atoms sharing one or more pairs of electrons. The bond is non-polar if the electrons are shared equally between the two atoms: it is polar if the electrons are attracted to one of the atoms more than the other one. Polar bonds exist when the two atoms have **significantly** different electronegativities[3], in which case the distribution of electron charge is unbalanced, with more negative charge on the more electronegative atom. Note that, if the electronegativities of the atoms are **very**

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[2] There are some exceptions to this rule, for example it is customary to read the top of the meniscus for mercury (which has a reverse meniscus, i.e. one that curves upwards) and for opaque liquids such a potassium permanganate and iodine solutions, but the diagram would have made it clear if these cases applied.

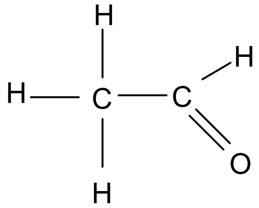
[3] Carbon-hydrogen bonds in organic molecules are generally considered to be non-polar, even though the Pauling electronegativity values are H = 2.1 and C = 2.5. Electronegativity differences between about 0.5 and 2.0 generally result in polar covalent bonds.

different (greater than 2 or more units), we consider that electrons will effectively be transferred from one atom to the other (more electronegative) atom, creating a positive ion and a negative ion, which means that the bonding will be ionic rather than covalent.

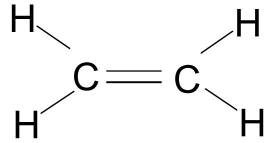
Although you are not given any electronegativity values for this question, it is fairly safe to say that any bond that is formed between atoms of different elements is likely to be polar, which eliminates keys A, C and D from consideration. There is some ambiguity in C, because the C–H bond is usually considered non-polar, but this is not the case in $CHCl_3$ because of the effect of the effect of three very electronegative chlorine atoms pulling electrons towards them, and thus increasing the electronegativity of the central carbon atom. Note that if you chose key D, it might have been because it refers to CCl_4, which you are used to seeing as an example of a non-polar **molecule**, where the symmetry of the molecule cancels out the polarity of the bonds.

You really only need to consider keys B and E, which both feature carbon-carbon bonds. Let us look more closely at the two molecules involved here, these are:

Key B refers to CH_3CHO (ethanal), the structural formula of which can be represented as:



Key E refers to C_2H_4 (ethene), which has the structural formula:



The first thing you are likely to notice in these two molecules is that they both contain double bonds. This simply means that there are **two** pairs of electrons involved in the bonding – it does not interfere with the polarity of the bonding. The C=O is polar because it contains atoms with different electronegativities. (Oxygen is more electronegative and so it attracts the electrons more than the carbon end.) The C=C bond is non-polar because it connects two of the same kind of atoms. You are, however, asked about the carbon-carbon bond in each molecule. On the face of it, it looks as though this should be non-polar in each case. The carbon-carbon bond in ethanal is, however, somewhat polarised because one of the carbons is connected to oxygen, and the electronegativity of the oxygen pulls electrons towards it – not just from the bond with the carbon that is nearest to it, but also from the bonds that are next "in line".

The ethene molecule is symmetrical about the carbon-carbon double bond, so that any electronegativity effects on the electrons is cancelled out, and the bond is truly non-polar. The answer to this question is therefore **E**.

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4. This was the question that was done best of all the questions on the exam, with about 82% of students getting the correct answer, although a fair number (about 18%) of teachers thought it was not on the curriculum. It concerned the electronic configuration of the sodium ion formed by **adding** an electron to a sodium atom. As electrons are negative, the ion formed will be an anion (negative). The catch here is, of course, that you are used to seeing sodium ions as cations (positive).

Sodium has an atomic number of 11, and so a neutral sodium atom has 11 electrons. The electron configuration of a sodium atom is therefore:

$$1s^2 2s^2 2p^6 3s^1$$

(This is the configuration given in key C, so that cannot be the correct answer.)

Adding one electron to this gives:

$$1s^2 2s^2 2p^6 3s^2$$

This is given in key **D**, which is therefore the correct answer.

Note that the main distractor in this question is key B, which is:

$$1s^2 2s^2 2p^6$$

This is the electronic configuration of the sodium cation, which corresponds to the electron configuration of the noble gas neon.

The other two electron configurations given are $1s^2 2s^2 2p^5$ and $1s^2 2s^2 2p^6 3s^2 3p^6$, which refer to fluorine and argon atoms respectively (or to chemical species that are isoelectronic with them).

The first version of this question had the electron configurations in the format 2.8.1 (for sodium), 2.8.2 (for the sodium anion) and 2.8 (for the sodium cation) etc. The reviewers thought that this format was confusing. Would you have had trouble with this?

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5. This question concerns oxidation states. About 70% of teachers thought that it was appropriate, whilst 7% had not yet covered the topic. About 20% of the teachers who responded to the questionnaire about the exam felt that it was too difficult, possibly because it involved a subject that is sometimes perceived as being difficult, or possibly because the question required interpretation of a diagram. About half the students chose the correct answer.

The diagram for the question is given on the next page. It shows a graph in which the abscissa (x axis) represents the atomic number of successive elements in the Periodic Table, and the ordinate (y axis) indicates possible oxidation states of these elements. The atomic number is defined as a number equal to the number of protons in the nucleus of an atom of the element. The number of protons is, of course, equal to the number of electrons in the neutral atom.

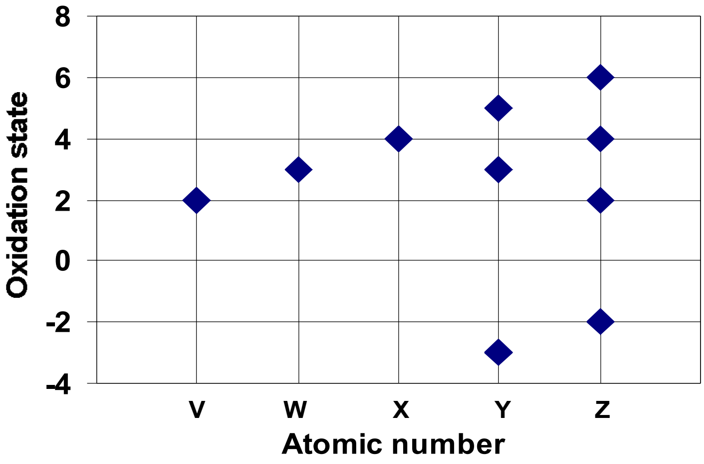
The oxidation state of an element in an ionic compound is represented by the charge on the ion in that

(continued on the next page)

compound. It is thus equal to the valency of that ion[4]. Oxidation states are, however, also used for elements that are covalently bonded. The oxidation states of elements in covalently bonded compounds are obtained in an arbitrary way by taking the oxidation state that each element in the compound would have had if the bonds were ionic. The algebraic sum of the oxidation states of the individual atoms in a compound is equated to zero. (Further information about the rules for assigning oxidation numbers are given in the Appendix to at the end of the solutions to Questions 21 to 25 of the NHSCE 2001.) In essence that oxidation state of an element in a compound gives an indication of the number of electrons that the element is using for bonding with other elements in the compound, irrespective of whether that bonding is ionic or covalent.

The important point to appreciate in this question is that it is the valency electrons (i.e. those electrons in the outermost shell of the atom) that are involved in bonding, whether the bonding is ionic or covalent, and that **the oxidation state of an atom cannot be greater than the number of its valency electrons**.[5]

Now let us take a closer look at the diagram given in Question 5:



In this diagram we can see that, for the five successive elements V, W, X, Y and Z, the maximum oxidation states are 2, 3, 4, 5 and 6. This means that the number of valency electrons that they have are 2, 3, 4, 5 and 6 respectively, and, in particular, element Z, which we are to focus on, will have a maximum of 6 valency electrons. Z is therefore likely to be in main group 6 of the periodic table (IUPAC group 16), which includes oxygen (atomic number = 8) and sulfur (atomic number = 16). It is just conceivable that Z might be in transition group 6 (like chromium, for example) but these elements do not have –2 oxidation states. Having now effectively eliminated keys A, B and C, we now have to decide how to choose between D and E. The easiest way of doing this is probably to start by considering what you know about oxygen and

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[4] In the early stages of learning chemistry we usually learn only the valencies of ions, although the concept of valency can relate to elements in covalently bonded compounds. Originally valency was determined by looking at the formulae of a number of different compounds, and establishing the number of hydrogens that could combine with, or replace, an element in the formula of a compound. Thus the valency of sodium is 1, because, when you compare NaCl and HCl one sodium replaces one hydrogen. The valency of magnesium is 2, because when you compare $MgSO_4$ and H_2SO_4, you can see that two hydrogens are needed to replace one magnesium. Strictly speaking valencies do not have charges attributed to them, but usually we think in terms of sodium and magnesium ions as being positive, whilst chloride and sulfate ions are negative. Both valency and oxidation states indicate the combining power of elements.

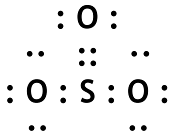
[5] Note that the valency electrons in the main group elements will be the electrons in the outermost shell (*s* and *p* electrons), for the transition metals and inner transition metals, *d* and *f* electrons from inner shells may be included.

sulfur. Beginners usually learn that oxygen has a valency of –2, although its oxidation states are –2, –1 (in peroxides) and +2 (when combined with fluorine). It does not have any higher oxidation states. Sulfur also has a valency of –2, but its oxidation states go much higher. For example, it has oxidation states of +2 in SF_2, +4 in SO_2 and +6 in SO_3. (Note that there is an oxide, SO, with sulfur in the +2 state, but it has only a transient existence: SF_2 exists in the gas state and is relatively stable .) The answer to this question is **E**, but you might wonder why oxygen does not have higher oxidation states.

There are various reasons for the lack of higher oxidation states in elements, such as oxygen, that are in the second period of the periodic table. The first reason applies to the ionic compounds. It is unlikely for elements to form highly charged positive ions, because removing negative electrons from a species that is positively charged becomes increasingly difficult as the charge is increased. Likewise it becomes increasingly difficult to force electrons onto a species that is already negatively charged. Ions rarely have charges greater than + 3 or –3, and even in these cases the compounds that are formed from them have considerable covalent character (because the electrons are partially shared between atoms rather than completely transferred from one atom to another).

Another reason for the lack of higher oxidation states in period 2 elements applies to covalent compounds. The atoms of the period 2 elements are very small, and there simply isn't room to put a lot of other atoms around them. Atoms of period 3 elements are larger, and so more atoms can be fitted around them. Furthermore, if the octet rule is broken (i.e. when there are more than eight electrons in the valency shell of the atom) then more orbitals are required to put extra electrons in. Period 2 elements have only two shells that contain electrons in the ground state, and the second shell is full when it has eight electrons in it (i.e. when the electronic configuration $1s^22s^22p^6$ has been reached). Period 3 elements have three shells, and, although a noble gas configuration is achieved at $1s^22s^22p^63s^23p^6$, there are empty d orbitals in the third shell that can be used (even though the 4s electrons are normally filled in before them).

For example if we draw the Lewis diagram for SO_3 with two single bonds and one double bond between the sulfur and the oxygen atoms, then the octet rule is obeyed. This is a molecule which is sometimes said to exhibit "resonance hybridisation", because the molecule can be drawn in different ways with one of the oxygens connected to the sulfur with the double bond. The three bonds are, in fact, equivalent, being somewhat stronger than a single bond.



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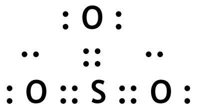
There is, however, some evidence that the bonds are even stronger and shorter than this would imply, and that the Lewis diagram of the molecule could be drawn with three double bonds, thus:



$$\begin{array}{ccc} & :O: & \\ \cdot\cdot & :: & \cdot\cdot \\ :O:: & S & ::O: \end{array}$$

In this case there would be 12 electrons round the central sulfur atom, breaking the octet rule, and requiring the use of 3d electron orbitals. The actual molecule probably involves some sort of hybridisation of all the possible structures. It should be noted that in both cases the sulfur is using all six of its valency electrons for bonding.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2005 continued

6. This question was very well done, with about 80% of students getting the correct answer. Most teachers (80%) felt that it was was fair, but a few of them said they thought it was too easy, and about 14% said that they had not yet covered it.

The question was concerned with indicators, and required students to appreciate that indicators change colour over a range of pH values. The table given in the question is shown below:

Indicator	pH range	Colour change
Methyl orange	3.2 – 4.4	Red → yellow
Bromothymol blue	6.0 – 7.6	Yellow → blue
Phenolphthalein	8.2 – 10.0	Colourless → red

This table shows that if you are adding alkali to acid, and are using methyl orange as an indicator, then you would expect the solution to change in colour from red (when the pH ≤ 3.2) to yellow (when the pH ≥ 4.4). In between pH 3.2 and 4.4 the colour changes from red to yellow through shades of orange (which is, of course, a mixture of red and yellow). In a similar way, bromothymol blue would change from yellow to blue, through shades of green (a mixture of yellow and blue) between pH 6.0 and 7.6. Phenolphthalein is slightly different in that it is colourless in solutions of pH ≤ 8.2, so that it gradually goes through shades of pink until it becomes truly red at around pH 10.0.

In order to answer this question you need to use the table to work out what colour each indicator will be when it is placed in a buffer solution of pH 7.0. This pH is above 4.4, so methyl orange will be yellow. At pH 7.0. however, bromothymol blue will be in the middle of its colour change range, and so it will appear green. Phenolphthalein will be below the start of its range, so that it will be colourless. The three indicators will therefore appear yellow, green and colourless, in that order, so the answer to this question is **D**.

It should be noted that when you are using an indicator to establish the endpoint of a titration, you need to choose an indicator that will be in the **middle** of its colour change range at the endpoint. For example, if you are expecting an endpoint at pH = 7.0, and you are titrating alkali with acid using bromothymol blue, then you would start with a blue solution in the flask and end the titration with a green solution. If the solution is yellow at the endpoint then you have added too much acid!

In fact when you are choosing an indicator for a titration you need to find an indicator the pK_{In} of which is roughly equal to the pK_a of the solution of the salt found at the equivalence point (endpoint) of the titration. The pK_{In} value lies approximately in the middle of the colour change range (although it may lie slightly "off centre" if the two colours involved are of markedly different intensity). You also need to choose an indicator that gives a good colour change for just one drop of the acid (or base) being added, in order for the endpoint to be as sensitive as possible, which means that the indicator must change colour in the part of the titration curve where the pH changes very rapidly.[1]

Note that an acid-base indicator is itself a weak acid (its pK_{In} value is in fact simply its pK_a value).[2] It is important therefore not to add more than 2 or 3 drops of indicator to an acid-base titration mixture, because otherwise it will make a significant change in the total amount of acid or base present. Indicators for other kinds of titrations (e.g. precipitation titrations) work differently, and may need to be used in larger volumes.

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[1] See the solution to Question 21 of this exam for further information on titration curves.

[2] An indicator exhibits one colour in its undissociated acid form (HIn, say) when it is in the presence of an acid stronger than itself, but it is a different colour when it is in its conjugate base form (In^-) in the presence of an alkali.

Questions 7 and 8 refer to the following reaction sequence, which you are told is used to prepare potash alum crystals from aluminum foil.

$$2Al(s) + 2KOH(aq) + 2H_2O(l) \rightarrow 2KAlO_2(aq) + 3H_2(g) \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;(1)$$

$$2KAlO_2(aq) + 4H_2SO_4(aq) \rightarrow K_2SO_4(aq) + Al_2(SO_4)_3(aq) + 4H_2O(l) \;.\;.\;.\;.\;.\;.\;.\;.\;(2)$$

This is an interesting pair of reactions, because, in them, aluminum displays its amphoteric properties, i.e. it exhibits both acidic and basic characteristics. In reaction (1) an aluminate salt is formed (potassium aluminate, $KAlO_2$): in this salt aluminum is associated with oxygen in the aluminate radical AlO_2^{-}, just as non-metals are often associated with oxygen in anions derived from acids (e.g. sulfur in the SO_4^{2-} radical). Reaction (1) is also unusual in that the potassium hydroxide is behaving like an acid by reacting with a reactive metal to release hydrogen. In reaction (2) potassium aluminate is behaving as the salt of a weak acid by reaction with sulfuric acid (which is strong): two salts of sulfuric acid are formed in this reaction – potassium sulfate and aluminum sulfate. In aluminum sulfate, the aluminum is present as a cation (Al^{3+}), i.e. it is behaving the way that metals usually do in salts – as though it had originally been part of a basic oxide or hydroxide that had reacted with the sulfuric acid to form the salt.

In **Question 7** you are told that about 0.6 g of aluminum foil is treated with 10.00 mL of KOH solution (2.00 mol L^{-1}) and the reaction is allowed to proceed until effervescence ceases, at which point the excess aluminum is filtered off. You have to find the volume of H_2SO_4 (1.00 mol L^{-1}) that needs to be added to the filtrate in order for reaction (2) to take place without any excess reagent remaining in the final solution.

Because you are told that the aluminum is added in excess at the beginning of reaction (1), you should not use its mass in the calculation. Instead you should base your calculations on potassium hydroxide, which is the limiting reagent. You need to find its chemical amount (in moles) in order to find the amount of H_2SO_4 that is needed, and thence its volume. The equation you need to use for this calculation is:

$n = cV$ Where n is the chemical amount in mol
c is the concentration in mol L^{-1}
and V is the volume in **L**

The chemical amount of KOH is therefore

$$= (2.00 \text{ mol L}^{-1} \times 10.00 \text{ mL}) / 1000 \text{ mL L}^{-1}$$

$$= 0.0200 \text{ mol of KOH}$$

Reading the equations you can see that 2 moles of KOH react to give 2 moles of $KAlO_2$, then these 2 moles react with 4 moles of H_2SO_4. In other words the mole ratio of KOH: H_2SO_4 is 2:4 (or 1:2). (Note that this is **not** the ratio you would expect if you were simply reacting KOH directly with H_2SO_4.)

The chemical amount of H_2SO_4 is therefore 2 x 0.0200 mol = 0.0400 mol.

You now need to find the volume of H_2SO_4 corresponding to this chemical amount, thus:

$$\text{Volume, } V = n/c \qquad = (0.0400 \text{ mol} \times 1000 \text{ mL L}^{-1}) / 1.00 \text{ mol L}^{-1}$$

$$= 40.00 \text{ mL of } H_2SO_4$$

The answer to question **7** is therefore **D**.

You may have been able to "see" the answer to this question without having to go through the full calculations in the way that is shown here, but, if you have time, this way will help you to avoid careless mistakes.

In **Question 8** you are given the formula of potash alum, which is a double salt. One mole of it contains one mole of K_2SO_4 and one mole of $Al_2(SO_4)_3$. You also have 24 moles of water, but as the reactions are done in aqueous solution, you don't have to worry about the water as this will be provided by the solvent water.

You can see from the chemical equations you are given that two moles of KOH are needed to produce one mole of each of the individual salts, and therefore one mole of potash alum (a KOH:alum ratio of 2:1). You can speed things up by using the information about the chemical amount of KOH that you determined in Question 7, i.e. that you started with 0.0200 mol of KOH. You will therefore obtain (0.0200 mol/2) = 0.0100 mol of potash alum.

You don't have to calculate the molar mass of potash alum, because it is given to you (the symbol M_r means relative molar mass – you just have to add the units of g mol^{-1}). You can determine the mass of potash alum obtained using the formula:

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

The mass of potash alum that can theoretically be obtained is therefore:

$$= 0.0100 \text{ mol} \times 948.8 \text{ g mol}^{-1}$$

$$= 9.488 \text{ g (or 9.49 g to 3 significant figures)}$$

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

This is the maximum mass that could be obtained, because, if you tried to do this experimentally, some mass would be lost in the process of filtering and transferring materials. In practice this is a very tricky experiment, but if you do it well you are rewarded by a product of beautiful potash alum crystals.

Most teachers felt that this pair of questions were appropriate, although some felt that Question 8 was too difficult. One teacher commented that the questions were long, but it should be noted that they were presented as a pair so that part of the calculations were common to both questions, which should have helped the students to save time[3]. About 67 % of students chose the correct answer to Question 7, but this dropped to about 60% for Question 8. It appears that students either didn't appreciate that they had been given a relevant molar mass, or that they did not understand what to do with the water of crystallisation given in the formula for potash alum.

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9. Again most teachers (87%) indicated that this question was appropriate, although some thought that it was too difficult and one commented that it was too long. About 60% of students chose the correct answer.

The question concerned the mineral glauberite. (I like to try and include at least one question with a geological connection on the exam.) Glauberite is an evaporite mineral that occurs in bedded salt deposits, along with halite (rock salt) and other minerals. You are told in the question that it contains sodium sulfate and calcium sulfate, and that it is the chief source of sodium sulfate, which is used in making glass. You

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[3] Note that students are allowed an average of just over two minutes per question, but some problems can be solved almost instantaneously, so that there should be time for more reflection on more difficult questions.

are given the calcium content of a small sample of glauberite, and you are required to work out from that how much sodium sulfate you might get from 1 tonne of the glauberite (i.e. on an industrial scale).

For this question you really need to know the formula of calcium sulfate, which is $CaSO_4$, because you need to know that one mole of calcium sulfate contains just one mole of calcium. You are given the mass of calcium, so you can work out the chemical amount of calcium and this gives you the chemical amount of calcium sulfate and hence its mass in the small sample. The mass of sodium sulfate can then be obtained by difference. Note that you are given the M_r values for calcium sulfate and sodium sulfate (although you don't really need the latter) so you don't have to do any calculations of molar mass. You can use the Periodic Table you are given to find the molar mass of calcium.

This is how the calculation works:

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

The chemical amount of Ca in the sample = 2.88 g / 40.08 g mol^{-1}
= 0.0718563 mol (or 0.0719 mol to 3 significant figures)
The chemical amount of $CaSO_4$ is therefore = 0.0719 mol

Using the formula $m = nM$

The mass of $CaSO_4$ in the sample = 0.0719 mol x 136.1 g mol^{-1}
= 9.780 g *

The mass of sodium sulfate in the sample is therefore

= (20.00 – 9.780) g
= 10.22 g

The mass of sodium sulfate in one tonne is therefore

= (10.22 g / 20.00 g) x 1000 kg
= 511 kg

* Note that if you use the rounded value of 0.0719 mol in your calculation, instead of using the numbers you have kept in your calculator, the mass of calcium sulfate in the sample comes out to 9.786 g and the mass of sodium sulfate in one tonne becomes 510.5 kg. The correct answer is thererore **B**.

The mineral glauberite actually contains a calcium sulfate:sodium sulfate ratio of 1:1, but, as you can see, you do not need to know this in order to solve the problem. In fact, ores containing glauberite are very likely to be impure, and could easily contain other minerals, including other calcium containing substances. So this method of determination would only give an approximate value in a "real life" situation.

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10. This question was rated as appropriate by most teachers (81%), with just a few feeling that it was too difficult or not on the curriculum. About two thirds of the students chose the correct answer. You have to find the molecular formula for a compound that is the chief constituent of pineapple flavouring, and it could have been done in two different ways.

The safest way of finding the answer, would be to use the data you are given. Start by using the percentages by mass of carbon (62.04%) and hydrogen (10.41%) in the compound, which you can use to calculate the empirical formula. But note that the values you are given do not add up to 100%. In this situation you can assume that the remainder of the compound consists of oxygen.[4]

The percentage by mass of oxygen is therefore (100 – 62.04 – 10.41) = 27.55 %. Now you can set up a calculation table to determine the empirical formula, thus:

	C	**H**	**O**
Mass, g	62.04	10.41	27.55
Molar mass, g mol^{-1}	12	1	16
Chemical amount, mol	5.17	10.41	1.72
Simplest ratio (obtained here by dividing through by the smallest number)[5]	3	6	1
Empirical formula	C_3H_6O		

Note that it is not necessary to use very precise values for the atomic molar masses, as the simplest ratio only needs to be a whole number.

Now that you have established an empirical formula, you need to consider the molecular formula. The first step in doing this is to consider formula masses. The formula mass for the empirical formula that you have determined (C_3H_6O) is (3 x 12 + 6 x 1 + 1 x 16) = 58 (g mol^{-1}). You are given an approximate relative molar mass (molecular formula mass) of 110 ± 10, which is a factor of (110/58) ≈ 2 times greater than the empirical formula mass. (Note that again we only need to look at approximate values, because whole numbers are required here.) The molecular formula therefore has twice as many atoms of each kind as the empirical formular. In other words the molecular formula is $C_6H_{12}O_2$, give or take a carbon or hydrogen atom or two (because the molecular formula mass is not known precisely).

Now we need to consider which structural formula might be possible. Let us consider each of the suggested answers in turn:

A. C_8H_{16} (octene)

This contains no oxygen, so it can quickly be ruled out as a possibility. Its relative molar mass is, however, 112.2, which is within the margins of error of the M_r value you are given. If you had not noticed that the percentages did not add up, this might have been a tempting possibility, as the ratio of the chemical amounts of C:H works out as 1:2.

/continued on next page

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[4] Traditionally the percentages of carbon and hydrogen are determined by a combustion method, nitrogen is determined by Kjeldhal's method (reduction to ammonia) and halogens are determined by Carius's method (via the silver halide). Oxygen cannot be so easily determined, therefore it is found by difference.

[5] There is a little ditty that you can use to help you with the steps in this kind of calculation:

"Percent to mass
Mass to mole
Divide by small
Multiply 'til whole"

In the present case you don't have to use the final line of the ditty, because you have already arrived at a whole number. You have to start multiplying if you end up with numbers ending in .5 (when you need to multiply by 2) or .33 or .67 (when you need to multiply by 3).

B. CH_3CH_2CHO (propanal)

This has a molecular formula of C_3H_6O, which is, of course the same as the empirical formula of our target compound. Tempting, but its molecular formula mass (58 g mol^{-1}) isn't right of course.

C. $CH_3CH{=}CHCH_2CH_3$ (pent-2-ene)

This is another compound that can be ruled out as it contains no oxygen. Its relative molecular mass (70.13) also makes it an impossible choice.

D. $CH_3(CH_2)_5CH_2OH$ (heptan-1-ol)

This contains oxygen, and has a relative molecular formula mass of 116. 2, which is within the margins of error, but its molecular formula is $C_7H_{16}O$, which doesn't work. This means the answer to the question must be E by process of elimination, but let's just check it out.

E. $CH_3(CH_2)_2COOCH_2CH_3$ (ethyl butanoate)

This contains oxygen, and has a relative molecular formula mass of 116. 2, which is within the margins of error, and its molecular formula is $C_6H_{12}O_2$ (or 2 x C_3H_6O) which is what you are looking for. The answer to this question is therefore **E**.

The second way of working out the answer to this question is to say that esters have pleasant fruity odours. $CH_3(CH_2)_2COOCH_2CH_3$ is the only option offered with an ester group (–COOC–) in it. Therefore the answer must be E. And you are then very quickly on to the next question!

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11. I felt that this was a very simple question and most of the teachers (88%) felt that it was appropriate, although a few felt that it was too difficult. About 62% of students chose the correct answer.

The question requires you to work out which one of five different substances has an unpaired electron in its Lewis structure, but you don't really need to draw out the Lewis structures for these molecules. All you need to do is count up the total number of valency electrons on the atoms in these molecules.

You have, in fact, got very few atoms to consider in this particular selection of molecules – just hydrogen, carbon, nitrogen and oxygen, which have 1, 4, 5, and 6 valency electrons respectively. If the total number of valency electrons in a molecule comes out as an even number, you know that all the electrons are likely to be paired – either in covalent bonds or in non-bonding (lone) pairs. If there are an odd number of electrons in the molecule, then it is going to have an unpaired electron in it.

Let us see how this method works out in practice, considering each of the molecules given in the question in turn:

A. NH_3 (ammonia)

One nitrogen + 3 hydrogen atoms gives a total of (5 + 3 x 1) = 8 electrons (an even number)

B. $N \equiv N$ (nitrogen)

Two nitrogen atoms give a total of (5 + 5) = 10 electrons (an even number)

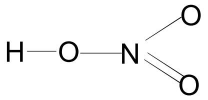
C. $N = O$ (Nitric oxide or nitrogen monoxide)

One nitrogen plus one oxygen atom gives a total of (5 + 6) = 11 electrons (an odd number). The answer to this question is therefore likely to be C, but to continue…

D. H—C ≡ N (hydrogen cyanide)

One hydrogen plus one carbon plus one nitrogen gives a total of (1 + 4 + 5) = 10 electrons (an even number)

E. HNO_3 (nitric acid)

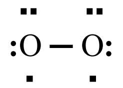


One hydrogen plus one nitrogen plus three oxygens gives a total of (1 + 5 + 3 x 6) = 24 electrons (an even number)

This means that the answer to the question is **C**. I am mystified as to why about 15% of the students chose NH_3 as an asnwer. I wonder whether they thought that the question was asking about lone pairs rather than odd electrons? Another 15% chose nitric acid, but perhaps this was because the nitrogen in this molecule has only 4 covalent bonds. It is possible that the students who chose this option were thinking that one of nitrogen's valency electrons was the odd one, whilst in fact the single bond to one oxygen contains two electrons that might be considered to originate from nitrogen, so that it is a dative covalent (or coordinate) bond rather than a "regular" covalent bond which would consist of one electron from nitrogen and one from oxygen.

There are a number of other "odd electron" molecules, which can be recognized by the fact that they have an odd number of valency electrons. Examples are NO_2 (nitrogen dioxide) and ClO_2 (chlorine dioxide). You might like to try drawing out the Lewis diagrams for these molecules. Note that nitrogen dioxide has a tendency to dimerize in the liquid state to give N_2O_4, in this way the "odd electrons" of two NO_2 molecules pair up to give a single covalent bond. The superoxide ion (O_2^-), which is found combined with some alkali metal ions, is another kind of an odd electron species.

The presence of unpaired electrons in a substance is indicated on a macro scale by the substance being attracted to a magnetic field. One particularly interesting example of this is oxygen, O_2, which is attracted to magnetic poles in its liquid form. Oxygen molecules have an even number of valency electrons, and you probably think of it as O=O. It could, however, exist as:



$$:\overset{\cdot\cdot}{\underset{\cdot}{O}} - \overset{\cdot\cdot}{\underset{\cdot}{O}}:$$

which would give it the observed magnetic properties. The reason for this anomaly might be that the oxygen molecule is very small, so that all the electrons in a double bond would have to be close together. The repulsive forces of so many negative electrons so close together would be relieved if one of the bonding pairs breaks apart to give odd electrons. Generally, however, odd electrons species tend to be somewhat unstable.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2005 continued

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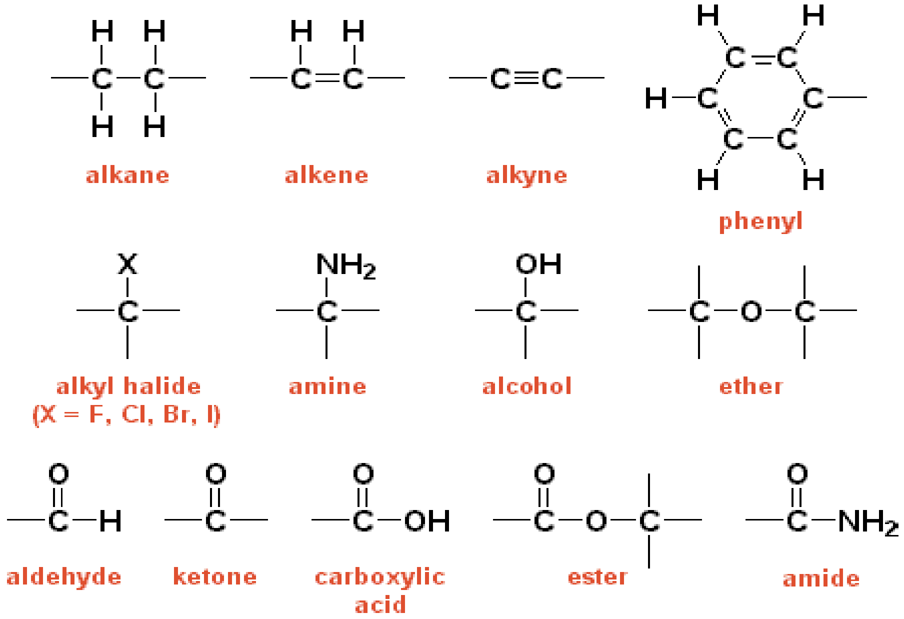
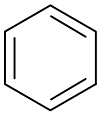
12. This question related to organic functional groups: most teachers (>60%) felt it was appropriate, although aaround 28% thought it was not on the curriculum. In the event, it was very poorly done with fewer than a quarter of the students choosing the correct answer.

The Pan-Canadian protocol states that students should know some organic functional groups, but it is not clear exactly which groups students are expected to know. Therefore, in the answer to question 6 of the 2002 NHSCE, I gave a list of organic functional groups that I expected students to be able to recognize. This is getting to be some time ago now, and students may not be trying to do exams from this far back. For that reason I shall reproduce here the diagrams of the groups that I expect students to know:

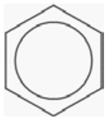


Note that it was also stated in these solutions that **phenol** would also be included in the NHSCE from that time on.

The use of condensed formulae has also been discussed in previous solutions, and formulae such as



and the aromatic ring



have been introduced for benzene.[1]

As a phenol involves a hydroxy group (–OH) attached to a benzene ring, it can appear as:

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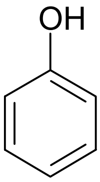
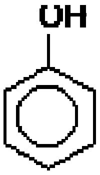
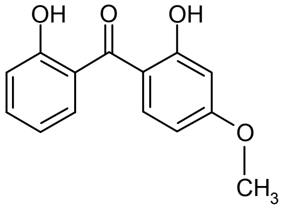
[1] See the solutions to questions 20 and 21 of the 2004 exam, which both refer to the formula of aspartame.



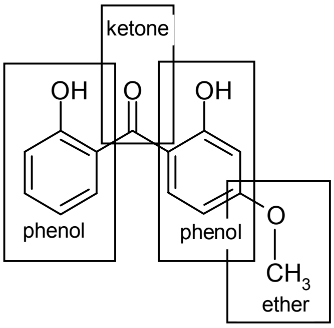
or as



The structural formula of the compound given in the question is:



The functional groups in this molecule are shown below:



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

Over 40% of students who answered this question chose “A” as the answer, indicating that they had correctly identified the condensed structures of the ether and ketone groups, but that they had failed to recognize the hydroxy group (–OH) as being a phenol rather than an alcohol. As one teacher said – this question is trickier than it looks.

The compound in this question is known by a variety of names, including benzophenone–8 or (2–hydroxy–4–methoxyphenyl)(2–hydroxyphenyl) methanone. The molecule contains a conjugated system i.e. one that has alternating double and single bonds. In such a system the second pair of electrons in the double bonds can actually spread across the single bonds so that all the bonds behave like “one-and-a-half” bonds, and these electrons can move throughout the entire conjugated system, i.e. they are delocalised (this results in a stabilising effect). Conjugated compounds are able to absorb energy without covalent bonds being broken. In the case of benzophenone–8 it is particularly good at absorbing UV radiation, which is why it is effective as a sunscreen.

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13. This question was moderately well done, with about 58% of candidates choosing the correct answer. Teachers, however, felt it was the least appropriate question on the exam – many of them felt that it was not on the curriculum, and others said that they thought it was too difficult. The question was concerned with different kinds of large molecules, and the easiest way of doing it is probably to try to identify the class of compound from the formula you are given, rather than try to think of all the formulae that might be associated with the different types of compounds that are suggested as answers. If this is not clear, then look at two methods that are given below!

The formula you are given is:

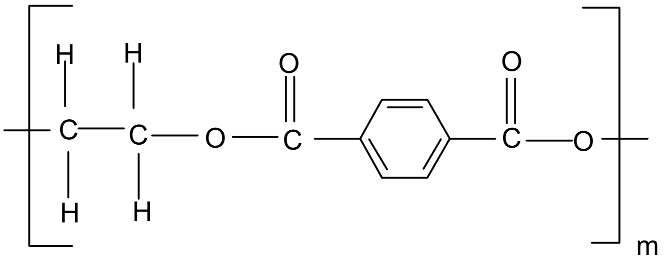
$$-\!\!\left(CH_2CH_2O_2CC_6H_4CO_2CH_2CH_2O_2CC_6H_4CO_2 \right)\!\!-_n$$

This is the repeat unit of a polymer that contains "n" such units. In fact this chunk of the formula contains two equivalent parts, so that the molecular formula could also be written as:

$$-\!\!\left(CH_2CH_2O_2CC_6H_4CO_2 \right)\!\!-_m$$

(where m = 2n.).

It is probably easiest to draw this repeating unit out as:



At this point you should be able to see that there are two ester groups (and a phenyl group) in this formula, so that you now know that represents a polymer with ester groups in it, i.e. that it is a polyester, and that the answer to this question is therefore **C**.

The alternative way of finding the answer to this question is to go through each of the suggested answers in turn, as shown below.

A. Detergent

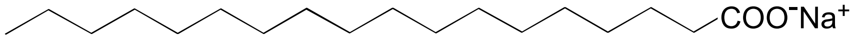
A detergent is a water-soluble cleansing agent. Detergent molecules contain a polar part that is attracted to water, and a non-polar part that is attracted to grease and dirt. The detergent molecules form a sort of chemical bridge between the dirt and water, reducing the surface tension of the water and enabling the water to "pull" the dirt away from the material it is attached to (such as human clothes and skin).

The detergent that you are most likely to have come across in your chemistry courses is soap, which is a mixture of salts of medium- and long-chain carboxylic acids. The general formula of a soap is $CH_3(CH_2)_nCOO^-Na^+$. An example of a soap is sodium octadecanoate (sodium stearate), for which n = 16, giving it a total of 18 carbon atoms (including the first and last carbons), which is indicated by IUPAC name ("octa" means 8, and "deca" means 10, thus "octadeca" means 18). The formula of sodium octadecanoate is shown below:

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO^-Na^+$

Non-polar tail Polar "head"

It can also be written in the following form:



Soaps have the disadvantage of reacting with calcium ions in hard water to form insoluble calcium salts (scum), so synthetic detergents have been developed. These have water-soluble calcium salts.

Some examples of different types of synthetic detergents are:

Sodium alkane sulfonates	$CH_3(CH_2)_nCH_2SO_2O^-Na^+$
Sodium alkyl sulfates	$CH_3(CH_2)_nCH_2OSO_2O^-Na^+$
Sodium alkylbenzenesulfonates	$CH_3(CH_2)_nCH(CH_3)C_6H_4SO_2O^-Na^+$

Note that the difference between the sulfonates and the sulfates is that the sulfonates contain a C–S bond and the sulfates have a C–O–S sequence of bonds. Also, a sulfonate group has only 3 oxygens in it, whilst a sulfate group has 4.

It is possible to have non-ionic synthetic detergents, which have a number of oxygen atoms in the molecule that form hydrogen bonds with water molecules. An example is:

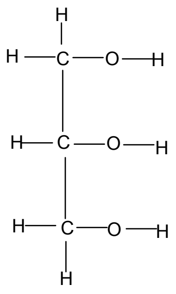
$$CH_3(CH_2)_nCH_2OCH_3(CH_2)_mCH_2OH$$

To go back to the question – none of these detergents has a formula that is anything like the one you were given in the question, so the answer cannot be A.

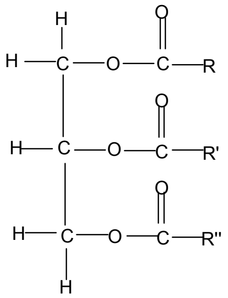
B. Natural oil or fat

Natural oils and fats are tri-esters of propane–1,2,3–triol, formerly known as glycerol, and long chain carboxylic acids ("fatty" acids). Three acid molecules are required to combine with the three alcohol groups in propane–1,2,3–triol, and these may be from the same acid, RCOOH, or from two or three different acids. The symbol "R" is used to represent an alkyl group in the acid. Thus octadecanoic acid ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$) and related acids can simply be represented by RCOOH, which, I think you will agree, is even simpler than writing $CH_3(CH_2)_nCOOH$. Alkyl groups with different lengths of chains, or with chains containing double bonds, can be represented by R′ or R″ etc.

The formula for propane–1,2,3–triol is shown below:



If this combines with three acid molecules, RCOOH, R′ COOH and R″COOH, the resulting molecule is a fat or oil, with the formula:



This is nothing like the formula you are given, so the answer to this question cannot be B.

Note that the difference between a fat and an oil is that a fat is solid, and an oil is liquid (at room temperature). Fats usually contain alkyl groups that are saturated (i.e. all the bonds between carbon atoms are single bonds), oils usually contain alkyl groups that are unsaturated (i.e. one or more of the bonds between carbon atoms are double bonds)[2]. The reason that unsaturated alkyl groups are associated with oils rather than fats, is that their chains tend to be bent by their double bonds, so that their molecules cannot make as many intermolecular bonds, nor are the molecules close enough together to make bonds that are as strong, thus they have low melting points (i.e. they are liquids are room temperature). Saturated alkyl groups can get closer together giving a greater number of stronger intermolecular bonds, so that compounds containing saturated alkyl groups have higher melting points than compounds containing unsaturated alkyl groups of the same chain length: they are usually solids rather than liquids at room temperature.

Oils with several double bonds are called polyunsaturated, and these are considered to be healthier to eat than saturated fats. Solid fats are, however, often considered to be easier to use, so sometimes oils are hydrogenated to turn them into saturated compounds, which are solid. Furthermore, some natural oils are actually poisonous, and must be hydrogenated in order to be edible at all. Either way, it is probably best to avoid foodstuffs that say they contain hydrogenated oils.

You may also have heard in recent news reports that so-called “trans fats” are bad for you. These are formed when polyunsaturated oils are partially hydrogenated, leaving one or two double bonds in the alkyl groups. It really has nothing to do with the answer to this question, but you might like to check out what is meant by the term “trans”, which is used to describe one kind of geometric isomer that is formed with double bonds (see the answer to question 5 of NHSCE 2001). The other kind of geometric isomers (“cis” isomers) are found in natural oils, such as olive oil, and are generally considered to be good for you.

You will probably have noticed that the carboxylic acids that we have discussed in this section, are very similar to the carboxylate salts that are found in soaps (see the discussion in A above). They are indeed very similar, because soaps are actually manufactured from fats, by reacting them with sodium hydroxide, NaOH (or with potassium hydroxide, KOH). This treatment is called saponification and it breaks the fat or oil down into propane–1,2,3–triol and the sodium (or potassium) salts of the acids RCOOH, R′ COOH and R″COOH found in the fat or oil.

C. Polyester

This has been discussed above.

/continued on the next page

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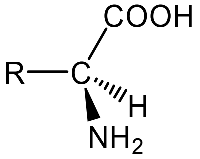
[2] Strictly speaking the term “alkyl” refers to a group with the formula $–C_nH_{(2n+1)}$. An unsaturated group would contain fewer hydrogen atoms. Nevertheless the carbon-hydrogen chains in fats and oils are generally referred to as alkyl groups, even where they contain some double bonds.

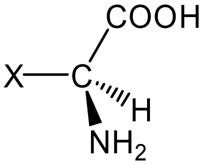
D. Protein

Proteins are large molecules that are considered to be derived from linked together amino acids. There are 22 different amino acids occurring in nature (two of which are very rare), and many proteins contain several thousand amino acid units. Proteins differ from synthetic polymers such as polyesters, because the amino acids in proteins do not necessarily repeat themselves in the same way throughout the molecule. This results in huge numbers of different proteins being formed from different arrangements using the 22 amino acids. For example, for a protein containing 5000 amino acid units, the number of possible arrangements is theoretically 22^{5000}, i.e. about 10^{6700}. This may seem daunting, but there is a simple picture of the arrangements of amino acids in a protein that you can easily learn to recognize.

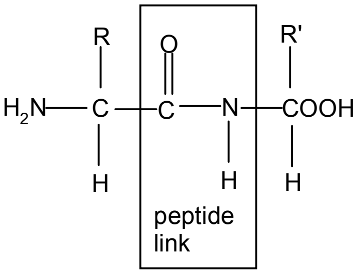
First of all, you need to be aware that an amino acid is an organic compound that contains both an amine group (NH_2) and carboxylic acid group (–COOH). It is often shown in textbooks as:



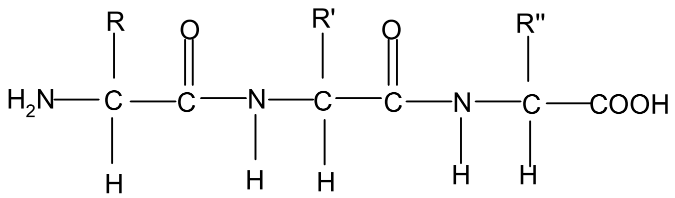
It should be noted that the "R" group in this formula can be an alkyl group (as discussed for oils and fats above) but it can also represent hydrogen or a phenyl group or an group that includes a hetero atom such as sulfur or a functional group (e.g. a hydroxyl group or more carboxylic acid or amine groups) . For that reason, you sometimes see the "R" in the amino acid replaced with "X", which is intended to include all these possibilities. Thus the general formula of an amino acid appear in some books as:



When two amino acids are joined together, the amine group of one molecule is connected to the carboxylic acid group of the other molecule (and a molecule of water is eliminated). This creates a sequence of atoms and bonds known as a peptide link, as shown below:



More amino acids can be added on, so that both the amine groups and the carboxylate groups of almost all the acids are involved in peptide links. (There is one unattached amine group and one unattached carboxylate group left at each end of the chain, of course.) Thus three amino acids will be joined up by two peptide links as shown below:



$$H_2N-CH(R)-CO-NH-CH(R')-CO-NH-CH(R'')-COOH$$

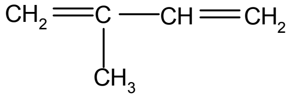
When a molecule contains large numbers of amino acids linked together it is known as a polypeptide. The order in which the amino acids are linked in the polypeptide molecule is known as its primary structure. A protein is a kind of polypeptide, but it is somewhat different in that it has additional characteristics, which are associated with its secondary and tertiary structures. In these structures further linkages occur between different parts of the molecule (forming intramolular bonds), which cause it to change its 3-dimensional shape, forming into pleats or coils for example. These complex structures give proteins their biological properties. Proteins are extremely important in life processes, and can function in many different ways, e.g. as enzymes, as hormones and as strucutural molecules (keratin, collagen etc.).

Irrespective of their function, the formula of a protein can be recognized by the characteristic –CONH– peptide link. This link is not in the formula given in this question, so the answer cannot be D.

E. Rubber

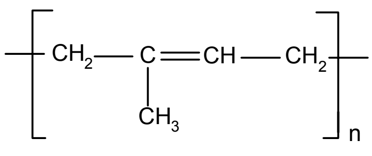
Rubbers are polymeric materials with elastic properties. Natural rubber can be obtained from the Para rubber tree. When the outer bark of the tree is cut a milky liquid called latex oozes out. Raw rubber can easily be precipitated from latex, but it is sticky and soft. Sulfur is often added to the latex to make the rubber harder by forming cross linkages between the polymer molecules: this process is called vulcanisation. Nowadays several different forms of synthetic rubber are available – these are generally cheaper than natural rubber, and can be designed to provide more useful properties.

Natural rubber can be considered to be an polymer of 2–methylbuta–1,3–diene (formerly known as isoprene), which has two double bonds. Its formula is:



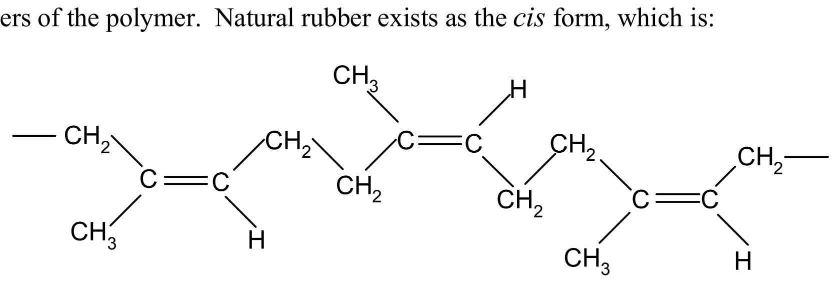
$$CH_2=C(CH_3)-CH=CH_2$$

Synthetic rubber, poly(2–methylbuta–1,3–diene) can be obtained by addition polymerisation. Note, however, that the polymerisation process only uses one double bond per molecule of 2–methylbuta–1,3–diene, the other double bond stays in the middle of the "mer" unit, thus:

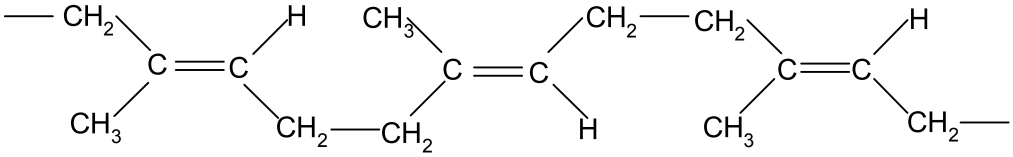


$$\left[-CH_2-C(CH_3)=CH-CH_2-\right]_n$$

Because there is a double bond in the middle of each mer unit, it is possible to have both *cis* and *trans* isomers of the polymer. Natural rubber exists as the *cis* form, which is:



The *trans* form is a synthetic polymer called gutta-percha, which is much less elastic than rubber, and has the formula:



Different synthetic rubbers can be made by addition polymerisation of other dienes or one of their derivatives, or by co-polymerisation of a diene with another compound. They all have one characteristic in common, however, and that is the presence of >C=C< bonds in the polymer molecules. This is not the case in the formula given in the question, therefore the answer cannot be E.

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14. Questions involving electrolysis seem to create problems every year, and this year was no exception, even though this question was intended to be easy. About half the teachers felt that it was appropriate although others felt that it was too difficult, not on the curriculum, or not yet covered. Only about a third of the students chose the correct answer.

The question concerned the industrial production of chlorine, and it is probably best solved by considering each suggested process in turn.

A. Treating sea water with bromine

Sea water varies a good deal in composition depending on the particular sea or ocean where it is found, but it generally contains considerable amounts of dissolved solids, principally sodium chloride. It also usually contains various concentrations of potassium, magnesium and calcium cations in addition to sodium ions, and bromide, hydrogencarbonate and sulfate anions in addition to chloride ions. Molecular chlorine is obtained by the oxidation of chloride ions, but there are much better sources of chloride than sea water, notably in solid deposits of sodium chloride in salt mines.

The main problem, however, with this suggested answer is that bromine **cannot** be used to oxidise chloride ions. This is because bromine is less reactive than chlorine in the reactivity scale of non-metals – bromine has a less positive standard reduction potential than chlorine (+1.09 Volts compared with +1.36 Volts). You should be aware that the reactivity of the halogens decreases as you go down the group, thus the order of their reactivity is $F_2 > Cl_2 > Br_2 > I_2$, even if you do not have a table of standard reduction potentials, or haven't yet "done" standard potentials in class.

What might have confused you here is that sea water is, in fact, used as a raw material for obtaining bromine (rather than chlorine). This is done by treating the sea water with chlorine (the more reactive element). The equation for this "redox competition" reaction is:

$$Cl_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$$

The reverse reaction does not occur, so that the answer to this question cannot be A.

B. Electrolysis of brine (sodium chloride solution)

Brine is usually obtained by "solution mining", that is by pumping hot water into salt mines to obtain a solution of sodium chloride. Alternatively rock salt can simply be mined, brought to the surface, and then dissolved in water. Trace amounts of other salts are also found in the resulting brine solutions, because salt deposits are usually created when inland seas dry up and then become covered by rocks. The ions present in the solid are likely to be very similar to those found in present-day sea water (with the exception of hydrogencarbonate ions, which will turn into carbonate as the water evaporates from the sea). Brine is electrolysed on an industrial scale using three different methods: the diaphragm cell, the membrane cell and the flowing mercury cathode (or Castner-Kellner) cell.

If we simply consider brine to be an aqueous solution of sodium chloride, then we can say that the ions in the solution will be Na^+, H^+, Cl^- and OH^-. The hydrogen ions and hydroxide ions come from the dissociation of water, according to the following equation:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

This equilibrium constant for this reaction, $K_w = 1.0 \times 10^{-14}$ (at 25°C), indicating that very few of the water molecules are ionised, however, if the equilibrium is disturbed by removing some of the ions, then the "stress" on the system will be relieved by the dissociation of more water molecules to replace the lost ions according to Le Châtelier's principle (and keeping K_w constant). Because there are two cations and two anions present in the brine, there will be a competition reaction at each electrode when the solution is electrolysed. Let us consider the possible reactions occurring at each electrode in turn.

At the anode

The anions, Cl^- and OH^- are attracted to the anode (positive electrode in an electrolysis cell) where they will compete to give up electrons. The oxidation processes that can occur at the anode are:

$$2Cl^-(aq) \rightarrow Cl_2(aq) + 2e^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^- \quad . \; . \; . \; . \; . \quad (2)$$

The standard reduction potentials (E^θ values) suggest that reaction (2) is the one most likely to occur.[3] The conditions are not, however, standard. By definition, standard conditions require the concentration of aqueous solutions to be 1.0 mol L^{-1}, and the concentration of chloride ions in brine is likely to be very much greater than this, whilst the concentration of hydrogen ions in water is very much less (1.0×10^{-7} mol L^{-1}). These concentration differences mean that chlorine is, in fact, preferentially discharged at the anode. Initially it dissolves in the water, but after that it is quickly released from solution as a gas, thus:

$$Cl_2(aq) \rightleftharpoons Cl_2(g)$$

Chlorine gas can thus be obtained from the electrolysis of brine. Unfortunately, as the electrolysis continues, the concentration of chloride ions drops, whilst the concentration of hydroxide ions rises due to reactions at the cathode (see on). This means that it is increasing likely that oxygen will be produced, contaminating the chlorine. The three different kinds of commercial cells deal with this problem in different ways, thus:

- in the flowing mercury cathode cell the sodium hydroxide is formed in a separate part of the apparatus, and brine is continuously added to the electrolysis cell

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[3] The reduction reactions that apply are the reverse of these oxidation reactions, i.e.

$$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)\ ;\ E^\theta = +1.36\ V$$

$$2H_2O(l) + O_2(g) + 4e^- \rightarrow 4OH^-(aq)\ ;\ E^\theta = +0.40\ V$$

Bearing in mind that the standard potential for the reduction reaction has approximately the same numerical value as that for the oxidation reaction, but with the opposite sign, we can see that the oxidation potential for reaction (1) = – 1.36 V, whilst that for reaction (2) = – 0.40 V, so that reaction (2) has the more positive (less negative) oxidation potential, and is most likely to occur **under standard conditions**.

- in the diaphragm cell the electrolysis is halted after a certain point and the solids in the solution are separated by fractional crystallisation, with the sodium chloride being recycled. (The diaphragm is used to keep the chlorine and the sodium hydroxide separate, so that they do not react.) Not surprisingly, the sodium hydroxide obtained in this process is contaminated with sodium chloride.
- in the membrane cell the membrane is an ion exchanger that contains the brine in the anode compartment, whilst the cathode compartment contains pure water. This process has the advantage of producing very pure sodium hydroxide.

At the cathode

The cations, Na^+ and H^+, will be attracted to the cathode (the negative electrode of an electrolysis cell), where they will compete for electrons. The reduction processes that can occur at the cathode are:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)\ ;\ E^\theta = \ 0.00\ V\ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ (3)$$

or $$Na^+(aq) + e^- \rightarrow Na(s)\ ;\ E^\theta = -2.71\ V\ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ (4)$$

Looking at these reactions one can see that reaction (3) is more likely to occur, because it has the more positive standard reduction potential (E^θ value), although, admittedly, the concentrations are not standard for either ion. Even if you have not learnt about standard reduction potentials, you should be able to see that it is extremely unlikely that sodium metal will form at the electrode, as it reacts very vigorously with water. Usually, therefore, hydrogen gas is the product at the cathode in the electrolysis of sodium chloride, with hydroxide ions being left in the solution as more and more hydrogen ions react to form hydrogen.

In the flowing mercury cathode cell, however, the reduction potentials are altered, and sodium is formed at the mercury cathode: the sodium, however, dissolves in the mercury (with which it forms a kind of alloy called an amalgam) and flows with it out of the electrolysis cell and into another chamber before being reacted with water in a controlled fashion, thus:

$$2Na(amalgam) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

The advantage of using the flowing mercury cathode cell is that sodium hydroxide is formed away from the electrolysis cell, so that there is no problem of it getting mixed with sodium chloride, nor does it get a chance to react with the chlorine formed at the anode. The disadvantage of using this process is that small amounts of mercury gradually leak out into the environment – and even these small amounts are seriously toxic and can create environmental problems.

To summarize: there are three industrial processes for the electrolysis of brine. Chlorine is produced in all three of them, along with sodium hydroxide and hydrogen. All three products are important commercially. The answer to this question could be B, but we should continue to examine the other suggested processes.

C. Electrolysis of molten sodium chloride

The electrolysis of molten sodium chloride is a much simpler process that the electrolysis of the aqueous solution, because there are no hydrogen and hydroxide ions present to compete with the sodium and chloride ions. The products of the electrolysis are chlorine gas at the anode (see reaction 1 above) and sodium metal at the cathode (see reaction 4 above). The electrolysis is done in a special cell (called a Downs cell) designed to ensure that the liquid sodium metal cannot come in contact with air, or with the chlorine produced.

So chlorine is produced industrially by this process, and the answer could be C.

D. Electrolysis of sodium hypochlorite solution

Sodium hypochlorite is the common name for sodium chlorate(I), NaOCl. It is usually made by reacting chlorine with sodium hydroxide, thus:

$$2NaOH(aq) + Cl_2(g) \rightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$$

It can also be produced by mixing the sodium hydroxide and chlorine produced in the electrolysis of brine and allowing them to react. Continuing the electrolysis and mixing process allows chlorate(I) ions to be oxidised to chlorate(III) at the anode, thus:

$$12ClO^-(aq) + 6H_2O(l) \rightarrow 4ClO_2^-(aq) + 12H^+(aq) + 8Cl^-(aq) + 5O_2(g) + 12e^-$$

At higher temperatures it is possible for chlorate(V) ions to form, thus:

$$3ClO^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq)$$

As you can see, chlorine is not produced in any of these reactions – in fact it is consumed during the electrolysis. So the answer to this question is not D.

You should realise that you do not need to know the details of these somewhat obscure reactions. This key is really only put into the question as a distractor. However, you might have been able to guess that it was a non-starter because sodium hypochlorite is a bleach, and, as such, it is a source of oxygen that reacts with dyes to form colourless products. It also gradually breaks down to oxygen if it is left in the bottle, thus:

$$2NaClO(aq) \rightarrow NaCl(aq) + O_2(g)$$

E. Electrolysis of aqueous hydrochloric acid

Hydrochloric acid solution contains hydrogen cations, and chloride and hydroxide anions. (The hydrochloric acid provides the hydrogen and chloride ions, whilst the solvent water provides hydrogen and hydroxide ions.) There is therefore no competition at the cathode when the solution is electrolysed – hydrogen is formed. At the anode there is a competition between the chloride and the hydroxide for which one of them will give up an electron, but the chloride usually wins because of concentration effects, as discussed for the brine solution above. Chlorine is thus a product of the electrolysis of hydrochloric acid solution, so the answer might conceivably be E. You should, however, be aware that hydrochloric acid is actually made by dissolving hydrogen chloride gas in water, and that this hydrogen chloride gas is made from burning hydrogen in chlorine. The sequence of reactions is:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

$$HCl(g) + aq \rightarrow HCl(aq)$$

(where “aq” indicates water in an unspecified molar amount).

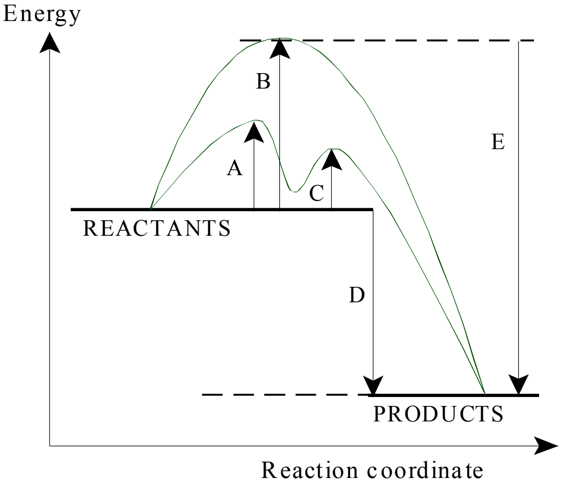
It would be a pointless exercise to use chlorine to make hydrochloric acid, which would then be electrolysed to make more chlorine, so obviously this is not done commercially, and the answer to this question is not likely to be E.

You are now left with two possible answers to the question “Which is the main process for the industrial production of chlorine?”. It could be B (the electrolysis of brine) or C (the electrolysis of molten sodium chloride), as both of these processes are used on an industrial scale to produce chlorine. The question is now reduced to “Which is the **main** process?”. And this is the electrolysis of brine, which creates the valuable co-products of sodium hydroxide and hydrogen. The electrolysis of molten sodium chloride is used principally in the production of sodium metal, and is much more expensive to operate because of the large amount of energy required to keep the contents of the cell molten. About 98% of all the chlorine produced in North America is, in fact, obtained from the electrolysis of brine, and so the answer to this question is **B**.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2005 continued

15. This question is concerned with the diagram that compares the energy profiles of a reaction and of the same reaction when it is catalysed. Most teachers (almost 90%) thought that the question was appropriate, and most students (> 70%) chose the correct answer.

The question refers to the following diagram, which was, in fact, essentially the same as the one used in the solution to Question 17 of the 2004 NHSCE. Students who are not familiar with this kind of diagram should refer to last year's solutions for a fuller explanation of activation energy and catalysis than that given below.



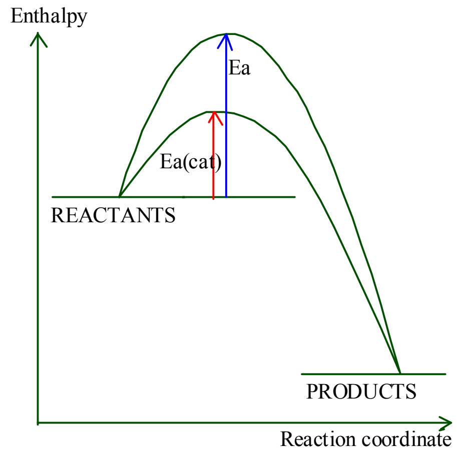
This diagram shows the energy changes that take place during the generalised reaction:

Reactants → Products

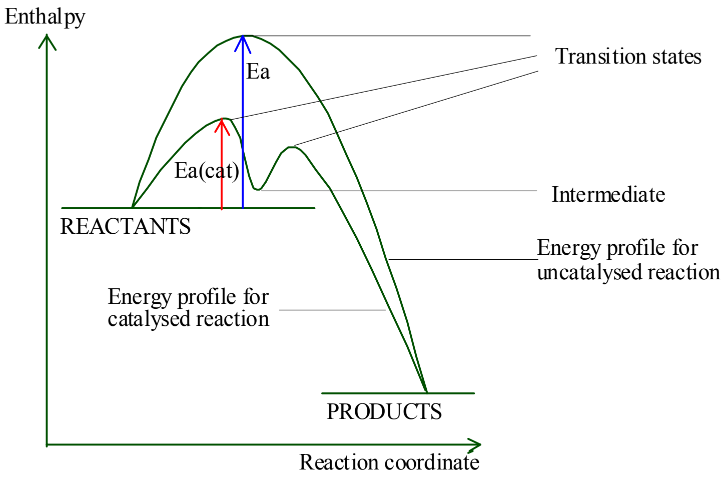
The reactants are at a higher energy (or enthalpy) level that the products, which means that energy will be given out in the reaction. This particular reaction is **exo**thermic. The enthalpy change (ΔH) for the reaction is negative and is represented by the downwards arrow, D.

The two curved lines on the diagram indicate the energy profile of the reaction, i.e. how the energy of the chemical species present in reaction mixture changes as the reaction proceeds. The upper curve indicates the energy changes for the uncatalysed reaction. This curve has a "bump" at the top: this is the point of maximum energy, where a highly unstable transition state is formed fleetingly. Energy is required by the system to create the transition state – this is the activation energy (E_a), and is indicated by the upwards arrow, B. Once the unstable transition state rearranges to form the products a considerable amount of energy is released, this is indicated on the diagram as E: it does not have a particular name, it is just the energy difference between the highest and lowest energies involved in this reaction.

As you probably know, a catalyst reduces the amount of energy required for a reaction to take place. It does so by changing the energy profile for the reaction. The lower curve on the diagram shows a possible energy profile for the reaction when it is catalysed. The curve for the catalysed reaction in this diagram has two "bumps" (transition states), but the diagrams you may have seen in textbooks often only show one maximum for the catalysed reaction, and you will have learnt to recognise that this lower "bump" is the one you use to measure the activation energy of the catalysed reaction ($E_{a(cat)}$). See the diagram on the next page.



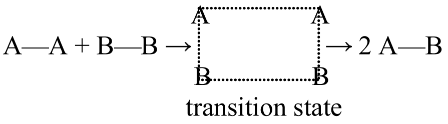
The curve shown on the diagram given in this question indicates that the reaction goes through one transition state (sometimes called an activated complex) to form an intermediate (indicated by the trough on the curve), and then goes through another transition state before it forms the products. The intermediate is stable enough to exist for a period of time that is usually measurable, but it is unstable in comparison with the final products (because it has a higher enthalpy than the products). Catalysed reactions usually involve the reaction of one of the reactants with the catalyst to form an intermediate, then another reactant reacts with the intermediate to form the products. The reaction profile for a catalysed reaction is thus much more likely to show two (or more) “bumps” than to have just one single transition state.



For the following hypothetical reaction:

$$A_2(g) + B_2(g) \rightarrow 2AB(g)$$

The uncatalysed reaction might follow the reaction path:



The reaction might go through something like the following reaction sequence with a catalyst "X":

$$2A—A + 2X \rightarrow \text{first transition state} \rightarrow 2(A—X)$$

followed by $$2(B—B) + 2(A—X) \rightarrow \text{second transition state} \rightarrow 2(A—B) + 2X$$

The same amount of catalyst is thus available at the end of the reaction as there was at the beginning. Note that the activation energies for both the first and second transition states of the catalysed reaction must be lower than that of the transition state for the uncatalysed reaction, if the catalyst is going to increase the rate of the overall reaction.

To return to the question: the problem now resolves itself into the problem of deciding which of the two activation energies shown in the "double bump" diagram will be the relevant one for the overall reaction. Even if you have not seen this diagram before, it should be fairly easy to work out that the bigger of the two energies is the one to choose, as the energy released in going from the highest energy (most unstable state) to a lower energy level (that of the intermediate in this diagram) will be sufficient to allow the formation of the second transition state. (This will hold true even if the first "bump" is not the bigger one.) The answer to this question is therefore **A**.

To recapitulate – The energies shown on the diagram given on the question are:

A. Activation energy of the catalysed reaction (the answer)
B. Activation of the uncatalysed reaction
C. Activation energy required to form the second transition state of the catalysed reaction from the initial reactants
D. The enthalpy change for the reaction
E. The energy released when the transition state of the uncatalysed reaction is converted to the products.

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16. This question concerned the characteristics of dynamic equilibrium, and was considered to be an appropriate level by about 85% of the teachers, although about 5% thought it was too easy. I found it somewhat surprising (even for semestered schools) that a further 5% said that they had not yet covered this topic. About 80% of students chose the correct answer.

I would expect students to know the essential features of chemical equilibrium systems, which involve dynamic equilibria. The four main characteristics of dynamic equilibria are:

(1) When an equilibrium state has been attained, the **macroscopic properties of the system are constant**, under the given conditions of temperature, pressure and intitial amounts of substances. (Macroscopic properties are the properties that are measurable in bulk – pressure, volume, mass, colour, concentration etc.)

(2) After equilibrium hass been attained, **microscopic (molecular scale) processes continue** to occur, but these are in balance, so that no overall (macroscopic) changes are observable. The particles take part in both forward and reverse reactions, but **the rate of the forward process is equal to the rate of the reverse process**, so that no overall change occurs.

(3) Reactions involved in equilibrium systems are reversible, so that **the same equilibrium can be attained starting with reagents from either side of the reaction** – reactants or products or a mixture of the two.

(4) **Equilibrium can only be attained in a closed system**, i.e. one in which there can be no loss or gain of material to or from the surroundiings. Equilibrium cannot be attained in an open system, i.e. one that allows matter to escape or enter.

Now let us consider each of the statements you are given in the question in turn:

A. Reactants form products as fast as they are formed from products

This is absolutely correct – see point (2) above. If you are short of time you could stop here, but it is always preferable to check all the alternatives.

B. The position of equilibrium can be altered using a catalyst

Not true, although it was the second most popular choice of students. A catalyst speeds up both the forward and backward reactions, so that equilibrium is established more quickly, but the equilibrium mixture will have the same composition as that obtained without a catalyst.

The reaction profile for the reverse reaction is the mirror image of that for the forward reaction (the reactants and products are the other way round), and, if you look at the energy profiles shown in the diagrams shown in the solution to question 15, you can see that the energy "bumps" will still have to be surmounted. The "bumps" on the catalysed reaction are still lower than that for the uncatalysed reaction, so the catalyst will still make the reaction go faster.

C. Rates of the forward and reverse reactions are both zero

Not true. The rates of the forward and reverse reactions may **appear** to be zero on the macroscopic scale, but on a molecular scale the forward and reverse reactions are continuing, but their rates are equal – see points (1) and (2) above.

D. Reactants can no longer react together to form products

Not true. Reactants continue to form products, but products are forming reactants at the same rate – see point (2) above.

E. Reactants and products are present in equal amounts

Not necessarily. This may be true in a few (rare) reactions, but it is much more usual for the equilibrium to establish itself with either more reactants or more products present.

It is possibly easier to see how this works if we consider the equilibrium for the hypothetical reaction:

$$\mathrm{A + B \rightleftharpoons C + D}$$

The equilibrium constant, K_c, for this reaction is given by:

$$\frac{\{\text{product of the concentrations of the products}\}}{\{\text{product of the concentrations of the reactants}\}}$$

$$= \frac{[\mathrm{C}] \times [\mathrm{D}]}{[\mathrm{A}] \times [\mathrm{B}]}$$

If the reactants and products are present in equal amounts in the equilibrium mixture, then $\{[\mathrm{C}] \times [\mathrm{D}]\} = \{[\mathrm{A}] \times [\mathrm{B}]\}$ and $K_c = 1$, but it is much more usual for either the products to predominate (in which case $K_c > 1$) or for the reactants to predominate (when $K_c < 1$).

E cannot therefore be generally considered to be true, so the answer to this question must be **A**.

---

17. This question is concerned with a calculation involving an acid dissociation constant (acid ionisation constant). About 70% of teachers indicated that they thought it was appropriate, although again a surprisingly large percentage (about 20%) had not yet covered the topic. About 43% of students chose the correct answer, but other responses were fairly evenly scattered, which I feel indicated that some guessing had been going on.

The question required you to calculate the pH of a solution of Vitamin C (ascorbic acid). This means that you must start by determining the initial concentration of the acid, then to use the pK_a value to find the concentration of hydrogen ions, and hence the pH.

You first need to determine the chemical amount of ascorbic acid in the tablet. For this you need to use the equation:

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

Thus the chemical amount of ascorbic acid

$$= 500 \text{ mg}/1000 \text{ mg g}^{-1} \ / \ 76.13 \text{ g mol}^{-1}$$

$$= 0.002839 \text{ mol}$$

To determine the intitial concentration of the acid in the solution you need to use the equation:

c = n/V Where c is the concentration in mol•L^{-1}
n is the chemical amount in mol
and V is the volume in **L**

Thus the intitial concentration of the acid

$$= \{0.002839 \text{ mol x } 1000\text{ml L}^{-1}\} \ / \ 100 \text{ mL}$$

$$= 0.02839 \text{ mol L}^{-1}$$

We shall refer to this concentration as c_o (mol L^{-1}) in the discussion below.

Ascorbic acid is a weak acid (as indicated by its pK_a value) so we now need to consider the dissociation equilibrium that occurs when it is dissolved in water. If we represent the acid by HA, then the equation for this equilibrium is:

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$

The dissociation constant for the acid,

$$K_a = \frac{[\text{H}^+] \text{ x } [\text{A}^-]}{[\text{HA}]}$$

We are given that the pK_a for ascorbic acid is 4.17,

so $$K_a = 10^{-4.17} = 6.7608 \text{ x } 10^{-5}$$

Now we shall consider the equilibrium in terms of the symbols often used by convention:

if the initial concentration of acid is c_o (mol L^{-1}),
and the concentration of hydrogen ions, H^+, at equilibrium is $\boldsymbol{x}$ (mol L^{-1})
then the concentration of anions, A^-, at equilibrium is also $\boldsymbol{x}$ (mol L^{-1})
and the change in concentration of acid is $-\boldsymbol{x}$ (mol L^{-1})
so the equilibrium concentration of acid becomes ($c_o - \boldsymbol{x}$) (mol L^{-1})

The dissociation constant for the acid now becomes

$$K_a = \boldsymbol{x}^2 / \{c_o - \boldsymbol{x}\}$$

Rearranging this expression gives $\boldsymbol{x}^2 = K_a (c_o - \boldsymbol{x})$

So that $\boldsymbol{x} = \sqrt{K_a} (c_o - \boldsymbol{x})$ . . . . (1)

If we assume that $(c_o - \boldsymbol{x}) \approx c_o$ then $\boldsymbol{x} = \sqrt{(K_a c_o)}$

But can we use this assumption? If we can, then it greatly simplifies the calculation. The assumption is justifiable if c_o is very much greater than $\boldsymbol{x}$, which it is likely be if the equlibrium lies mainly to the left (undissociated acid) side, i.e. if the equilibrium constant is very much less than one (pK_a value is high). However, you also need to consider the intitial concentration of the acid, c_o, because if this is low then the ion concentration, $\boldsymbol{x}$, must be even lower if we are to be able to ignore it. The "rule of thumb" that is often applied here is to look at the ratio c_o / K_a. If this is greater than 1000 then it is reasonable to assume that $(c_o - \boldsymbol{x}) \approx c_o$.

In this question $c_o / K_a = 0.02839 / 6.7608 \times 10^{-5}$ (data from calculations on the previous page)

≈ 420.

This means that we cannot really make the simplifying assumption, **except that** you are only asked to determine the **approximate** pH of the Vitamin C solution.

So let us see what happens when you use the approximation, thus:

The hydrogen ion concentration of the solution is given by

$$\boldsymbol{x} = \sqrt{(K_a c_o)}$$

$$= \sqrt{(6.7608 \times 10^{-5} \times 0.02839)}$$

$$= 0.001385$$

And $\log \boldsymbol{x} = -2.8584$

Therefore $pH = 2.86$

The answer to this question is therefore **B** (approximate pH = 2.9)

To see what would happen if you did not use the simplified method of solving the problem, then we need to go back to equation (1), which is:

$$\boldsymbol{x} = \surd K_a \, (c_o - \boldsymbol{x})$$

This can be rewritten as $\boldsymbol{x}^2 = K_a \, (c_o - \boldsymbol{x})$

or $\boldsymbol{x}^2 + K_a\boldsymbol{x} - K_a \, c_o = 0$

This last equation is in the general formal of a quadratic equation, which is generally given the following form in mathematics:

$$ax^2 + bx + c = 0$$

This equation has the following solution:

$$x = \frac{-b \pm \surd\{b^2 - 4ac\}}{2a}$$

Subsituting the general symbols for acid dissociation into this equation gives:

$$\boldsymbol{x} = -K_a \pm \surd \, \{K_a^2 + 4K_a \, c_o\}$$

If you solve this equation for the values of K_a and c_o relevant to this question, then you find that:

$$\boldsymbol{x} = 0.001352$$

And $\log \boldsymbol{x} = -2.8690$

Therefore pH = 2.87

This approximates to the same value as before (i.e. pH = 2.9), so that the answer to this question does not change.

Note that the error obtained by using the simplified method to determine the hydrogen ion concentration is about 2.4%. You cannot use the pH value to determine the error (because it is a log value) but the two values of pH are so close that you would be unlikely to be able to distinguish between them using the kind of pH meters available in most high schools.

For the record: I do not intend to include questions that involve solving quadratic equations onto Part A of the NHSCE – they just take too long to solve in a multiple choice context.

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18. This question is concerned with the calculation of the solubility of calcium phosphate from its solubility product. About 63% of teachers thought it was appropriate, although about 20% had not covered it, and 12% said it was not on their curriculum. About 35% of students chose the correct answer.

Ths solubility of a substance is the concentration of a saturated solution that is in equilibrium with the solid substance (at a specified temperature). For calcium phosphate this equilibrium can be represented by the following equation:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

The equilibrium constant for this reaction is:

$$K_c = \frac{[Ca^{2+}(aq)]^3 \text{ x } [PO_4^{3-}(aq)]^2}{[Ca_3(PO_4)_2(s)]}$$

where the concentrations given in square brackets refer to equilibrium concentrations. Note, however, that the concentration of the undissolved calcium phosphate is constant (and equal to its density). This holds true irrespective of the total amount present, because it is in a different phase (solid rather than solution), and therefore its value can be incorporated into the equilibrium constant, which is then redefined as the solubility product constant, thus:

$$K_{SP} = [Ca^{2+}(aq)]^3 \text{ x } [PO_4^{3-}(aq)]^2$$

This value is sometimes referred to as the ionic product of the saturated solution. The "concentration" of undissolved calcium phosphate is not required to determine this value. It should, however, be noted that this value can only really be considered to be a constant for very sparingly soluble substances[1]. For more soluble substances, for which the ionic concentrations are higher, ion pairing can occur, and the ionic product will change with the concentration (so it will not be constant).

We now need to set up the equations for calculating the solubility from the solubility product constant. Let us denote the solubility as $\boldsymbol{s}$ (mol L^{-1}). (Note that the units needed for the calculation are moles per litre, and not grams per litre as required for the final answer.)

Going back to the chemical equation:

$$\underset{\boldsymbol{s}}{Ca_3(PO_4)_2(s)} \rightleftharpoons \underset{3\boldsymbol{s}}{3Ca^{2+}(aq)} \underset{+}{+} \underset{2\boldsymbol{s}}{2PO_4^{3-}(aq)}$$

In other words, we can say that, for every $\boldsymbol{s}$ moles of calcium phosphate dissolved in a litre of solution, we will have $3\boldsymbol{s}$ moles of calcium ions and $2\boldsymbol{s}$ moles of phosphate ions.

The solubility product constant can now be expressed in terms of solubility, thus:

$$K_{SP} = (3\boldsymbol{s})^3 \text{ x } (2\boldsymbol{s})^2$$

$$= 27\boldsymbol{s}^3 \text{ x } 4\boldsymbol{s}^2$$

$$= 108\,\boldsymbol{s}^5$$

The solubility, in mol L^{-1}, is therefore given by

$$\boldsymbol{s} = \sqrt[5]{\{K_{SP}/108\}}$$

$$= \sqrt[5]{\{1.0 \text{ x } 10^{-26}/108\}} \text{ at } 25^{o}C$$ [2]

The solubility is therefore $= 2.4735 \text{ x } 10^{-6}$ mol L^{-1}

This is not yet the answer to the question, however, as you need to find the solubility in g L^{-1}. This can be

---

[1] Note that it is useful for a fertiliser such as calcium phosphate to be sparingly soluble, because the ions are slowly released over a period of time. This means that one relatively large application can be used to fertilise a crop for several months, rather than having to use several small applications to obtain the same effect with a more soluble fertiliser.

[2] You need to know how your calculator works in order to find this fifth root. Every calculator is a liitle bit different, but for mine for example I have to punch in the following sequence:

1 EXP ± 26 ÷ 108 (this gives $9.259 \text{ x } 10^{-29}$) then 2ndF $\sqrt[x]{y}$ 5 (this gives $2.4735 \text{ x } 10^{-6}$)

done using the molar mass that you are (effectively) given, thus

The solubility (in g L^{-1}) $= 2.4735 \times 10^{-6}$ mol L^{-1} x 310.2 g mol^{-1}

$= 7.6728 \times 10^{-4}$ g L^{-1}

The answer to this question is therefore **B**. The other answers are obtained if you make an error along the way of this rather tricky calculation – or if you forget to change to the right units at the end (when you would have chosen A).

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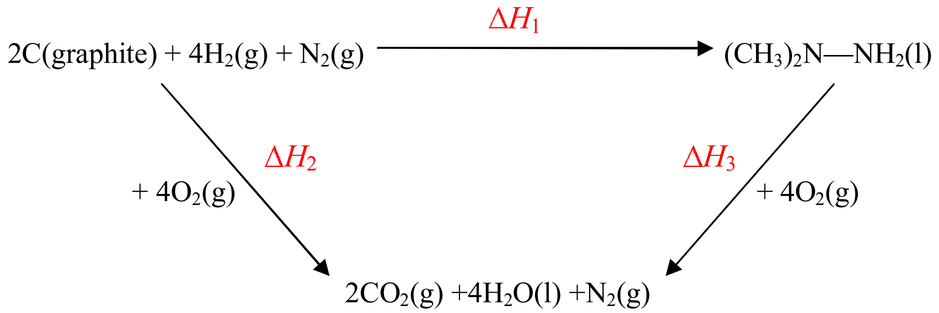
19. This question requires students to determine an enthalpy change of reaction using a Hess's Law diagram. Two thirds of the teachers felt that this was appropriate, the remainder were divided between thinking it was too difficult, not on the curriculum or not yet done. About 37% of the students chose the correct answer.

The Hess's Law cycle involved is given below:



(The red ΔH symbols have been added to the diagram given in the question in order to help with the explanation.)

In this question you need to calculate the standard enthalpy change of combustion, $\Delta H^{\ominus}_{c}$, of UDMH[3]. (1,1–dimethylhydrazine, $(CH_3)_2N—NH_2$). Remember that the standard enthalpy change of combustion is defined as the enthalpy change that occurs when one mole of a substance undergoes complete combustion with oxygen under standard conditions. For a compound containing carbon this means that all the carbon in the compound must be converted into carbon dioxide. In the diagram above you can see that this enthalpy change is indicated by ΔH_3. (Note that nitrogen does not have to be converted to a nitrogen oxide for complete combustion to have been deemed to occur. Nitrogen will not react directly with oxygen in ordinary combustion reactions, only at very high temperatures – for example those found in lightning strikes – and even then the yields of nitrogen oxide are very small.)

By considering the directions of the three arrows shown in the diagram, we can see that

$$\Delta H_1 = \Delta H_2 - \Delta H_3$$

or that

$$\Delta H_3 = \Delta H_2 - \Delta H_1$$

We now need to establish values for ΔH_1 and ΔH_2 then we should easily be able to determine ΔH_3.

---

[3] The initials UDMH stand for unsymmetrical dimethylhydrazine, which is a non-systematic name for 1,1–dimethylhydrazine. UDMH is used as a rocket fuel, and you can see why if you look at the equation for its combustion because 7 moles of gas are produced for each mole of UDMH. If these gases are vented to the rear of the rocket they will create tremendous forward momentum.

First of all, ΔH_1 refers to the following reaction:

$$2C(graphite) + 4H_2(g) + N_2(g) \rightarrow (CH_3)_2N—NH_2(l)$$

This is the enthalpy change of formation of 1,1–dimethylhydrazine, which, by definition, refers to the formation of one mole of a substance from its constituent elements under standard conditions. (This means that all the substances given in the equation must be in their standard states, and, in particular, it means that the carbon allotrope of graphite must be used.) The list of standard enthlpy change values that you are given in the question include the standard enthalpy change of formation of 1,1–dimethylhydrazine, $\Delta H^{\ominus}_f\{(CH_3)_2N—NH_2\}(l) = +48.3$ kJ mol^{-1}. Therefore we know that

$$\Delta H_2 = +48.3 \text{ kJ mol}^{-1}.$$

We now need to consider the third arrow of the cycle, for which the enthalpy change is ΔH_2 which refers to:

$$2C(graphite) + 4H_2(g) + N_2(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) + N_2(g)$$

This actually involves two different reactions, these are:

$$2C(graphite) + 2O_2(g) \rightarrow 2CO_2(g) \;.\;.\;.\;.\;.\;.\;.\;.\;.\; \text{(i)}$$

and $$4H_2(g) + 2O_2(g) \rightarrow 4H_2O(l) \;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \text{(ii)}$$

Both these reaction can be considered to be combustion reactions, but you are not given any information on standard enthalpy changes of combustion. You are, however, given values for the standard enthalpy changes of formation for carbon dioxide and water and these can apply here equally well. Remember, though, that standard enthalpy changes of formation apply to the formation of **one** mole of a compound from its constituent elements.

Equation (i) refers to the formation of **two** moles of carbon dioxide from its constituent elements, therefore the enthalpy change for this reaction is

$$2 \text{ x } \Delta H^{\ominus}_f\{CO_2(g)\}$$

$$= 2 \text{ x } (-393.5 \text{ kJ mol}^{-1})$$

$$= -787.0 \text{ kJ mol}^{-1}$$

Similarly **Equation (ii)** refers to the formation of **four** moles of water from its consitutent elements, therefore the enthalpy change for this reaction is

$$4 \text{ x } \Delta H^{\ominus}_f\{H_2O(l)$$

$$= 4 \text{ x } (-285.8 \text{ kJ mol}^{-1})$$

$$= -1143.2 \text{ kJ mol}^{-1}$$

Therefore $$\Delta H_2 = -787.0 + (-1143.2) \text{ kJ mol}^{-1}$$

$$= -1930.2 \text{ kJ mol}^{-1}$$

What we really need is the enthalpy change of combustion of 1,1–dimethylhydrazine, i.e.

$$\begin{aligned}\Delta H_3 &= \Delta H_2 - \Delta H_1\\ &= -\,1930.2 - (+\,48.3)\ \text{kJ mol}^{-1}\\ &= -\,1978.5\ \text{kJ mol}^{-1}\end{aligned}$$

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

---

20. This question was concerned with bond lengths and strengths, and only just over half of the teachers felt that it was appropriate, whilst fully one third of them felt that it was outside the curriculum. This judgement that it was outside the curriculum was possibly due to the fact that the question referred to bond energy (as a measure of bond strength), although bond energies are on the Pan-Canadian protocol so they should be on most of the provincial curricula, if not all of them. In fact the students did not seem to be too fazed by the terminology, because around 70% of them chose the correct answer.

One of the problems with bond energies is that there are a number of different formal definitions that are used to describe them (even to the extent of giving the numerical value different signs according to whether the definition refers to bond breaking or bond forming). In the answer to Question 23 of the 2002 NHSCE we defined bond enthalpy term 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 dissociation enthalpy is similarly defined but refers to a specific bond in a particular compound. 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.”

As we are looking at bond breaking (endothermic) processes in our definition of bond energy, the value we obtain will always be positive. (It would have the same numerical value, but with a negative sign,if we were to define it in terms of bond formation.)

To simplify all this, we are essentially saying that the bond energy is the energy required to break the force of attraction between two atoms that are bonded together. This means that bond energy is a measure of the strength of a bond.

We can also say that, if the bond is strong, then the two atoms involved in the bond will be pulled closer together, i.e. the bond will be shorter.

Furthermore, the more electrons that are involved in forming a particular bond, the stronger it is likely to be. Thus a double bond, which involves two pairs of electrons, is likely to be stronger than a single bond, which involves only one pair of electrons, because because there will be a greater amount of negative charge helping to attract the two positive nuclei and thus pull them together. A triple bond can be expected to be even stronger than a double bond.[4]

The present problem gives the bond length and bond energy of the $C=O$ double bond, and asks you to identify the equivalent figures for the $C-O$ single bond. Using the reasoning given above, a single bond

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[4] It is not, however, the case that a double bond is twice as strong as a single bond, nor is a triple bond three times as strong as a single bond. This is because there are some repulsion effects – having several negative electrons close together will tend to spread out the bond to some extent.

should be weaker and longer than a double bond. We are therefore looking for a bond length > 0.122 nm, meaning that answers A, B and C can be ruled out. The we are looking for a bond strength that is < 740 kJ mol^{-1}, which rules out E. This means that the answer to this question must be **D**.

The table below shows the values you were given in the question, together with the actual bonds they apply to:

Bond	**Bond length, nm**	**Bond energy, kJ mol^{-1}**
C – O in CH_3OH	0.113	335
C ≡ O (carbon monoxide)	0.113	1080
C = O (carbon dioxide)	0.116	805
C – O (average)	0.143	360
No particular bond	0.143	1080

Note the variation between the C – O in CH_3OH and the average values (note that the question only asks you to identify which of the pairs of values given in the table is **most likely** to be correct). Also note the difference between the values for C = O double bond in carbon dioxide and the values you are given for C = O in the question (bond length = 0.122 nm and bond energy = 740 kJ mol^{-1}), which are average values for the C = O bond. You should be aware that considerable discrepancies exist between average values and values for specific bonds, and that using bond energy terms to calculate the enthalpy change of a reaction will not usually give as precise a value as using enthalpy changes of formation or combustion.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2005 continued

21. This question concerned the interpretation of a titration curve. About 80% of teachers thought it was appropriate, but about 12% had not yet covered it. About 70% of students chose the correct answer.

The graph given in the question shows the changes of pH that occur when sodium hydroxide solution (0.1 mol L^{-1}) is added to 25.00 mL of ethanoic acid solution (0.1 mol L^{-1}), and you are asked to identify what is in the solution at a particular point X.

In order to establish this you need to consider what is happening in the titration. You would typically start off with the ethanoic acid solution in an Erlenmeyer flask, and add the sodium hydroxide solution to it from a burette. The reaction that takes place as the titration proceeds will be:

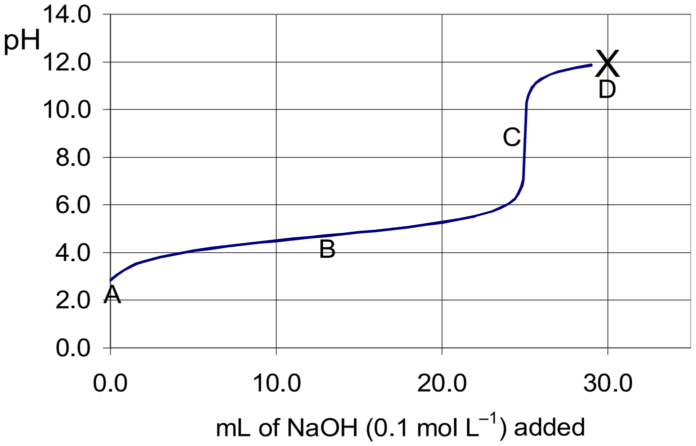
$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

At the very beginning of the titration, the solution in the flask will contain only acid. As you add sodium hydroxide the salt (sodium ethanoate, CH_3COONa) will start to form, but the solution will still contain excess acid because only part of it will have been able to react. The endpoint (or equivalence point)[1], of the titration will occur when the acid and the sodium hydroxide have completely reacted, but there is no excess of either reagent: at this point the solution contains only the salt. On the diagram you are given, this occurs when around 25 mL of the sodium hydroxide solution have been added. After this point there will no longer be any acid in the solution, and, if you continue to add sodium hydroxide, the solution will simply contain the salt plus excess base.

The answers that you are given to choose from in this question are:

A. Acid only B. Acid + salt C. Salt only D. Base + salt E. Base only

The regions of the curve corresponding to the first four answers are shown superimposed on the diagram below:



Note that “E” is not shown on the diagram, because at no stage can the solution contain only base.

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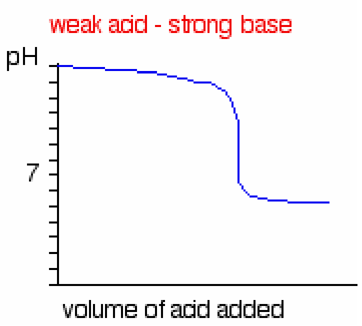
[1] Strictly speaking we should refer to the equivalence point of the titration as being the point at which the reactants have completely reacted and there is no excess of either reagent. The endpoint is the point at which the indicator has just begun to change colour. The endpoint will be the same as the equivalence point if we have chosen an appropriate indicator – i.e. one that has a colour change range within the steep part of the curve, where the pH changes rapidly with only very small additions of reagent.

At the point X shown on the diagram, the solution is at the stage where it contains base plus salt , so the answer to this question is **D**.

Note that it is possible to have a solution containing only base in a titration, if you start with a base solution in the conical flask (and then add acid from the burette). In this case it is, however, impossible to have only acid in the solution at any point. A sketch of the type of graph that you might expect for this kind of titration is given below:



This graph was taken from the website www.chemguide.co.uk/physical/acidbaseeqia/phcurves.html. This is an excellent website to visit if you would like to learn more about titration curves. You might also like to click on the link from this page to acid-base equilibria and from there to acid-base indicators, buffer solutions etc.

Note that, although most books show diagrams of titration curves that involve adding base to acid, this is best avoided if possible in practice, because strong bases such as sodium hydroxide and potassium hydroxide tend to react with carbon dioxide in the air to form carbonates. Solutions of sodium and potassium carbonates dry out rapidly, often clogging the burette tip with solid, which is very difficult to clean out. One can usually arrange acid-base titrations so that the acid is run into the base solution rather than vice versa.

22. This question is concerned with alkene isomers. About 64% of teachers thought that it was appropriate, although 14% said they had not yet covered it, and around 19% said that it was not on their curriculum. About 30% of candidates chose the correct answer.

The task was to find the number of non-cyclic isomers of C_5H_{10}. As this conforms to the general formula of C_nH_{2n} it refers to alkenes, and, because n = 5, it refers to pentene isomers. The only way I know of working out the number of isomers is to draw them out, but you need to do this systematically if you are not to get caught out by repeating a diagram or by missing one out. This need not take a lot of time in an exam if you only draw the carbon skeleton, but we shall draw the full diagrams here in order to show you that all the valencies are correct.

I start with all the possible straight chain isomers, then I shorten the chain by one carbon atom at a time. Next I fix the position of the functional group and introduce methyl groups onto the shortened chain one at a time[2]. I don't consider the geometric isomers until I have dealt with all the carbon chain and positional isomers. I always work from the same end of the chain, and I always start by putting substituents onto the same side of the chain. This is how my method works for the isomeric pentenes, starting with the straight chain isomers, which are:

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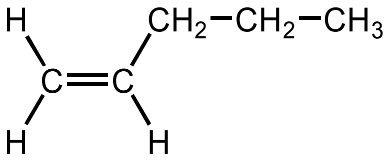
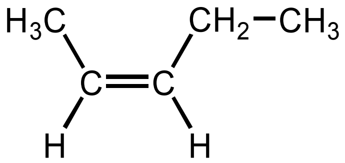
[2] If you get to the point where you are able to take two carbon atoms off the straight chain, then you need to consider the possibility of (1) a side chain comprising an ethyl group, or (2) two methyl group branches: and if you are adding alkyl group(s) you must consider whether they are going to become the part of the main (longest) chain of carbons.



1–pentene or pent–1–ene

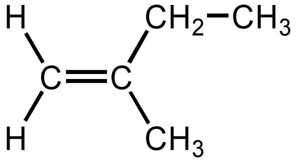
and



2–pentene or pent–2–ene

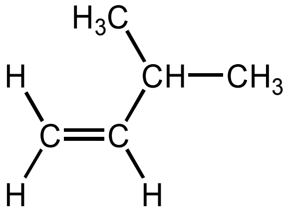
Note that, because we have a chain of 5 carbons, we have 4 sets of carbon–carbon bonds. The symmetry of the molecule means that we cannot have any more positional isomers for the straight chain once we are half-way along the chain – an isomer with a double bond in the "3" position would simply be the same as 2–pentene, and an isomer with a double bond in the "4" position would be the same as 1–pentene, counted from the other end of the chain.

Now shortening the chain by one carbon and putting the double bond into the number "1" position: this gives us:



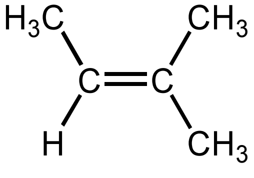
2–methyl–1–butene or 2–methylbut–1–ene

and



3–methyl–1–butene or 3–methylbut–1–ene

Now we have to see if there are any possibilities with the double bond in the number "2" position. Yes, there is one, it is:



2–methyl–2–butene or 2–methylbut–2–ene

As the double bond is in the middle of the chain, there are no other possible chain branch isomers.

Now we should consider shortening the chain by yet another carbon, to give us a 3-carbon chain with two methyl groups attached. This would be a possible isomer if we were looking at alk**a**nes (we could have 2,2–dimethylprop**a**ne after all) but it doesn't leave us with any place to put the double bond. We have now come to an end of the possibilities of finding another isomer by juggling the carbon skeleton and alkene positions. We have 5 isomers so far, but we have not yet considered the possibility of geometric isomers – and you can be pretty sure that there will be some of those by the way the question is worded!

Geometric isomers occur because molecules cannot rotate about a double bond[3]. This means that if both of the carbons involved in a C=C bond are attached to two different groups, then it is possible for two isomers to form, one with a given set of groups on the same side of the double bond as each other, and the other with those groups on opposite sides. Each of the pair of geometric isomers has the same structure in that the carbon chain is the same and the functional group is in the same position. This means that we need to check the structural (constitutional) isomers that we have identified above to see if it is possible for them to represent geometric isomers. We can eliminate any molecule that has two groups the same on either one of the carbons involved in the double bond. Let's consider each of the above molecules in turn:

1–pentene: The left hand carbon of the double bond on this molecule has two hydrogens attached, so the molecule cannot have geometric isomers.

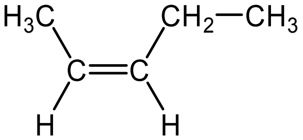
2–pentene: The left hand carbon of the double bond is attached to one H and one CH_3 group, the right hand carbon is attached to one H and one C_2H_5 group. This means that the formula can represent a pair of geometric isomers.

2–methyl–1–butene: The left hand carbon of the double bond on this molecule has two hydrogens attached, so the molecule cannot have geometric isomers.

3–methyl–1–butene: The left hand carbon of the double bond on this molecule has two hydrogens attached, so the molecule cannot have geometric isomers.

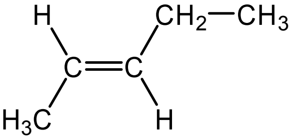
2–methyl–2–butene: The left hand carbon of the double bond is attached to one H and one CH_3 group, the right hand carbon is attached to two CH_3 groups, so the molecule cannot have geometric isomers.

2–Pentene is thus the only one of the molecules identified above that can exist as geometrical isomers. The two isomers are drawn out below:



cis–2–pentene or *cis*–pent–2–ene

and



trans–2–pentene or *trans*–pent–2–ene

You may also meet alternative names for these isomers, e.g. (*Z*)–2–pentene for *cis*–2–pentene and (*E*)–2–pentene for *trans*–2–pentene. These names are based on priority rules and are not usually met in high school text books.

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[3] Compounds other than alkenes can also have geometric isomers, e.g. cyclic compounds.

This has brought the total number of pentene isomers up to 6 from 5 (don't count the structural isomer in with its geometric isomers!), which means the answer to this question is **C**.

You can always check that you have got the correct number of isomers by looking the molecular formula up in the CRC Handbook of Chemistry and Physics (the "Rubber" book) – that's assuming that your're not working under exam conditions!

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23. This question involved standard reduction potentials. About two-thirds of the teachers said that they thought it was appropriate, but a whopping one-third of teachers said that they had not yet covered it. Despite this, about 70% of students chose the correct answer.

You are asked to calculate the standard potential for this following reaction:

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

You are told that this reaction is a disproportionation reaction, but, even if you didn't know what this means, you can probably see that you have an element in one oxidation state that is being simultaneously oxidised and reduced in the same reaction – which is what disproportionation means. (Copper(I) is simultaneously oxidised to copper(II) whilst being reduced to copper(0).) You don't really have to know what "spontaneous" refers to in this context either, however it does help a bit, because it tells you that the standard potential must be postive, which means that you can eliminate answers A and B, which involve negative values.

You are given standard **reduction** potentials for the following half reactions:

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s) \qquad E^{\ominus} = +\,0.52\text{ V} \;.\;.\;.\;.\;.\;.\;.\;. \quad \text{(i)}$$

$$Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq) \qquad E^{\ominus} = +\,0.16\text{ V} \;.\;.\;.\;.\;.\;.\;.\;. \quad \text{(ii)}$$

To obtain the overall reaction you have to combine the reduction reaction (i) with the oxidation reaction, which is the reverse of reaction (ii).

To obtain the standard potential for the overall reaction you have to subtract the standard reduction potential for the oxidation half cell from the standard reduction potential of the reduction half cell, thus:

$$= +\,0.52\text{ V} - 0.16\text{ V}$$

$$= +\,0.36\text{ V.}$$

So the answer to this question is **C**.

Note that the criterion for predicting that disproportionation will occur spontaneously is not simply that the standard potential for the overall reaction is positive, but that it is **more** positive than the average of the standard reduction potentials for the two reduction half reactions. Here the average of the standard reduction potentials is (+ 0.52 + 0.16)/2 = + 0.34 V, which is less than + 0.36 V, so disproportionation is likely to occur[4]. The copper(I) oxidation state is always unstable in aqueous solution: it can, however, be

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[4] Note that standard potentials, being thermodynamic values, can only predict whether a reaction is **likely** to take place or not. They tell us nothing about whether the reaction will actually occur. It is possible that a reaction might be thermodynamically unstable but kinetically stable, i.e. the activation energy might be so high that it effectively prevents the reaction from taking place even if it has a positive standard potential.

stabilised by being "locked" in a water-insoluble solid (such as CuCl) or in a complex (such as $CuCl_3^{2-}$). Alternatively relatively stable copper(I) compounds can be created in the absence of water (e.g. Cu_2SO_4)[5]. Note also that similar reactions can occur in which two different oxidation states of an element can combine to give just one oxidation state. This kind of reaction is called **comproportionation**. An example of comproportionation is:

$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$$

Here the sulfur in hydrogen sulfide is oxidised from the –2 state to the 0 state, whilst the sulfur in sulfur dioxide is reduced from the +4 state to the 0 state. This is the key reaction in the Claus process for the production of elemental sulfur from hydrogen sulfide found in "sour" natural gas and in flue gases produced from burning fossil fuels. The elemental sulfur produced is generally used to produce sulfuric acid.

24. This question requires students to be able to apply Le Châtelier's principle to an equilibrium reaction that had two other equilibrium reactions feeding into it. About 62% of teachers thought it was appropriate, but 28% felt it was too difficult. Students did very poorly on it, with only around 18% choosing the correct answer.

The idea behind the question was to involve the students in considering a somewhat unusual application of Le Châtelier, namely the reversible reaction that causes limestone rock, $CaCO_3(s)$, to dissolve and form again in caves. The equation given for this process is:

$$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca(HCO_3)_2(aq) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (i)$$

Stalagmites and stalactites form in the caves when the reaction goes to the left. You need to consider the forward reaction as given, however, as you are asked to consider which of several possible processes will **inhibit** the formation of stalagmites and stalactites. Note that the amount of $CaCO_3(s)$ present is irrelevant to the equilibrium as it is a solid and the other components of the system are in solution (see also the solution to Question 18 of this year's exam).

The first of the subsidiary equations that you are given is:

$$CO_2(aq) \rightleftharpoons CO_2(g)$$

Note that, strictly speaking, this equation should be written as:

$$CO_2(aq) \rightleftharpoons CO_2(g) + aq \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (ii)$$

Where "aq" refers to an unspecified amount of water. (We are not told the concentration of the carbon dioxide solution, so that we cannot specify the amount of water that remains when the carbon dioxide gas has been released from it.) The "aq" was omitted in the exam paper, as the reviewers felt that students would not have met it before, and it could confuse them.

The other subsidiary equation is:

$$H_2O(l) \rightleftharpoons H_2O(g) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (iii)$$

Note that you cannot really tell whether equation (i) refers to an exothermic or an endothermic reaction. It could go either way as it involves dissolving a solid in a liquid. Equations (ii) and (iii), however, both refer to endothermic reactions. Heat is required to drive a gas out of solution (always) and also to vaporize a

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[5] It should be noted that the standard reduction potentials given in the question refer to **aqueous** solutions of the copper ions only. Other conditions will be governed by different equilibrium processes.

liquid (always).

Armed with this information, we can now consider each of the proposed answers to the question in turn:

A. Global warming

Increasing temperature will force the endothermic processes (ii) and (iii) to the right. This will remove CO_2(aq) and H_2O(l) from the main equilibrium system (i), causing it to "swing" back to the left. This aids the formation of $CaCO_3$(s) (stalagmites and stalactites) so the the answer cannot be A.

B. Low pressure weather systems

Reducing the atmospheric pressure will make little difference to the main equilibrium system (i), because it does not directly involve gases, however it will affect both reaction (ii) and (iii). A reduction in gas pressure will cause the gases involved in these reactions to be released, removing CO_2(aq) and H_2O(l) from the main equilibrium system (i), and causing it to "swing" back to the left. This aids the formation of $CaCO_3$(s) (stalagmites and stalactites) so the the answer cannot be B.

C. Increasing the flow of air through the caves

Increasing the flow of air through the caves will blow away the gases produced by reactions (ii) and (iii), reducing the amount of CO_2(aq) and H_2O(l) in the main equilibrium system (i), causing it to "swing" back to the left. This aids the formation of $CaCO_3$(s) (stalagmites and stalactites) so the the answer cannot be C.

D. Removing stack gases from local coal-fired power plants

Stack gases contain carbon dioxide, water vapour and other (polluting) gases. Removing these gases from the atmosphere in the vicinity of the caves will deplete the gases produced by reactions (ii) and (iii), removing CO_2(aq) and H_2O(l) from the main equilibrium system (i), causing it to "swing" back to the left. This aids the formation of $CaCO_3$(s) (stalagmites and stalactites) so the answer cannot be D.

E. Increasing humidity from the breath of visitors to the caves

The moisture in the breath of visitors to the caves increases the amount of H_2O(g) in the air of the caves, and thus the H_2O(l) in reaction (i). This reduces the concentration of $Ca(HCO_3)_2$(aq), shifting the equilibrium to the right and causing the limestone to dissolve. In other words this inhibits the growth of the stalagmites and stalactites, so the answer to this question is therefore **E**. Note that the breath of the visitors contains carbon dioxide gas as well as moisture, and this will also inhibit the growth of stalagmites and stalactites. In fact the growth of the rock formations is not simply inhibited by the visitors to caves, but, in some cases, the rocks are actually dissolving away. As a result of this, some caves have been closed to the public, and the numbers of visitors allowed into other caves have been restricted.

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25. This question involved calculating the error in the value of an equilibrium constant determined experimentally. Although about 56% of the teachers thought it was appropriate, 29% felt it was too difficult, and 14% had not yet covered it. The students bombed it, with only about 13.4% of them choosing the correct answer – in this respect it was the worst question in the exam. But then it was also the last question, which traditionally tends to be tricky.

The real problem seemed to be understanding what the question was about, because once that was overcome, the calculation was very straightforward. You need to focus on what the students **think** they have in the mixture, because this is what they have to base their calculation on. The reaction involves the acid catalysed hydrolysis of the ester, ethyl ethanoate, to give ethanoic acid and ethanol. The equation is given as:

$$CH_3COOC_2H_5(l) + H_2O(l) \overset{H^+}{\rightleftharpoons} CH_3COOH(l) + C_2H_5OH(l)$$

The students are told to begin by mixing 0.05 mol of $CH_3COOC_2H_5$ and 0.28 mol of H_2O, and this is what you need to use for the calculation. The fact that they have only 0.045 mol of ester is irrelevant, because they don't **know** this. (There is, therefore, no need to try to correct for the extra amount of water.)

The students find that they have 0.03 mol of ethanoic acid, CH_3COOH, in the equilibrium mixture, which means that they also have 0.03 mol of ethanol, C_2H_5OH. It also means that the change in the amounts of ethyl ethanoate and water will both be 0.03 mol, so that the equilibrium amounts are:

$$CH_3COOC_2H_5 = (0.05 - 0.03) = 0.02 \text{ mol}$$
$$\text{and} \quad H_2O = (0.28 - 0.03) = 0.25 \text{ mol}$$

Now let us consider the equilibrium constant expression, which is:

$$K_c = \frac{[CH_3COOH(l)] \times [C_2H_5OH(l)]}{[CH_3COOC_2H_5(l)] \times [H_2O(l)]}$$

The next difficulty that some teachers mentioned was concerned with the fact that you hadn't been given a volume of reaction mixture, so that you couldn't express the equilibrium constant in terms of concentration. But let us say that this volume is V litres. You can now substitute values into the equilibrium constant expression thus:

$$K_c = \frac{(0.03/V) \times (0.03/V)}{(0.02/V) \times (0.25/V)}$$

Note that the volume, V, **cancels out** in this equation. (This will always be the case where the stoichiometric equation for the equilibrium reaction shows that the total number of moles of reactants is equal to the total number of moles of products.)

So we can say that

$$K_c = \frac{0.03 \times 0.03}{0.02 \times 0.25}$$

$$= 0.18$$

Now all we have to do is to calculate the error (this is based on the accepted value of K_c, which is given in the question as 0.27).

The general equation for calculating errors is:

$$\text{Error} = \frac{(\text{experimental value} - \text{accepted value})}{\text{accepted value}} \times 100\%$$

$$= \frac{0.18 - 0.27}{0.27} \times 100\% = - 33\%$$

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

Note that even if you cannot remember the general equation for calculating errors, you could probably guess that the error has to be the difference between the experimental and accepted values, and that it would need to be calculated as a percentage of the accepted value. If the experimental value is lower than the accepted value then the error will be negative, and if it is greater then the error will be positive.

Some teachers criticised this question, because they felt that it is unnecessary to consider this aspect of errors. Most of the error analysis that goes on in high schools focusses on errors in reading equipment, and how these errors impact on the error of the final value obtained. Whilst it is important to recognize these errors, it should be appreciated that reading errors are usually randomly distributed (some readings will be too high, but they may equally well be too low) so that their impact on the final result can be reduced by repeating the experiment multiple times. The problem with a systematic error, such as impurities in the reactants used, is that they simply will not "go away" if readings are repeated.

I find it very useful to have students calculate the error in their result in comparison with an accepted value, and then have them try to work out what aspect of the design of the experiment might contribute to this error – and in particular, to have them consider what might cause a systematic error, which will continually give a value that is too high or too low.

Organic liquids are often contaminated with water (even those that are not usually considered to be water-soluble), and the present experiment is a good example of the effect that such contamination might have. In fact the determination of the equilibrium constant for the hydrolysis of an ester is often used as a means of determining the equilibrium constant for the esterification process (i.e. the reverse reaction). This can be done because the equilibrium constant of the forward reaction is simply the reciprocal of the equilibrium constant of the reverse reaction, thus:

$$K_c(\text{forward}) = 1/\, K_c(\text{reverse})$$

By using the hydrolysis reaction, we have only one reagent that might be contaminated with water, whereas the reverse reaction (esterification) requires two organic chemicals, both of which might be contaminated.