ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2006

These answers are designed to help students who are preparing to take the Canadian National High School Chemistry Examination in 2007 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 2005 exams (questions and answers) before attempting the 2006 examination.

Students should try to do the questions in Part A of the 2006 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. 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. It should be pointed out, however, that students in different parts of the country sometimes 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 emphasize different aspects of the curriculum.

Students and teachers also need to be aware that questions in the exam often involve applications of simple principles: it is not expected that students will necessarily have met these particular applications before. The applications are intended to increase the interest level of the exam for students, and, whilst it is hoped that the student will remember these, it is not intended that they should consciously work on memorising them, as they are not likely to reappear in future exams.

This year we have included information about the discrimination index of the questions based on the results for British Columbia (the only province for which such information is available). This index indicates the extent to which an item differentiates between high-scoring (top 27%) and low-scoring (bottom 27%) students. For the 2006 examination discussed here, the discrimination ability of the questions have been classified thus:

> discrimination indices >0.45 = very good, between 0.38 and 0.45 = good, between 0.25 and 0.38 = moderate, between 0.20 and 0.25 = poor, and <0.20 = very poor.

Difficulty levels for the questions have been calculated for all reporting regions, with questions rated for the purposes of this discussion according to the average scores obtained by the students, thus:

> >90% = very easy, 75 – 90% = easy, 60 – 70% = moderately easy,
> 40 – 60% = moderately difficult, 25 – 40% difficult, and <25% = very difficult.

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 fourth year that the National High School Chemistry Exam (NHSCE) has had a question on it that relates to WHMIS (Workplace Hazardous Materials Information System), and this year it seemed to be better done than in previous years. About 70% of responding teachers thought it was appropriate although 22% thought it was not on the curriculum: only 2% of teachers said it was too difficult, whilst 7% said it was too easy. The statistical data for BC (the only province for which such data was available) indicates that the level of difficulty was moderate, and the discrimination index was good.

This question is concerned with the categories of substances[1] shown below. Note that the letters here refer to the answer keys and not to the official reference codes for the different classes of compounds.

A. Flammable and combustible material[2] (Class B), e.g. white phosphorus, acetone and butane. These materials should be kept away from heat.

B. Oxidizing material (Class C), e.g. Potassium chlorate, sodium nitrate and hydrogen peroxide. These materials should be kept away from combustible materials.

C. Poisonous and infectious material – other toxic effects (Class D, Division 2), e.g. acetone (irritant), asbestos (carcinogen), These are materials **other than** Class D Division 1 materials, such as sodium cyanide and hydrogen sulfide, which have immediate and serious toxic effects (this class of compounds has a skull and crossbones symbol), and Class D Division 3 materials, which are biohazardous and infectious (see key E below). Protective clothing and/or respiratory equipment should be worn when handling these materials.

D. Dangerously reactive material (Class F), e.g. butadiene, sodium metal, 2,4,6–trinitrotoluene (TNT). These materials should be kept away from heat, shock, air and/or moisture.

E. Biohazardous infectious material (Class D Division 3), e.g. cultures or diagnostic specimens containing salmonella bacteria or the hepatitis B virus. These materials should be handled only in areas designed to prevent biological contamination.

To go back to the question actually given in the 2006 exam, which was:

> A certain substance has the following WHMIS symbol on the label of its bottle.
>
> 
>
> Which one of the following instructions is best indicated by this symbol?
>
> A. Keep the material away from heat
> B. Keep the material away from combustible materials
> C. Wear protective clothing and/or respiratory equipment
> D. Keep the material away from heat, shock, air and/or moisture
> E. Handle the material only in areas designed to prevent biological contamination.

It can be seen from the information given above for the symbol indicates that the material is dangerously reactive, so the correct answer to this question is **D**.

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[1] The instructions for this are paraphrased from the University of Victoria Engineering website at http://www.coop.engr.uvic.ca/engrweb/whmis/symbols.html .

[2] Note the difference between flammable and combustible materials: *flammable* liquids such as acetone are more easily ignited than *combustible* liquids such as kerosene.

2. Most teachers (98%) thought that this question was appropriate, and, in BC, students found it to be the easiest question on the exam, although in other provinces it was not as well done. The discrimination index was moderate. One teacher indicated that s/he did not recognise the symbol M_r (which is the symbol recommended by IUPAC for relative molar mass). Students might have been able to guess the meaning of the symbol, or they could have calculated the molar mass from the formula (but in the latter case they would have lost precious time).

The formula given in the question is $MnSiO_3 \cdot 3Mn_2O_3$, and the question focuses on understanding what this type of formula means. The "dot" in the middle of the formula is often used for hydrated salts (e.g. $Na_2CO_3 \cdot 10\ H_2O$, see Question 5) and for minerals: it is more informative than the empirical (simplest) formula, because it gives some indication of the compounds included in the structure. Here the formula indicates that one manganese(II) silicate[3] unit is combined with three manganese(III) oxides, with the units intertwined in a regular but complex crystalline network.

In this question, however, we really need to know the empirical formula in order to be able to calculate the percentage of manganese in the mineral.

$MnSiO_3$ contributes	1 x Mn	+	1 x Si	+	3 x O
$3Mn_2O_3$ contributes	3 x 2 x Mn	+	0 x Si	+	3 x 3 x O
TOTAL	7 x Mn	+	1 x Si	+	12 x O

The empirical formula of braunite is therefore Mn_7SiO_{12}.

The percentage by mass of manganese in braunite is therefore given by

$$\frac{\{7 \times M_r(\mathrm{Mn})\}}{M_r(\mathrm{MnSiO_3 \cdot 3Mn_2O_3})} \times 100\ \%$$

$$= \frac{\{7 \times 54.94\}}{604.7} \times 100\ \%$$

$$= 63.6\ \%$$

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

Calculations of this sort are, of course, important in ascertaining how much of an element such as manganese can be extracted from a particular ore, although, it has to be said, that braunite is not commonly used as a source of manganese.

Note that the formulae given for minerals often uses the convention in which the oxide component is given before any other constituent of the mineral, thus braunite might be written as $3Mn_2O_3 \cdot MnSiO_3$: I felt, however, that stating the formula in this way would be too easily misinterpreted by students (who might easily think that the whole formula needed to be multiplied by three). Other methods of writing mineral formulae are also used, depending on how much is actually known about the structure, thus braunite is sometimes written as $Mn^{2+}Mn^{3+}{}_6\,SiO_{12}$, which would show a knowledge of the two oxidation states of manganese present in the compounds, but which would indicate that the oxide and silicate oxygens are probably interlinked in a more complex fashion than is implied by the formula $MnSiO_3 \cdot 3Mn_2O_3$.

3. This question was found to be the second easiest question on the exam in BC, with about 83% of students there choosing the correct response: other provinces found the question more difficult, with only

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[3] Note that SiO_3^{2-} silicate ion does not exist as a simple ion in $MnSiO_3$ but as a chain of silicon and oxygen atoms that are covalently linked and that bear extra electrons in the ratio of 2 electrons per SiO_3. Silicon and oxygen can form many other kinds of structures including 2-dimensional sheets and 3-dimensional networks with different ratios of silicon to oxygen.

around 62% getting the answer right in one instance. About 93% of responding teachers found the question appropriate, although, surprisingly, about 4% thought it was not on the curriculum. The discrimination index was moderate.

The question essentially relates to determining the empirical formula of a particular uranium oxide, which can be done in a tabular format, thus:

	U	**O**
Mass, g	11.902	2.136
Molar mass, g mol^{-1}	238.03	16.00
Chemical amount, mol	0.05	0.134
Simplest ratio (obtained here by dividing through by the smallest number)[4]	1	2.67
Empirical formula	U_3O_8	

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

Note that it would not be appropriate to try to calculate the percentage of uranium in the oxide, and then to compare the value you obtain with the percentages of uranium in the oxides given in the suggested answers. This is because of the possibility that hydrogen might be present, and that you have not been given its mass in the sample. In this particular case the difference of mass attributable to hydrogen would probably be negligible, because of the large atomic mass of uranium, but it is a consideration you should bear in mind when solving this type of problem.

Note also that the oxide U_3O_8 must first be converted into UO_2 before it can be used in CANDU reactors.

4. This was another question that students in most (but not all) provinces found easy, but its discrimination index was very poor. About 72 % of teachers felt that it was appropriate, but 13% said that they had not yet covered the topic, and about 9% thought that it was not on the curriculum.

Essentially the question asks the students to work out the molar mass of an acid from titration data, this is something that they might have done in class as a practical assignment. Once they have obtained a value, then all they have to do is to compare it with the relative molar masses given for the acids given in the suggested answers. The fact that the acids all play a role in human metabolism has really nothing to do with the exercise, apart from indicating an application that students might find interesting[5].

The students are told that all the acids are monoprotic, so, if we represent them by the general formula, HA,

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[4] This method of calculation was discussed in the solution to Question 10 of the 2005 exam, when a little ditty was presented to help you remember the steps you need to follow when doing this kind of calculation:

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

(Thompson, J.S., *J. Chem. Educ.*, **1988**, *65*, 704)

Last year you didn't need to use the final line of the ditty, because you had already arrived at a whole number, but in this year's question you have to start multiplying. If you end up with numbers ending in 0.5 (then you need to multiply by 2) or if the number ends in 0.33 or 0.67 (as in this year's question) then you need to multiply by 3.

[5] Thank you to Lew Brubacher (University of Waterloo) for suggesting the particular acids for this question.

then the equation for the titration reaction is:

$$HA + NaOH \rightarrow NaA + H_2O$$

If you like to see state symbols in your equations then this would be:

$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$$

(Distilled water would need to be added to the solid acid to dissolve it, otherwise the acid and the alkali would not be able to mix thoroughly as the titration proceeds.)

You are given the mass of acid used and you need to find its molar mass, so you need to find the chemical amount of acid (in moles). You can do this by using the data given for the sodium hydroxide solution to find its chemical amount, which, according to the equation, is the same as that of the acid.

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 NaOH is thus:

$$= (0.1 \text{ mol L}^{-1} \times 23.25 \text{ mL}) / 1000 \text{ mL L}^{-1}$$

$$= 0.002325 \text{ mol of NaOH}$$

The chemical amount of acid is therefore = 0.002325 mol

The equation that you now need to determine the molar mass of the acid is

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

The molar mass of the acid is thus:

$$= 0.200 \text{ g} / 0.002325 \text{ mol}$$

$$= 86.(02) \text{ g mol}^{-1}$$

The answer to this question is therefore **C**.
Note that this is not quite the same numerical value as is given in the question, which is $M_r = 86.1$, but the concentration of the sodium hydroxide solution is given very imprecisely (to one significant figure), so that we are well within the limits of error that might be expected for this experiment. Note that it would, in fact, be very difficult to distinguish between acids A and B (and possibly even C and D) using this experiment.

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5. About 79% of teachers said that this question was appropriate, about 13% felt it was too difficult, 2% felt it was too easy, and about 6% thought that it was not on the curriculum. The statistics show that students found it moderately difficult, and that it had a good discrimination index.

This question is a "storyline" question, intended not just to assess the student's ability to do the necessary calculation, but also to inform students about the uses of the compound concerned and about what an analyst does.

Essentially you are required to find the value of x in the "formula"[6] $Na_2CO_3 \cdot xH_2O$, which refers to the composition of the partially dehydrated washing soda. In other words we need to find the mole ratio **H_2O: Na_2CO_3 in the partially dehydrated washing soda** which equals x. There are a number of different methods of performing this calculation, but the one given below is the simplest method I can think of.

The process of partial dehydration of the washing soda can be represented by the following equation:

$$Na_2CO_3 \cdot 10\ H_2O(s) \rightarrow Na_2CO_3 \cdot xH_2O(s) + (10 - x)H_2O(g)$$

We know the masses of the original washing soda and the soda that is left in the box after it has become partially dehydrated. We can find the chemical amount (moles) of the original washing soda, because we have a definite formula for it, and therefore we can calculate its molar mass (which, to make things easier, is given in the question), and hence its chemical amount. Note that the chemical amount of Na_2CO_3 is the same as the chemical amount of $Na_2CO_3 \cdot 10\ H_2O$.

We cannot find a molar mass for the partially dehydrated soda, because we do not know its formula. We do, however, know the formula of water, so we can calculate its molar mass. We can also calculate the mass of water lost (from the difference between the original mass of soda and the final mass). Knowing these two values we can obtain the chemical amount of water that has been lost from the soda, and hence the ratio **H_2O lost : Na_2CO_3 which equals $(10 - x)$.** Once we have found $(10 - x)$ it is easy to find x.

We can set up the calculation as a table, thus:

	$Na_2CO_3 \cdot 10\ H_2O$	H_2O lost
Mass	1.50 kg = 1500 g	1.50 kg – 1.34 kg = 0.16 kg = 160 g
Molar mass, g mol^{-1}	286.1	18.02
Chemical amount, mol	5.24(3)	8.87(9)
Ratio of chemical amounts, $(10 - x)$	1	1.69(4)
x	(10 – 1.69) = 8.3(1)	

The composition of the powder in the box is therefore $Na_2CO_3 \cdot 8.3\ H_2O$, and answer to this question is **D**.

Note what a high proportion of the mass of washing soda is due to the water of crystallisation, which does not contribute anything to its effectiveness as a laundry aid. It just makes it a heavy item to carry home from the supermarket, and increases the cost of transporting it in bulk. Nevertheless customers seem to prefer the large, clear lumps of sodium carbonate decahydrate to less hydrated forms that are white and powdery. Once the seal on the packet is open, however, the washing soda quickly deteriorates into the less attractive form. The exact composition of the less hydrated form will depend on the conditions under which it is kept (the atmospheric pressure and humidity can make a big difference to the composition). It should be noted, however, that it does not break down into the fully anhydrous form (with no water of crystallisation) under normal ambient conditions – it needs to be heated to over 110°C for this to occur.

Although it is often considered to be a somewhat old-fashioned laundry aid nowadays, washing soda is nevertheless very effective. It is a moderately strong alkali (a one molar solution has a pH of about 11.3),

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[6] Note that this is not a true formula, because it does not refer to a pure compound. $Na_2CO_3 \cdot xH_2O$ is likely to be a mixture of different hydrated (and possibly anhydrous) forms of sodium carbonate, with the parts of the powder that are in contact with the atmosphere likely to be less hydrated than other parts. The composition of the solid is also likely to vary from day to day, as it will be affected by different atmospheric conditions of pressure and humidity.

so it reacts with oils and greases to form soaps[7], so it not only helps to remove oily dirt but also lowers the surface tension of the water, which helps to dissolve all kinds of dirt and stains. (Further information about oils and detergents is given in the answer to question 13 of the 2005 NHSCE.)

Washing soda also acts as a water softener, because it removes dissolved calcium ions in hard water by precipitating them as calcium carbonate, the equation for the reaction is:

$$Ca^{2+}(aq) + Na_2CO_3\ (s\ or\ aq) \rightarrow CaCO_3(s) + 2Na^{+}(aq)$$

(The anions associated with $Ca^{2+}(aq)$ are spectators in this reaction: they might be various different ions, e.g. chloride, sulfate or hydrogencarbonate, depending on the source of the water, but they do not affect the precipitation reaction.) Although softened water does not waste soap by reacting with it to give a scum, the precipitated calcium carbonate remaining in the water after it has been softened with washing soda can leave it feeling gritty and can wear away fabrics that are washed in it.

Nowadays the main use for sodium carbonate is in the production of glass, in which it is fused with calcium carbonate and silicon dioxide (and possibly other compounds, depending on the properties required of the glass) to give a complex mixture of sodium and calcium silicates.

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[7] Alkalis feel soapy to touch because they react with the oil in your skin. They are, however, very corrosive, so you should avoid contact with them. It is particularly dangerous if you get alkali in your eye: if this happens you should immediately wash your eye with copious amount of water.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2006 continued

6. About 72% of responding teachers considered that this question was appropriate, with 13% indicating that they thought it was difficult, and 11% saying that they had not yet covered it. A statistical analysis of the results from BC (the only province for which these were available) indicated that it had a moderate discrimination index with students there finding it moderately difficult. Students in some other provinces, however, seemed to find it more difficult.

Although this is a "storyline" question, it really just requires a knowledge of acid-base chemistry to work out the answer. Essentially students need to know that (1) indicators change colour according to whether they are in contact with acids or bases, (2) substances with low pH values are acidic and (3) carbon dioxide is the only acidic gas in the 5 most common gases found in air. The answer to this question is therefore **E**.

We concentrate so much on "acid rain", meaning rain containing dissolved pollutants such as sulfur oxides and nitrogen oxides, that we can sometimes forget that even the purest rain is acidic because of the carbon dioxide it dissolves as it falls through the atmosphere. Although rain containing carbon dioxide is not nearly as acidic as polluted rain, it can still weather limestone rocks and damage buildings.

The gluestick containing a little alkali and phenolphthalein gives the characteristic pink colour of the indicator when the glue is first put onto paper, so that we can see exactly where we have put the glue. After a little while, however, the indicator reacts with carbon dioxide and turns colourless, so that it doesn't show once the paper has been stuck down. Phenolphthalein is also used as an indicator in plaster. Decorators can see from the pink colour exactly where they have patched up cracks and blemishes in walls, but, after a while the colour fades, so it won't show up when they have painted over it.

Another make of gluestick is blue in the tube. This is because it contains methylene blue indicator, which works on a completely different principle from phenolphthalein. Methylene blue is a redox indicator: the reduced form of this indicator is blue, whilst the oxidized form is colourless. The indicator (and therefore the glue) becomes colourless when it reacts with oxygen in the air.

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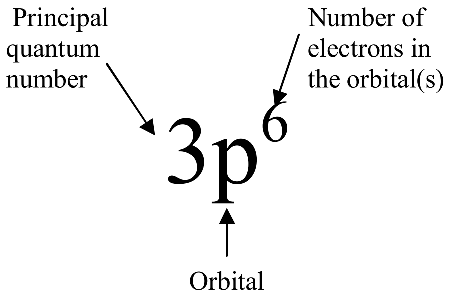
7. This question was done with very different degrees of success in different parts of the country. The BC statistics indicated that it was moderately difficult with a moderate discrimination index. Alberta and Quebec students found it much more difficult, however, and, in Alberta, it was the worst done question in the exam. This difference can be explained by comparing the results with the comments from teachers in Alberta and Quebec, most of whom said that the topic was not on the curriculum. (Compare this with the Ontario where 78% of teachers said it was appropriate, although 19% said they had not yet covered the topic, with the remaining Ontario teachers feeling that it was too difficult.) It should be noted that the topic is not on the Pan-Canadian protocol for Grades 11 and 12, although simple atomic structures are covered in the Grade 9 framework. In my experience Grade 12 textbooks cover the subject at the level required, although, in some cases, the discussion is not very illuminating.

The question requires the identification of a species with the ground state electronic configuration:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ .$$

This uses the most common method of identifying electrons used in chemistry, but it should be observed that it uses to a blend of two different concepts, namely quantum numbers and orbitals. What we really need to know is which energy levels have electrons in them, and the energy levels are defined by quantum numbers. Each energy level has a unique set of quantum numbers, which are: the principal quantum number, the subsidiary (or secondary) quantum number, the magnetic quantum number, and the spin quantum number. I do not propose to go into detail of exactly what these values signify, as most first year university textbooks discuss them, even if they are not in your high school textbook. Suffice it to say that they are all numerical values, rather than letters. The letters shown in the electronic configuration convention refer to *orbitals*, which define the space in which the electron may be found. Each orbital, however, is associated with a particular subsidiary energy level, so by defining it we obtain information about energy levels.

If we look at the series of numbers and letters that we are given, we can break it apart into sets each of which contains a number, a letter and a superscript number. The first number in each set gives the principal quantum number, the letter gives the orbital and thus the subsidiary quantum number, and the superscript number shows the number of electrons in that subsidiary energy level. An example is given below:



Note that you can find the total number of electrons in the species you are investigating by adding together all the superscript numbers in the series you are given, thus for

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$$

the total number of electrons is {2+2+6+2+6+10} = 28. This eliminates As^{3-} with 36 electrons (answer A), Ge^{2+} with 30 electrons (answer B), and Kr with 36 electrons (answer C). Both Ni and Zn^{2+}, however, have 28 electrons, so we need to look at exactly **which** energy levels are filled.

We are told that the species is in its ground state, which means that the electrons are in the lowest possible energy levels, consistent with each electron having a unique set of quantum numbers, i.e. conforming to the aufbau principle[1] and the Pauli exclusion principle[2], however we need to remember that the actual energy levels are different in different atoms, even when they are given the same electron configuration. The $1s^2$ level, for example, becomes lower and lower as electrons are added to levels above it, meaning that the $1s^2$ level becomes increasingly stable, and it becomes increasingly difficult to remove electrons from it.[3] Energy levels also become closer and closer together at higher levels. Furthermore, the position of the levels relative to each other can actually change. This question is testing whether you know what happens to electron configurations around the 3d and 4s energy levels, which tend to change position relative to one another.

Before we continue to consider what is happening in this particular case, we need to remember that, for a particular atom or ion, the electronic (potential) energy of the ground state will be as low as possible. This means that the energy levels with lower principal quantum numbers will be the ones most likely to contain electrons, so they will usually fill up in the order 1, 2, 3 etc. Within any level defined by a particular principal quantum number, one might expect that the levels indicated by the lower subsidiary quantum numbers will be filled up first, which, in orbital terms, means that the levels will be filled in the order s, p, d, f, with each s orbital being able to take a maximum of 2 electrons, each p orbital being able to take a maximum of 6 electrons, each d orbital being able to take a maximum of 10 electrons, and each f orbital being able to take a maximum of 14 electrons. It is, however, usual for 4s energy levels to be filled in

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[1] The aufbau (building up) principle states that each electron added must be placed in the lowest available energy level in an atom or ion.

[2] The Pauli exclusion principle states that no two electrons in the same species can have the same set of 4 quantum numbers.

[3] Note that the theory of electronic energy levels is supported by ionization energy data, c.f. the answer to Question 14 of the 2006 MHSCE.

before 3d, and 5s before 4d, due to overlap of the energy levels. Energy levels with higher principal quantum numbers, such as 6s, 5d and 4f, are also filled in an unlikely-looking order. Note that, once the filling-in process has been completed, the order of the energy levels reverts to that indicated by the principal quantum number, i.e. the 4s level returns to a higher energy level than the 3d level (which now has more than one or two electrons). The reason for this new "inversion" of energy levels is not easily explained, but it probably has something to do with the spatial arrangement of the electrons: because if electrons come very close together they will repel each other, and this will elevate their energy level.

In this question we can see that each set of subsidiary energy levels is complete, but we can also see that we are missing the 4s energy level that might be expected to come in before the 3d level, thus:

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,\mathbf{4s^2}\,3d^{10}$$

Adding the extra two electrons would, however, would give us a 30-electron species, such as a zinc atom. What we have to remember, however, is that, although electrons go into the 4s level before the 3d level for atoms, **the electrons come off the 4s level before the 3d level when the ion is formed from the atom**. The species that is formed by removing the $4s^2$ electrons from the zinc atom is the Zn^{2+} ion, so the answer to this question is **E**.

For your information the electron configurations of the species presented as alternative answers in this question are:

A. As^{3-} $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6$ (Note how the energy levels have reverted to the "normal" pattern here – with the principal quantum numbers written in order – once the 3d and 4s levels have been filled up, and the 4p level started.)

B. Ge^{2+} $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}$

C. Kr $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6$

D. Ni $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}$

E. Zn^{2+} $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$

Note that all these species have their outer orbitals completely filled, which confers some stability, but only As^{3-} and Kr have complete outer p orbitals, which is what is needed for the greatest stability (noble gas configuration).

Note also how we have established an electron configuration for the atoms or ions using only two of the four quantum numbers[4]. We can do this because the energy levels indicated by the subsidiary quantum number are degenerate, which is to say that they are equal in the absence of a magnetic field, so the magnetic quantum number does not come into play. Thus, for example, the three p orbitals, which can be designated p_x, p_y and p_z, and which can be differentiated in a magnetic field, are all at an equivalent level. Each of the p_x, p_y and p_z orbitals contains two electrons, with each of these two electrons in a p ortibal having a different spin. The spin does not affect the way in which the energy levels fill up in this case, but it may do so in other cases[5].

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[4] It is still possible to distinguish Zn^{2+} from the other species given in this question, even if you were only using the simplified electronic configuration convention that is sometimes taught in Grade 9. This convention shows only the number of electrons in each shell (which is equivalent to the number of electrons with each principal quantum number) in turn. In this system Zn^{2+} is 2.8.18, compare this with As^{3-} 2.8.18.8, Ge^{2+} 2.8.18.2, Kr 2.8.18.8 and Ni 2.8.18.2.

[5] The rule to apply when putting electrons into degenerate energy levels is Hund's rule. This states that one electron is put into each of the equivalent energy levels until all these levels contain a single electron, each with a parallel spin, after which a second electron (with the opposite spin) is placed in each level.

8. The statistical analysis of BC results indicates that this students found this question easy and that the discrimination index was moderate. Students in Alberta also did well on this question, but it was less well done in other provinces, presumably because teachers had not covered it. Overall about 46% of teachers said that they had not yet covered the material, whilst 52% said the question was appropriate and 2% said it was too easy.

The question refers to a reaction involving borax, $B_4O_7^{2-}$, so it could easily have become a "storyline" question, because borax is a common household product used as a laundry detergent enhancer. Borax is alkaline, so it works like washing soda. We had already had a question about washing soda on this exam, so having a second question on detergent enhancers seemed a bit excessive.

The question required a simple application of the rules of calculating oxidation numbers. These rules have been discussed several times in the solutions to the NHSCE, and a detailed explanation can be found at http://www.cheminst.ca/outreach/hsexam/cicfrm_index__e.htm under CIC/CCO Examination for 2001 in the Appendix to the solutions to Questions 21 to 25.

The question gives the equation for the reaction between borax (sodium borate) and hydrochloric acid:

$$Na_2B_4O_7(aq) + 2HCl(aq) + 5H_2O(l) \rightarrow 4H_3BO_3(aq) + 2NaCl(aq)$$

and asks students to determine the change in the oxidation number of each boron atom in this reaction. Essentially this means that the oxidation number in boron needs to be determined in two compounds, $Na_2B_4O_7$ and H_3BO_3. In order to do this you need to know the total of the oxidation numbers of the other elements in each of the compounds, then you need to apply the rule stating that in neutral compounds the algebraic sum of the oxidation numbers = 0.

(1) Determining the oxidation number of boron (B) in $Na_2B_4O_7$

For sodium (Na) you need to apply the rule that states that all Group I elements have a valency of +1. There are two sodiums in the formula, so that the contribution from sodium is (2 x +1) = +2

For oxygen (O) you need to apply the rule that states that the oxidation number of oxygen is always –2[6]. There are seven oxygens in the formula, so that the contribution from oxygen is (7 x –2) = –14.

The combined contribution from all the sodiums and oxygens in the formula is therefore (+2 –14) = –12.

As the algebraic sum of all the oxidation numbers must be zero, then the contribution due to all 4 of the borons in the formula must = +12

and the contribution from each individual boron must = +12/4 = 3

The oxidation number of boron in $Na_2B_4O_7$ is therefore = +3.

(2) Determining the oxidation number of boron (B) in H_3BO_3

For hydrogen (H) you need to apply the rule that states that the oxidation number of hydrogen is +1[7]. There are three hydrogens in the formula, so that the contribution from hydrogen is (3 x +1) = +3.

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[6] The complete rule states that the oxidation number of oxygen is always –2 (except in peroxides when it is –1, and in OF_2 when it is +2).

[7] The complete rule states that the oxidation number of hydrogen in all its compounds, except metal hydrides, is +1. (In metal hydrides it is –1.)

For oxygen you again need to apply the rule that states that the oxidation number of oxygen is always –2. There are 3 oxygens in the formula, so that the contribution from oxygen is (3 x –2) = –6.

The combined contribution from all the hydrogens and oxygens in the formula is therefore (+3 –6) = –3.

The contribution of the single boron to the neutral compounds must therefore be +3.

The oxidation number of boron in H_3BO_3 is therefore = +3.

There is therefore no change of oxidation number in this reaction, therefore the answer to the question is **C**. Note that the number of formulas shown in the equation (stoichiometry of the **reaction**) does not change the oxidation numbers of the elements in the compounds, which is affected only by the number of symbols in the formulae (stoichiometry of the **compound**).

This is a kind of trick question, because we tend to link the presence of different numbers of oxygens in a formula to differences in oxidation number of a "central" atom, e.g. in H_2SO_4 sulfur is in an oxidation state = +6, whilst in H_2SO_3 it is in an oxidation state = +4, but such differences in oxidation number tend to occur only with non-metals on the right hand side of the Periodic Table, or with transition metal elements. In Groups 1, 2 and 3 the elements usually show only their group oxidation state (+1, +2 or +3, respectively), so we would expect the oxidation number of boron to = +3.

In the covalent compound H_3BO_3 boron is the central atom connected to three oxygens, and the formula is perhaps better written as $B(OH)_3$. $Na_2B_4O_7$ contains two Na^+ ions for every $B_4O_7{}^{2-}$, however the $B_4O_7{}^{2-}$ is probably only one unit in a complex polymeric network, in which boron atoms and oxygen atoms are covalently bonded, with some of the oxygen atoms carrying an extra negative charge. Some non-metals (e.g. S) and transition metals (e.g. Cr) form similar compounds, so it cannot be assumed that their oxidation numbers will change in every reaction they are involved in, even though they are the kind of elements which can have a number of different oxidation numbers.

It is often possible to check yourself on exactly which kind of reaction is taking place by seeing whether other elements in the equation are changing their oxidation numbers. If two elements in an equation are changing oxidation numbers (with one number increasing and the other decreasing) then you have a redox reaction, whereas if you just have a change in the number of oxygens associated with one element in a compound, and no other element is changing oxidation number, then the reaction is like to be a polymerisation reaction or a condensation (polymerisation/elimination) reaction.

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9. Students found this question difficult, and the discrimination index was poor. The majority (72%) of teachers found it appropriate, although 15% felt it was too difficult, and 9% thought that it was not on the curriculum.

The question was concerned with the ratio between the size of an ion compared with the corresponding atom. I feel that students should know that, when an atom loses an electron, its radius shrinks. This is because the positive protons in the nucleus outnumbers the negative electrons in the outer part of the ion, and so the remaining electrons are pulled in closer. The more electrons that the atom loses, the smaller its radius will become. Conversely the radius increases when electrons are added to an atom, because the ability of the nucleus to attract all the electrons is reduced. The more electrons that the atom gains, the larger the negative ion becomes.

We can therefore say that the ratio of ionic radius to atomic radius is <1 for Na^+:Na, B^{3+}:B and Al^{3+}:Al, but >1 for N^{3-}:N and F^-:F. This means that we can eliminate Na^+:Na, B^{3+}:B and Al^{3+}:Al from consideration, as their ratios will definitely be smaller than those for N^{3-}:N and F^-:F. It also looks likely that the ratio for N^{3-}:N will be greater than that for F^-:F, because the negative charge on the ion is greater. The only thing that could make the comparative ratios difficult to estimate would be a large difference in the size of the original atoms – which would be the case if the atoms were in different periods of the periodic table, for example. This is not the case here, however, as nitrogen and fluorine are in the same period of the periodic table and have atoms of very similar sizes. The greatest ratio of ionic radius to atomic radius of the examples given is therefore N^{3-}:N, so the answer to this question is **D**.

Note that it would have been more difficult to assess the relative ratios of Na^{+}:Na, B^{3+}:B and Al^{3+}:Al, because boron is in a different period of the periodic table than sodium and aluminum. Boron is in the same **group** as aluminum, but it is in the previous period, so its atoms will have one less shell of electrons than aluminum and its radius will be smaller. We can also say that $B^{3+} < Al^{3+}$, but assessing the ratio of ionic to atomic sizes is problematic.

When looking at sodium and aluminium atoms there is also the question of size to complicate matters. Remember that the sizes of atoms within a particular period of the periodic table starts off relatively large in group 1, but decrease going from left to right of the period, becoming fairly similar on the right hand side. This variation in atomic size is due to the electron being added into a fresh shell in Group I, so that the nucleus has only a limited power to attract it (because the electron is further away, and it is also shielded by the filled shells that have come before). As electrons are added into the new shell, protons are also added into the nucleus, so the attraction between protons and electrons inceases, and the atom actually becomes smaller than the one before it. Towards the right hand side of the table, however, the effect is limited, because the negative electrons in the outer shell begin to repel each other, and this makes it more difficult for the atom to decrease much in size.

10. Students found this question easy, but the discrimination index was poor. The majority of teachers (73%) thought it was appropriate , but 18% said that they had not yet covered the topic, and 11% thought it was too difficult.

The question concerned kinetics (rates of reaction), which is not actually on the Grade 11 and 12 curriculum of the Pan-Canadian protocol. In the past, however, teachers have suggested that it should be on the NHSCE, and so, as it is, in fact, in the Grade 10 section of the protocol, it has been included. Realising that Grade 10 work would not likely to be uppermost in the minds of most students taking the exam, care was taken to keep the question simple by referring to a reaction that students would be familiar with – one that they may even have met in the context of a rates experiment in the laboratory – namely the reaction between marble (calcium carbonate) and hydrochloric acid according to the following equation:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Students are asked to identify the graph that would best show the change in concentration of hydrochloric acid during the course of the reaction, assuming that the marble is in the form of chips of roughly the same size and shape.

In order to be able to work out the answer, students need to appreciate that hydrochloric acid is a reactant (because it is on the left hand side of the equation given), so that its concentration will decrease with time. This eliminates responses B, D and E. In order to choose between responses A and C students must realise that the change in concentration occurs most rapidly at the beginning of the reaction, when there is plenty of acid around to be in contact with the marble. The reaction slows down as it goes along because there is less acid around, and it takes some time for acid and marble to meet. At the end of the reaction, there is no acid left, and the reaction stops. This is the pattern shown in the first graph, so the answer to this question is **A**. In graph C, although the concentration does eventually drop to zero, it does not change at all at first, so it is not a likely pattern for the reaction.

It would, perhaps, be easier for students if they remembered that the rate of reaction can be defined as change in concentration with unit time. Rate is thus indicated by the slope[8] of concentration vs time graphs

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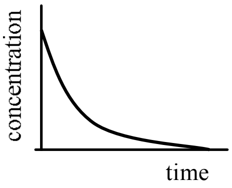
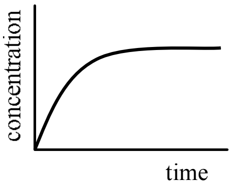
[8] The usual convention is to ignore the sign of the slope, so that a steep slope indicates a fast reaction, irrespective of whether the concentration is increasing or decreasing.

such as these. In graph A, we can see that the rate of reaction is fast at first and then tapers off to zero. In graph B, we can see a similar pattern in the rate, although the sign of the slope is different because it is a graph for a product rather than a reactant concentration. Graphs similar in shape to those shown in the other keys may also be obtained sometimes. Graph C, where the rate is slow at first, and then increases, might be observed in an autocatalysed reaction[9] (although the rate would need to flatten out again at the end of ther reaction). In D the concentration does not change with time: this is because the measured reactant does not, in fact, affect the rate of reaction. You may also have seen a graph similar in shape to that shown in E, but this would be a rate vs concentration graph (rather than a concentration vs time graph) for an enzyme reaction.

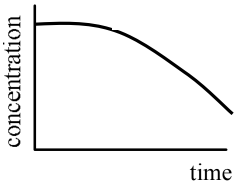
A



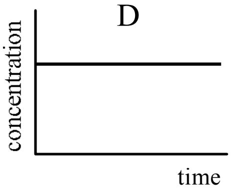
B



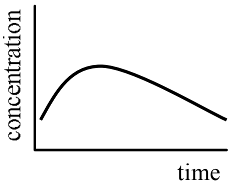
C



D



E



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[9] An autocatalyzed reaction is one in which a product of the reaction is a catalyst for the reaction: this means that the reaction will go faster and faster until the concentration of reactants becomes so low that the reaction has to slow down and stop.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2006 continued

11. A statistical analysis of the results from BC (the only province for which these were available) indicated that this question had a moderate discrimination index with students there finding it moderately difficult. Only 47% of teachers thought that this question was appropriate, with 38% saying that they had not yet covered it, and 11% saying that it was too difficult.

I felt that the results for this question were disappointing in view of the fact that the it concerned the electrolysis of brine (sodium chloride solution), a topic that was extensively discussed in the solution to Question 14 of the 2005 NHSCE. The explanation for the electrolysis is repeated below.

> 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.[1] 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 hydroxide 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:

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[1] 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**.

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

Chlorine gas is thus obtained at the anode in the electrolysis of brine, and the answer to Question 11 of the 2006 NHSCE is therefore **E**.

The discussion about the electrolysis of brine continues.

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 increasingly 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 process the sodium hydroxide is formed in a separate part of the apparatus, and brine is continuously added to the electrolysis cell
- in the diaphragm cell process 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 process 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: the flowing mercury cathode cell, the diaphragm cell and the membrane cell. Chlorine is produced in all three of them, along with sodium hydroxide and hydrogen. All three products are important commercially.

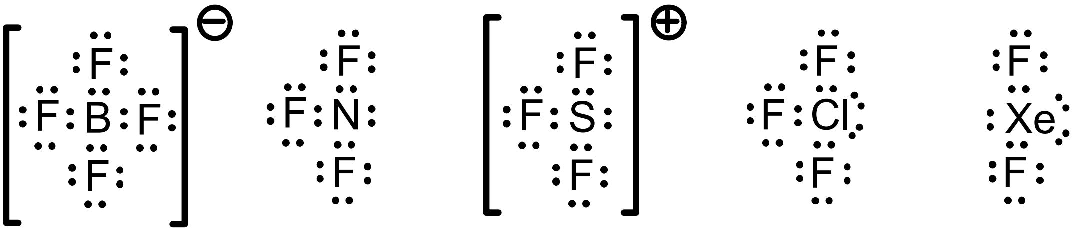
12. Students found this question to be moderately difficult and it had a good discrimination index. 78% of teachers indicated that it was appropriate, but 7% felt it was too difficult and 11% said that it was not on their curriculum.

This question is concerned with the electronic structures (essentially the Lewis diagrams) of five covalent species, each of which consists of a central atom bonded to fluorine. Students have to figure out the number of bonding pairs and lone pairs around the central atom. The logic for working this out is summarized in the table below. Note that the numbers of electrons due to fluorine have not been shown in this table, but it should be remembered that each fluorine atom has 7 electrons, so it will have 3 lone pairs of electrons and will contribute one electron to each bond with the central atom.

	A. BF_4^-	B. NF_3	C. SF_3^+	D. ClF_3	E. XeF_2
1. Central atom	B	N	S	Cl	Xe
2. Group in the periodic table of the central atom (IUPAC number)	3	15	16	17	18
3. Number of electrons contributed by the central atom	3	5	6	7	8
4. Electrons involved in the overall charge	1 added	0	1 subtracted	0	0
5. Total number of electrons contributed by bonds with fluorine to the central atom	4	3	3	3	2
6. Total number of electrons around the central atom (bonding and non-bonding)	3+1+4 = 8 (4 pairs)	5+3 = 8 (4 pairs)	6–1+3 = 8 (4 pairs)	7+3 = 10 (5 pairs)	8+2 = 10 (5 pairs)
7. Total number of bonding pairs of electrons around the central atom (from step 5)	4	3	3	3	2
8. Total number of non-bonding pairs of electrons (lone pairs) around the central atom (from steps 6 and 7)	4–4 = **0**	4–3=**1**	4–3=**1**	5–3=**2**	5–2=**3**

The species with two, and only two, lone pairs of electrons around the central atom is therefore ClF_3, and the answer to this question is therefore **D**.

The Lewis diagrams for the ions and molecules given in this question are shown below:



It is important to be able to work out the number of bonding and non-bonding pairs of electrons around a central atom, and to draw the Lewis diagrams, because these can help you to establish the shape and symmetry of a molecule or an ion (c.f. the solution to Question 15 below), and, from these, the polarity of the species. Once you know the polarity you can begin to predict some of the properties of the substance, such as its viscosity or its behaviour in an electric field.

13. Students generally found this question easy but it was a very poor discriminator. 72% of teachers said that they thought it was appropriate, 9% thought it was too difficult, and 17% had not yet covered it. The problem involved a series of single displacement reactions, i.e. reactions between a metal and the salt of another metal in aqueous solution. Although these are redox reactions, they are often studied at the beginning of chemistry courses because they involve simple substances. Students often do this kind of experiment for themselves, or they may see the "Christmas tree" demonstration in which a piece of copper wire is twisted into a tree shape, and dipped into silver nitrate solution, where the tree shape gradually becomes covered with sparkling silver and the colourless solution may gradually become blue as aquated copper (II) ions are formed. The equation for the reaction is:

$$Cu(s) + 2AgNO_3(aq) \rightarrow 2Ag(s) + Cu(NO_3)_2(aq)$$

Alternatively an ionic equation may be written, thus:

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

(The nitrate ions are spectators in this reaction, which means that they can be omitted from the ionic equation.)

It can be seen from the ionic equation that this reaction involves the transfer of electrons. Copper atoms give electrons to silver ions, forming silver atoms and copper ions. Electron transfer like this is a characteristic of redox reactions. In simplified terms we are looking at a series of competition reactions here. In each case the more reactive metal will give up its electrons and "take the anion away from" the less reactive metal. We can establish a reactivity series of metals simply by looking at how many reactions each metal will do.

When students do the reactions for themselves they often use common metals, such as copper, iron, magnesium and zinc, together with solutions of their salts. I chose a different group of metals here, because I wanted students to use logic rather than rely on their memories in order to establish an order of reactivity. To be honest, I don't really know that the reactions would work exactly as the reactivities of the metals might indicate, because the rate of reaction might be very slow, or a metal might be rendered passive by an insoluble oxide layer, or the anion involved might interfere with the reaction. For the purposes of the question, however, you can assume that, if a reaction occurs between metal A and the salt of metal B, then the reaction between metal B and the salt of metal A will not occur. Conversely, if a reaction does not occur between metal C and the salt of metal D, then it is likely that the reaction between metal D and the salt of metal C will occur (although this cannot be relied on "in real life").

Looking at the table you are given in the question, you can see that there are two cases in which "No data" has been recorded.

Metal / Solutions	Ni	Ca	Cr	Ag
$AgNO_3$	Silver formed	Silver formed	Silver formed	No reaction
$CaCl_2$	No reaction	No reaction	No reaction	No reaction
$NiCl_2$	No reaction	No data	Nickel formed	No reaction
$CrCl_3$	No reaction	Chromium formed	No reaction	No data

In the case of the reaction between Ca and $NiCl_2$ we need to look at what happened in the reaction between Ni and $CaCl_2$. No reaction occurred between Ni and $CaCl_2$, so it is **likely** that nickel will be formed in the reaction between Ca and $NiCl_2$. In other words, calcium is probably more reactive than nickel.

In the case of the reaction between Ag and $CrCl_3$ we need to look at what happened between Cr and $AgNO_3$. Here we can see that silver was formed, so that we can be fairly sure that chromium is more reactive than silver. Now we can modify the table, as shown below:

Metal / Solutions	Ni	Ca	Cr	Ag
$AgNO_3$	Silver formed	Silver formed	Silver formed	No reaction
$CaCl_2$	No reaction	No reaction	No reaction	No reaction
$NiCl_2$	No reaction	Nickel probably formed	Nickel formed	No reaction
$CrCl_3$	No reaction	Chromium formed	No reaction	No reaction
Number of reactions done by the metal	1	3	2	0

Looking at the number of reactions done by each metal we can say that the order of reactivity of these 4 metals must be Ca > Cr > Ni > Ag, so that the answer to this question is **B**.

Note that, in order to simplify the question, the information given in the table in this question has been modified from the kind of table of observations that you might record in your laboratory notebook. When you are doing an experiment you should only note down what you see, and leave your formal interpretation of the data until later. Your table of observations for this experiment might look something like this:

Metal / Solutions	Ni	Ca	Cr	Ag
$AgNO_3$	Grey-black solid formed	Grey-black solid formed	Grey-black solid formed	X
$CaCl_2$	No apparent reaction	X	No apparent reaction	No apparent reaction
$NiCl_2$	X		Grey-black solid formed	No apparent reaction
$CrCl_3$	No apparent reaction	Grey-black solid formed	X	

Points to note in this table are:

- It is not necessary to react a metal with one of its own salts in this experiment, because one would not expect a reaction here. These parts of the table can therefore be crossed out.
- Instead of saying "No reaction" it is better to write "No apparent reaction" because reactions can occur without any observable effect. (Think of the reaction between hydrochloric acid and sodium hydroxide solution to make salt and water. This reaction would just appear as two colourless liquids combining to form a colourless liquid.)
- You should report what you observe rather than name the substance that you think you have obtained. Here I have assumed that all the solids will appear grey-black, but they could look slightly different colours, or some of them might form shiny crystals, and this should be noted down. Changes in colour of the solution should also be noted, as should the formation of gas (which might occur, for example, when calcium reacts with some of the more acidic salt solutions).

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14. Students found this question moderately difficult and it had a moderate discrimination index. Teachers comments indicated that 80% thought it was appropriate, 7% considered it to be too difficult, 9% said it was not on the curriculum and 4% had not yet covered the topic.

This question requires students to interpret a graph showing molar ionization energies (E_m) for removing successive electrons from atoms of a particular element, Z. It should be remembered here that the term *molar ionization energy* may be defined as the energy required to remove one mole of electrons from a particular energy level from one mole of a particular type of atom or ion (one electron from each atom or ion) in the gas state at standard temperature and pressure. Thus for the first electron to be removed from atoms of an element Z, the molar ionization energy, E_{m1}, would refer to the following reaction:

$$Z(g) \rightarrow Z^{+}(g) + e^{-} \; ; E\text{m}_1$$

The ionization reaction for the second electron to be removed is:

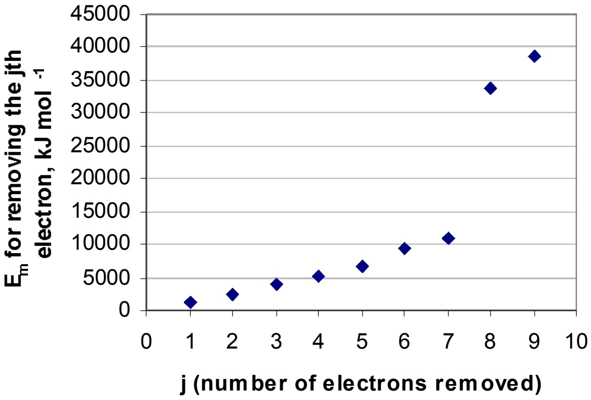
$$Z^{+}(g) \rightarrow Z^{2+}(g) + e^{-} \; ; E\text{m}_2$$

and the general equation for the jth electron is:

$$Z^{(j-1)+}(g) \rightarrow Z^{j+}(g) + e^{-} \; ; E\text{mj}$$

Remember that the ionization energies refer to one electron being removed at a time: the ionization energies are not cumulative. Note also that, following the usual convention, the equations refer to one mole of each species involved in the reaction.

The graph given in the question is shown below:



It can be seen from this graph that the ionization energy, E_m increases as the number of electrons removed increases. This is not surprising when one considers that the successive electrons are being removed from ions with increasing positive charges. The electrostatic attraction between outer electrons and the nucleus of the ions becomes greater and greater, making it more and more difficult for ionization to occur.

The relationship between E_m and j is not, however, linear. There is, in particular, a large difference in ionization energy for removing the seventh electron and that for the eighth electron. This big "jump" indicates that the first seven electrons are in the outer valency shell, but the eighth electron is in an inner shell. Inner shells are closer to the nucleus, and therefore the force of attraction between inner shell electrons and the nucleus is much greater than for outer shell electrons, so the ionization energies for inner shell electrons are much greater than those for outer shells.

As the graph shows that there are 7 electrons in the outer shell of the atoms, we can say that it is likely that

Z is in Group 7 (IUPAC Group 17). The only Group 7 element amongst the options to choose from in this question is chlorine, so the answer to this question is **B**.

The other options in the question are: sulfur which is in Group 6 (IUPAC Group 16), argon Group 8 (IUPAC Group 18), calcium Group 2 (also IUPAC Group 2) and scandium Group 3 (also IUPAC Group 3).

If you look closely at the graph, you may be able to see a small "jump" in ionization energies between electrons 5 and 6. This occurs after the 5 p-orbital electrons have been removed, when there is a slight increase in energy required to remove an electron from a complete s orbital, which has some stability. Sometimes one can also observe a "jump" when a half-filled set of p orbitals is broken into: it is not very easy to see in this diagram, but it might be expected between electrons number 2 and 3. Patterns in ionization energy values like this provide support for the theory of electron energy levels. (Compare this with the solution to Question 7 of the 2006 NHSCE.)

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15. Students found this question to be moderately difficult and it had a moderate discrimination index. 70% of teachers thought that the question was appropriate, 17% said that the topic was not on their curriculum, and 14% were divided equally between saying that they had not yet covered the topic or that it was difficult.

The question was concerned with the shapes of three molecules containing sulfur, and in such problems the first step is to establish the arrangement of electrons around the central atoms of the molecules. Here the central atom in all three molecules is sulfur (because it is less electronegative than either oxygen or chlorine). There are two methods for determining the arrangement of electrons:

Method 1: Determing the number of lone pairs by counting valency electrons

This method is similar to that described above for Question 12. The process is shown in the table below:

	SCl_2	SO_3	$SOCl_2$
1. Number of valency electrons on S (Group 16)	6	6	6
2. Number of valency electrons attributable to Cl atoms (Group 17)	2 x 7 = 14	0	2 x 7 = 14
3. Number of valency electrons attributable to O atoms (Group 16)	0	3 x 6 = 18	1 x 6 = 6
4. Total number of valency electrons (from steps 1, 2 and 3)	20	24	26
5. Total number of valency electrons needed for every atom in the molecule to have an octet	3 x 8 = 24	4 x 8 = 32	4 x 8 = 32
6. Number of bonding electrons around the S atom (from steps 4 and 5)	24 – 20 = 4 (2 pairs)	32 – 24 = 8 (4 pairs)	32 – 26 = 6 (3 pairs)
7. Number of electrons in the octet around the S atom	8 electrons (4 pairs)	8 electrons (4 pairs)	8 electrons (4 pairs)
8. Number of non-bonding, lone pair electrons on the S atom (from steps 6 and 7)	2 pairs	0	1 pair

Method 2: Determining the number of lone pairs using oxidation numbers

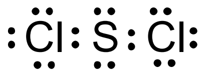
You will probably find this way easier if you have learnt about oxidation numbers in class. Remember that the oxidation number tells you the number of electrons that an atom is using for bonding. This method is shown on the next page.

For SCl_2: Cl has an oxidation number (state) of –1 (when it is an outer atom of the molecule)
Two Cl atoms contribute (2 x –1) = –2, which must be balanced by S in the neutral molecule
S is therefore in the +2 oxidation state, which means it contributes 2 electrons to the bonding
S is in Group 16, so it has 6 valency electrons,
So there must be (6–2) = 4 non-bonding electrons i.e. 2 lone pairs of electrons on the sulfur.

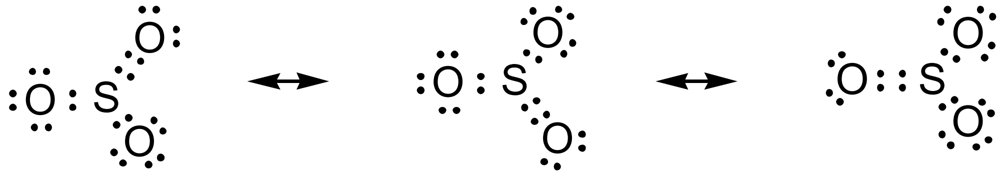
For SO_3: O has an oxidation number of –2
Three O atoms contribute (3 x –2) = –6, which must be balanced by S in the neutral molecule
S is therefore in the +6 oxidation state, which means it contributes 6 electrons to the bonding
S is in Group 16, so it has 6 valency electrons,
So there must be (6–6) = 0 non-bonding electrons, i.e. there are no lone pairs of electrons on the sulfur.

For $SOCl_2$: Cl has an oxidation number of –1 (when it is an outer atom of the molecule), and O has an oxidation number of –2
Two Cl atoms (2 x –1) = –2 and one O atom contributes –2, for a total of –4, which must be balanced by S in the neutral molecule
S is therefore in the +4 oxidation state, which means it contributes 4 electrons to the bonding
S is in Group 16, so it has 6 valency electrons,
So there must be (6–4) = 2 non-bonding electrons i.e. one lone pair of electrons on the sulfur.

The next stage in the process of establishing the shape of the molecules is to draw the Lewis diagrams. SCl_2 is fairly simple because it just has 2 bonding pairs and 2 lone pairs of electrons so its Lewis diagram looks like this:



For SO_3 the process is a little more complex. If we assume that there is an octet (4 pairs) of electrons around the central sulfur atom, then we have to decide on how to spread these electrons over 3 bonds with oxygen. This can be done by having one double bond and two coordinate bonds[2]. (Note how this uses all 6 of the electrons from the sulfur atom as indicated by its oxidation number of 6.) There is, however, no real difference between the bonds – they all behave like 1⅓ bonds in terms of length and strength. We often say that the bonds are "hybridised" and draw them with a series of equivalent structures called resonance hybrids, some possible variations of which are shown below:



We can draw other resonance hybrid stuctures for the SO_3 molecule: these structures require the sulfur atom to "disobey" the octet rule. Sulfur is able to have more that 8 electrons in the valency shell, because it has empty d orbitals that can be brought into use. The d orbitals are, however, at a higher energy level than the s and p orbitals, so that they are less likely to be involved, and the data for bond strength and length suggest that resonance hybrids involving >8 electrons around the sulfur are unlikely to represent more than about 5% of sulfur trioxide molecules in the gas phase.

Some possible structures are shown on the next page:

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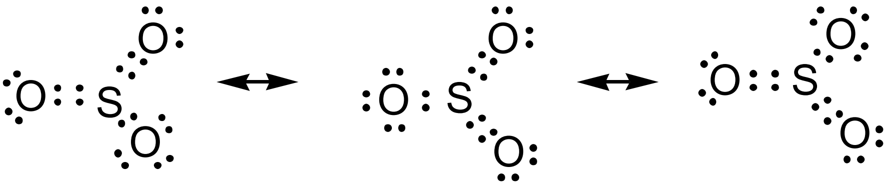
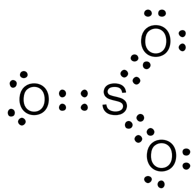
[2] A coordinate bond (also sometimes called a dative covalent bond) is a single bond in which both electrons are considered to originate from one atom. Note that, when a coordinate bond has been formed, there is no way of distinguishing it from any other single bond: the electrons in the bond are not "marked" in any way as coming from a particular atom.

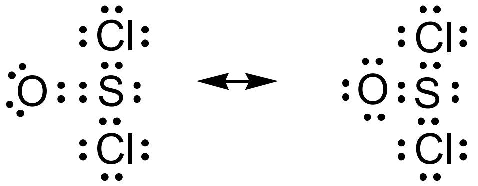


Some authors draw SO_3 with **3** double bonds around the central sulfur atom. This means that sulfur is using all 6 of its own electrons plus 6 electrons from oxygen atoms, so that it has 12 electrons instead of 8 around it. The Lewis structure for this arrangement is shown below:

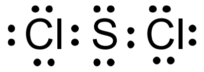


If this arrangement of electrons were to predominate then the electron density between the sulfur and oxygen atoms would be significantly greater than with the octet arrangement, the bond length would be shorter and the bond strength would be greater, but the figures for these values suggest that the contribution from this structure is, in fact, minimal. The direction of the bonds would, however, be unchanged, and this is what is important in determining the shape of the molecule.

The Lewis diagram for $SOCl_2$ is usually drawn so that the octet rule is obeyed, with a coordinate bond to oxygen, "regular" single bonds to the chlorine, and a lone pair on the sulfur, but it is also sometimes shown as having a double bond between sulfur and the oxygen (i.e. with an expanded valency shell on sulfur). The areas of electron density are not affected by these differences. The two possible hybrid structures are shown below:



Once the Lewis diagrams have been established, the next job is to establish the shape of the molecule based on the VSEPR theory[3]. Remember that it is important to consider non-bonding electron pairs as well as bonding electrons when establishing a molecular shape. The first molecule, SCl_2, can easily trick you here, particularly if you draw the Lewis diagram as:



It is very tempting to say that this molecule is linear, thus:

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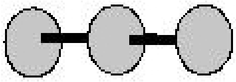
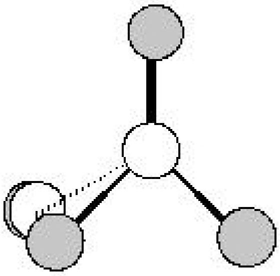
[3] VSEPR stands for Valence Shell Electron Pair Repulsion. VSEPR is a bonding model that is used for predicting the geometry of molecules. It was developed by Canadian chemist, Ronald Gillespie, and states that pairs of electrons that surround the central atom of a molecule repel each other and arrange themselves in space in such a way that they are as far apart as possible. Where double or triple bonds are involved we can modify this to say that groups of electrons (or areas of electron density) around the central atom repel each other and arrange themselves in space so that they are as far apart as possible.

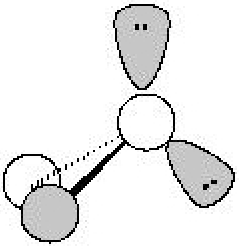


but this is **NOT** the case, because we have to remember the two lone pairs on the sulfur atom, which will affect the shape.

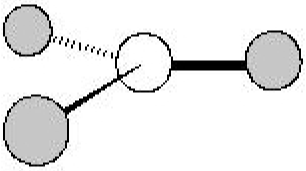
Whenever we have 4 pairs of electrons around a central atom we can expect a molecular shape that is **based on** a tetrahedron, because the 4 regions of electrons density are distributed through 3-dimensional space. (We are NOT looking at a 2-dimensional square.) A diagram of a tetrahedral molecule is shown on below:



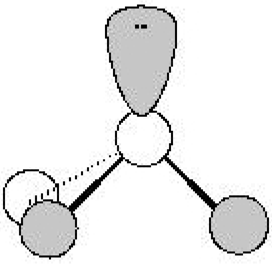
SCl_2 is not, however, a tetrahedral molecule, because only the atoms in the molecule count when we name the shape, and two of the positions in the tetrahedron are here occupied by lone pairs. The shape of this molecule is therefore angular (or bent) as shown below:



With SO_3 we are looking at only three areas of electron density, all of which are involved in bonding (with no lone pairs) so the molecule is trigonal planar (or triangular) as shown here:



The third molecule involved in this question, $SOCl_2$, involves four areas of electron density, one of which involves a lone pair. This gives a trigonal pyramidal shape, as shown on the next page:



We can therefore say that the 3 molecules SCl_2, SO_3 and $SOCl_2$ have the following shapes: angular, trigonal planar and trigonal pyramidal, respectively. This means that the answer to this question is **D**.

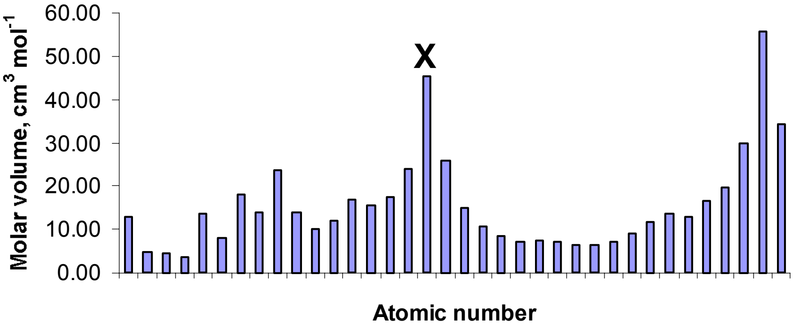
ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2006 continued

16. A statistical analysis of the results from BC (the only province for which this was available) indicated that students found this question to be difficult, but that it had a good discrimination index. Only 52% of teachers indicated that it was appropriate, with 33 % saying that they felt that it was difficult, and 11% indicated that the topic was not on their curriculum.

This question is concerned with a version of the classic graph produced by Lothar Meyer in 1869, in which he plotted "atomic volume" against "atomic weight"[1]. Using this graph he was able to demonstrate the periodic nature of atomic volume, even though he only knew of 57 elements (the noble gases, in particular, were unknown at that time). He drew similar graphs for other physical properties of the elements, and proposed a Periodic Table similar to that prepared by Mendeleev. Unlike Mendeleev, however, Meyer did not leave spaces for unknown elements, nor did he predict their properties.

The modern version of Lothar Meyer's graph shown in this question is a plot of "molar volume" against "atomic number". The term "molar volume" makes it quite clear that we are looking at the volume of a whole mole of atoms, rather than the volume of just one atom. Note, however, that the molar volume is affected not just by the size of the individual atoms of the element, but also by the space between them, which, in turn, is affected by the strength of the bonding and by the way the atoms are packed together. It is important to use the density of all the elements in the same (solid) state in order to calculate the molar volume, because the density of the liquid state is likely to be less than the solid (due to weaker bonding and no regular packing arrangement), and gases are very considerably less dense than either solids or liquids (because they have no bonding or packing). There is some measure of "unfairness" in choosing the solid state for comparison purposes, because the elements that are not solids at standard temperature need to be cooled (sometimes to very low temperatures indeed) until they become solid, and the density of substances generally increase with temperature, meaning that the molar volume of non-solid elements appears smaller than it might otherwise be.

Atomic number is used instead of relative atomic mass in the modern graph, because it refers to the number of protons in the nucleus of the atom, which defines the element more effectively than the atomic mass (which is affected by the varying number of neutrons in the nucleus). The modern graph also uses all the elements in the range, including noble gases. This helps to reinforce the appearance of periodicity (repeat patterns) in the graph given in the question, which is shown below.



The question asks students to identify the group of the periodic table that element "X" belongs in, noting that the scale for the atomic numbers does not start at 1. Element "X" is at a peak in the graph, i.e. it has a high molar volume relative to other elements with similar atomic numbers. This tells us that the atoms are probably relatively large, and that they are loosely bonded and packed in a fairly open arrangement in the solid.

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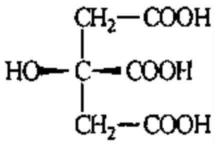
[1] "Atomic weight" is the old name for relative atomic mass (no units). "Atomic volume" was determined by dividing atomic weight (given the units g/mol) by the density of the element (in units of g/cm^3).

The size of atoms in a particular period of the Periodic Table is largest in Group 1 (the alkali metals)[2], so the answer to this question is likely to be B. This opinion is reinforced by knowing that the bonding in the alkali metals is weak (metallic bonding with only one electron per atom feeding into the "electron sea"), and the structure is body centred cubic (not close-packed)[3]. The answer is indeed **B**.

17. Students found this question very difficult, and the discrimination index was very poor. Teachers were almost equally divided between thinking that it was A. appropriate, B. difficult, D. not on the curriculum, and E. not yet covered. This is disappointing in view of the fact that the titration of citric acid was extensively discussed in the solution to the 2004 NHSCE (Question 5).

The structural formula for citric acid, 2-hydroxypropane-1,2,3-tricarboxylic acid ($C_6H_8O_7$), is:



$$\begin{array}{l} \quad\;\, CH_2-COOH \\ \quad\;\;\; | \\ HO-C-COOH \\ \quad\;\;\; | \\ \quad\;\, CH_2-COOH \end{array}$$

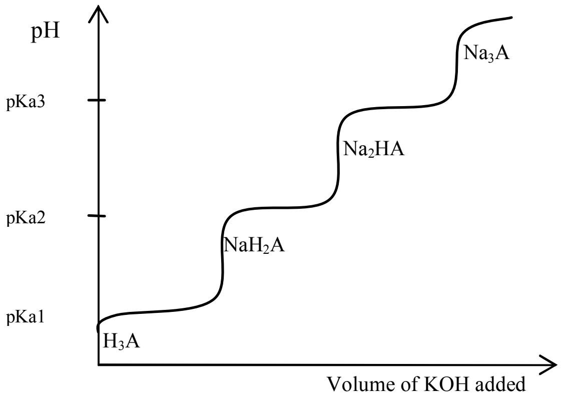
Students do not, however, need to know this. They are told that citric acid is triprotic, so they can represent it by the general formula H_3A. Its reaction with potassium hydroxide solution occurs in three stages, which take place according to the following equations:

$H_3A(aq) + KOH(aq) \rightarrow KH_2A(aq) + H_2O(l)$ . . . . . . Stage 1

$KH_2A(aq) + KOH(aq) \rightarrow K_2HA(aq) + H_2O(l)$ . . . . . Stage 2

$K_2HA(aq) + KOH(aq) \rightarrow K_3A(aq) + H_2O(l)$ . . . . . . Stage 3

One might expect a titration curve for this series of reactions to look something like that shown in the sketch below, with the vertical parts of the curve showing the equivalence point and the product for each stage.



Possible titration curve for a hypothetical triprotic acid, H_3A

The flat parts of the curve are called the buffer zones, because the addition of alkali makes very little difference to the pH in these parts of the titration. In the middle of each buffer zone, where the

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[2] The size effect is discussed in the answer to Question 9 of the 2006 NHSCE.

[3] Most students will have seen a video or a demonstration of the reaction of alkali metals with water, which show the metals floating on water even as they react with it. The fact that the metals float on water is an indication of low density, which is explained by the effects discussed here.

concentrations of acid and its salt are exactly equal, the pH of the solution is given by the pK_a value of the acid it is formed from[4].

Simply reacting equal volumes of equimolar solutions of H_3A with potassium hydroxide would cause the reaction to go to completion of Stage 1, and no further. At this point the solution will contain only the potassium dihyrogen salt of the acid (KH_2A), and the pH will be at the middle of the vertical part of the curve, between the first two flat buffer regions. The pH might therefore be expected to be somewhere between the values for pKa_1 (3.13) and pKa_2 (4.76). There is only one value within this range amongst the response keys, and that is 3.8: the answer to this question is therefore **B**.

A closer value for the pH may be found by averaging the the first two pKa values, thus:

$$\text{pH} \approx (3.13 + 4.76)/2 = 3.945$$

This, however, would be the pH of a 1.0 mol L^{-1} solution of potassium dihydrogen citrate, whereas the solution we have is 0.1 mol L^{-1}. This is because mixing equal volumes of equimolar (0.2 mol L^{-1}) solutions of citric acid and potassium hydroxide would result in a 0.1 mol L^{-1} solution of potassium dihydrogen citrate[5].

Note that a solution of 0.1 mol L^{-1} potassium dihydrogen citrate can be used as primary standard solution for pH: it has an exact pH value of 3.776 at 25°C. Determining the pH of this solution by treating it as an acid with pK = 4.76, using the standard method of calculation gives you a pH ≈ 2.88 (you can try it), and this value is not improved even if you use a quadratic equation. The reason for this difference is that, since citric acid is triprotic, its various anions will be interlinked by a series of equilibria. Each anion will hydrolyse to give hydroxide ions in solution, making the solution more basic than might be expected. The equations for these hydrolysis reactions are:

$$A^{3-}(aq) + H_2O(l) \rightleftharpoons HA^{2-}(aq) + OH^-(aq)$$

$$HA^{2-}(aq) + H_2O(l) \rightleftharpoons H_2A^-(aq) + OH^-(aq)$$

$$H_2A^-(aq) + H_2O(l) \rightleftharpoons H_3A(aq) + OH^-(aq)$$

It should be possible to calculate the pH of potassium dihydrogen citrate taking all these different species into account, but such a calculation would be very long, and would take far more time than is allowed for a question on this exam (which is just over 2 minutes per question). You need to know when you can use estimation techniques to find the answer in a multiple choice exam, rather than doing the longer kind of calculation that might be needed in a problem-solving exercise.

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[4] We can see how this occurs by considering the equation relating pH and pK_a for Stage 1 of the reaction sequence:

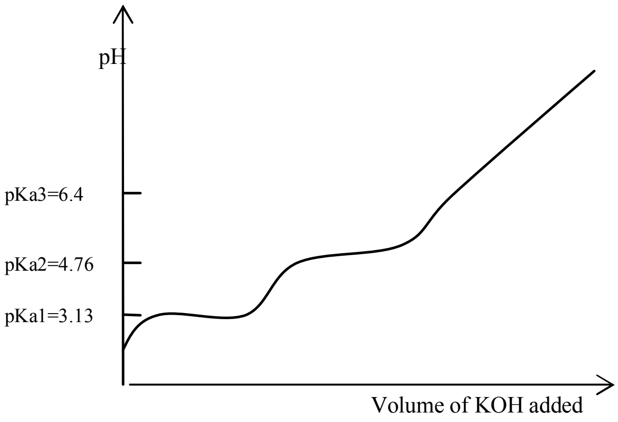
$$\text{pH} = pK_{a1} - \log [H_3A(aq)]/[KH_2A(aq)]$$

where $[H_3A(aq)]$ is the concentration of $H_3A(aq)$ in mol L^{-1}
and $[KH_2A(aq)]$ is the concentration of $KH_2A(aq)$ in mol L^{-1}

In the middle of the buffer zone the concentrations of H_3A and KH_2A are equal,
so $[H_3A(aq)]/[KH_2A(aq)] = 1$, and $\log [H_3A(aq)]/[KH_2A(aq)] = 0$, therefore $\text{pH} = pK_{a1}$.

[5] The concentration is half that of the two original solutions, even though each solution will contain the same chemical amount (number of moles) because the total volume of the final solution is double that of either of the original ones.

Finally, it should also be noted that the titration curve for citric acid, is, in fact, very different from the possible titration curve shown above for a hypothetical triprotic acid. The steps on the curve are not evenly spaced because the pKa values are fairly close[6]. The vertical parts of the curve, marking the equivalence points where KH_2A and K_2HA are formed are not nearly so clear as in the hypothetical curve, and the final equivalence point, where K_3A is formed is barely noticeable. The titration curve might be expected to look something like the sketch shown below.



Rough sketch of a titration curve for citric acid

18. Students found this question very difficult, and its discrimination index was negative, indicating that weaker students did better at it than students who were generally expected to do better! About 38% of teachers thought it was appropriate, 26% felt it was difficult, and 34% thought that it was not on their curriculum.

The question involved knowing about some classic laboratory tests used to distinguish between different kinds of hydrocarbons. Some of the reactions involving bromine that are used for these tests are summarized in the following table:

Reagent	**Alkane**	**Alkene**	**Alkyne**	**Benzene**
Br_2 dissolved in 1,1,1–trichloroethane (dark)	No reaction	Bromine decolorized, No gas given off	Bromine decolorized (slowly)	No reaction
Br_2 dissolved in 1,1,1–trichloroethane (UV light)	Bromine decolorized, Gas given off	Bromine decolorized, No gas given off	Bromine decolorized (slowly)	Possible slight decolorization of bromine, No gas detectable.
Bromine water, i.e. $Br_2(aq)$	No reaction	Bromine decolorized, No gas given off	Bromine decolorized (slowly)	No reaction

The reaction between bromine and alkanes is very distinctive, because it occurs only in the presence of ultraviolet light. This is because it is a free radical substitution reaction, which requires the bromine molecules first to be dissociated into bromine atoms (using energy that is provided by the light) before it can take place, as described on the next page.

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[6] The Ka value (and therefore the pKa) for each acid hydrogen will depend on how difficult it is to remove each successive proton. It will, of course, become increasingly difficult to remove protons from species that are more negatively charged, but interactions between atoms within a particular acid molecule or anion will determine just how difficult the removal of a specific proton will be. The Ka value gets smaller and the pKa value gets larger as the difficulty increases.

Taking cyclohexane as the example of an alkane, the reaction with bromine occurs according to the following overall equation:

$$C_6H_{12} + Br_2 \longrightarrow C_6H_{11}Br + HBr$$

This substitution reaction takes place in a number of steps as shown below. Note that free radicals are atoms or groups of atoms with unpaired electrons, and that these unpaired electrons are represented in the schema by the symbol ▪.

Step 1: Initiation

$$Br\text{–}Br \xrightarrow{\text{UV light}} 2\ Br^{\blacksquare}$$

Steps 2 and 3: Propagation

Once a bromine radical is formed it can react with cyclohexane as shown in Step 2, thus:

$$C_6H_{12} + Br^{\blacksquare} \longrightarrow HBr + C_6H_{11}^{\blacksquare}$$

The cyclohexyl radical formed in Step 2 can then react with a bromine molecule to form a bromine radical, as shown in Step 3, thus:

$$C_6H_{11}^{\blacksquare} + Br\text{–}Br \longrightarrow C_6H_{11}Br + Br^{\blacksquare}$$

The bromine radical can then react with another cyclohexane molecule as in Step 2. Steps 2 and 3 can be repeated many times until all the reactants are used up, or until termination, when two free radicals react as shown in Step 4.

Step 4: Termination

e.g. $C_6H_{11}^{\blacksquare} + C_6H_{11}^{\blacksquare} \longrightarrow C_6H_{11}\text{–}C_6H_{11}$

This termination step is very unlikely (although something like it may occur with simpler radicals such as the methyl $CH_3^{\blacksquare}$ radicals). Somewhat more likely is that two bromine radicals might recombine to give a bromine molecule again (a reverse of Step 1). Alternatively a bromine radical might combine with a cyclohexyl radical to give $C_6H_{11}Br$: this is the product of the overall reaction, but it will not propagate the reaction, because it does not produce a bromine radical which is necessary to keep the reaction going.

Once one bromine atom has been substituted for hydrogen in the cyclohexane molecule, further substitutions are also possible, for example:

$$C_6H_{11}Br + Br_2 \rightarrow C_6H_{10}Br_2 + HBr$$

Pure liquid bromine is not, however, appropriate for monitoring this reaction as it is very concentrated, and it is therefore difficult to see any decolorization of the very dark brown colour occurring as the bromine molecules are used up in the reaction. For the purpose of this test bromine is therefore diluted in an inert solvent so that the colour change can be observed. Traditionally the solvent used was tetrachloromethane (carbon tetrachloride), but this is carcinogenic and harmful to the environment, therefore 1,1,1–trichloroethane, which is somewhat less harmful, is more likely to be used nowadays[7].

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[7] Note that 1,1,1–trichloroethane (being a partially substituted alkane) does react slowly with bromine in the light, so it is important to make up this reagent close to the time of use, and to keep it in a dark bottle.

It can be seen from the table given above, that bromine dissolved in water does not give a reaction with alkanes. This is because water does not behave as an "inert solvent". Bromine reacts with water according to the following equation:

$$Br_2(l) + H_2O(l) \rightleftharpoons H^+(aq) + Br^-(aq) + HOBr(aq)$$

The bromine preferentially forms ions rather than free radicals in aqueous solution, so that the free radical substitution reaction cannot take place.

In addition to the information given to you about "Reagent X", you are also given a clue to the nature of "Gas Y", which, according to the proposed answers to the question, may be either hydrogen or hydrogen bromide. Of these two gases, only hydrogen bromide will react with ammonia to give a white "smoke", which it does according to the following equation:

$$NH_3(g) + HBr(g) \rightarrow NH_4Br(s)$$

(Similar reactions are undergone between the other hydrogen halides and ammonia, giving ammonium halide "smokes".)

Using these clues we can check the possible answer keys as follows:

A. Reagent X is $Br_2(l)$. This will react with alkanes (although a visible decolorization is unlikely), but Gas Y would be HBr not H_2, therefore the answer cannot be A.

B. Reagent X is $Br_2(aq)$. This does not react with alkanes, so there would be no decolorization and no gas would be produced, therefore the answer cannot be B.

C. Reagent X is Br_2 dissolved in 1,1,1–trichloroethane. This reacts with alkanes in the presence of ultraviolet light (specified in the introduction to the question), giving HBr as Gas Y, therefore the correct answer is **C**.

D. Reagent X is HBr(aq). This is colourless, so it can't be decolorized, and in any case the hydrogen given as Gas Y will not give a "smoke" with ammonia, therefore the answer cannot be D.

E. Reagent X is HBr dissolved in 1,1,1–trichloroethane. Again this is colourless, so it can't be decolorized, and in any case the hydrogen given as Gas Y will not give a "smoke" with ammonia, therefore the answer cannot be E.

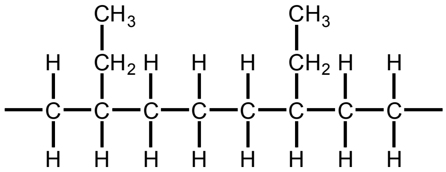
Note that the reactions of bromine with alkenes and alkynes are addition reactions rather than substitution reactions, and no gases are given off in these reactions. For example the reaction between bromine and hexene occurs as follows:

$$C_6H_{10} + Br_2 \rightarrow C_6H_{10}Br_2$$

The reactions of bromine with benzene **is** a substitution reaction, but it needs a catalyst before it will occur. Hydrogen bromide gas is given off, but the catalysed reaction will take place in the dark as well as in the light. Other aromatic hydrocarbons (e.g. cumene, a.k.a. isopropylbenzene) react readily with bromine in the presence of UV light (benzylic bromination), and could be mistaken for alkanes in this test.

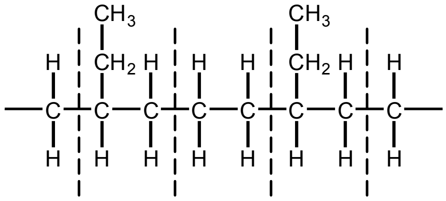
19. Students found this question very difficult and it had a poor discrimination index. 64% of teachers thought that it was appropriate, but 28% said that it was not on their curriculum.

The question was concerned with a plastic used for food wrapping. Part of the molecule of the plastic was given in the question, and this is shown below:

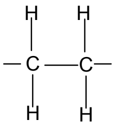


The question says that the plastic is an addition copolymer. Students are expected to know that an addition polymer is one that is formed when two or more simple molecules (monomers) undergo an addition reaction – that is one in which no compound is formed other than the polymeric molecule. Where the two monomer molecules are the same, then the empirical formula of the polymer will be the same as that of the monomer. A copolymer is one that is formed by the addition of two or more different monomer molecules, so its empirical formula will be the weighted average of the formulae of the component molecules. The question requires the students to identify the monomers used in this particular copolymer.

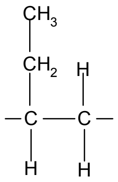
The first step in solving this problem is to identify the repeat units (mer units) within the polymer. These can be seen in the diagram below:



The two different mer units are therefore:

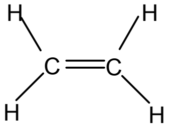


(1) and (2)



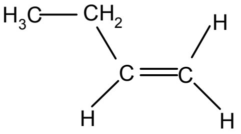
These mer units are shown with “half bonds” (single electrons) on each end: these link up with the half bonds on other mer units to form the polymer chain. The monomer molecules from which these units are derived contain double bonds between the carbon atoms. When polymerisation takes place one of the bonds between the carbons stays in place, while the other one “opens up” to form the half bonds of the mer unit.

The monomer from which mer unit (1) is derived is:

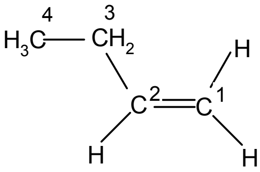


This is an alkene with just two carbons so its suffix is “eth-”, and the name of the compound is ethene, which means that D and E cannot be the correct responses to this question.

The monomer from which mer unit (2) is derived is:



This has four carbons in a chain, so its suffix is "but-", and it has the double bond between two end carbons. According to the nomenclature rules, which says that number has to be kept as low as possible, we need to number the carbons from the end with the double bond, and the name of the compound is therefore 1–butene (or but–1–ene).



The two monomers from which the copolymer is formed are thus ethene and 1-butene, so the answer to this question is therefore **B**.

20. Students found this question very difficult, and the discrimination index was very poor. 62% of teachers thought that the question was appropriate, whilst 30% said that the topic was not on their curriculum. The question involved identifying the correct structural formula of an ester, given its IUPAC name.

Esters are compounds that can be considered to be derived from a carboxylic acid and an alcohol. If we denote the acid as RCOOH and the alcohol as R′OH (where R and R′ represent alkyl groups, which may be the same or different), then the ester might[8] be formed according to the following reaction:

$$RCOOH + R'OH \rightarrow RCOOR' + H_2O$$

Note how the characteristic ester linkage –COO– has its carbon attached to the alkyl group of the acid. In the IUPAC nomenclature system this carbon has to be included in the name of the acid from which the ester is derived: the acid does not simply take its name from the alkyl group R. Thus for CH_3COOH, R = CH_3 (methyl), but the acid has two carbon atoms in it, so it is given a name with "eth" in it (ethanoic acid).

The ester is named with the alcohol alkyl group, R′, coming first, even though it is usually shown at the end of the formula. The second part of the name is taken from the acid with the "ic" ending of the acid replaced with the "oate" ending. Thus an ester formed from ethanoic acid will be called an ethanoate. (Note that the "oate" ending is also used for salts of the acid, e.g. sodium ethanoate, as well as for esters.)

Applying these rules to the ester given in the question, we can see that ethyl 3-methylbutanoate must be derived from the alcohol ethanol and the acid 3-methylbutanoic acid. The structures of these two compounds are shown on the next page:

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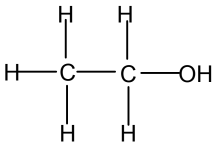
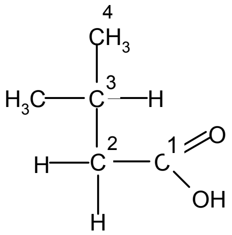
[8] This reaction is not an efficient means of preparing esters, because yields are often poor (esterification is generally governed by an equilibrium constant close to one, meaning the reactants and products are evenly distributed through the system): it also tends to be slow, even in the presence of a catalyst. These two factors mean that esters are usually prepared by indirect methods.

Ethanol



3–methylbutanoic acid



Writing these structures in the condensed format gives the familiar formula for ethanol, CH_3CH_2OH, which gives rise to the end group $–OCH_2CH_3$[9], meaning that the answer to this question cannot be A or B. The condensed formula for 3–methylbutanoic acid is $(CH_3)_2CHCH_2COOH$, so that the formula for the ester must be $(CH_3)_2CHCH_2COOCH_2CH_3$, and the answer to this question is therefore **D**.

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[9] Note that isotopic labelling studies of ester hydrolysis reactions under aqueous acidic conditions (the reverse of esterification) indicate that one oxygen in the –COO– group comes from the alcohol, and one comes from the acid, rather than both oxygens being derived from the acid.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2006 continued

21. A statistical analysis of the results of the 2006 exam for BC (the only province for which this was available) indicated that students found this question moderately difficult, and it had a moderate discrimination index. 43% of teachers said that they thought the question was appropriate, but 37% said they had not yet covered the topic, and 11% indicated that it was not on their curriculum.

The question was concerned with calomel (mercury(I) chloride, Hg_2Cl_2), which used to be taken as a laxative, despite the fact that mercury compounds are highly poisonous. The reason that it is possible to ingest this compound is because it has an extremely low solubility, and the question is designed to demonstrate this by requiring the students to determine the solubility of a saturated solution of calomel dissolved in water[1], given its solubility product. The problem is somewhat complicated by the fact that mercury(I) cation exists in the Hg_2^{2+} form, but this information is effectively given in question in the formula for the solubility product constant, K_{SP}.

The equation for the solution reaction is:

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq)$$

If we let the solubility of mercury(I) chloride be s mol L^{-1}, then we can write the ionic concentrations in terms of "s" thus:

$$[Hg_2^{2+}] = s \text{ mol L}^{-1} \text{and } [Cl^-] = 2s \text{ mol L}^{-1}$$

The solubility product constant expression is given in the question as:

$$K_{SP} = \{[Hg_2^{2+}][Cl^-]^2\}$$

which can be written in terms of the solubility as:

$$K_{SP} = s \times (2s)^2 = 4s^3$$

Substituting the value given for the solubility product constant, gives:

$$4s^3 = 1.60 \times 10^{-18}$$

$$s^3 = 0.40 \times 10^{-18} = 4.0 \times 10^{-19}$$

$$s = 7.3(6) \times 10^{-7} \text{ (mol L}^{-1})$$

Therefore the mass of Hg in the dissolved in one litre of saturated Hg_2Cl_2 solution

$$= 7.3(6) \times 10^{-7} \times 200.59 \times 2 \text{ g}$$
$$= 2.95 \times 10^{-4} \text{ g} \approx 3.0 \times 10^{-4} \text{ g}$$

And the mass of Hg dissolved in 100 mL $\approx 3.0 \times 10^{-5}$ g

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

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[1] The medication would be inbibed as a slurry containing solid mercury(I) chloride in aqueous solution, which means that the solution part of the mixture would be saturated, and the conditions necessary for solubility calculations would apply.

22. Students found this question moderately difficult and its discrimination index was good. 37% of teachers thought it was appropriate, but others (a whopping 57%) said that they had not yet covered it.

The question was concerned with the chemical reaction taking place in a cell of a car battery (accumulator) as it discharges. The overall reaction is given as:

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

The aim is to determine the cell potential[2] for this reaction.

As with all cell reactions, this is a redox reaction, and it can be considered to be a combination of two half-cell reactions – one oxidation and one reduction.

You are given the standard reduction potentials for three half-cell reactions that look very similar in that they all involve lead(IV) oxide, but you can only possibly need two of them. (This is a simplified version of the sort of problem that you may easily meet if you are using tables of standard reduction potentials, which have many different values in them, and in which several of the values given can look as though they might relate to a particular redox reaction.)

The half-cell reduction reactions that you are given are:

(1) $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$; $E^\ominus = -0.36$ V
(2) $PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$; $E^\ominus = +1.46$ V
(3) $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$; $E^\ominus = +1.69$ V

These most likely pair that you will need to combine will be the pair that give the greatest difference in reduction potential. This is because the reaction involved in an electrochemical cell, such as that used in a car battery, will be spontaneous, which means that its cell potential will be positive[3]. The biggest difference in half-cell potentials is between reaction (3) and reaction (1), which gives a value of

$$E^\ominus(\text{overall}) = +1.69 - (-0.36)\text{V} = 2.05\text{ V}$$

This would mean that the answer to the question would be **D**.

You can check yourself by combining the two half-cell reactions to see whether they give the correct overall reaction, as given in the question. Note that the half cell reaction with the less positive (more negative) standard reduction potential (Reaction 1) is the one that must be reversed to give the oxidation half-cell (anode) reaction, thus:

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

Combining this reaction with Reaction (3), the reduction half-cell (cathode) reaction, gives the overall cell reaction:

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[2] We are actually going to be calculating the electromotive force (e.m.f.) of the cell, which is effectively the maximum potential the cell can have (see the solutions to Question 24 the 2004 NHSCE for further information on this topic).

[3] The e.m.f. of a cell is a thermodynamic predictor of whether a reaction will occur or not. The more positive its value is, the more likely the reaction is to occur, but one can never be absolutely sure whether the reaction will occur or not, as one also has to consider the kinetics of the reaction. A reaction might be predicted to be thermodynamically likely, but it could be kinetically stable (in other words it could only take place very slowly indeed).

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- + Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2H_2O(l) + PbSO_4(s) + 2e^-$$

"Tidying up" this equation, by cancelling the electrons on either side, and combining species that appear more than once on the same side of the equation (sulfate ions on the left hand side, and lead sulfate on the right hand side) gives:

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

which is the overall equation given in the question. The answer D is thus confirmed.

Note that, in problems like this, you might find that the number of electrons on either side of the overall equation and not the same. In this case you will need to multiply one or both of the half-cell reactions in order to be able to cancel the electrons, e.g.

(4) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; $E^\ominus = + 0.34$ V
(5) $Ag^+(aq) + e^- \rightarrow Ag(s)$; $E^\ominus = + 0.80$ V

The cell potential for the overall reaction is

$$E^\ominus(\text{overall}) = +0.80 - (+ 0.34)\ \text{V} = + 0.46\ \text{V}$$

The overall cell potential is positive so the reaction is spontaneous and Equation (4) must be reversed to give the oxidation half-cell (anode) reaction, thus:

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

Combining this with Equation (5) the reduction half-cell (cathode) reaction, gives:

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

This reaction has different numbers of electrons on either side of the equation, so you cannot cancel electrons. You need to multiply Equation (5) by two, thus:

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

Including this in the overall equation gives:

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

The final equation is:

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

The important point to note here is that **the cell potential for the overall equation does not change**, even though you have doubled the chemical amounts (number of moles) of some of the subtances in the equation. Extra material in the electrochemical cell simply means that it runs at its particular voltage for longer before the substances run out. If a higher voltage is required for a particular application then several cells must be placed in series. Thus a car battery usually has 6 cells in series, allowing it to provide a maximum voltage of (6 x 2.05)V = 12.30 V.

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23. Students found this question difficult, and its discrimination index was poor. 65% of teachers thought it was appropriate and 24% felt it was difficult.

The question was concerned with the neutralisation reaction, which is usually taken as referring to the ionic equation:

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

(where the anion of the acid and the cation of the base are passive spectator ions). The standard enthalpy change for the reaction, $\Delta H^\ominus$, is -57.9 kJ mol^{-1}, but this value only applies where a strong acid reacts with a strong base. Experimental values for systems involving a weak acid and/or a weak base are typically less negative than this value.

This question asks students to identify the reason why the data book value for the reaction of ethanoic acid[4] with sodium hydroxide gives a value of $\Delta H^\ominus = -56.1$ kJ mol^{-1} (which is less negative than the enthalpy change for the reaction of hydrogen ions with hydroxide ions given above). Ethanoic acid is, of course, a weak acid, whilst sodium hydroxide is a strong base. The equation for this reaction is given in the question as:

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

Let us consider each of the options offered as an explanation in turn:

A. Energy is lost to the surroundings

If energy is lost to the surroundings, the temperature rise measured after the reactants are mixed will be lower than if no energy was lost.

The enthalpy change, $\Delta H^\ominus$, is usually calculated using the equation:

$$\Delta H^\ominus = -\,mCp\,\Delta T^\ominus/n$$

where m is the mass of solution (of acid and base combined), in g
Cp is the specific heat capacity of water[5], in Jg^{-1}K^{-1}
$\Delta T^\ominus$ is the temperature rise, in K
and n is the chemical amount of the limiting reagent, in mol
(in this case there is no limiting reagent so the chemical amount of either acid or base may be used – they are equal)

It can be seen from this equation that the enthalpy change will be less negative if the temperature rise is less positive, so it might appear a logical reason for the anomalous result. You are, however, told that the **data book** value is less negative than it should be, and values in data books might be expected to be corrected for this sort of problem. The answer is therefore unlikely to be A.

B. Energy is used in dissociating the ethanoic acid

Ethanoic acid is a weak acid, and so a solution of ethanoic acid in water exists as an equilibrium of

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[4] Ethanoic acid is often referred to by its common name, acetic acid, even in textbooks. It is the main constituent of vinegar.

[5] The mass of the solution is usually determined from its volume using mass = volume x density, with the density being taken as the density of water. The dissolved solids in the solution are dispersed within the water, and so taking the density and specific heat capacity of the solution to be those of water has a negligible effect on the result of the calculation.

undissociated ethanoic acid molecules along with hydrogen ions[6] and ethanoate ions, thus:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

When a solution of ethanoic acid reacts with the hydroxide ions in a basic solution, the hydrogen ions in the acid solution are assumed to react first: this stresses the equilibrium, so that some ethanoic acid molecules ionize to replace the hydrogen ions. This continues until all the ethanoic acid molecules have ionized, and all the hydrogen ions have been neutralized.

At this point you need to remember that bond breaking uses energy, whilst bond forming gives out energy. The combination of hydrogen ions and hydroxide ions to give water is a bond forming reaction, so it gives out energy (the temperature of the solution rises and the enthalpy change is negative, as discussed in A above.) The ionization (or dissociation) of ethanoic acid is bond breaking, therefore it uses energy, and, in this case, the energy it uses comes from the neutralization energy, making the enthalpy change less negative than it would otherwise be.

Some teachers complained that their students had not met the term “dissociation” in the context of acids: they use the term “ionization”. As far as the discussion above is concerned the two terms on synonymous. “Dissociation” was chosen for this question, because one reviewer expressed the opinion that full ionization is unlikely to occur in this type of system. The hydroxide ion of the base is much more likely to be attracted to the acid molecule, forming some sort of intermediate, which dissociates before the molecule has a chance to ionize. The intermediate then breaks down to the acid anion and water, thus:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow [CH_3COOH...OH^-] \rightarrow CH_3COO^-(aq) + H_2O(l)$$

Even in this case the acid molecules still need energy to break apart, and that energy will still come from the enthalpy change of neutralization. So, either way you look at it, the break-down of the enthanoic acid will make the enthalpy change of neutralization less than it would otherwise be.

The answer to this question is therefore likely to be B, but we shall continue to consider the other options on offer.

C. Energy is used in dissociating the sodium hydroxide

Sodium hydroxide is a strong base, so it is almost completely ionized[7] when it dissolves to form an aqueous solution[8,9], thus:

$$NaOH(s) + aq \rightarrow Na^+(aq) + OH^-(aq)$$

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[6] A rather better method of describing this process is to show the ethanoic acid molecules reacting with water molecules to form hydroxonium ions and ethanoate ions, thus:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

This indicates that the proton does not simply break off from a molecule of ethanoic acid in the presence of water, but that it is involved in a “push-pull” equilibrium between the acid and the water molecules.

[7] In very concentrated solutions the sodium ions and hydroxide ions may clump together to form ion pairs. These ion pairs are very different from the dissolved molecules that occur in solutions of weak acids and bases.

[8] Note that the process of dissolving solid sodium hydroxide in water is highly exothermic. The temperature of the mixture rises as heat is given out by the reaction. This is because the bonds forming between the ions and water are very much stronger than the ionic bonds between the sodium and hydroxide ions in the solid. (Some of the bond-forming energy is used for breaking apart the ionic bonds.)

[9] The symbol “aq” is used in the following two equations to denote water used as solvent in an unspecified amount.

Note that, even in the solid state, sodium hydroxide consists of sodium ions and hydroxide ions, so that some authors show the above equation as:

$$Na^+OH^-(s) + aq \rightarrow Na^+(aq) + OH^-(aq)$$

Once the solution has been formed there is no further bond breaking to be done, so none of the energy created by the neutralization reaction is lost. The difference in enthalpy change of neutralization is therefore not due to the dissociation of sodium hydroxide, so the answer to this question cannot be C. Considering that the ethanoic acid is mainly present as molecules in the solution, and sodium hydroxide is present as ions, the equation for the reaction between the two is sometimes given as:

$$CH_3COOH(aq) + Na^+(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq) + H_2O(l)$$

Note how the sodium ethanoate formed in the reaction is generally shown as being ionic, although the ethanoate ion is susceptible to hydrolysis, thus:

$$CH_3COO^-(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + OH^-(aq)$$

and the "neutralized" solution remains somewhat alkaline due to the presence of hydroxide ions.

D. Energy is used in heating up the acid and the base as well as the water

This sounds as though it might be a likely scenario, but, in fact, the heat capacity of a dilute aqueous solution is very close to that of pure water, because the solute particles are dispersed into spaces between the water molecules. The answer to this question is not D.

E. The two values are essentially the same within the limits of experimental error

Again this looks plausible – we are not, however, looking at a single set of experimental results, but at a data book value. The values quoted would be the result of repeat experiments by many different workers, and, although the precision of the values has not been quoted, the fact that they are given to 3 significant figures is an indication that they are probably known to within $\pm$ 0.1 kJ mol^{-1}, so that experimental error is not a valid reason for the difference, and the answer is not E.

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

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24. Students found this question difficult, and its discrimination index was poor. 65% of teachers considered it to be appropriate, 17% thought it was difficult, and 11% said it was not on their curriculum.

High school textbooks often give very simplistic definitions of the enthalpy change of solution, for example:

> **Heat of solution (ΔH_{soln})**: the enthalpy change that occurs when a solution forms from a solute and a solvent[10].

This definition covers the basic concept of the enthalpy change of solution, but it does not say anything about what is considered standard for the solution reaction. In particular it does not say anything about the concentration of the solution that is formed. I would prefer to see the following definition:

> **Enthalpy change of solution (ΔH_{soln})**[11]: the enthalpy change that occurs when one mole of a

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[10] McGraw-Hill Ryerson Chemistry 12, Mustoe et al, Publ. 2002.

[11] I prefer to use the term "enthalpy change" rather than "heat": firstly because it clearly encompasses the possibility of reactions losing heat as well as giving it out, and it also makes it clear that a change is

> substance dissolves in such a large volume of solvent that an addition of more solvent produces no further enthalpy change of dilution, under standard conditions of temperature and pressure.

The concept of "infinite dilution" is important, because the value of the enthalpy change of solution varies considerably with the concentration of the solution formed. This can be explained if one considers the solution process as taking place in two steps. Step 1, breaking apart of the solid lattice, is an endothermic process (energy is required to break the solid apart): Step 2, forming bonds between the solution particles and the solvent, is an exothermic process (energy is given out). The overall solution process may be exothermic or endothermic, according to which step involves the greater enthalpy difference. Where the solutions formed are very dilute, i.e. where they is much larger number of moles of solvent than solvent, there is a much greater opportunity for bonding, and the process of solution becomes increasingly exothermic. This is demonstrated in the following table of values for magnesium chloride and water:

Mole ratio, H_2O:$MgCl_2$	**ΔH, kJ mol^{-1}**
10:1	– 140.35
20:1	– 150.19
50:1	– 154.62
100:1	– 156.13
200:1	– 157.05
500:1	– 157.76
1000:1	– 158.18
2000:1	– 158.58

The table shows that even with a mole ratio of 2000:1, there is some interaction between the ions in magnesium choride and water, however the enthalpy change of solution is becoming closer to a limiting value (that of infinite dilution).

This question deals with an experiment that I designed for students to do for themselves to investigate the enthalpy change of solution at different concentrations. (I do not, however, expect students doing this exam to have done the experiment.) I chose anhydrous magnesium chloride as the solute, because it has a very exothermic enthalpy change of solution when it dissolves in water[12]. This means that temperature changes should be easily observed using the kind of thermometers generally available in high schools, which tend not to be very precise. It should be noted, however, that, although the enthalpy change becomes more negative in more dilute solutions, the temperature increase becomes smaller, because the heat energy is spread through a much larger mass of water[13].

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occurring (which would also be unclear if the simple term "enthalpy" is used). Better would be the use of the term "enthalpy difference", because it indicates that the difference is independent of the path between the intial and final states, whereas "enthalpy change" implies that the value is dependent on the path, which, of course, it is not. Unfortunately the term "enthalpy difference" is not in common usage, although the symbol Δ (the Greek equivalent of the letter D) implies that it has been considered (D for difference).

[12] Anhydrous magnesium chloride dissolves in water partly by a simple physical solution process, thus:

$$MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)$$

However it also undergoes a chemical reaction with water (hydrolysis) thus:

$$MgCl_2(s) + H_2O(l) \rightarrow Mg(OH)^{+}(aq) + H^{+}(aq) + 2Cl^{-}(aq)$$

This hydrolysis reaction is highly exothermic and contributes significantly to the very negative enthalpy change for the solution process.

[13] For very dilute solutions, it is difficult to measure out the very small mass of solute required with

The enthalpy change, $\Delta H^\ominus$, is usually calculated using the equation shown on the next page (which is very similar to the equation used to determine the enthalpy change of neutralisation in the last question):

$$\Delta H^\ominus_{\text{(soln)}} = -\, \text{m}Cp\, \Delta T^\ominus/\text{n}$$

where m is the mass of solution (here taken as the mass of water), in g
Cp is the specific heat capacity of the solution (again taken as that of water), in $\text{Jg}^{-1}\text{K}^{-1}$
$\Delta T^\ominus$ is the temperature change, in K
and n is the chemical amount of the limiting reagent (here the solute), in mol

Remember also that the mass of solution can be determined from the volume using the equation, $\text{m} = \rho \times \text{V}$, where ρ is the density of the solution (here taken as the density of water), which is given as $1.00\ \text{g mL}^{-1}$, and V is the volume of water in mL. This means that the mass (in g) and the volume (in mL) of the solution are numerically equal.

The chemical amount (in mol) of the limiting reagent, anhydrous magnesium chloride, can be determined using the equation $\text{n} = \text{m}/M_\text{r}$, where m is the mass of MgCl_2 (given as 4.76 g) and M_r is its relative molar mass (given as $95.2\ \text{g mol}^{-1}$). The chemical amount used is thus = $\{4.76\ \text{g} \times 95.2\ \text{g mol}^{-1}\} = 0.05$ mol.

Using these equations we can determine two values: (1) the correct or accepted value, which the students should have obtained if they had done the experiment as they were meant to, with 90.0 mL of water, and observing a temperature increase of 20.1^oC (20.1K), and (2) the incorrect or experimental value, which the students obtained using 180.0 mL of water, and observing a temperature increase of 10.1^oC (10.1K). Note that the students had *measured out* the180.0 mL of water, so they *knew* that they had this volume (and therefore they used a mass of 180.0 g in their calculation).

The two values can be determined as follows (although you can probably also think of shorter ways of doing the calculations):

(1) determining the correct or accepted value

$$\begin{aligned}\Delta H^\ominus_{\text{(soln)}} &= -\ \{90.0\ \text{g} \times 4.18\ \text{J g K}^{-1} \times 20.1\ \text{K}\}/\ 0.05\ \text{mol} \\ &= -\ 151.2\ \text{kJ mol}^{-1}\end{aligned}$$

(2) determining the incorrect or experimental value

$$\begin{aligned}\Delta H^\ominus_{\text{(soln)}} &= -\ \{180.0\ \text{g} \times 4.18\ \text{J g K}^{-1} \times 10.1\ \text{K}\}/\ 0.05\ \text{mol} \\ &= -\ 152.0\ \text{kJ mol}^{-1}\end{aligned}$$

These two values do not look a lot different, but there *is* a slight error involved. The question is how to determine the numerical value of this error. The equation that I have always used for determining percentage error is:

$$\text{Error} = \frac{\{\text{Experimental value} - \text{Accepted value}\}}{\text{Accepted value}} \times 100\% \quad . . . . \quad (1)$$

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sufficient precision using balances generally available in high schools. (The extra water was not used for the other solutions, because this would have required a lot of extra solute, and that would have been expensive.) The volume (and thus the mass) of water required to make up the most dilute solution was therefore doubled, so that the mass of solute could also be doubled, thus improving the precision of the measurement. This confused some students, and the problem posed in this question is indicative of what actually happened in some cases.

This equation gives a value for the error of $\dfrac{\{-152.0\ \text{kJ mol}^{-1} - (-151.2\ \text{kJ mol}^{-1})\}}{-151.2\ \text{kJ mol}^{-1}} \times 100\%$

$$= +0.53\%\ (\approx +0.5\%)$$

During the review process for this question I discovered that some textbooks use another equation, which is

$$\text{Error} = \frac{\{\text{Accepted value} - \text{Experimental value}\}}{\text{Accepted value}} \times 100\% \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

This equation gives a value of the error of $\dfrac{\{-151.2\ \text{kJ mol}^{-1} - (-152.0\ \text{kJ mol}^{-1})\}}{-151.2\ \text{kJ mol}^{-1}} \times 100\%$

$$= -0.53\%$$

As you can see the two conventions result in different signs for the error. Another convention simply uses the difference between the accepted and experimental values, chosen so that the error value is always positive. Because of these differences in convention, and because, as a matter of principle, the answer to a question should not depend on memorizing a particular formula, it was decided to make all the options for the answer to the question positive. The answer to this question is therefore **A** (+ 0.5%).

There is an advantage to using equation (1) for calculating the error, which is that it makes it quite clear that if the experimental value is numerically too large, the error is positive, whilst, if it is too small, the error is negative. It is always good practice to look for errors in experiment design that can cause systematic errors, i.e. ones that will cause a bias towards a positive or negative overall error. These are not usually included in the error assessment, where one is looking for errors in individual readings which can equally easily be positive or negative. For example, the error in reading a thermometer might be to ± 0.1°C, which would mean an error in the calculated temperature difference of ± 0.2°C. However, unless the system is perfectly insulated, then the size of the temperature difference will always be smaller than it should be.

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25. Students found this question difficult, but it was a moderately good discriminator. 50% of teachers thought that it was appropriate, 24% thought it was difficult, and 24% said they had not yet covered the topic.

The question involved the equilibrium reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Students were given the information needed to determine the equilibrium constant for the reaction (Step 1), which they then had to use to determine the yield of one of the products in a new equilibrium mixture (Step 2).

Step 1: Determining the equilibrium constant. Given that a yield of 1.00 mol of hydrogen is obtained at equilibrium when 1.45 mol of carbon monoxide and 1.45 mol of water vapour are mixed in a closed container (with no carbon dioxide or hydrogen).

First note that you are only given information about the chemical amounts (number of moles) of the substances: no information is given about the volume of the container. This is because the volume will cancel out in the equilibrium constant expression[14]. You can check this as follows:

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[14] Some teachers have said that their students have not met the symbol *K*c (they have only used *K*, without the modifier "c"). *K*c simply means that the equilibrium constant is written in terms of concentration,

$$Kc = \frac{[CO_2(g)]_{eqm} \text{ x } [H_2(g)]_{eqm}}{[CO(g)]_{eqm} \text{ x } [H_2O(g)]_{eqm}}$$

where $[CO_2(g)]_{eqm}$ is the equilibrium concentration of $CO_2(g)$ in mol L^{-1}
$[H_2(g)]_{eqm}$ is the equilibrium concentration of $H_2(g)$ in mol L^{-1}
$[CO(g)]_{eqm}$ is the equilibrium concentration of $CO(g)$ in mol L^{-1}
and $[H_2O(g)]_{eqm}$ is the equilibrium concentration of $H_2O(g)$ in mol L^{-1}

Therefore

$$Kc = \frac{n\{CO_2(g)_{eqm}\}/V \text{ x } n\{H_2(g)_{eqm}\}/V}{n\{CO(g)_{eqm}\}/V \text{ x } n\{H_2O(g)_{eqm}\}/V}$$

where $n\{CO_2(g)_{eqm}\}$ is the chemical amount of $CO_2(g)$ at equilibrium in mol
$n\{H_2(g)_{eqm}\}$ is the chemical amount of $H_2(g)$ at equilibrium in mol
$n\{CO(g)_{eqm}\}$ is the chemical amount of $CO(g)$ at equilibrium in mol
$n\{H_2O(g)_{eqm}\}$ is the chemical amount of $H_2O(g)$ at equilibrium in mol
and V is the volume of the container in L

The volume cancels out in this expresion, which then becomes

$$Kc = \frac{n\{CO_2(g)_{eqm}\} \text{ x } n\{H_2(g)_{eqm}\}}{n\{CO(g)_{eqm}\} \text{ x } n\{H_2O(g)_{eqm}\}}$$

We thus only need to know the chemical amounts in order to determine the concentrationequilibrium constant. The chemical amounts for the equilibrium:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

are summarised in the following table (the values given in the question being shown in **bold**):

Substance / Amount, mol	$CO(g)$	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
At start	**1.45**	**1.45**	**0**	**0**
Change	– 1.00	– 1.00	+ 1.00	+ 1.00
At equilibrium	(1.45 – 1.00) = 0.45	(1.45 – 1.00) = 0.45	1.00	**1.00**

The equilibrium constant for this reaction, *K*c, is therefore:

$$= \frac{1.00 \text{ mol x } 1.00 \text{ mol}}{0.45 \text{ mol x } 0.45 \text{ mol}}$$

$$= 4.94$$

This is the value that can be used in the next step of the calculation.

Step 2: Using the equilibrium constant to determine the chemical amount of product in a new equilibrium (at the same temperature)

The chemical amounts for Step 2 are given in the table below (the starting values for $CO(g)$, $CO_2(g)$ and

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compare this with *K*p, which refers to the equilibrium constant written in terms of partial pressures of the gases involved in the reaction.

$H_2(g)$, are the same as the equilibrium values established for Step 1: the unknown value is the chemical amount of $H_2O(g)$, which is given the value $\boldsymbol{x}$ mol):

Substance / Amount, mol	$CO(g)$	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
At start	0.45	$\boldsymbol{x}$	1.0	1.0
Change	– 0.42	– 0.42	+ 0.42	+ 0.42
At equilibrium	(0.45 – 0.42) = 0.03	($\boldsymbol{x}$ – 0.42)	1.42	**1.42**

Using the value of the equilibrium constant found in Step 1 gives the expression:

$$4.94 = \frac{(1.42 \text{ x } 1.42)}{0.03\,(\boldsymbol{x} - 0.42)}$$

Solving this gives $\boldsymbol{x} = 15.0$

This is not, however, the end of the question, because you were asked to find the **extra** moles of water vapour required to obtain the desired amount of hydrogen.

The extra amount of water = ($\boldsymbol{x}$ – 1.45) = 13.55 mol

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

The scenario described in this question is quite realistic. Chemical engineers will generally try to manipulate a reaction in such a way that the yield of the most useful product is maximised (hydrogen in this case). They do this by increasing the proportion of one of the reactants, stressing the equilibrium so that it "swings" to the product side. They generally choose to increase the amount of the cheaper reactant (H_2O), and in so doing they will ensure that a greater proportion of the more expensive reagent (CO) will get used up. In this case, the more expensive reagent is toxic, and there will be the added benefit that the chances of any of it getting into the environment will be minimized if more of it is used up. It should, however, be borne in mind that most industrial-scale production reactions are not left to come to equilibrium. Industrial processes are generally continuous flow systems, in which some yield is forfeited in order to have a good rate of production.

The shift reaction was first discovered by an Italian called Felice Fontana in 1780 (see Wikipedia.com). It has been used to produce hydrogen on an industrial scale for use in processes such as methanol synthesis, ammonia production, and in fuel cells. Nowadays hydrogen is more likely to be produced from the reaction between steam and natural gas or petroleum naphtha, because the high temperature required for the shift reaction requires a lot of energy to maintain, however research is still going on to find a suitable catalyst that will enable the shift reaction to take place more economically at lower temperatures.