ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2004

These answers are designed to help students who are preparing to take the Canadian National High School Chemistry Examination in 2005 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, 2002 and 2003 exams (questions and answers) before attempting the 2004 examination.

Students should attempt to do the questions in Part A of the 2004 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.

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

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/.

The people involved in preparing the NHSCE very much appreciate all the comments and feedback that we get from teachers. This year we have tried to incorporate some of these comments in with the solutions. We have also tried to indicate a little more about how students did in particular questions. It should be pointed out, however, that students in different parts of the country do very differently in the examination. We feel that this is, in part at least, because the provincial curricula do not necessarily follow the Pan-Canadian protocol, or, if they do, then they empahasize different aspects of the curriculum.

Please note that from 2005 onwards, the method of indicating multiple units will be changed to conform to IUPAC standards. The bullet between individual units will be omitted and only spaces will be used to separate the component units, e.g. $mol{\bullet}L^{-1}$ will become $mol\ L^{-1}$, and $kJ{\bullet}\ mol^{-1}$ will become $kJ\ \ mol^{-1}$.

Please also note that the units on the axes of graphs will be labelled with a solidus (slash), / , instead of being separated with a comma or being shown in brackets, e.g. mass, g or mass (g) will become mass/g .

The solidus will not be used in any representation of multiple units.

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 question concerns WHMIS (Workplace Hazardous Information System), which everyone working in Canada is (supposedly) trained in. It is useful for high school students to learn these symbols in preparation for their working life – and, of course, they need to know about the hazards of any material that they are likely to meet in the school laboratory.

   The first symbol shown in this question is:

   This pictogram shows a gas cylinder, and warns of the hazards associated with a compressed gas (Class A Material). A compressed gas cylinder is usually quite heavy and if the valve is broken, or the cylinder is ruptured, it can become a projectile which is capable of causing significant damage. Gas cylinders (including those using for inflating helium balloons) should always be kept chained to a wall, or chained in a trolley if they are being moved.

   Of the substances given in the question, only hydrogen and oxygen are gases, so the answer to the questions must be either B or D. (In the absence of any other information alcohol is taken to mean ethanol, which is a liquid at ambient temperatures and pressures – but even if another alcohol were indicated it would not be a gas. Similarly the term "oil" can mean a number of different chemical substances, but it indicates a substance normally in the liquid state. Sodium, of course, is a solid at ambient temperatures and pressures.)

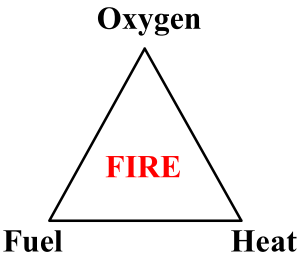
   The second symbol shown is:

   This pictogram shows a flame, and warns of the hazards associated with a flammable substance (Class B material). Flammable or combustible materials will ignite and continue to burn if exposed to a flame or source of ignition. All the substances suggested as answers in this question will burn **except** oxygen, but A, C and E have all been eliminated because they are not gases. The correct key is therefore **B**.

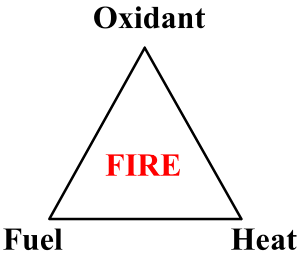
   You need to be careful not to confuse the symbol for a flammable material with that given below:

   This pictogram shows a flame, but it has a large "O" at the bottom of it, indicating that is is an oxidant. (Class C material). An oxidant is required to react with a flammable substance in order for combustion to occur. The third factor that is required is heat.

The three necessary factors are often shown in the “fire triangle” that is used for training firefighters, thus:



A more general version of the fire triangle would be:



The more general form of the fire traingle is needed because there are all sorts of other oxidants apart from oxygen that substances can burn in, e.g. chlorine or nitrogen dioxide. Solid substances such as nitrates or chlorates are also considered to be oxidising substances because they can release oxygen, nitrogen dioxide etc. when they are heated.

The fuel indicated in the triangle could be any flammable substance, not just gasoline or oil etc. It could be wood or paper – or absolutely anything that can burn. And heat doesn’t need to be a flame – it may be a spark, or simply something that is very hot such as an engine part or exhaust pipe – or it may simply the heat available in a room (substances such as white phosphorus, for example, often undergo spontaneous combustion because there is enough heat available in the surroundings at room temperature).

It should be noted that the reaction between the fuel and the oxidant in a combustion reaction is a special kind of redox reaction, in that the reaction will continue once it has been started by the heat. Combustion reactions do not require heat to be supplied once the reaction has been started. This is because combustion reactions are so highly exothermic that the heat released during the reaction (ΔH) is greater than the activation energy (E_a). You might like to consider what the potential energy diagram of such a reaction looks like.

2. This question concerns the stoichiometry of the double displacement reaction[1] between solutions of a metal nitrate (of formula $M(NO_3)_x$, say) and potassium iodide to give potassium nitrate and a precipitate of the metal iodide. It may be represented by the following equation:

$$M(NO_3)_x(aq) + xKI(aq) \rightarrow MI_x(s) + xKNO_3(aq)$$

Note that, because both nitrate ions and iodide ions are monovalent, formulae of the type $M_y(NO_3)_x$ and M_yI_x are not possible. (This eliminates answer A.)

This reaction may also be represented by an ionic equation, thus:

$$M^{x+}(aq) + xI^{-}(aq) \rightarrow MI_x(s)$$

The nitrate ions and the potassium ions are not considered in this equation, because they are "spectator ions" and serve only to maintain the electrical neutrality of the solutes.

The problem now boils down to finding a value for "x" in this equation. And this can be done by finding the ratio

moles of I^- : moles of M^{x+} (which equals x : 1) -- (1)

You are given the concentration of the metal ions in the metal nitrate solution (1•0 $mol•L^{-1}$). You are also given the concentration of the potassium iodide solution (1•0 $mol•L^{-1}$) – and this means that the concentration of iodide ions in the solution is also 1•0 $mol•L^{-1}$ (since the formula tells you that there is one mole of iodide ions for each mole of KI).

The question also tells you that each of the test tubes contains 3•0 mL of the metal nitrate solution. This means that you can calculate the chemical amount of metal ions in each test tube using the formula:

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

You can see from this that for two solutions of equal concentration the chemical amount will be proportional to the volume. But if you wish to calculate the chemical amount it can be done as follows:

The chemical amount of metal ions (M^{x+}) = 1•0 $mol•L^{-1}$ x 3•0 mL/ 1000 $mL•L^{-1}$
= 3•0 x 10^{-3} mol

Now you need to work out the volume (and thus the chemical amount) of iodide solution used. This can been done using the graph provided in the question.

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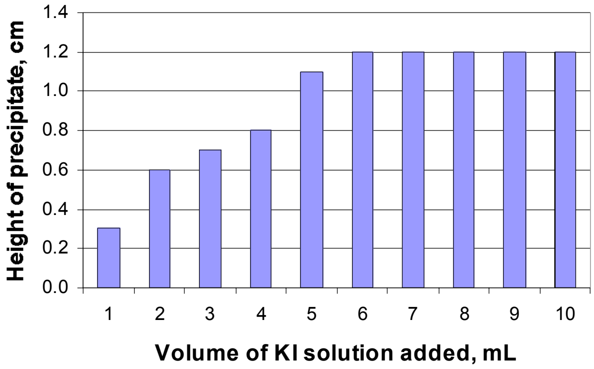
[1] Double displacement reactions are also sometimes known as double decomposition or metathesis reactions.



It can be seen from this graph that the height of the "secret" metal iodide precipitate gradually increases as potassium iodide solution is added to the metal nitrate solution, until it reaches 1.2 cm, at which point it remains constant. No more precipitate is being formed because all the metal ions have been used up. The metal nitrate is the limiting reagent, and adding excess potassium iodide cannot cause any further reaction.

The important thing to note is that the height of the precipitate reaches its maximum when a volume 6•0 mL of potassium iodide has been added. This is when

the chemical amount of iodide ions (I^-) $= 1•0 \text{ mol•L}^{-1} \text{ x } 6•0 \text{ mL/ } 1000 \text{ ml •L}^{-1}$
$= 6•0 \text{ x } 10^{-3}$ mol

Going back to (1) above, it can be seen that the ratio we need is:

moles of I^- : moles of M^{x+} $= 6•0 \text{ x } 10^{-3}$ mol : $3•0 \text{ x } 10^{-3}$ mol
$= 2 : 1$
$=$ x

The formula of the metal iodide is therefore MI_2 and the correct answer to this question is **C**.

This experiment does actually work, using, for example, lead(II) nitrate as the metal nitrate (one teacher said that this was his "Experiment 10"!). Lead(II) nitrate reacts with potassium iodide to give a beautiful orange-yellow precipitate of lead(II) iodide, which, however, tends to settle gradually with time, making it difficult to measure the heights reliably. I have also tried it using metal hydroxide precipitate, but these tend to be rather gelatinous, forming throughout the solution and not settling well enough to be properly measured.

3. This question concerns the valencies (oxidation states) of iron in the oxide Fe_3O_4. I can think of no more elegant way of solving this problem other than by trial and error.

   You need to start by considering the oxygen. Using the rules for assigning oxidation states given in the Solutions to the 2001 NHSCE (Appendix to the Solutions to Questions 21 to 25), you can see that the oxygen in Fe_3O_4 is in the –2 state, so that four oxygens will contribute a total charge of (4 x –2) = –8 in the formula. This is the charge that has to be balanced by the + charges of the iron in its two valency states, i.e. the iron must contribute a charge of +8 for the oxide to be electrically neutral.

   Now we need to consider each key in turn, bearing in mind that there are two atoms of one valency for every atom of the other:

   A. 1 and 2

   This could be considered as {(1 x +1) + (2 x +2)} = +5

   Or as {(1 x +2) + (2 x +1)} = +4

   Neither of these give +8 so the answer cannot be A

   B. 2 and 3

   This could be considered as {(1 x +2) + (2 x +3)} = +8

   (It could also be considered as {(1 x +3) + (2 x +2)} = +7, but as we need the answer +8, we can stop at the first combination of oxidation states.)

   You should know that the two valencies of iron are +2 and +3 so there is really no need to go any further, and the answer to this question is **B**. (But you could continue going through the keys to make absolutely sure that you have the correct answer.)

   Magnetite is a fascinating substance. It is one of only a few minerals that are magnetic, and it is the only common one that behaves as a strong magnet without being heated. Its old name is lodestone, meaning “guiding stone”, because it was used to make the directional needle in compasses. The name magnetite comes from Magnesia in Asia Minor (Turkey), and it is associated with the fable of Magnes, a shepherd who discovered it when he was climbing a mountain in this region. (He found that the nails in his shoes were attracted to the ground.)

   Magnetite has an unusually high electrical conductivity (it is about 10^6 times more conducting than Fe_2O_3), probably because valency electrons are able to interchange between the two oxidation states of iron. And it is believed that this movement of electrons that causes the magnetic effect.

   Magnetite is a widely distributed mineral, and is important as an ore in the production of iron and steel. It is a member of the spinel family of minerals, which have a smilar structure and common formula (AB_2O_4, where A and B are usually different metals – one divalent and the other trivalent). Many spinels are beautiful gemstones, some forms being very like ruby,: magnetite, however, is just a dull black colour.

4. Yes, these definitions of the chemical term "mole" really were based on definitions found in old textbooks. It just goes to show that you should never simply accept something in a textbook – you should always think about whether it makes sense or not! But, to be fair, scientists are always thinking about the definitions of the words they use, and polishing them as their ideas develop.

Let us consider each of the definitions in turn:

A mole is:

A. 6.02×10^{23} molecules

We all tend to think of a mole as being 6.02×10^{23} "things" , and we often speak about molecules when we really mean atoms or ions or other entities, so could this definition be considered to be reasonable? Well no, I don't think so. We still have to consider the number itself. 6.02×10^{23} is the number we tend to memorize as being Avogadro's number [2], but different books give different values, for example: $6.022\,05 \times 10^{23}$ or $6.022\,045(31) \times 10^{23}$. The NHSCE Data Sheet gives $6.022\,14 \times 10^{23}$. Which one is correct? The answer is that we cannot say. It is an experimentally determined value that we are improving on as we devise better experiments to determine it. But even if we think of the most precise value as the "best value" [3], it may not be the one we use in a particular calculation, because it is not generally appropriate to use a very precise value when all the other numbers we are using in a calculation are substantially less precise.

B. The Avogadro number of any particle of definite composition

This begs the question again about what the Avogadro number actually is, but it could be a reasonable definition if it referred to a correct definition of the Avogadro number. This definition, however, makes a good point about the kind of particle being counted needing to be of a definite composition. Essentially this is because we usually need to know the mass and the molar mass of a substance before we can find its chemical amount (number of moles). It is possible to find the chemical amount of a mixture if we know its exact composition so that we can find its average molar mass, but generally it is more satisfactory to stay with pure substances with known chemical formulae.

C. The quantity of a substance that has a mass in grams numerically equal to its molecular mass

This makes some sense, but nowadays we use the term "amount of substance" (or chemical amount), rather than quantity, when we are referring to moles. Molecular mass is an old-fashioned term meaning molar mass – but, strictly speaking, it only refers to the molar mass of molecules so it doesn't cover all the possible "things" that might be being counted. Furthermore the molecular mass would need to be measured in units of $\mathrm{g{\bullet}mol^{-1}}$ for the statement to be really valid.

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[2] In fact, strictly speaking we should refer to Avogadro's constant, rather than Avogadro's number, and use the unit of $\mathrm{mol^{-1}}$, thus Avogadro's constant (which is given the symbol N_A or L) might have the value of $6.02 \times 10^{23}\ \mathrm{mol^{-1}}$.

[3] We should also bear in mind that a precise value is not always accurate. For example, a stopped clock can give you a time to minutes and seconds, but that does not mean it is the correct time.

D. A mass unit defined as that mass of material containing 6.02 x 10^{23} molecules, atoms or other units

This is probably the worst definition of all, although in one province it was the favourite answer! First of all a mole is not a mass unit, it is a unit of amount of substance (or chemical amount). Secondly the word “units” is used twice in this sentence, each time with a different meaning. In the first part of the sentence it refers to a unit of measurement (a mole), meaning “a standard amount of a physical quantity”. In the second part “unit” is used to mean “a single undivided entity”. And finally we are back to the fact that Avogadro’s number is given as a specific value, which it cannot have.

Well none of the definitions in keys A through D are really satisfactory, so we are left with **E**, which is, in fact, the correct answer.

The definition given in the IUPAC Gold Book is as follows:

> The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, ...
>
> **author:** A D McNaught & A Wilkinson: IUPAC Compendium of Chemical Terminology (updated 1998).

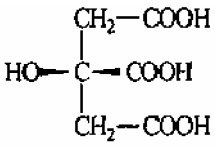
We could however criticize even this definition! Although it is actually more correct to work in kilograms rather than grams (because the the kilogram is a base unit of the SI system), it is, in my opinion, rather better to refer to an “exact” mass, rather than to specify the precision with which the mass is given. This is because it allows for improvements in measuring mass. I also dislike the use of the term “elementary entities” as this could create an impression that the term mole only applies to elements (and not to compounds etc.)

The final definition given in this question was

The amount of substance that contains the same number of specified entities as there are atoms in exactly 12 g of carbon-12. It is essentially the definition given by Whitman et al. in Chemistry Today 1 (Third Edition), Publ. Prentice-Hall Canada Inc. 1988.

We shall draw a veil over where the other definitions came from!

5. This is a question about citric acid, the structural formula of which is:



$$\begin{array}{c} CH_2-COOH \\ | \\ HO-C-COOH \\ | \\ CH_2-COOH \end{array}$$

As you can see from this formula, citric acid has **three** –COOH groups, which means it is really a triprotic (or tribasic) acid. However, the question tells you that, **under the conditions given**, it behaves as a diprotic (or dibasic) acid. (Actually I have since found out that it does not, in fact, behave as a diprotic acid under these conditions, but we'll discuss that below. We shall work through the solution of the question as it stands.)

Because the citric acid is behaving as a diprotic (or dibasic) acid, we know that two moles of sodium hydroxide will react with each mole of acid. And if we simplify matters by writing the dibasic form of citric acid as H_2A, then we can consider the reaction equation to be:

$$H_2A + 2NaOH \rightarrow Na_2A + 2H_2O$$

I shall be showing you a schematic method using this equation for solving the problem later, but first of all we shall use a more conventional method. Either way a useful tip for solving problems is that you often have to start with the **last** bit of information given in the question. (The beginning of the question is usually taken up with setting out the problem.)

So starting with the sodium hydroxide solution, we shall work out its chemical amount (number of moles) from its concentration and volume. This means using the formula:

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

The chemical amount of sodium hydroxide used is therefore

$$= (0.100\ \text{mol}\bullet\text{L}^{-1} \text{ x } 25.00\ \text{mL}) / 1000\ \text{mL}\bullet\text{L}^{-1}$$
$$= 2\bullet 50 \text{ x } 10^{-3}\ \text{mol}$$

Now since the acid:base ratio is 1:2, the chemical amount of acid used

$$= (2\bullet 50 \text{ x } 10^{-3})/2\ \text{mol}$$
$$= 1\bullet 25 \text{ x } 10^{-3}\ \text{mol}$$

This value, together with the volume of drink given, can be used to find the concentration of the citric acid in the drink. (The equation above must be rearranged first, to give $c = n/V$.) Note that the volume of water added to dilute the drink does **not** enter into the calculation. This is because we need to find the concentration of the citric acid in the drink not in the solution being titrated.

The concentration of citric acid in the drink is therefore

$$= (1\bullet 25 \text{ x } 10^{-3}\ \text{mol x } 1000\ \text{mL}\ \bullet\text{L}^{-1}) / \ 10.00\ \text{mL}$$
$$= 0\bullet 125\ \text{mol}\bullet\text{L}^{-1}$$

So the answer to the question is **B**.

A summary of the route used to do this calculation is given in the diagram below. (You start with sodium hydroxide and follow the arrows to arrive at the answer.)

	H_2A	+	2NaOH	→	Na_2A	+	$2H_2O$
c, mol•L^{-1}	**0•125**	↑	0•100	↓			
V, L	0•010		0•025				
N, mol	1•25 x 10^{-3}		2•50 x 10^{-3}				

← 1:2 mole ratio

Now for the question of whether the citric acid is, in fact, going to behave as a diprotic acid or not under the conditions given. I have known students use this experiment (which was taken from a laboratory manual) in science projects, with apparent success, but I don't suppose they ever really had a known value of the citric acid content of their drink against which they could compare their final result. However, they should, in any case, have verified the method using a standard solution of citric acid. This is another instance where a textbook could not be taken on trust! Here is the reason why:

Citric acid is a triprotic acid with $pK_1 = 3.128$, $pK_2 = 4.761$ and $pK_3 = 6.396$ at 25°C [4]. The gaps between these values are close enough that even in a titration with a pH meter, it would be very difficult to detect the equivalence points except at the end of titrating all three. In any case, phenolphthalein has a $pK_{In} = 9.5$, with a range between pH 8.2 to 10.0. This means that the **third** endpoint would have been reached well before the phenolphthalein would change colour, so it would be a very inaccurate means of measuring even this endpoint. For the second endpoint, occurring at $pH \approx 4.8$, an indicator such as bromocresol green, with $pK_{In} = 4.9$ and range between pH 3.8 and 5.4 would be a possibility, although the closeness of the endpoints might make the indicator insensitive (i.e. a small drop might not give a clear colour change because the pH is only changing very gradually as the base is added). It would probably be best to titrate to the third endpoint, occurring at $pH \approx 6.4$ and use an indicator such as bromocresol purple with $pK_{In} = 6.4$ and range between pH 5.2 and 6.8.

Another acidulant used in soft drinks is phosphoric acid, H_3PO_4, which is also triprotic (tribasic) with $pK_1 = 2.15$, $pK_2 = 7.09$ and $pK_3 = 12.32$ at 25°C. It can be seen that these three values are much better separated than those of citric acid, and therefore phosphoric acid is much more amenable to titration using an indicator. There is, however, no indicator that is suitable for an endpoint pH as high as 12, so that phosphoric acid **is** generally titrated to the second endpoint. Furthermore, phenolphthalein is commonly used to indicate this endpoint, although an indicator with a pK_{In} closer to 7 (e.g. bromthymol blue with $pK_{In} = 7.30$ and range from pH 6.0 to 7.6) might be better.

Many thanks to Professor Brubacher (University of Waterloo) who pointed out the problem with this question, and who calculated the titration curves. I am sorry that we didn't catch it before the exam was published.

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[4] pKa values have been taken from the Merck Index, 12th Edition, 1996

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2004 continued

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6. This question requires you to find the following masses in this order:

Mass of zinc in the pill → Mass of copper in the pill → mass of copper oxide in the pill

Finding the mass of zinc in the pill requires you to use the molar mass of $ZnSO_4$. You are given M_r, which is the **relative** molar mass. This is the molar mass measured relative to the molar mass of standard carbon–12 atoms and it has no units. It is, however, numerically equal to the molar mass, which has units of $g{\bullet}mol^{-1}$. The molar mass of $ZnSO_4$ is therefore 161.4 $g{\bullet}mol^{-1}$. You will also need to use the molar mass of zinc, which is given in your data sheet as 65.39 (again this has no units because it is relative to carbon-12, but you can give it units of $g{\bullet}mol^{-1}$).

The mass of zinc in the pill is therefore $(65.39\ g{\bullet}mol^{-1}/161.4\ g{\bullet}mol^{-1}) \times 49.37$ mg
$= 20.00$ mg

The ratio of Zn:Cu by mass has to be 10.1, therefore the mass of copper in the pill needs to be (20.00 mg/10)
$= 2.00$ mg

Using the relative molar masses of $M_r = 79.5$ for CuO (given) and 63.55 for Cu (from the data sheet), the mass of copper oxide that should be added to the pill is $(79.5\ g{\bullet}mol^{-1}/63.55\ g{\bullet}mol^{-1}) \times 2.00$ mg
$= 2.50$ mg

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

You could argue, that there is no need to consider the units of molar mass in this question because they cancel out, but it is always a good idea to put them in as a means of checking yourself. Sometimes units can be very similar, but differ in powers of ten.

This question was seeking to inject a little verisimilitude into the exam. It is absolutely true that people take zinc pills to boost their immune systems, although, whether this works or not is open to debate. (Zinc does, however, appear to have other benefits.) It is also true that zinc impairs the absoroption of other minerals, and that copper is added to maintain a balance, and that the ratio of Zn:Cu used is often about 10:1 by mass. A calculation of the sort given in this question is therefore necessary to establish how much of a copper compound is needed. When I investigated the sort of formulations actually used, however, I noted that they generally combine ZnO with CuO or $ZnSO_4$ with $CuSO_4$, however I did not choose to use these combinations in the question, because the molar masses of Zn and Cu are so close (and therefore the molar masses of their oxides or sulfates are also close) so that possible answers to the question would not look significantly different.

It is,interesting to consider what difference the various formulations can have on absorption of the zinc and/or copper by the body. Zinc oxide is amphoteric, and dissolves only with difficulty in strong acids and bases. Copper oxide is basic, but usually needs to be heated before it will dissolve in strong acids. It is therefore unlikely that either of these oxides will dissolve very well in the hydrochloric acid in the stomach. Both the sulfates are water-soluble, but zinc sulfate is reported to cause gastric inflammation and copper sulfate is toxic (but presumably not harmful at the low levels used in pills). More expensive supplements often have the zinc present as its gluconate, citrate, aspartate or as an amino acid chelate. There is some evidence that forms that involve protein breakdown products (amino acids and their derivates) naturally facilitate the absorption of the zinc.

It is probably better to avoid using pills at all, and to rely instead on incorporating natural sources of zinc into a well balanced diet. Good sources of zinc include whole-grain products, wheat bran and germ; seafoods and animal meats. Vegetables generally do not provide zinc in an easily absorbed form.

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7. We shall take this question at face value to start with, then, when we have solved it, we shall look into the whys and wherefores of the effect described.

First of all you need to appreciate that a strong crystal lattice will require a lot of energy to break it up (either by melting it or causing it to decompose). A high melting point or decomposition point means that a lot of heat energy has to be provided for the break up because the crystal lattice is strong.

Next you need to look at the charges on the ions formed by the elements given in the question, and the formula of the compound formed when they pair up as indicated. Once you have the formulae then you have the ratio of the ions. After that you can only hope that something stands out as having best fulfilled the criteria given for having a strong lattice.

A.	Li, O	Ionic charges: Li (1+), O (2–)	Formula: Li_2O
B.	Mg, O	Ionic charges: Mg (2+), O (2–)	Formula: MgO
C.	Ag, O	Ionic charges: Ag (1+), O (2–)	Formula: Ag_2O
D.	Li, F	Ionic charges: Li (1+), F(1–)	Formula: LiF
E.	Mg, F	Ionic charges: Mg(2+), F(1–)	Formula: MgF_2

Well yes, something does stand out. Only MgO and LiF fulfil the criterion of having a 1:1 mole ratio. And in MgO both the ions are divalent, whereas in LiF they are both monovalent, i.e. the ions in MgO are more highly charged, so that this compound will have the strongest crystal lattice and the highest melting or decomposition point. The answer is therefore **B**.

The actual values for the melting points are:

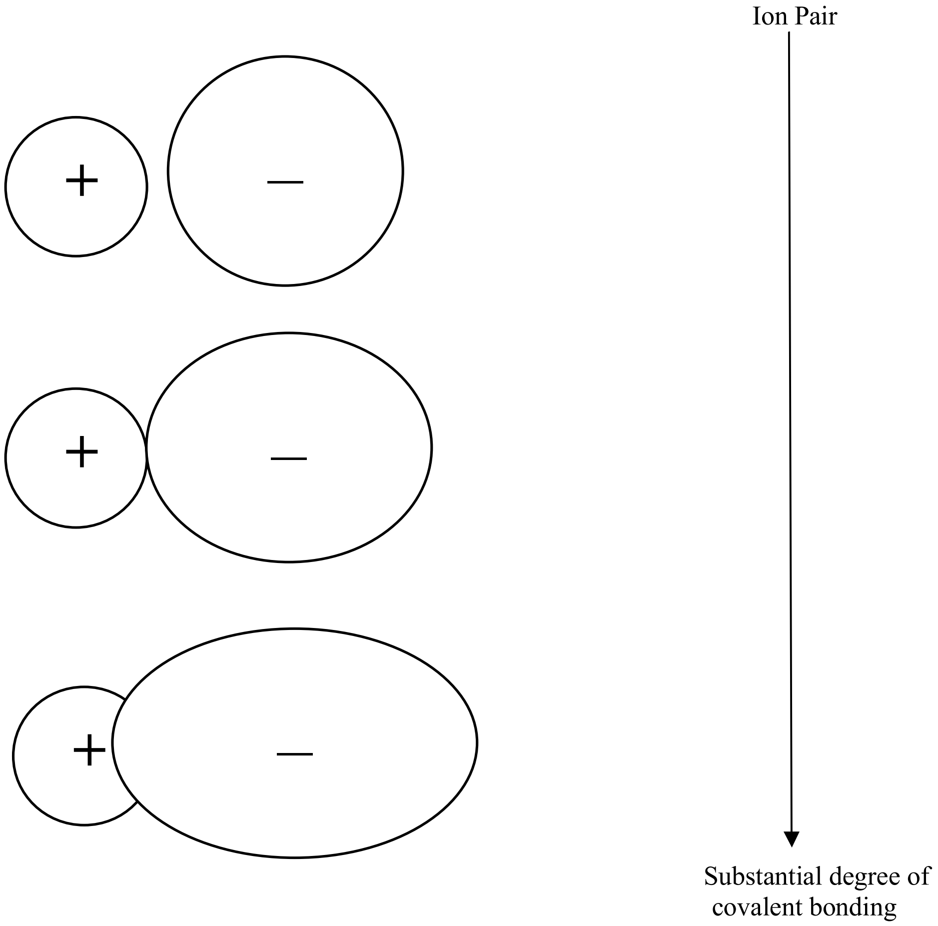
Li_2O, 1570 ^oC MgO, 2825 ^oC Ag_2O, $\approx$ 200 ^oC (decomposition) LiF, 848 ^oC MgF_2, 1263 ^oC

Magnesium oxide has one of the highest melting points of any compound, and it is therefore used to make bricks for furnace linings.

This question addresses two important factors that affect the strength of the crystal lattice (and thus the melting point). The first effect is the bonding. In the early years of chemistry we tend to think of bonding in absolute terms, thus: metal/metal bonding is metallic, non-metal/non-metal bonding is covalent and metal/non-metal bonding is ionic. Later we begin to think of a "bonding continuum" in which intermediate forms of bonding are possible. For example, in simple molecular compounds a pure covalent bond only really exists between atoms of the same element. Where the bond is between atoms of two different elements then the electronegativity difference between them will polarize the bond, creating a dipole. And, if the electronegativity difference is large enough, the compound will have ionic characteristics.

We can also consider this phenomenon starting from the point of view of ions. You probably remember that when ions are formed from atoms of approximately the same size, then the positive ions (cations) are generally smaller that the negative ions (anions). This is because the atoms lose electrons when they form positive ions, which means that the nucleus is more effective at attracting the remaining electrons, and therefore pulls them in, causing the ion to be smaller than the atom. On the other hand, when electrons are added to an atom to form a negative ion, the nucleus is not able to attract them nearly as well as in the atom, and the ion is therefore bigger than the atom.

When cations and anions are involved in ionic bonding the positive and negative charges of the ions attract each other and hold the ionic lattice together. The anions, however, tend to become distorted away from the spherical shape that we usually imagine ions to have. A cation can pull at the "electron cloud" around an anion, so that a "bulge" forms on the side of the anion nearest the cation. The cation is said to polarize the anion. This increases the electron density on the axis between the ions, making the bonding more covalent in character. The diagram below shows how this might happen for one pair of ions.



The increase in covalent character strengthens the bonding, and the effect is enhanced if polyvalent ions are involved. A high charge on a cation, especially if it is small, will increase its ability to polarize the anion, because it is more "electron hungry": a high charge on the anion, especially if it is large, increases its polarizability because the nucleus is less able to control the electron cloud surrounding it.

The strength of the bonding is not the only factor to affect the strength of a crystal lattice. The stoichiometry of the compound is also important, as indicated in the question. A 1:1 stoichiometry is helpful, because the ions generally fit together neatly in the lattice. A 2:1 stoichiometry, for example, would mean that two of one kind of ion would have to be fitted in to the lattice for every one of the other kind. These two ions of the same charge tend to repel each other and open up the lattice, making it weaker.

8. Like question 9 in the 2003 NHSCE, this question was presented in tabular form to simulate an "Observation" table that a student might put into his or her laboratory notebook if asked to investigate some unknown substances. But this year's question was a good deal easier than last year's, requiring only a knowledge of one of the reactions of acids plus some simple tests for gases.

You should know that metal carbonates react with acids to form a salt, water and carbon dioxide. Thus, sodium carbonate reacts with hydrochloric acid as follows:

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

The test for carbon dioxide is that it turns limewater milky, so that the answer to this question must be **D**.

The reaction of hydrochloric acid with a sodium carbonate is an example of a general reaction of acids in which a strong acid reacts with the salt of a weaker acid, thus:

Strong acid + salt of weak acid → Salt of strong acid + weak acid

In the case of sodium carbonate the weak acid may be considered to be carbonic acid (H_2CO_3)[1] which breaks down very easily into carbon dioxide and water.

The reaction of carbon dioxide with limewater (aqueous calcium hydroxide solution) is an acid-base reaction in which an insoluble salt (calcium carbonate) is formed as a white, milky precipitate, thus:

$$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$$

(The carbon dioxide may be considered to be reacting as an acid in this reaction, because it is an acid anhydride[2].)

Let us consider what could be happening in the rest of the suggested responses.

A. Solid does not dissolve

This means that the solid is not water soluble (remember that water is present in the aqueous solution of hydrochloric acid) so it cannot be a sodium salt[3]. It could conceivably be a water-soluble salt of a metal ion that forms a water insoluble chloride when it reacts with hydrochloric acid. Bearing in mind the solubility rules, this could be a salt of Ag(I), Pb(II) or Hg(I). Lead(II) nitrate, for example, is be a water-soluble white

---

[1] Some people consider carbonic acid to be no more than water and carbon dioxide molecules that are hydrogen bonded together. In any case solutions of the "acid" exist in equilibrium with carbon dioxide and water, and, unless the system is enclosed (as in a bottle of soda) the carbon dioxide will escape from the solution as a gas until no more acid is left. Thus:

$$H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(aq) \rightleftharpoons H_2O(l) + CO_2(g)$$

[2] An acid anhydride may be defined as a substance that is formed by elimination of water from an acid. This definition applies to both organic and inorganic anhydrides, although the structures of the two types of compounds are very different.

[3] Students are expected to know the solubilities of common inorganic compounds. The "Solubility Rules" that I am using are given in the Answer to Question 17 of the 2002 NHSCE.

solid, but it would react with hydrochloric acid to form a coating of insoluble lead(II) chloride, and so it would not, in fact, dissolve.

B. Solid dissolves, but does not give off a gas

This means either that the that the solid is water-soluble (and does not react with hydrochloric acid to form an insoluble compound) or that is a base that dissolves by reacting with hydrochloric acid to form a salt and water (but no gas).

C. Solid dissolves, giving off a vinegary smell

This could be a water-soluble salt of ethanoic acid (acetic acid), e.g. sodium ethanoate (acetate). As the salt of a weak acid this would react with hydrochloric acid to give ethanoic acid, which is somewhat voltaile and has a vinegary smell. (Vinegar is an aqueous solution the principal solute of which is ethanoic acid.)

D. Solid dissolves, giving off a gas that turns limewater milky

This is the correct answer for the reasons given above.

E. Solid dissolves, giving off a gas that relights a glowing splint

This concerns a reaction that you may not have met before. You should, however, know that the gas released is oxygen, because it relights a glowing splint. The solid could, in fact, be a peroxide, e.g. sodium peroxide (Na_2O_2), which is the oxide usually formed when sodium burns in the presence of a good supply of oxygen. The peroxide radical O_2^{2-} seems to behave like a weak acid radical realeasing hydrogen peroxide when it reacts with a strong acid, thus:

$$Na_2O_2(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O_2(aq)$$

$$\text{followed by } H_2O_2(aq) \rightleftharpoons H_2O(l) + O_2(g)$$

(It should, however, be noted that hydrogen peroxide cannot really be considered to be a weak acid, as its solutions in water are neutral.)

The oxides, peroxides and superoxides of Group I and II metals have very interesting structures and poperties, but a discussion of them is unfortunately beyond the scope of these exam answers. I strongly recommend that you do some research on them for yourself.

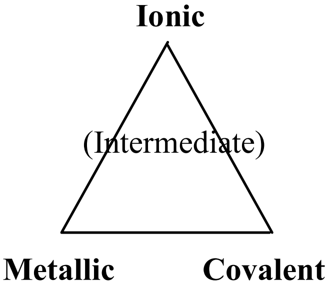
9. This question is concerned with the properties of substances that are held together by different kinds of attractive forces.

Where the melting point is concerned, we are essentially looking at the strength of different kinds of bonding, as in Question 7. (The question is worded in terms of "attractive forces" because some people feel that these forces are too weak to be considered to be "real" bonding).

The three main types of bonding that we generally consider are ionic, covalent and metallic bonding. Covalent bonding involves the sharing of electrons between atoms, and is generally the strongest kind of bonding. Ionic bonding involves electrostatic attraction between positive ions (i.e. atoms that have lost one or more electrons) and negative ions (i.e. atoms that have gained one or more electrons). Ionic bonding is usually moderately strong. Metallic bonding involves positive ions that are held together by a delocalised "sea" of electrons. Pure metallic bonding is usually fairly weak.

We must bear in mind, however, that there are two types of covalent bonding – network and molecular. But if we consider only the network covalent bonding, and compare it with ionic and metallic bonding (which are also network), we can translate the bond strengths to **very approximate** melting points for the three types of substances. Thus substances with network covalent bonding might have melting points in the low thousands, substances with ionic bonding might have melting points in the high hundreds, and substances with metallic bonding might have melting points in the low hundreds of degrees Celsius.

These are only very approximate temperatures, because there are also intermediate types of bonding (c.f. the solution to Question 7 above). The three main types of bonding are sometimes shown as being at the "cornerstones" of a bonding triangle, as shown below:



Substances that have ionic bonding with a fair amount of covalent character can be expected to have stronger bonding and therefore higher melting points than those with simple ionic bonding. Metallically bonded susbstances formed from positive ions with more than one electron feeding into their delocalized system will tend to form electron "clumps" between the ions, which will make the bonds more like covalent bonds, and therefore stronger. So the melting points of these substances will be higher than those of metals with just one electron feeding into the system. And on the third side of the triangle there are alloys, which are formed from more than one metal. If the metals in the alloy have different electronegativities then the bonding between them will become more like ionic bonding, which will affect the bonding strength and melting point.

A detailed version of the bonding triangle, with specific examples of substances with different kinds of network bonding is given at the end of the solution to this question.

Before we go on to considering electrical conductivity we should go back to looking at the strength of covalent molecular bonding. Here we need to differentiate between the kind of bonding **inside** the molecules, which is strong covalent bonding, and the attractive forces **between** the molecules, which are weak. Melting a substance that is covalently bonded causes the weak forces between the molecules to break apart, whilst the strong covalent bonds keep the molecules intact. Substances with covalent molecular bonding typically have very low melting points – often they are liquids or even gases at room temperature, or, if they are solids, they may have melting temperatures below 100^oC. Even substances with very large molecules such as polymers rarely have melting points above 300^oC.

There are two main types of covalent molecular substances, which are differentiated according to the polarity of their molecules:

> Polar molecules – these molecules exist as permanent dipoles, so that the attractive forces between them are dipole-dipole interactions.
>
> Non-polar molecules – these molecules can only have temporary dipoles, so that the attractive forces between them are induced dipoles. These forces are know as London forces or dispersive forces. The term Van der Waals forces is best avoided as some people use it to refer to both kinds of intermolecular interactions, whilst other people use it only for induced dipole intereactions.

There is a third type of intermolecular force, namely hydrogen bonding. This is really just a special case of interactions between molecules with permanent dipoles. It occurs in the special case of molecules that have hydrogen atoms that can form a bridge between small electronegative atoms (such as oxygen, nitrogen or fluorine) on two different molecules.

Having said all this, the melting point of 681^oC points towards an ionic substance, but it is also possible that it could be a metal, or some substance with intermediate bonding. To confirm our suspicions, we need to consider the information given to us about the electrical conductivity. We are most familiar with electrical conductivity in metals in the solid form. However, the delocalized electrons in the metal allow electric current to flow through the metal whether it is solid or liquid. (So the answer to this question cannot be B.)

Electricity can also be carried by other charged particles, particularly ions, provided that the ions can move. In the solid state, ions are trapped in a crystal lattice, so that they cannot conduct electric current. In the liquid state (or in solution) they can move, and so they can conduct electricity.

Neither network nor molecular covalent compounds can conduct electricity (unless there is a significant amount of intermediate bonding with metallic or ionic character involved). The correct answer to this question is therefore **A**. (It could be potassium iodide, which has the correct melting point of 681^oC, but you are not expected to memorize this.)

The diagram on the next page shows a more detailed version of the bonding triangle discussed above.

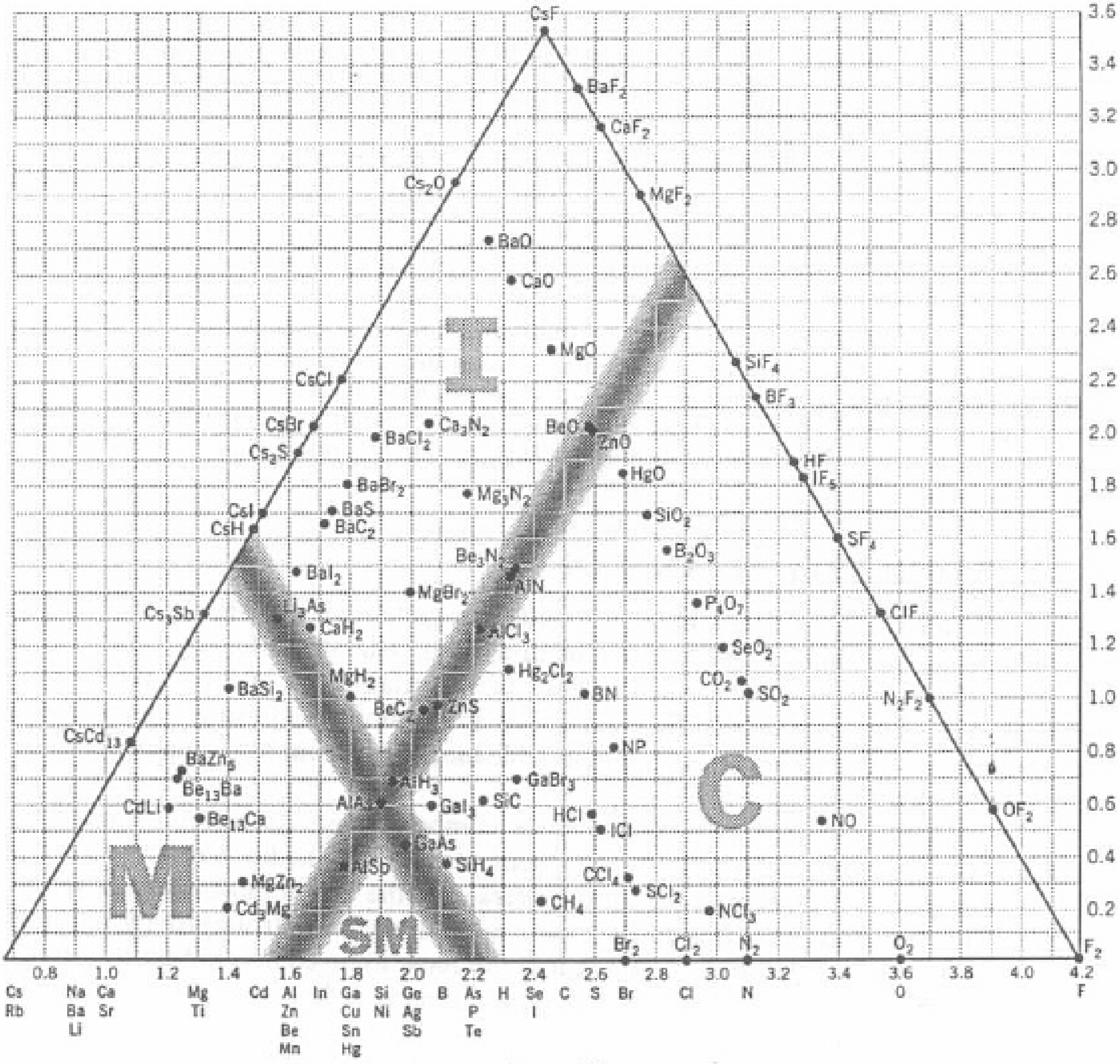
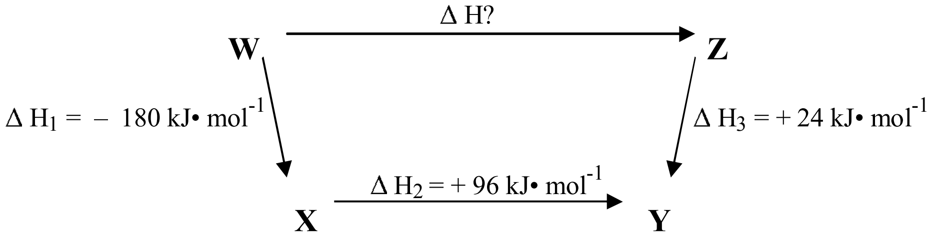


FIGURE 5.10 Bond type triangle for elements with electronegativities ranging from Cs to F. The lines separating the regions into ionic (I), metallic (M), covalent (C), and semimetallic compounds (SM) may be determined empirically and correspond approximately to lines parallel to the triangle sides drawn through Al and Te. (from Purdue University workshop by Dr. George Bodner)

10. This question requires the student to determine an enthalpy change using a Hess's Law Diagram, i.e it requires a visualization technique rather than purely algebraic manipulation. We shall first re-label the diagram, so that we can distinguish between the different values of ΔH, thus:



The enthalpy change that we need to calculate for the reaction W → Z is shown on the diagram as ΔH?. We are told that this cannot be determined directly, but we can establish an alternative route from the diagram. This shows that we can use a series of reactions, thus:

$$W \rightarrow X \rightarrow Y \rightarrow Z$$

Note that it is very important to "follow the arrows" on the diagram. We need to know the enthalpy change going from Y → Z, but we are only given an enthalpy change for the reverse reaction Z → Y. We therefore need to reverse the sign of the enthalpy change for this reaction.

Now we can formulate an expression for the enthalpy change value that we are trying to calculate, thus:

$$\Delta H? = \Delta H_1 + \Delta H_2 - \Delta H_3$$

Susbtituting the values given in the diagram allows us to obtain the answer, thus:

$$\begin{aligned}\Delta H? &= -\ 180\ \text{kJ}\bullet\text{mol}^{-1} + (+\ 96\ \text{kJ}\bullet\text{mol}^{-1}) - (+\ 24\ \text{kJ}\bullet\text{mol}^{-1})\\ &= -\ 108\ \text{kJ}\bullet\text{mol}^{-1}\end{aligned}$$

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

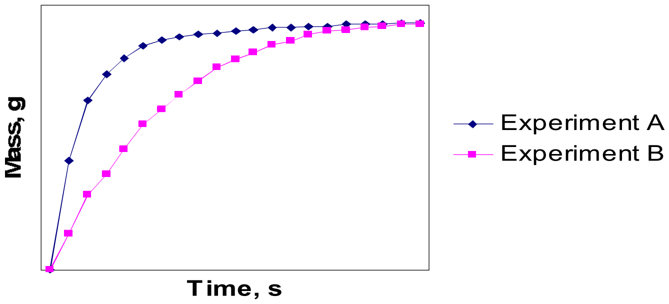
This is a fairly simple example of using a Hess's Law Diagram to determine an enthalpy change. Expect more complex examples in the future. Visualization techniques are important in chemistry, so it is a good idea to develop the ability to use them.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2004 continued

11. This questions refers to a graph that was plotted using data that really were obtained by a student investigating the rate of a reaction. I didn't want to give the precise reaction that he was studying in the question, because it is an experiment that is so often done in schools that this might mean that it could be answered from memory rather than by working it out. As a result the question ended up being rather wordy, for which I apologise.

You were given the information that the data came from two trials – experiments A and B – and that these were obtained by changing just one of the reaction condiditons. The "storyline" of the question says that the student has lost some of his notes. (Had he been writing on loose sheets of paper, rather than in his lab book, I wonder?) When the student tried to reconstruct what he had done, he made a mistake. The suggested answers to the question are possible mistakes that he could have made in different circumstances. You are not told exactly what the student was trying to do, so you have to think of various possibilities. And you have to choose the statement that is incompatible with the graph, whatever the circumstances.

It is probably easiest to start off by taking a good look at the graph, and trying to make out what it is telling you. The graph is given below for reference:



First of all, we can see that it is a graph of mass against time, and that the mass is increasing with time. This tells you that it is a product of the reaction that is being monitored. (The mass of a reactant would be decreasing with time.) Statement D is thus correct, and cannot therefore be the answer to the question.

The line for Experiment A starts off more steeply that that for Experiment B. This tells you that the initial rate of reaction is higher in Experiment A than in Experiment B, so statement E is correct, and cannot therefore be the answer to the question.

The lines for Experiment A and Experiment B converge, levelling off at the same mass by the end of the experiment. This tells you that the same mass of product was formed in the two experiments, and therefore that the same mass of limiting reagent was probably used in the two trials. Although you cannot be absolutely sure, it is likely that the same amount of all the starting reactants were used in the two experiments. Statement A is thus likely to be correct, and cannot therefore be the answer to the question.

Furthermore, the fact that the two lines level off tells you that the rate of reaction at the end of **both** experiments is zero. It is therefore INCORRECT to say that the **final** rate of reaction was greater in Expreiment A than in Experiment B. This means that the solution to this question is key **B**.

Even though we now know the solution to this question, we shall consider the fifth statement. This suggests that the reaction temperature was higher in Experiment A than in Experiment B. This would result in a greater initial rate of reaction for Experiment A, which is indeed indicated by the graph. Statement C cannot there fore be the answer to the question. Having said this it should be noted that this graph was not, in fact, obtained in an experiment to determine the effect of temperature on rate of reaction. The experiment was investigating the effect of particle size on the rate of reaction between marble (calcium carbonate) chips and hydrochloric acid solution, according to the reaction:

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

It was the mass of carbon dioxide formed in the reaction that was being monitored. In the faster reaction (Experiment A) smaller chips of calcium carbonate were used than in Experiment B. The hydrochloric acid was the limiting reagent. (The smaller chips reacted faster because they present a higher surface area to the acid than the larger chips.)

Other experiments that might have given similar results would be experiments to find the effect of concentration on the rate of reaction. In the example above, it would (in theory) have been possible to use chips of the same size with different concentrations of acid. The line for Experiment A, in this case, would be obtained with the more concentrated acid. (This experiment would not be very easy to do in practice because marble chips do not come in exactly uniform sizes, so it would be difficult to hold this factor constant in the two experiments.)

Another factor that you might have done in a school experiment, and that might give similar-looking results, would be one looking a the effect of different masses of catalyst. A greater mass of catalyst would give a line like Experiment A, because it would promote a faster reaction than a smaller mass, which would give a line like Experiment B. I can't think of a way that this might be done with the calcium carbonate/hydrochloric acid reaction, but it would work for the decomposition of hydrogen peroxide using different masses of manganese(IV) oxide catalyst.

There are often many different ways in which the rates of the same reaction can be studied. You might like to reflect on how many variations in methodology you could use in some different cases.

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12. This is a very straightforward question involving application of Le Châtelier's Principle to the Haber process reaction for the manufacture of ammonia.[1] The equation for this reaction is given as:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\text{ ; } \Delta H = -92\text{ kJ}\bullet\text{mol}^{-1}$$

You are asked which one of the changes in the process conditions given in the answer keys will NOT help to increase the amount of ammonia produced from a given amount of hydrogen.

We shall consider each of the changes in turn:

A. Increasing the temperature

The ΔH value that you are given is negative, which means that the reaction is exothermic, i.e. heat is given out in the reaction. (Heat can be considered as a product of the reaction.)

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[1] Remember that equilibrium considerations are only used to establish the best conditions for operating a chemical plant. In practice the process is not a batch process, but a continuous process, and is operated under steady state conditions.

Increasing the temperature will increase the heat supplied to the system, adding to the heat created in the reaction and thus causing the reaction to reverse. This will result in less ammonia being formed. Increasing the temperature will NOT help to increase the amount of ammonia produced, so the answer is **A**. [2]

You could, of course, move on to the next question at this point, but we shall continue to consider the other keys.

B. Increasing the pressure

This reaction involves different chemical amounts of gas on either side of the equation, so that it will be affected by pressure. The equation shows a total of 4 moles of gas on the left hand side, and 2 moles of gas on the right hand side. The left hand side of the equation is thus the "high pressure side".

If the pressure is increased then the equilibrium swings towards to "low pressure side" of the reaction (the right hand side) so that more ammonia will be formed. The answer to the question cannot therefore be B.

The pressure actually used in this process was, at one time, as high as 600 atm, but nowadays it is more likely to be in the region of 250 atm. It should be noted, however, that even at this pressure, it is necessary to use expensive equipment, which can withstand the pressure, and which will not allow leakage of gases. (A common student mistake is to assume that you can react nitrogen and ammonia under lab conditions. It should also be remembered that, even under the extreme conditions used in the manufacturing process, the yield of ammonia is very low.)

C. Recycling the reactants

The yield of ammonia is low for a single pass of reactants through the system, but the reactants need not be wasted. The ammonia formed is usually liquefied and removed from the mixture, then the unreacted gases are recycled through the system again, along with fresh reactants. This process is repeated continuously, thus ensuring that as much of the reactants as possible can be converted into ammonia. The answer to the question is therefore not C.

D. Removing ammonia as it is formed

Ammonia is the product of the reaction, so that removing it means that the equilibrium swings to the right, producing more ammonia to replace the product that has been removed. The answer to the question is therefore not D.

In the manufacturing process, the reaction takes place as the gases are moving over the catalyst. Ammonia is liquefied in a separate chamber from the reactor, so that it is not really being removed from the reaction mixture until after the reaction has taken place.

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[2] In fact this process is actually operated at a moderate temperature (usually around 450^{o}C) rather than at a very low temperatures, because this keeps the reaction going at a reasonable rate.

E. Increasing the amount of nitrogen relative to the hydrogen used

Increasing amount of just one of the reactants will stress the left hand side of the reaction, causing more product to be formed relative to the other reactant. More product means more ammonia, so the answer to the question cannot be E.

Hydrogen is the more expensive reactant in this process, so that increasing the proportion of the other reactant (nitrogen) in the feedstock, ensures that as much of the more expensive reactant as possible gets used in the reaction.

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13. This question provoked an extended discussion amongst reviewers of the exam about what exactly we mean by the term "*isoelectronic*". Clearly "iso" means "the same" [3] and "electronic" refers to electrons. The problem was that different books define the term differently. In some books "isoelectronic" means that two or more species must have exactly the same arrangement of **all** the electrons; in other books the term just refers to valency electrons being the same. For example, using the second definition HCl and HBr would be isoelectronic, whereas under the first definition they would not. We therefore added the provisor that the Lewis structures must be the same, in order to obtain an unambiguously correct answer irrespective of which definition was used.

Now we shall consider what this means for the structures given:

A. CO, N_2

In CO the constituent atoms have the electronic configurations: carbon: 2, 4 and oxygen: 2, 6

This gives a total number of electrons = 14, and a number of **valency** electrons =10

If both of the atoms are to obey the octet rule, then a total of 16 electrons are somehow going to be needed. This means that 6 electrons have to be shared, i.e. a triple bond is needed between the atoms. The oxygen atom gives 4 electrons into the triple bond, and the carbon gives 2 electrons, but, once the triple bond has been formed, all the electrons are equivalent, and you cannot tell which atom they came from. One lone pair is left on each of the atoms, thus the molecule can be represented as:

$$:C\equiv O:$$

In N_2 both atoms in the molecule are nitrogen atoms, with electronic configuration of 2, 5.

This gives a total number of electrons = 14, and a number of **valency** electrons = 10 (just like for carbon monoxide). As in the carbon dioxide molecule, the nitrogen molecule has a triple bond between its two atoms. The nitrogen molecule can be represented as:

$$:N\equiv N:$$

Note that even though both the nitrogen atoms contribute 3 electrons each to the triple bond (rather than the 4/2 split seen in the carbon monoxide molecule), the distinction is not evident once the molecules

---

[3] Consider words such as isobar meaning equal pressure (isobars are lines shown on weather maps that show places where the pressure is equal) or isosceles meaning equal "legs" (as in a triangle with two sides of equal length).

have been formed. CO and N_2 are isoelectronic (whichever definition you use), so the answer to this question is **A**.

Even though we have established the correct answer, we shall go through the rest of the answer keys to see how these work out.

B. CO_2, SO_2

In CO_2 the carbon atom has the electronic configuration of 2, 4 and the oxygens have each got 2, 6. This gives a total number of electrons = 22, and a number of valency electrons = 16.

In SO_2 the sulfur atom has the electronic confuguration of 2, 8, 6, and the oxygens have each got 2, 6. This gives a total number of electrons = 22, and a number of valency electrons = 18.

CO_2 and SO_2 molecules cannot possibly be isoelectronic by either definition, so the answer to this question cannot be B.

C. CS_2, $BeCl_2$

In CS_2 the carbon atom has the electronic configuration of 2, 4 and the sulfur atoms have each got 2, 8, 6. This gives a total number of electrons = 36, and a number of valency electrons = 16.

In $BeCl_2$ the beryllium atom has the electronic configuration of 2, 2 and the chlorine atoms have each got 2, 8, 7. This gives a total number of electrons = 38, and a number of valency electrons = 16.

CS_2, and $BeCl_2$ molecules have different total numbers of electrons, but the number of valency electrons are the same, so can these two molecules be isoelectronic according to the valency electron definition? We must think a bit more about the arrangement of electrons within the molecule to answer this.

In both cases, the molecule has 3 atoms and therefore 24 valency electrons are nominally needed for each atom to have an octect. Each molecule only has 16 valency electrons so 8 more electrons are somehow needed, indicating that two double bonds are required.

This works for carbon disulfide, thus:

$$\mathrm{S{=}C{=}S}$$

(There are also two sets of lone pair electrons on each of the sulfur atoms.)

Beryllium, however, only has 2 electrons in its valency shell, so it simply doesn't have enough electrons to contribute 4 electrons to two double bonds, and, if the chlorine atoms were to contribute another electron each this would break into their lone pair electron systems. Beryllium cannot form an octet in this compound, and so the electron arrangement is:

$$\mathrm{Cl{-}Be{-}Cl}$$

(There are also three sets of lone pair electrons on each of the chlorine atoms.)

Thus $BeCl_2$ has single bonds where CS_2 has double bonds, and the disposition of lone pairs is different. So the two species do not have the same Lewis structure and so the answer to this question cannot be C.

D. CO_2, NO_2^-

In CO_2 the carbon atom has the electronic configuration of 2, 4 and the oxygens have each got 2, 6. This gives a total number of electrons = 22, and a number of valency electrons = 16.

In NO_2^- the nitrogen atom has the electronic configuration of 2, 5 and the oxygens have each got 2, 6, and **there is also an extra electron to provide the negative charge on the ion**. This gives a total number of electrons = 24, and a number of valency electrons = 18.

CO_2 and NO_2^- cannot be isoelectronic by either definition, so the answer to this question cannot be D.

You might, however, like to think about a very similar pair of species: CO_2 and NO_2^+. These two species both have a total number of electrons = 22, and a number of valency electrons = 16. Are their Lewis structures the same?

E. CN^-, NO

In CN^- the carbon atom has the electronic configuration of 2, 4 and the nitrogen has got 2, 5, and there is also an extra electron to provide the negative charge on the ion. Thhis gives a total number of electrons = 14, and a number of valency electrons = 10.

In NO, the nitrogen atom has the electronic configuration of 2, 5 and the oxygen has got 2, 6. This gives a total number of electrons = 15, and a number of valency electrons = 11.

CN^- and NO cannot be isoelectronic by either definition, so the answer to this question cannot be E.

You might, however, like to compare CN^- with CO and N_2. These species all have the same total number of electrons and number of valency electrons. Are their Lewis structures the same?

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14. The idea for this question came from the Chemical Insitute of Canada's annual crystal growing competition (see http://www.cheminst.ca/outreach/ncw/cicfrm_index__e.htm) in which students compete to produce a single large crystal from a given amount of starting material. One year a group of students produced a truly gigantic crystal because they started off with more material than they were meant to (they used the material intended for several groups by mistake). This question shows how you can work out what the maximum possible size of the crystal can be from a given mass of starting material.

In order to make a single large crystal, the starting material must be completely dissolved in water, and the solution left to evaporate until it becomes saturated and some small crystals form. A single well-shaped small crystal is chosen, and a piece of thread is fastened round it so that it can be suspended, fully immersed, in the saturated solution, without touching the sides or the bottom of the container. The solution is allowed to evaporate away slowly and the single crystal gradually grows bigger, and (one hopes) it also grows in a perfect shape for its type (e.g. triclinic for copper sulfate pentahydrate). The crystal needs constant nurturing, as it is important to keep any other crystals from forming in the solution and competing with the chosen crystal. Any small crystals that do form are removed, and can be used to make a further supply of saturated solution. This extra solution may be needed to keep the main crystal covered if it gets really big.

In this question we have to assume that all small crystals have been dissolved and included in the saturated solution remaining at the end of the experiment. In other words the starting mass of $CuSO_4•5H_2O$ is now divided between the solid single crystal and the dissolved material in the saturated solution. We are given the solubility[4] of $CuSO_4 \bullet 5H_2O$ at the temperature of their experiment – it is 1.39 $mol \bullet L^{-1}$.

In order to be able to work in masses we need to change the units of solubility into $g \bullet L^{-1}$. This means that we need to use the equation for intercoverting mass and chemical amount[5], which is:

$n = m/M$ Where n is the chemical amount in mol
m is the mass in g
and M is the molar mass in $g \bullet mol^{-1}$.

Rearranging this equation to put what we are trying to calculate onto the left hand side of the equation means that

$$m = nM$$

and therefore the mass of $CuSO_4 \bullet 5H_2O$ dissolved in one litre of saturated solution at the temperature of the experiment $= 1.39 \text{ mol} \times 249.7 \text{ g} \bullet \text{mol}^{-1}$

$$= 347.1 \text{ g}$$

The solubility can therefore be expressed as 347.1 $g \bullet L^{-1}$

The volume of solution left at the end of the experiment is 100 mL, so that the mass of $CuSO_4 \bullet 5H_2O$ in this volume of solution

$$= 347.1 \text{ g} \bullet \text{L}^{-1} \times 100 \text{ mL}/ 1000 \text{ mL} \bullet \text{L}^{-1}$$

$$= 34.71 \text{ g}$$

We started with a mass of 100 g of crystals, and just 34.71 g of this mass is left in the solution around the big single crystal. The mass of the single crystal is therefore

$$= (100 - 34.71) \text{ g}$$

$$= 65.29 \text{ g}$$

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

---

[4] Remember that solubility is defined as the concentration of a saturated solution that is in equilibrium with undissolved solid.

[5] Students sometimes have difficulty is seeing why we can ignore the "L^{-1}" here. However if you look at the fact that the solubility/concentration is given as 1.39 $mol \bullet L^{-1}$, then you know that a chemical amount of 1.39 mol is dissolved in each litre. Simply converting this chemical amount of 1.39 mol into the equivalent mass will therefore give you the mass dissolved in each litre.

15. This question generated a certain amount of controversy, because the assumption you are told to make is not valid (see below). But you just need to take it at face value.

First of all, let us simply consider the dissociation of sulfuric acid when it is dissolved in water, without taking into account any reaction it might have with water. This dissociation can be shown by the following equation:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$$

If the sulfuric acid is **fully dissociated** (which is what you are told to assume) then this equation becomes:

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

We can see from this equation that two moles of hydrogen ions are thus produced from every mole of sulfuric acid.

Car battery acid containing sulfuric acid of concentration $4.0\ mol{\bullet}L^{-1}$ thus has a concentration of hydrogen ions equal to $8.0\ mol{\bullet}L^{-1}$ (assuming complete dissociation.)

The pH of a solution can be defined by the equation:

$$pH = -\log[H^+]$$

where $[H^+]$ is an abbreviation for "hydrogen ion concentration".

The pH of the car battery acid is therefore $= -\log(8.0\ mol{\bullet}L^{-1})$

$= -0.903$

(This value has no units because logarithms do not have units.)

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

A negative pH may appear unlikely, but remember that this is only a **theoretical** pH. The sulfuric acid is NOT, in fact, completely dissociated in solution. The first step of the dissociation

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

is usually considered to be complete as its K_a value is very high. The second stage of the dissociation:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

is definitely not complete, as the K_a value is in the order of 1.0×10^{-2}. This effect is exacerbated by the fact that we are looking at a relatively high concentration of sulfuric acid ($4.0\ mol{\bullet}L^{-1}$), which is well outside the standard concentration of $1.0\ mol{\bullet}L^{-1}$. It must be remembered that, at high concentrations, ion pairing is likely to occur, and that this will reduce the concentration of free hydrogen ions in the solution.[6]

---

[6] Strictly speaking, all equilibrium constants, including acid dissociation constants, should be written in terms of activities rather than concentrations. Activities are values that have been corrected for effects such as ion pairing, but they are difficult to determine, so we often use the approximate values given by substituting concentration values into equilibrium constant expression.

Some people say that pH can only really be established by measurement with a pH meter, and that it cannot effectively be calculated (even if the activity of the hydrogen ion is used instead of concentration in the pH expression). Apparently, even when a strong acid is fully dissociated, it is difficult to get a pH meter reading lower than pH = 2.0. Nevertheless, the concept of pH is a useful one and the theoretical calculation of pH can often give a good indication of the actual pH, especially around the middle of the pH scale for dilute solutions.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2004 continued

16. Although it looks unlikely on the face of it, this question requires you to know some simple reactions of acids. To recap these briefly, they are:

(1) Acids react with bases to form a salt and water

(2) Acids react with reactive metals to form a salt and hydrogen

(3) Acids react with the salts of weaker acids to form a salt of the stronger acid plus the weak acid (see solution to question 8 on this year's exam), and

(4) Acids react with indicators to change their colour. (This is really just a special example of reaction 3, because the indicator needs to be in the form of the salt of the indicator acid[1], and the indicator acid must be weaker than the acid being tested.)

An aqueous solution that reacts with magnesium ribbon to form hydrogen gas is likely to be an acid solution undergoing reaction (2) above. If you have learnt about the reactivity series of metals, you probably remember that it goes:

Potassium, sodium, calcium, magnesium, aluminium, zinc, iron, lead, [hydrogen], copper, mercury, silver, gold

Most reactive ⟵⟶ Least reactive

(The list you have learnt might contain slightly different metals, but it will probably be very similar to this.)

Hydrogen is listed amongst the metals, because the more reactive metals (potassium through lead) will displace it from acids, whilst the less reactive metals (copper through gold) will not. **Very** reactive metals such as potassium and sodium will react violently with acids, so it is not too good an idea to use them for testing for acids in the school laboratory![2] Less reactive "reactive" metals are not used either, because they tend to react too slowly, and lead barely reacts at all (largely because the salts produced in the reactions with most acids are water insoluble, so the acid is blocked from reaching the lead). Magnesium is "just right" for use as a testing material.

The question now becomes "Which of the substances given will produce an acid solution when dissolved in water?" so that the acid solution will react with magnesium to give hydrogen. None of them are actually acids as such. The first four of the substances given are salts, and the fifth is ammonia solution (which is a weak alkali i.e. a base).

---

[1] Do not allow yourself to become confused! The salt of an indicator acid is often called the "base" form of the indicator. This is because the anion of the salt is a base according to the Brønsted-Lowry theory. It is the complete salt (anion + cation) that you need to consider here.

[2] Even water reacts like an acid with very reactive metals, to produce hydrogen, e.g.

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

Using potassium, sodium, or even calcium, will therefore not work when testing aqueous solutions for acidity (see also solution to question 24).

Salts can be hydrolysed to give acidic (or alkaline) solutions, and you possibly know how to determine what the pH of a salt solution is, given the right kind of data. You are not, however, given any data, so you need to know how to work out whether the solution is likely to be acidic or alkaline from your general chemical knowledge. (You won't be able to say for sure exactly what the pH will be.) What you need to know is which acid and which base will react to form a particular salt (cf reaction (1) above), and whether they are strong or weak. If a strong acid reacts with a strong base then the salt is likely to give a neutral solution (pH ≈ 7). A weak acid with a weak base is also likely to give a solution with pH ≈ 7. If a strong acid reacts with a weak base then the pH will be < 7, and if a weak acid reacts with a strong base then the pH will be > 7.

Now let us consider each of the suggested substances in turn:

A. LiCl

Lithium chloride can be produced by reacting lithium hydroxide (or oxide) with hydrochloric acid, thus:

$$LiOH + HCl \rightarrow LiCl + H_2O$$

$$(\text{ or } Li_2O + 2HCl \rightarrow 2LiCl + H_2O)$$

Note that I am omitting state symbols in the equations given in this section as they are not relevant to the logic here.

Lithium is an alkali metal (it is in Group I of the Periodic table) and so its hydroxide is a strong base. Hydrochloric acid is a strong acid, as are all the hydrohalic acids[3] (except hydrofluoric acid). Lithium chloride can therefore be expected to dissolve in water to give a neutral solution. So the answer to this question cannot be A.

B. NaBr

Sodium bromide can be produced by reacting sodium hydroxide (or oxide) with hydrobromic acid, thus:

$$NaOH + HBr \rightarrow NaBr + H_2O$$

Like lithium, sodium is an alkali metal so its hydroxide is a strong base. Hydrobromic acid is a hydrohalic acid so it is a strong acid. Sodium bromide can therefore be expected to dissolve in water to give a neutral solution, so the answer to this question cannot be B.

C. KI

Potassium iodide can be produced by reacting potassium hydroxide (or oxide) with hydroiodic acid, thus:

$$KOH + HI \rightarrow KI + H_2O$$

Potassium is an alkali metal so its hydroxide is a strong base. Hydroiodic acid is a hydrohalic acid so it is a strong acid. Poatssium iodide can therefore be expected to dissolve in water to give a neutral solution, so the answer to this question cannot be C.

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[3] A hydrohalic acid is formed when binary compound containing hydrogen and a halogen is dissolved in water. And a halogen is an element in Group 7 (IUPAC 17) of the Periodic Table.

D. NH_4Cl

Ammonium chloride can be produced by reacting ammonium hydroxide (ammonia solution) with hydrochloric acid, thus:

$$NH_4OH(aq) + HCl(aq) \rightarrow NH_4Cl\ (aq) + H_2O(l)$$

Ammonium hydroxide is a weak alkali ($pK_b = 4.8$), whilst hydrochloric acid is a strong acid, so that a solution of ammonium chloride is acidic. It will therefore react with magnesium to give hydrogen, so the answer to this question is **D**.

It should be noted that this equation, which we often use in high school, is probably incorrect because molecules of ammonium hydroxide do not really exist. Instead, when ammonia gas is dissolved in water it forms hydrated species, such as $NH_3 \bullet H_2O$, $NH_3 \bullet 2H_2O$ etc. in which molecules of ammonia are linked with molecules of water by means of hydrogen bonds. These hydrated species exist in equilibrium with ammonium ions and hydroxide ions, for example:

$$NH_3 \bullet H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \ldots\ldots\ldots\ldots(1)$$

This equilibrium lies well to the left hand side, and the equilibrium constant is just the same as that given for ammonium hydroxide.

The neautralization equation for producing ammonium chloride is therefore better written as:

$$NH_3 \bullet H_2O(aq) + HCl(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$$

The following equation is also used sometimes, although water is not shown as a product in this case:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

When ammonium chloride hydrolyses, a series of reactions can be considered to occur. First of all the ammonium chloride itself dissociates into ammonium ions and chloride ions:

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq) \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

The water itself is, of course, partially ionized, thus:

$$H_2O(l) \rightleftharpoons H^+\ (aq) + OH^-(aq) \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

The ammonium ions then meet up with some of the hydroxide ions and “ammonium hydroxide” or, better, ammonia hydrate is formed, reversing reaction (1), thus:

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3 \bullet H_2O(aq) \ldots\ldots\ldots(4)$$

The hydroxide ion concentration in the mixture is therefore significantly reduced, stressing the equilibrium shown in (3), so that more hydrogen ions are needed to maintain the balance. It is this excess of hydrogen ions that cause the solution to be acidic.

The acidic properties of ammonium chloride are exploited in its use in cleaning metals before electroplating them or coating them with other metals e.g. in tinning where an object is coated by dipping it in molten tin. The ammonium chloride presumably removes the layer of oxide in an acid-base reaction (the oxide would reduce the adhesion of metal on metal). Ammonium chloride has a similar use as a flux, which means it is added to a molten metal before it is used to coat another metal, e.g. ammonium chloride flux is added to molten zinc before an iron object is dipped into the zinc to galvanize it (coat it with zinc). In this case the ammonium chloride will prevent the formation of an oxide layer in the first place.

E. NH_3 (aq)

This is aqueous ammonia solution, which is essentially the solution of hydrated species that we have just been discussing, and it is, of course, a weak alkali, so it will not react with magnesium, and the answer to the question is not E.

It is not unknown for alkalis to react with metals. For example aluminum reacts with aqueous solutions of strong alkalis such as sodium hydroxide, to give hydrogen, thus:

$$2Al(s) + 2NaOH(aq) + 2H_2O(l) \rightarrow 2NaAlO_2(aq) + 3H_2(g)$$

This sort of reaction only takes place between strong alkalis and weak, amphoteric, metals. So ammonia solution would not be involved, nor would magnesium metal.

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17. Teachers predicted that this question would be done the best of any in the examination, and, indeed it was well done in most provinces. Was it too easy?

A catalyst can be defined as a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. If one assumes that the reactants and the products are exactly the same in the catalyzed reaction as in the uncatalyzed reaction (i.e. that their temperature, pressure and physical states are the same) then their enthalpy levels will be the same in both cases, and the catalyzed and uncatalyzed reactions will have the same enthalpy change. (This means that A, C and D can be eliminated as possible answers.)

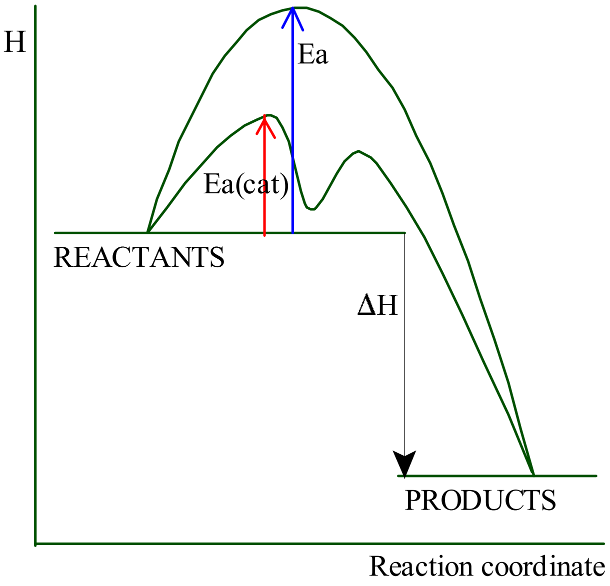
The activation energy is the energy barrier that has to be surmounted in order for the reaction to take place. A catalyst works by providing a lower energy barrier than that of the uncatalyzed reaction. The reactant particles will have the same distribution of energies in both cases, but more of them will have sufficient energy to overcome the barrier if that barrier is lower. This means that more particles react in a given time, i.e. the rate of reaction is faster.

The diagram on the next page shows how the enthalpy (H) might change during the course of an exothermic reaction. During the course of the reaction the reactants (which have a specific enthalpy) turn into the products (which have a different enthalpy). The enthalpy of the products is lower than that of the reactants because the reaction is exothermic. Note that the enthalpies of the reactants and products are not known in absolute terms, so that no values are shown on the "H" axis. Note also that the enthalpy change is the same whether the reaction is catalyzed or uncatalyzed (and can usually be measured).

It is plausible to say that the activation energy is decreased by the catalyst, which means that the answer to the question is **B**. However, one of the teachers who did the exam with his/her class, pointed out that is it is not, strictly speaking, correct to say that the catalyst decreases the activation energy of the reaction. The catalyst actually changes the way in which the reaction proceeds, so that the reaction profiles are different in the catalyzed and uncatalyzed reactions. Very often a catalyst forms an unstable intermediate with one of the reactants, which then reacts with another reagent to give the products. The reaction profile for the kind of reaction appears "bumpy", but even the biggest of the bumps is lower than the bump of the uncatalysed reaction. (The diagram on the next page shows just one bump for the catalyzed reaction, but it is possible to have a whole series of them.) The activation energy for the uncatalyzed reaction, Ea, is thus lower than that for the uncatalyzed reaction, Ea(cat).

Notice that the formation of an intermediate means that the catalyst has undergone a chemical reaction, but it is changed back into its original chemical form by the end of the reaction. This is why we are very careful to say in our difinition that it does not itself undergo any **permanent** chemical change during the course of the reaction.

Diagram showing the differences in energy profiles between a catalyzed and an uncatalyzed reaction



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18. The first ionization energy can be defined as the enthalpy increase that occurs when one mole of electrons is removed from one mole of atoms in the gas state to form one mole of gaseous ions each with a single positive charge, under standard conditions. Thus for atoms of element "X" the first ionization enthalpy is the enthalpy change for the reaction:

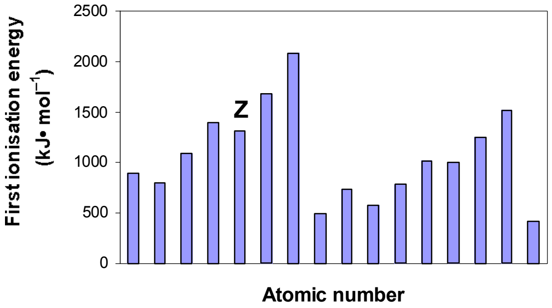
$$X(g) \rightarrow X^{+}(g) + e^{-}$$

This definition is somewhat cumbersome to use in explanations of ionization energy values, so we shall just consider what is happening with one atom losing one electron. Scaling up to mole amounts simply means that the effect is more easily measurable.

The values of first ionization energies are generally lower for larger elements than for smaller elements, because the electron that is removed is on the outer part of the atom. In a larger atom this will be a greater distance from the nucleus, so the attractive force of the nucleus will be less: there will also be more shells of electrons between the nucleus and the electrons in the outer part of the atom, and this reduces the attraction still more.

First ionization energies for elements in the same period of the Periodic Table do not, however, increase with atomic number. The atoms actually shrink in size going from left to right of a period, as more electrons are placed in the same outer shell, whilst more protons are placed in the nucleus, effectively increasing the attractive force of the nucleus. Removing electrons generally becomes more difficult as the atoms decrease in size, so the first ionization energy increases across the period. The increase is not, however, smooth across the period, due to the effect of electron configurations in the outer shell. It is most difficult to take on electron away from a stable configuration, in particular from the noble gas configuration of s^2, p^6. A noble gas therefore has the highest first ionization energy of its period. The s^2 arrangement (found in Group 2 elements) also has some stability, but its effect is not so pronounced. A minor effect is also found with a half-filled p orbital (p^3 configuration), which also has some stability. The opposite effect can be observed, however, when a stable configuration is formed **after** the electron has been removed: thus Group 1 elements have very low first ionization energies, because, once the s^1 electron has been removed, the ion has very stable configuration of the noble gas from the previous period.

When looking at ionization trend graphs like the one given in this question, the first thing you need to do is to check for a high ionization energy, followed immediately afterwards by a low ionization energy. Assuming that the elements are in order of consecutive atomic number (which is specified here) this means that you can identify the position of a noble gas element (the one with the high ionization energy) followed by a Group 1 element (the one with the low ionization energy). The element, Z, whose group you are trying to identify, is the 5th element along, but this does not mean that it is in Group 5, because the 7th element along has the highest ionization energy, and the next one after that has a very low value. The 7th element along must therefore be a noble gas, i.e. it is in Group 8 (IUPAC 18). Working back from that gives Z as being in Group 6 (IUPAC 16), so the answer to the question is **D**.



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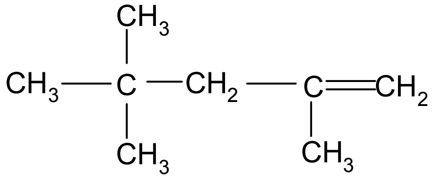
19. This question requires you to find the systematic IUPAC name for the following compound:



$CH_3-C(CH_3)_2-CH_2-C(CH_3)=CH_2$

In order to establish the name you need to work through a set of nomenclature rules [4].

Rule 1: Determine the principal group in your compound. When a compound contains more than one kind of functional group, the principal group is that which has the highest precedence. This characteristic group will be cited as suffix; all other groups are cited as prefixes.

In this case, the principal group is a carbon-carbon double bond.

Rule 2: Determine the parent hydrocarbon. If the principal group occurs in a chain (as in our case), the principal chain is selected as the longest chain containing the functional group of the highest seniority.

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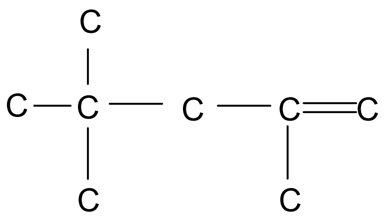
[4] These rules were kindly provided by Dr. S. Skonieczny, University of Toronto, Chemistry Department.

The carbon skeleton for the compound you are given is:



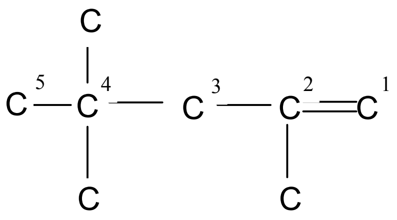
This is an easy example in which to determine the longest chain, because it does not matter whether you simply look at the horizontal line of 5 carbons, or substitute one (or two) carbons at the chain end. (The longest chain is often one that "bends around", you cannot assume that the carbons you want will be drawn in a straight line.)

Check that both carbon atoms bonded by a carbon-carbon double bond are included in parent hydrocarbon. They are, so the parent hydrocarbon must be pentane.

Rule 3: Name the parent structure and the principal group(s). Give the parent the same stem name as an alkane, but replace -*ane* with the suffix characteristic of the functional group of the highest priority
In this case, the suffix is –*ene*, so the main part of the name is pent*ene*.

Rule 4: Number the carbon atoms consecutively from the end of the chain nearer the functional group of the highest priority.

In this compound we need to start numbering the longest chain from the right hand side (rather than the left hand side, which might seem more natural), because the double bond is at that end. The double bond comes between carbons 1 and 2 (not 4 and 5), thus:



In order to maintain the lowest possible number in the name of this compound, we refer to the "ene" as being on number 1 carbon. We now know that we have a name that involves "1–pentene" (sometimes written as pent–1–ene).

Note that the actual name of the compound is NOT 1–pentene, because there are a total of 8 carbon atoms in the molecule.

Rule 5: Name alkyl groups, halides and other substituents and determine their position on the chain by the numbering established by Rule 4.

In our example we have: 2-methyl, 4-methyl, and 4-methyl.

Rule 6: Assign the stereochemistry to chiral cabon atoms (stereocenters) and the double bond(s).

This rule is not applicable in this case because our compound is not a stereoisomer.

Rule 7: Write the complete name of the compound as a single word with the correct locants for all substituents, which are listed in alphabetical order.

a) If a substituent appears more than once, multiplicative prefixes are used (di-, tri-, tetra-, etc.).
b) The prefixes di-, tri-, tetra-, etc., do not alter the alphabetical ordering of substituents.
c) The numbers indicating the locations of branches are separated by commas.
d) The letters and numbers are joined by hyphens.

The name of the compound is thus 2, 4, 4–trimethyl–1–pentene (or 2,4,4-trimethylpent-1-ene). So the answer to this question is **D**.

The common name for this compound is diisobutylene, and, when I was researching information about it on the web, I found several sites where the systematic name was given incorrectly!

In this question you are told that this compound is used as an additive in gasoline to improve its octane value. The octane value (or octane number) of a gasoline mixture is a measure of the fuel's ability to resist engine knocking. Knocking is a pinging sound that occurs when unburnt gasoline vapours explode spontaneously before the flame from the spark plug reaches them. This gives a double explosion, and results in a reduction of power and can cause engine damage.

The different compounds in a gasoline mixture have different octane numbers (these correlate fairly well with the volatility of the compounds). Different isomers can have very different octane values, for example the isooctane (2,2,4–trimethylpentane) has an octane number of 100, whilst normal octane has a value less than zero. The octane number of a particular fuel is the percentage of 2,2,4–trimethylpentane in a mixture of 2,2,4–trimethylpentane (octane number = 100) and normal heptane (octane number = 0) which knocks at the same compression ratio as the fuel.

The untreated gasoline fraction obtained from petroleum distillation has an octane number of about 70. However, regular grade gasoline from the pump has an octane number of about 87, whilst premium grade as on octane number of about 93. The increase in octane number is achieved by blending additives into the "straight run" gasoline. It is not, however, practical just to add more 2,2,4–trimethylpentane into the mixture.

A number of additives have been found effective in increasing the octane number. The classic additive used to be tetraethyl lead, however this resulted in toxic emissions of lead compounds, and it also poisons the catalyst used in the converter that is now used in cars to ensure complete combustion of the gasoline. Nowadays other high octane compounds are added, for example shorter-chain alkanes, more branched-chain alkanes, aromatic hydrocarbons, alcohols, ethers and alkenes, but some of these also have disadvantages, and their use is becoming increasingly restricted. For example, the use of highly volatile fuels (which tend to have high octane values) is becoming increasingly restricted due to toxicity and flammability issues. For these reasons the use of alkenes, including 2, 4, 4–trimethyl–1–pentene[5], is now being controlled in California. The use of the ether 2–methoxy–2–methylpropane (MTBE) is also restricted, because it is toxic and water soluble so it can pollute water supplies. However, other oxygenated compounds (especially alcohols) look more promising, and they also have the added advantage of assisting the complete combustion of the fuel.

Even if 2, 4, 4–trimethyl–1–pentene is no longer going to be used as an antiknocking agent in gasoline, it is likely still be used for other purposes, especially in making paints and resins and as a solvent in the production of rubber chemicals.

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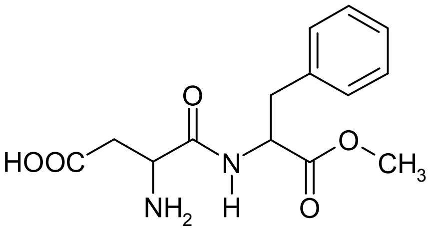
[5] The octane value of 2, 4, 4–trimethyl–1–pentene on its own is 86, but it can give very high octane values (up to 153) when it is combined with other materials in a blend.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2004 continued

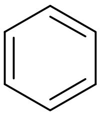
Questions 20 and 21 refer to aspartame, which is used as a sweetener in diet drinks. Its structural formula is given as:



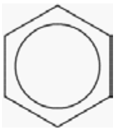
It is perhaps interesting to note that this is another formula which was incorrectly given on the web – this time on several, apparently reliable, websites. It just goes to show that you have to be very careful when using the web!

20. This question was generally well done, and it was the question that was done the best of all in the exam by the Alberta cohort of candidates.

In this question you need to find the number of carbon atoms in aspartame. The structural formula that you are given uses two different systems to represent carbon atoms. Some are clearly shown with the "C" symbol, but others are just shown as a bend in a zig-zag line. You will probably be used to seeing benzene written just as a hexagon with double bonds, thus:

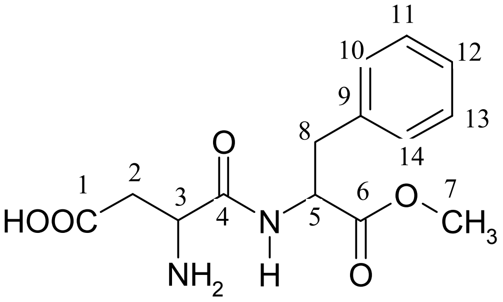


or as a hexagon with a ring inside it:



Both these diagrams are used to represent the C_6H_6 molecule, and, in both of them, each corner of the hexagon represents a carbon atom. In addition, with this kind of formula every carbon atom is taken to have sufficient hydrogen atoms attached to it to make up its valency of four. These hydrogen atoms are not shown, although atoms other than carbon or hydrogen are shown.

Looking at the aspartame molecule again we can now count the carbon atoms, both those indicated by a symbol and those indicated by a bend in a line (or corner of a ring), thus:



We can now see that aspartame has 14 carbon atoms, so the answer to this question is **C**.

You might like to see if you work out where all the hydrogen atoms are on this molecule – some of them are indicated by the H symbol, and some are implied on "corner" carbons. (The molecular formula is $C_{14}H_{18}N_2O_5$.)

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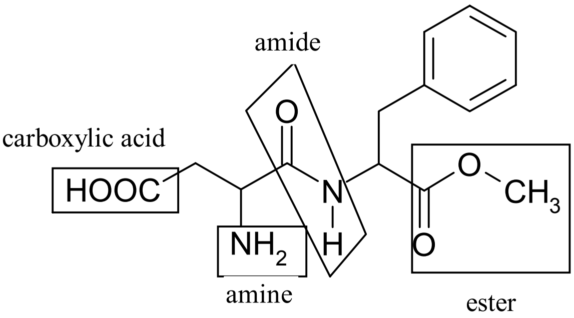
21. This question also refers to the aspartame molecule. This time you have to identify the functional groups in the molecule. There are, in fact, four functional groups[1], although the suggested answer only requires you to identify three of them. The four groups are amide, amine, carboxylic acid and ester. They are outlined on the formula below:



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

Note that the amide group was not included in this question as it is an *N*–substituted amide[2], so it looks a bit different from the $-CONH_2$ group you may have learnt. (The structures of some organic funtional groups that it would be useful for you to learn are given in the answer to Question 6 of the 2002 NHSCE.)

As usual, the suggested answer to this question included some traps for the unwary. You might have thought that the C=O group in the ester or the amide was a ketone group, but note that the carbon on theC=O is not connected to two other carbons, as is needed for a ketone. You might also have thought that the OH of the COOH was an alcohol group, which it is not. You need to be aware that whenever more than one group is attached to a single carbon atom then the groups will influence each other's reactions, and so the combination is considered to be a distinct functional group in its own right.

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[1] This excludes the benzene ring (also referred to as a phenyl group or an aromatic ring) which is also considered to be a functional group even though it is part of the carbon skeleton.

[2] In biochemistry this is also known as a peptide link. It is the characteristic link that joins amino acids, and it is found in polypeptides and proteins. The aspartame molecule is actually the methyl ester of a dipeptide formed between phenylalanine and aspartic acid.

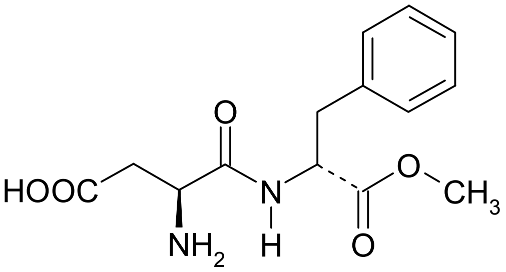
If you look carefully at the structural formula given for you to use in questions 20 and 21, you may be able to see that the molecule has two stereocentres [3] in it, i.e. carbon atoms that are attached to four different atoms or groups of atoms. (These are at carbons 3 and 5 according to the numbered diagram given above in the solution to Question 20.) This means that the molecule can form stereoisomers. However it should be noted that the structure is not drawn in such a way that you can tell exactly what the stereochemistry of the molecule is.

Various semi-systematic names have been suggested for aspartame, e.g. *N*–L–α–aspartyl–L–phenylalanine 1–methyl ester[4], but none of them are very satisfactory. The best name for the structure actually shown is probably:

3–amino–3–[N–(1–methoxycarbonyl–2–phenyl)ethyl]aminocarbonylpropanoic acid.

Note that this name does not include any stereochemical notation such as "α" and "L" .

The structure for aspartame that indicates its stereochemistry is:



The systematic name for this structure is

(*S*)-3-amino-3-[N-(*S*)-(1-methoxycarbonyl-2-phenyl)ethyl]aminocarbonylpropanoic acid.[5]

Some common names for aspartame are APM, SC-18862, Canderel™, Equal™, and NutraSweet™.

Aspartame acts as a sweetener because the molecule can arrange itself into a configuration that allows two of the oxygen atoms to fit into the receptors of the taste buds that react to sweetness. It is about 180 times more effective than sucrose at doing this, which means that you need a much smaller mass of it to be effective, which means a big reduction in calories – an important consideration for weight watchers. These stereoisomers have the same structural formula as that shown in this question, but the atoms are arranged differently in space. The stereoisomers will affect the taste buds differently, and at least one of them has a bitter taste.

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[3] Stereocentres are often referred to as "chiral centres" in textbooks, but this is confusing as it implies that the molecule overall will be chiral (i.e. that a mirror image of the molecule can exist), which is not necessarily the case.

[4] See The Merck Index, Twelfth Edition.

[5] This name uses the Cahn-Ingold-Prelog (*R* , *S*) convention for describing the arrangement of groups attached around a stereocentre. The Rosanoff (D, L) convention is a different system that is still widely used, particularly in carbohydrate chemistry. The α and β designations are generally used to indicate whether a substituent on a ring is in an axial or equatorial position relative to the ring. None of these terms are required knowledge for the NHSCE.

There is some evidence that aspartame is unsafe to use as a sweetener, because it appears to be toxic to some people. This may be because the breakdown products of its metabolism in the body are poisonous, or because the aspartame is contaminated by one of its stereoisomers, which may be toxic.

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22. This question requires you to balance the equation for the reaction between iodine and sodium hydroxide (in hot concentrated solution). The reaction is a disproportionation reaction, which you are told is a reaction in which one of the elements is both oxidized and reduced. You could probably solve the problem just by fiddling around with the numbers, but it is more reliable to work through it systematically, using the oxidation number method.

Let us first consider the equation with all the stoichiometric coefficients removed:

$$I_2(s) + NaOH(aq) \rightarrow NaIO_3(aq) + NaI(aq) + H_2O(l)$$

We need to work out the oxidation numbers of all the elements in all the species shown in this equation.

Looking at the left hand side of the equation:

I_2	Iodine is present in its elemental form, so its oxidation number is 0.
NaOH	Sodium is in the +1 state, oxygen is in the –2 state and hydrogen is in the +1 state (these are the usual states for these elements)

On the right hand side of the equation we have:

$NaIO_3$	Sodium is in the +1 state, and each of the three oxygens are in the –2 state, so the iodine must be in the +5 state to give a neutral compound.
NaI	Sodium is in the +1 state, so that iodine must be in its –1 state to give a neutral compound.

(It should now be fairly easy to see how the redox process is going to go, but to complete the exercise we can say that:

H_2O	Each of the two hydrogens are in the +1 state, and the oxygen is in the –2 state.)

Clearly it is the iodine that is going to be both oxidised and reduced in this reaction.

Iodine is oxidized from the 0 state in I_2 to the +5 state in $NaIO_3$. This is an increase of 5 oxidation numbers.

On the other hand, iodine is reduced from the 0 state in I_2 to the –1 state in NaI. This is a decrease of one oxidation number.

In order for the increase and the decrease to equalize each other we are going to need 5 iodine atoms to be reduced for each iodine atom that is oxidized. We are therefore going to require a total of six iodine atoms i.e. three I_2 molecules.

And there will be one $NaIO_3$ produced from the one iodine that is oxidized, and five NaI formulae from the five iodine atoms that are reduced.

The equation has now become:

$$3I_2(s) + ?NaOH(aq) \rightarrow NaIO_3(aq) + 5NaI(aq) + ?H_2O(l)$$

This has actually given you the two stoichiometric coefficients that you need to answer this question. The stoichiometric coefficient for $NaIO_3$ (given as **p** in the question) is 1, and the stoichiometric coefficient for NaI (**q** in the question) is 5. The answer to this question is therefore **E**.

If you need to find the rest of the stoichiometric coefficients this can be done in the usual way. With six Na atoms established on the right hand side of the equation you can see that will need six NaOH formulae on the left hand side. Now you have six O atoms on the left and three on the right so you need three more on the right, giving you three H_2O molecules. (You are told that the stoichiometric coefficients for I_2 and H_2O are the both "a", so this agrees.) Finally, checking the H atoms you can see that you have six on either side of the equation. The completely balanced equation is therefore:

$$3I_2(s) + 6NaOH(aq) \rightarrow NaIO_3(aq) + 5NaI(aq) + 3H_2O(l)$$

Disproportionation reactions such as this one are fairly common with elements that have several oxidation states. Oxidation states have different stabilities, and reactions tend to occur when the combined stability of the product oxidation states is greater than that of the original state.

Reactions that are essentially the opposite of disproportionation can also occur. Again the reactions are driven by differences in stability of the different oxidation states, but in this case the reactions involve combining two different oxidation states of an element into a single state. These reactions are called comproportionation (or symproportionation) reactions. An example of a comproportionation reaction is used in the Claus process for the production of sulfur from sulfur dioxide and hydrogen sulfide, thus:

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

(In this reaction the sulfur is in the +4 state in SO_2, the –2 state in H_2S and in the 0 state in S.)

This process provides a good way of using the hydrogen sulfide that contaminates natural gas, and the sulfur dioxide that pollutes stack gases from burning coal. The sulfur produced can be converted to sulfuric acid – an important industrial chemical with many different uses.

23. This question is about bond enthalpies and requires you to know the definition of bond enthalpy term or bond energy, <*D*>. The size of this value indicates the strength of a covalent bond, and may be defined as the **average** enthalpy change that accompanies the homolytic dissociation[6] of one mole of that type of bond to give individual atoms. The value of the bond enthalpy term is an average of the values obtained in a number of different compounds or species, under standard conditions of temperature and pressure.

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[6] Homolytic dissociation of a bond occurs when a covalent bond breaks apart in such a way that the two electrons in the bond split up, leaving one electron with each of the atoms that were originally bonded together. The species that are formed in the dissociation may be individual atoms or free radicals, i.e the unpaired electron can be on a single atom or on a group of atoms. The opposite of homolytic dissociation is heterolytic dissociation in which both electrons in the bond stay with one of the atoms, making it a negative ion, whilst the species on the other side of the bond becomes a positive ion. Homolytic fission is more usual where the electronegativities of the atoms are similar: heterolytic fission is more common where the electronegativities of the atoms are substantially different, i.e. when the covalent bond is polarized.

The bond enthalpy term can be measured in various ways, depending on whether the bond is between two atoms of the same kind or between two different kinds of atoms, for example:

(a) for X–X bonds, the bond energy is the molar enthalpy change for the process $X_2(g) \rightarrow 2X(g)$

(b) for X–Y bonds, the bond energy is the molar enthalpy change for the process

$$1/n\ XY_n(g) \rightarrow 1/n\ X(g) + Y(g)$$

This second method is the one that applies to measurement ot the bond enthalpy of C–F bonds, in which case the equation may be written as:

$$1/4\ CF_4(g) \rightarrow 1/4\ C(g) + F(g);\ \langle D \rangle = +\ 485\ \text{kJ}\bullet\ \text{mol}^{-1}\ldots\ldots\ldots\ldots(1)$$

Now all the suggested answers to this question involve the decomposition of one mole of CF_4 molecules, rather than 1/4 of a mole, so we need to multiply equation (1) by 4 to give us

$$CF_4(g) \rightarrow C(g) + 4F(g);\ \Delta H = +\ 1940\ \text{kJ}\bullet\ \text{mol}^{-1}\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

After checking that the ΔH value obtained is the same as the value required, we can see that the answer to this question is **E**.

There are other ways of tackling this question, one of which is to consider the atomization enthalpy of tetrafluoromethane (CF_4). The standard atomization enthalpy of a compound is defined as the enthalpy change that occurs when one mole of the compound in its standard physical state is broken down into gas atoms under standard conditions. For tetrafluoromethane[7] this is reaction (2) shown above. This atomization can be considered to take place in a series of steps as follows:

$$CF_4(g) \rightarrow CF_3(g) + F(g)\ ;\ D_1$$

$$CF_3(g) \rightarrow CF_2(g) + F(g)\ ;\ D_2$$

$$CF_2(g) \rightarrow CF(g) + F(g)\ ;\ D_3$$

$$CF(g) \rightarrow C(g) + F(g)\ ;\ D_4$$

Note that in each step of the reaction a C–F bond is being broken, and that the fission is homolytic. Species such as CF_3, that have odd unpaired electrons on them like this are as free radicals.

The values D_1, D_2, D_3 and D_4 are the bond dissociation enthalpies[8] for each of the steps of the reaction. They have slightly different values because each of the C–F bonds being broken are in different chemical environments. The

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[7] Tetrafluoromethane is a gas in the standard state, but you did not need to know this in order to be able to work out the answer to this question.

[8] The bond dissociation enthalpy (or energy), is defined as the enthalpy change that accompanies the homolytic breaking of one mole of a **particular bond** in a covalently bonded species, to give individual atoms and/or radicals, with both the original species and the resulting fragments being in their standard states and at standard temperature and pressure. The bond dissociation enthalpy will be identical to the bond enthalpy term for X_2 molecules, but the two values can vary considerably where the bond dissociation enthalpy is measured in more complex species.

bond enthalpy term, <*D*>, is the average value of these four dissociation enthalpies. The sum of these four values is the enthalpy change of atomization given in equation (2), so that the bond enthalpy term is
(+ 1940 kJ• mol^{-1})/4 = 485 kJ• mol^{-1}.

The incorrect answers that are suggested in this question are based on some possible mistakes that students might make in defining the enthalpy change of atomization, in particular you should remember that the products of the atomization reaction are NOT elements in their standard states, but atoms in the gas state. The enthalpy change of atomization is NOT the reverse of the enthalpy change of formation.

24. This question was done the worst of any in the exam, largely becauses it covers a topic that is largely not taught in high schools throughout the country, despite being on the Pan-Canadian protocol. Please note, however, that redox chemistry, including electrochemistry and electrolysis will continue to be included in the exam. It is not intended to make the questions on these topics excessively difficult, so that it should be possible for students to prepare for the exam by independent study.

    The idea for the question came from the Chemical Society of Japan who run a miniature car race for school students (elementary, junior high and senior high). The students have to make their own batteries for their car and the group whose car goes the furthest wins. The students are supplied with a pencil lead (carbon graphite) and cooking foil (aluminum) to make the electrodes, plus a variety of electrolytes. I have not been able to establish which electrolytes they are actually provided with for the competition, but I feel that it is a safe bet that sodium chloride is one of them. If you were going to participate in a competition like this, it would be a good idea to start by looking at what you might expect in the way of a maximum voltage from the various materials supplied.

    In order to make a working electrochemical cell you need to combine two half reactions. The e.m.f. values for half reactions shown in tables are usually shown as standard **reduction** potentials, i.e. where the oxidation number of the atoms or ions are being reduced. Note that these values refer to measurements made under standard conditions of 298K, 1 atm pressure and concentrations of mol•kg^{-1} (usually taken as mol•L^{-1} in practice). The e.m.f. (electromotive force)[9] or potential difference of the cell is calculated by taking the standard reduction potential of the cathode (where **reduction** actually occurs) and subtracting from it the standard reduction potential of the anode (where **oxidation** occurs) [10]. The e.m.f. obtained when the two half-cells are combined must be positive if the reaction is to be spontaneous.

    All the values given in this question are for aqueous solutions, so the sodium chloride must be dissolved in water if it is to be used as an electrolyte here. One person wrote in to criticize the fact that we had an e.m.f. value for the reduction of hydrogen ions in the data given, when there was no acid in the list of materials supplied. Whilst it is true that no acid was given, a low concentration of hydrogen ions would be present in the water, and it is important to remember this when doing this type of question (see on for a more detailed discussion of this).

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[9] The e.m.f. is the largest potential difference that can be obtained with a particular pair of half reactions, and it is only obtained when the cell is not connected up. When the cell is connected (working) its potential will be smaller than the e.m.f. value.

[10] It does not matter if you have a spontaneous system (i.e. one that is producing electricity) or a forced reaction (as in electrolysis), the way in which the e.m.f. of the cell is calculated from the standard reduction potentials of the half reactions is always the same, $\Delta E^{\ominus} = E^{\ominus}$ (cathode) – $E^{\ominus}$ (anode).

Using the standard reduction potentials given we can draw up a table as follows:

Reduction half-reactions	Standard **reduction** potential	Corresponding oxidation half-reactions
$Na^+(aq) + e^- \longrightarrow Na(s)$	$E^\ominus_{red} = -2.71$ V	$Na(s) \longrightarrow Na^+(aq) + e^-$
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	$E^\ominus_{red} = -1.66$ V	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	$E^\ominus_{red} = 0.00$ V	$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

On the face of it we get the largest positive e.m.f. value by combining the reduction half-reaction

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad E^\ominus_{red} = 0.00 \text{ V}$$

with the reverse of the following half-reaction (an oxidation)

$$Na^+(aq) + e^- \longrightarrow Na(s) \qquad E^\ominus_{red} = -2.71 \text{ V}$$

This would give an overall reaction of

$$2Na(s) + 2H^+(aq) \longrightarrow 2Na^+(aq) + H_2(g)$$

with an e.m.f. value of

$$0.00 \text{ V} - (-2.71 \text{ V}) = +2.71 \text{ V}$$ [11]

The most obvious snag with this is that we are not, in fact, given any sodium metal in our list of materials, so this reaction cannot possibly apply here. Another difficulty is that the sodium would react vigorously (even violently) with the hydrogen ions provided by water present or in an aqeuous solution, whether or not it is connected up in a cell (or working), so that it would not be much use as an electrode (c.f. the solution to question 16).

This brings us to the second best combination of half reactions, namely the reduction half-reaction

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad E^\ominus_{red} = 0.00 \text{ V}$$

combined with the reverse of the following half-reaction (oxidation)

$$Al^{3+}(aq) + 3e^- \longrightarrow Al(s) \quad E^\ominus_{red} = -1.66 \text{ V}$$

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[11] See also Footnote 10. Note also that the number of moles of reactants and products shown in the equation does NOT affect the size of the e.m.f. value generated by the cell. The amounts of substances used in the cell will, however, affect the length of time that the cell will produce electricity before the limiting reagent is all used up.

to give the overall reaction of

$$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$$

with an e.m.f. value of

$$0.00\ V – (– 1.66\ V) = + 1.66\ V$$

Aluminum **is** one of the materials provided, and it does not react with water (under standard conditions), so that this is a valid combination of half reactions, and therefore the answer to this question is **D**.

Note that the substance (solute) dissolved in the water does not affect the value of the e.m.f. in this problem. The solute simply has to provide ions that can carry the charge to and from the electrodes. In practice, however, the electrolyte can affect the resistance of the cell, so that the working potential may be very different with different solutes. The way to determine the best battery for the car race may well have to be determined by trial and error, and the race itself is likely to be won by the team that manages to build the best rig for its battery to ride on.

We shall now return to considering the question of the hydrogen ions in the aqueous solution. These are provided by the autodissociation of water molecules thus:

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

Although the concentration of hydrogen ions in water is very low under standard conditions (1.00 x 10^{-7} mol•L^{-1}), we can see that any hydrogen ion that reacts will be immediately replaced by the dissociation of a water molecule in order for the equilibrium to be maintained (according to Le Chatelier’s principle).

Looking at a list of standard reduction potentials for the ions of reactive metals (which we can now define as metal ions with a negative standard reduction potential), it is really quite difficult to determine which metals are likely to react with water (with its hydrogen ion concentration of 1.00 x 10^{-7} mol•L^{-1}) or which ones need a higher concentration of hydrogen ions (1.00 mol•L^{-1} for a standard hydrogen ion solution, i.e. an acid). The situation is complicated by the fact that many reactive metals react with oxygen in the air to give a protective oxide layer, and, if this oxide is water-insoluble and adhers reasonably well to the metal, then the metal will not react with water, but it may react with acid because its oxide will be removed by reaction with the acid. The best we can say is that metal ions with standard reduction potentials that are more negative than about – 2 V, will belong to metals that react with water. Metal ions with reduction potentials between about 0 and – 1 V, will belong to metals that react with acids but not with water. Between – 1 and – 2 V it is really not easy to make a prediction. It should be noted, however, that aluminium is one of the metals that has a protective oxide layer: aluminium does not dissolve in water, but it does dissolve in acid solutions. (Aluminium ions have a standard reduction potential of – 1.66 V as given above.) An acidic substance such as vinegar would probably not be an effective electrolyte to use in the car battery because the aluminium would undergo a short circuit reaction with the hydrogen ions rather than produce a flow of electrons around the external circuit.

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25. Although most students will have done the basic theory required for this question, there is a lot of scope for error in it, and it turned out to be the question that was the worst done of the whole exam in some provinces, with a more or less even spread of answers chosen amongst the five keys.

The reaction of ammonium thiocyanate with iron(III) solutions is often used to illustrate the principles of equilibrium, or as a system for which an equilibrium constant can be found, in the school laboratory. Few textbooks or lab manuals really explain what is going on in the system, and the experimental method often relies on a “black box” approach using a computer, with the students simply following instructions to get their results. The fact that the system takes place in a series of steps, however, means that the concentrations of the reagents must be strictly controlled in order to ensure that the reaction is limited to the first step. The colorimetric procedure is also tricky because both the iron(III) ions and the complex ion have a brownish colour in aqueous solutions, so a suitable wavelength for making the absorbance measurements is difficult to determine. (Iron(III) ions are yellowish-brown in aqueous solution, and the monothiocyanate iron(III) ions are reddish-brown.)

In this question, however, you are simply given the information you would have culled from doing the experiment in order to calculate the equilibrium constant, K_c. The reaction equation is given you as:

$$Fe^{3+}(aq) + CNS^{-}(aq \text{ or } s) \rightleftharpoons [Fe(CNS)]^{2+}(aq)$$

Note that this is an ionic equation. The anion that is associated with the iron(III) ions and the cation that is associated with the thiocyanate ions are spectator ions, which are there to ensure that the ions in the solution are electrically balanced. The spectator ions are also chosen to ensure that the reactants are water soluble, and that no precipitates occur when the reactants are mixed.

Note also that the equation shows that thiocyanate can be in aqueous solution or in the solid form for the reaction to occur, but only the aqueous solution is relevant to this question.

Using the stoichiometric equation you can write an expression for the equilibrium constant. This is:

$$K_c = \frac{[[Fe(CNS)]^{2+}(aq)]_{eqm}}{[Fe^{3+}(aq)]_{eqm} \times [CNS^{-}(aq)]_{eqm}}$$

Note that in this expression the numerator involves two sets of square brackets. The inner set, which is also shown in the stoichiometric equation, indicates that the species is a complex ion, the outer set is used to denote the concentration of the species whose formula is inside the brackets. Note that all the concentrations shown in the the expression are equilibrium concentrations, as indicated by the subscript "eqm".

The volumes and concentrations of the two solutions that are mixed at the beginning of the experiment are given to you, but these are not, of course, the equilibrium concentrations. It is important to note that you cannot use these concentrations directly for determining the equilibrium concentrations, because once they are mixed the volume they occupy changes to the total volume of the mixture. Mixing 45.00 mL of iron(III) solution with 5.00 mL of thiocyanate solution gives you a total of 50.00 mL of solution. The chemical amounts (moles) of the two reacting species are now spread out in a bigger volume, so there concentrations are less than before they were mixed. (In order to determine their starting concentrations you need to ignore the fact that they will react almost instantaneously when they are mixed.)

Determining the effective starting concentrations of the reactants is done using a two-step process involving (1) finding the chemical amount (moles) of the solute dissolved in the original volume of solution, then (2) using this chemical amount to determine the concentration of the solute in the larger volume of the combined reagents.

Both the steps involve manipulating the equation:

$c = n/V$ Where c is the concentration of the solution in $g{\bullet}L^{-1}$

n is the chemical amount of solute in mol

and V is the volume of solution in **litres** (L)

Thus for the iron(III) solution:

Step 1: n = cV The chemical amount of iron(III) $= (0.200 \text{ mol•L}^{-1} \text{ x } 45.00 \text{ mL})/1000 \text{ mL•L}^{-1}$
$= 0.0090 \text{ mol}$

Step 2: c = n/V The concentration of iron(III) in the combined solution
$= (0.0090 \text{ mol}/50.00 \text{ mL}) \text{ x } 1000 \text{ mL•L}^{-1}$
$= 0.1800 \text{ mol•L}^{-1}$

Similarly for the thiocyanate solution:

Step 1: The chemical amount of thiocyanate $= (0.00200 \text{ mol•L}^{-1} \text{ x } 5.00 \text{ mL})/1000 \text{ mL•L}^{-1}$
$= 0.0000100 \text{ mol}$

Step 2: The concentration of thiocyanate in the combined solution
$= (0.0000100 \text{ mol}/50.00 \text{ mL}) \text{ x } 1000 \text{ mL•L}^{-1}$
$= 0.000200 \text{ mol•L}^{-1}$

Note the great disparity between the concentrations of the two solutions – the iron(III) solution is 900 times more concentrated than the thiocyanate solution, making the thiocyanate the limiting reagent by a large margin. This is done to ensure that only the first complex of the series of complexes is formed, i.e. that only $[Fe(CNS)]^{2+}$ is formed, and that the reaction does not continue. If more thiocyanate were present then it would be possible for higher complexes such as $[Fe(CNS)_2]^+$ or $[Fe(CNS)3]^0$ to form. (Five complexes have in fact been observed between iron(III) and thiocyanate ions, but the higher ones have very small equilibrium constants.)

Now that we have the starting concentrations we can treat the calculation in the usual way, listing the values we are using under the formulae given in the equation, thus:

	$Fe^{3+}(aq)$	+	$CNS^{-}(aq)$	$\rightleftharpoons$	$[Fe(CNS)]^{2+}(aq)$
Starting conc.	$0.1800 \text{ mol•L}^{-1}$		$0.000200 \text{ mol•L}^{-1}$		0 mol•L^{-1}
Eqm. conc.	$(0.1800 - 1.99 \text{ x } 10^{-4}) \text{ mol•L}^{-1}$		$(0.000200 - 1.99 \text{ x } 10^{-4}) \text{ mol•L}^{-1}$		$1.99 \text{ x } 10^{-4} \text{ mol•L}^{-1}$ (given in the question)

Substituting the equilibrium concentration values into the expression for the equilibrium constant gives us:

$$K_c = \frac{1.99 \text{ x } 10^{-4} \text{ mol•L}^{-1}}{(0.1800 - 1.99 \text{ x } 10^{-4}) \text{ mol•L}^{-1} \text{ x } (0.000200 - 1.99 \text{ x } 10^{-4}) \text{ mol•L}^{-1}}$$

$$= \frac{1.99 \text{ x } 10^{-4} \text{ mol•L}^{-1}}{0.1798 \text{ mol•L}^{-1} \text{ x } (0.1000 - 10^{-6}) \text{ mol•L}^{-1}}$$

$$= 1107 \text{ (mol}^{-1}\text{•L)}$$

The answer to the question is therefore **E** ($1.1 \text{ x } 10^3$)

The data book value for this equilibrium constant[12] is 891 at standard temperature and pressure. Although we carefully did not specify the equilibrium temperature in this question, the values used were established by working backwards from this value of the equilibrium constant. The reason for the difference lies in the precision to which we are working. With the precision of the values given in the question, we can only really work to one significant figure, i.e. the answer should really be quoted as 1×10^3, which is in the same approximate order of magnitude as the data book value. We stretched the point by giving the results to two significant figures in order to make the result appear more meaningful.

The problem of significant figures was highlighted out by François Gauvin (University of Manitoba) in the design stage of the question. He pointed out that subtracting 1.99×10^{-4} from 0.000200 mol^{-1}•L (in the first part of the calculation of K_c), gives 1×10^{-6} mol^{-1}•L with ONE significant figure due to the subtraction. Since the latter value is used in the calculation of K_c, the latter should only have ONE figure, which does not look too good. To avoid this, we should adjust the volume of the original SCN^- solution to 5.000 mL, which would lead to a concentration of 0.002000 mol•L^{-1}. This level of precision is feasible for 5.000 mL pipettes. The final concentration of $[Fe(SCN)]^{2+}$ would also gain one figure to become 1.990×10^{-4}.mol•L^{-1}. All this would allow us to get the same value of the final concentration of SCN^- but now with 2 figures (1.0×10^{-6} mol•L^{-1}), and we could then quote a K_c value with 2 figures.

Dr. Gauvin kindly prepared tables that summarize these ideas (see below), but when we were writing this question we felt that the high precision pipettes required would rarely, if ever, be available in high school chemistry labs so we decided to compromise on this aspect of the question. It should, however, be born in mind that while we often overlook the details of precision when we are learning the basic principles of how to do a calculation at high school, precision is considered much more important in university courses.

BEFORE ADJUSTMENT OF SIGNIFICANT FIGURES:

mol•L^{-1}	Fe^{3+}(aq) +	CNS^-(aq or s) $\rightleftharpoons$	$[Fe(CNS)]^{2+}$(aq)
Initial	0.180	0.000200	0
Change	-0.000199	-0.000199	+0.000199
Equilibrium	$0.179\underline{801}$	0.000001	0.000199

Underlined figures are not significant. Equilibrium concentration of SCN^- counts only 1 figure. Since it is used in the calculation of K_c, the final result of K_c should not have more than one figure as well if we strictly apply the rules of significant figures.

AFTER ADJUSTMENT OF SIGNIFICANT FIGURES:

mol•L^{-1}	Fe^{3+}(aq) +	CNS^-(aq or s) $\rightleftharpoons$	$[Fe(CNS)]^{2+}$(aq)
Initial	0.180	0.0002000	0
Change	-0.0001990	-0.0001990	+0.0001990
Equilibrium	$0.179\underline{8010}$	0.0000010	0.0001990

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[12] The name given to equilibrium constants relating to complexes is "stability constant", and this is the term you need to use if you are looking up the values in a data book. However, some textbooks assign the term "stability constant" to the reverse reaction, whilst referring to the equilibrium constant of the forward reaction as the "formation constant". This second definition may make more sense, but I have not found it used in data books.

Underlined figures are still not significant, however the equilibrium concentration of SCN^{-} now has two significant figures (1.0 x 10^{-6} mol•L^{-1}). Since it is used in the calculation of K_c, the final result of K_c can also have two figures according to the rules, thus $K_c = 1.1 \times 10^{3}$.