ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2003

These answers are designed to help students who are preparing to take the Canadian National High School Chemistry Examination in 2004 or subsequent years. Note that information given here will generally not include material from the 2001 or 2002 answers, so that students should go through the 2001 and 2002 questions and answers before attempting the 2003 examination.

Students should attempt to do the questions in Part A of the 2003 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, and they discuss subjects arising from the questions, as well as how to work out the answers. They also contain tips about how to set about doing a multiple choice examination in general.

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

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.

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1. This question concerns the following WHMIS symbol:

Most students correctly identified this as being the symbol associated with a corrosive substance (Key **C**), although some weaker students chose Key A (acidic). It is important to remember that both acidic and alkaline substances are corrosive. In fact alkalis can sometimes be more dangerous than acids, particularly if they come in contact with the eyes.

Some teachers felt that this question was too easy for the National High School Chemistry Exam (in fact they identified it as being the easiest question) other teachers thought that the topic was not on the curriculum. WHMIS symbols are, in fact, on the Pan-Canadian protocol, although they may not have reached some provincial curricula or textbooks. I introduced a simple WHMIS question into the examination this year, as I intend to put some more advanced questions on the subject into future exams.

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2. Again some teachers felt that this question was somewhat easy (in fact students in general found it to be the easiest question on the exam). I was responding to requests for formulae and valencies to be included on the examination, but the question was kept simple by not requiring the student to provide the symbol of tin or the formula of sulfate. More questions on this topic can be expected in the future – and they may not be so easy!

The response to the question is determined as follows: the valency of tin in tin(IV) sulfate is +4 (from the name), and students should know that the sulfate radical has a valency of –2, so "cross-multiplying the valencies" to give a neutral compound gives $Sn_2(SO_4)_4$. Simplifying this gives $Sn(SO_4)_2$, which is Key C.

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3. This question is designed to emphasize the importance to students of their being able to work from experimental data. One hopes that they will have done this sort of experiment themselves in the laboratory.

Considering the original Epsom salts ($MgSO_4•7H_2O$):

Mass = (25.395 – 20.465) g = 4.930 g
Chemical amount = 4.930 g / 246.48 $g•mol^{-1}$ = 0.0200 mol.

(Remember that M_r means relative molar mass, which has no units [1]. The molar mass is numerically equal to this but has units of $g•mol^{-1}$.)

Each mole of Epsom salts contains one mole of $MgSO_4•7H_2O$, so 0.0200 mol of Epsom salts contains 0.0200 mol of $MgSO_4$.

Considering the residue: this will contain the same chemical amount of $MgSO_4$ as the original Epsom salts (but it will have a different amount of water in it).

The amount of $MgSO_4$ in the residue is therefore 0.0200 mol.

Considering the water lost on heating:

Mass = (25.395 –23.593) g = 1.802 g
Chemical amount = 1.802 g / 18.016 $g•mol^{-1}$ = 0.100 mol

The chemical amount of water lost per mole of $MgSO_4$ is therefore 0.1000 mol / 0.0200 mol

i.e. 5 mol of water are lost per mole of $MgSO_4$

Now as there were 7 mol of water per mole of $MgSO_4$ in the original Epsom salts, then 2 mol of water must remain **in the residue**, so the formula of the residue is $MgSO_4•\mathbf{2}H_2O$ and the correct answer is **B**.

Predictably, perhaps, some students forgot this last (essential) step in the calculation and gave the answer as D ($MgSO_4•\mathbf{5}H_2O$). It is always important to check with the original question before choosing a key.

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4. Students are expected to know how to determine oxidation states for the NHSCE, although some teachers say that they do not cover this until after the exam date. It is therefore intended that future questions on the topic will be fairly simple ones.

   It should be pointed out, however, that it can be very useful to know how to determine oxidation states, in contexts other than the redox unit that is so often taught at the very end of high school. For example, the oxidation state of an element in a compound tells you how many electrons it is using for bonding, and this can help to establish Lewis diagrams and molecular shapes.

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[1] Some teachers said that their students had not met the symbol M_r, although it has been used in the National High School Chemistry Exam for several years now. Please note that all symbols used will be, as far as possible, IUPAC recommended symbols, and not those used in a particular textbook. Different textbooks seem to use different symbols even within Canada.

In order to answer this particular question students need to consider ammonium nitrate as comprising two ions, NH_4^+ and NO_3^-. The rules for assigning oxidation numbers [2] that need to be applied are:

Rule 3: In ions, the algebraic sum of the oxidation numbers equals the charge on the ion.

Then for the NH_4^+ ion the rule to be applied is:

Rule 5: The oxidation number of hydrogen in all its compounds, except metal hydrides, is +1. (In metal hydrides it is -1.)

Thus the four hydrogens in the NH_4^+ ion contribute +4, so the nitrogen must contribute –3 for the overall charge on the ion to be +1 (since +4 –3 = +1).

For the NO_3^- ion the rule to be applied is:

Rule 6: The oxidation number of oxygen is always –2 (except in peroxides when it is –1, and in OF_2 when it is +2).

Thus the three oxygens in the NO_3^- ion contribute (3 x –2) = –6, so the nitrogen must contribute +5 for the overall charge on the ion to be –1 (since +5 –6 = –1).

The two different oxidation states of nitrogen in the compound NH_4NO_3 are therefore –3 and +5 so the correct answer is **D**.

Note that these two oxidation states are the minimum and maximum states of nitrogen respectively. The (simple) electron configuration of nitrogen is 2,5. In order to achieve a theoretical noble gas configuration is can either lose 5 electrons in order to have just 2 electrons like helium, or it can add 3 electrons to achieve a 2,8 configuration like neon (although it is unlikely that such high charges would actually exist in such a small atom, they are, nevertheless, considered as theoretical possibilities when considering oxidation states).

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5. This question tests various aspects of knowledge about atomic and ionic radii. The negative aspect of the question (you are looking for a series that is **NOT decreasing**) might have created difficulties for students, but in fact this question had the third most correct responses of any in the exam.

Let us consider each of the suggested answers in turn:

A. Li > Be > B

Lithium, beryllium and boron are in Groups 1,2 and 3 respectively in the same period of the Periodic Table. Atomic **size is decreasing** going from left to right of a period (electrons are added into the same outer shell, whilst added protons increase the power of the nucleus to pull in these electrons), so the answer cannot be A.

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[2] The rules for assigning oxidation numbers are fully discussed in the Appendix to the NHSCE answers for the 2001 exam (given at the end of the Answers to questions 21 to 25).

B. $Na^{+} > Mg^{2+} > Al^{3+}$

These ions are isoelectronic with each other and with neon, i.e. they all have the same electron configuration (2,8), however their nuclear charges are increasing (because the sodium, magnesium and aluminum are in Group 1,2 and 3 respectively of the same period). This means that the nucleus has increasing power to pull in the electrons and reduce ionic size (this decrease in size is even more dramatic than that observed for the atoms, which have to deal with an increase in electron numbers). As the ionic **size is decreasing** the answer cannot be B.

C. $P^{3-} > S^{2-} > Cl^{-}$

These ions are isoelectronic with each other and with argon (electron configuration 2,8,8). The only difference here is that electrons have been added to achieve the noble gas configuration rather than subtracted (as in the case of the cations given in B). The nuclear charges are increasing (because phosphorus, sulfur and chlorine are in Group 15, 16 and 17 respectively of the same period) whilst the electrons stay the same, so the ionic **size is decreasing**, and the answer cannot be C.

D. $Cl^{-} > Ar > K^{+}$

Here again we have three isoelectronic species. Potassium is, however, in the period following chlorine and argon: this means that chlorine has to add an electron, whereas potassium has to lose an electron in order to achieve the argon electronic configuration (2,8,8). The nuclear charges are increasing whilst the electrons stay the same, so the **size is decreasing**, and the answer cannot be D.

E. Cl > Ar > K

Well, having got this far, the answer must be E, but you should always check yourself if you can. Chorine and argon are in the same period , but potassium is in the next period up, so its final electron gets added into a new, bigger shell, and, even though it has another proton, the ensuing increase in nuclear charge cannot pull the electrons in to anything like the same extent as would be the case if the electron were going into the same shell. (Although atomic radii can vary in size according to the type of bonding they are involved in, my data book gives comparable values for Cl, Ar and K of 0.180 nm, 0.190 nm and 0.280 nm respectively.) The true order of atomic size is therefore Cl < Ar < K, i.e. the radii are not given in order of decreasing size in this key, and so the answer is **E**.

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6. I understand that some teachers gave students Solubility Data tables in order to help them do this question. I would like to make it quite clear that **teachers should not give students any material other than that provided in the NHSCE package**. All questions can be answered without the use of any additional aids.

   As stated in the answer to Question 17 of the 2002 exam, it is expected that students should have some idea of the solubilities of some common inorganic substances at room temperature The rules that they are expected to know are given again below.

The Solubility Rules

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

In this question we are essentially looking at a variety of conductimetric titrations. In a conductimetric titration the solutions involved are mixed in an electrolytic cell, and monitored using an ammeter. The apparatus is set up in such a way that the current measured by the ammeter is proportional to the conductivity of the solution in the cell. This conductivity depends on the concentrations of the various ions in the cell[1], which change gradually as the titration proceeds – concentrations of the reactant decrease while product concentrations increase. At the endpoint[2] there is generally a sharp change in conductivity because all the products of the reaction being studied have been formed. (The conductivity change at the endpoint needs to be sharp, otherwise this method of monitoring the titration does not work very well.) After the endpoint any conductivity change is gradual and is due to an excess of one reactant being added to the mixture.

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[1] Note that the conductivity of the solution does not depend only on concentration – it also depends on the nature of the ions in solution. Different ions have different conductivities at the same concentration, so that their contribution to the overall conductivity will differ.

[2] Here the term endpoint is being used as a synonym for equivalence point. This is the ideal situation! Often the point at which a titration is ended is slightly beyond the equivalence point, particularly in cases in which a colour change is being used to indicate the equivalence point.

The really important thing to do in solving this question is to look at the products of each reaction, and to determine which of them contribute ions to the endpoint mixture. However, in order to help students to understand what is actually happening throughout the titrations, we shall discuss what happens to the ions in each reaction in turn:

A. $\{H^+_{(aq)} + Cl^-_{(aq)}\} + \{Na^+_{(aq)} + OH^-_{(aq)}\} \rightarrow \{Na^+_{(aq)} + Cl^-_{(aq)}\} + H_2O_{(l)}$

Note that this reaction produces molecules of water, the ionic concentration of which is negligible. When the reaction is written like this it can be seen that there is a reduction in the number of ions as the reaction proceeds to the endpoint (after the endpoint the conductivity builds up again as additional ions of titrant are added). At the endpoint, however, there will still be plenty of sodium and chloride ions present, which means that the endpoint solution will still conduct electricity.

B. $\{Ag^+_{(aq)} + NO_3{}^-_{(aq)}\} + \{Na^+_{(aq)} + Cl^-_{(aq)}\} \rightarrow \{Ag^+ Cl^-\}_{(s)} + \{Na^+_{(aq)} + NO_3{}^-_{(aq)}\}$

In this reaction a precipitate of silver chloride is formed, which "locks away" the silver and chloride ions in the solid [3]. However there are still sodium and nitrate ions in the solution at the endpoint, meaning that it still conducts current.

Note that this reaction is used in a common test for chloride ions in solution in which silver nitrate solution (in the presence of nitric acid) is added to the unknown solution. A positive result involves the formation of a white precipitate of silver chloride (which rapidly becomes greyish in light as it decomposes to form silver metal).

C. $\{2Na^+_{(aq)} + CO_3{}^{2-}_{(aq)}\} + 2\{H^+_{(aq)} + Cl^-_{(aq)}\} \rightarrow \{Na^+_{(aq)} + Cl^-_{(aq)}\} + H_2O_{(l)} + CO_{2(g)}$

In this reaction the molecular compounds water and carbon dioxide[4] are formed, but there are still plenty of sodium and chloride ions left in the solution at the endpoint, so that it still conducts electricity.

Note that a common test for carbonate ions in solution involves the addition of acid (usually nitric acid because it does not form insoluble salts with any common cations). A positive result is indicated by effervescence of carbon dioxide (which can be confirmed by reaction with limewater).

D. $\{2H^+_{(aq)} + SO_4{}^{2-}_{(aq)}\} + \{Ba^{2+}_{(aq)} + 2OH^-_{(aq)}\} \rightarrow \{Ba^{2+} SO_4{}^{2-}\}_{(s)} + H_2O_{(l)}$

In this reaction a precipitate of barium sulfate is formed, which "locks away" the barium and sulfate ions. The only other species formed is water, which is molecular, so that there are virtually no ions present at the endpoint. It looks as though the answer to this question could be D, but you should check key E to make sure.

Note that a common test for sulfate ions in solution is the addition of a solution of barium ions (usually barium nitrate in the presence of nitric acid). A positive result involves the formation of a white precipitate of barium sulfate.

E. $CH_3COOH_{(aq)} + \{Na^+_{(aq)} + OH^-_{(aq)}\} \rightarrow \{CH_3COO^-_{(aq)} + Na^+_{(aq)}\} + H_2O_{(l)}$

Here the sodium hydroxide is present as ions in solution, although the ethanoic acid is only slightly ionized (because it is a weak acid). As the reaction proceeds sodium ethanoate is formed along with molecules of

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[3] In fact the bonding in silver chloride has considerable covalent character. However this does not affect the logic required to determine that the remaining solution conducts electricity.

[4] At these low concentrations carbon dioxide may be dissolved in the solutions rather than appearing as a gas, but again this does not affect the logic required to solve the problem.

water. The sodium ethanoate is fully ionized in solution, so that there will be plenty of ions present at the endpoint, and the solution will conduct electricity.

The correct answer to this question is therefore **D**. The titration between sulfuric acid and barium hydroxide is the classic example of a conductimetric titration, largely because the endpoint of almost zero conductivity is so easily observed. Note, however, that the barium hydroxide solution used in the titration has a concentration of 0.1 mol•L^{-1}, which is near the limit of its solubility. It also tends to react with carbon dioxide in air to form very insoluble barium carbonate so that standard barium hydroxide solutions are difficult to prepare and maintain.[5]

7. Almost every year the NHSCE includes a question on Brønsted-Lowry acid–base theory. This year the question required a knowledge of the theory to be combined with an understanding of equilibrium constants, which made it a little more difficult for weaker students. Some teachers indicated that they did not expect their students to recognize the symbol K_c (although it is a symbol that has been used for the last few years on the NHSCE). Their textbooks use either K or K_{eq}. K_c is intended to indicate that the equilibrium constant expression is written in terms of concentrations of solutions, although, strictly speaking, they should be written in terms of activities [6]. K_c values are sometimes given with units (powers of concentration units), but in this particular case no units are necessary because the sums of the stoichiometric coefficients on either side of the equation are the same. [7]

   In this question all the suggested answers could act as a base in an appropriate reaction, however there can be only two bases in the reaction given, which is:

$$HPO_4^{2-}(aq) + CH_3COOH(aq) \rightleftharpoons H_2PO_4^{-}(aq) + CH_3COO^{-}(aq)$$

   In this reaction HPO_4^{2-} is a base, because it accepts a proton to become its conjugate acid $H_2PO_4^{-}$. CH_3COOH is the acid that donates a proton to become its conjugate base CH_3COO^{-}. H_2O is simply the solvent in this reaction. This simplifies the question into which of the two bases HPO_4^{2-} or CH_3COO^{-} is the stronger.

   As $K_c = 290$ for this reaction (i.e. greater than one) then the equilibrium must lie to the right of the equation as shown. This means that the stronger of the two bases is HPO_4^{2-} (it is "pushing" the reaction to the right) and the answer to the question is **B**.

   Note that an equilibrium always favours the side of the weaker reagents, be they acids, bases, oxidizing or reducing agents. In a sense this is the meaning of "stronger" and "weaker".

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[5] Barium hydroxide solution is in fact a more sensitive indicator for carbon dioxide than lime water (calcium hydroxide solution). This is because barium hydroxide is more soluble in water than calcium hydroxide, whereas barium carbonate is more insoluble.

[6] Activity values take into account the fact that in all solutions containing ions, other than extremely dilute solutions, ion pairs tend to form, changing the effective concentrations of the ions. For this reason the equilibrium law expression does not give a completely constant value when concentration values are substituted into it. Activities are designed to give constant K_c values, but they are difficult to determine. Note that activity values have no units, which is why equilibrium constants are often given without units.

[7] The symbol K_p has also been used in the NHSCE. It is applied to reactions involving gases, and indicates that the equilibrium constant expression is to be calculated from partial pressure values, giving a value that might appear with units of pressure. Questions involving K_p values have, however, been discontinued as the topic is not on the Pan-Canadian protocol.

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8. This is a very straightforward question that was, however, poorly done by weaker students (it gave the biggest range of discrimination of the entire examination). Part of the problem might lie in the fact that some teachers had not covered redox before the date of the examination. Redox is, however, on the Pan-Canadian protocol, and I would like to reiterate that there will be some redox questions on the NHSCE. Students require some knowledge of this topic if they are going to take university courses in chemistry, and it needs to be thoroughly covered by the end of the year.

   Students should know that electrolysis is a process in which an electric current is passed through a molten electrolyte[8], or a solution of an electrolyte. During electrolysis the electrolyte is usually decomposed, although, in some cases the solvent or an electrode may react preferentially. In the case of molten sodium chloride there is no solvent to compete, and it can be assumed that the electrodes are inert, in which case only the elements (sodium and chlorine) can be formed in the decomposition reaction. This means that only B, C and D need be considered as correct keys.

   This question also relies on knowing the two rules that were given in the answer to Question 5 of the 2002 exam. These are:

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

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

   In this question only two of the keys have oxidation equations in them. These are A and D. In these equations the electrons are on the right hand side of the equation, showing that they are lost to the electrode. Just by considering the two previous paragraphs it can be seen that the correct answer must be **D**.

   It should be appreciated that the charges on the electrodes in electrolytic cells are the opposite way round from the charges on the electrodes in electrochemical cells. Although oxidation occurs at the anode in both electrochemical and electrolytic cells, in electrochemical cells it is spontaneous whereas in electrolytic cells it is not. In an electrolytic cell electrons are pushed around the circuit using a power supply[9]. The cathode is negatively charged (so that positive ions – cations – are attracted to it and forced to accept electrons) whilst the anode is positively charged (so that negative ions – anions – are attracted to it and forced to give up electrons).

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9. This question tests some essential knowledge about acids and bases that I would expect students to have covered in the very early stages of chemistry, however students found it the second most difficult question on the exam. I do not feel that it would have helped to have given students a solubility chart to assist them in answering this question, nor is it necessary for them to have any highly specific knowledge about copper chemistry (although a knowledge of the colours of copper compounds might help).

   The logic of the solution is as follows:

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[8] An electrolyte is a compound that will conduct electricity when in the molten state or when dissolved in water or other ionizing solvent. Many salts and bases are electrolytes (although not all of these are water-soluble, they usually conduct electricity when molten), acids are electrolytes only when dissolved in an ionizing solvent (in their pure state they are molecular compounds).

[9] Electrolysis is a decomposition process. This means that it needs energy to break bonds, i.e. it is endoergic. The energy used is electrical energy provided by the power supply.

- Copper is a metal (it is to the lower left hand side of the zig-zag line on the Periodic Table).
- Copper is not in Group 1 or Group 2 of the Periodic Table (i.e. it is not an alkali metal or alkaline earth) therefore its oxide is not water soluble. This eliminates E as a possible answer.
- Because copper is a metal its oxide must be basic [10], which means that copper oxide will dissolve in an acid to form a salt and water ONLY. No gases of any kind are formed. This means that **B** is the only possible answer.

This question was presented in tabular form to simulate an "Observation" table that a student might put into their laboratory notebook if asked to investigate some unknown substances. Note that nitric acid was chosen as the acid in this question because all its salts are water soluble. When a metal oxide reacts with an acid that would give a water-insoluble salt with it, the oxide tends to simply get coated with the insoluble salt and the reaction stops.

What could the unknown substances be? (Several people who commented on this question seemed to get really hung up on this – although it doesn't really matter.) In fact there is no indication in the question that the substances described in the keys have anything to do with copper (apart from the one that must be the answer).

I can think of no copper compound that would fit the bill for A (most copper compounds are coloured), but it could be something like barium sulfate or silicon dioxide.

B, of course, is copper(II) oxide, which is black. It dissolves in nitric acid to give blue copper(II) nitrate, thus:

$$CuO_{(s)} + 2HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + H_2O_{(l)}$$

C could be metallic copper (orange-brown), which is attacked vigorously by nitric acid to give copper(II) nitrate plus the brown gas nitrogen dioxide (although it is generally unreactive to acids). This is a rather complicated redox reaction, which depends on the concentration of the acid and/or the presence of air, but it can be considered as:

$$Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)}$$

D could be copper carbonate, which is a water-insoluble green powder. This reacts with nitric acid to give copper(II) nitrate plus carbon dioxide (the colourless gas), thus:

$$CuCO_{3(s)} + 2HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

E could be a water soluble copper salt, such as copper(II) sulfate or copper(II) nitrate, both of which give blue solutions. If the crystals dissolve in water, they will also dissolve in nitric acid, which consists mainly of water.

Note that I would expect that students to know some fundamental acid-base definitions which are usually inroduced early on in their chemistry course – or even in General Science courses before they begin chemistry. Specifically I would expect them to know the Arrhenius definition of an acid as a substance that dissolves in water [11] to give hydrogen ions as the only positive ions. The definition of a base is more contentious. Many textbooks define a base as a substance that dissolves in water to give hydroxide ions. But even if this is modified to say that the hydroxide ions are the only negative ions (so that it parallels the acid definition) the definition does not "work" for most bases, which are water-insoluble (it only works for alkalis.) Note that

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[10] Metal oxides might also be amphoteric, although this is not the case for copper oxide. Amphoteric oxides also react with acids to form a salt and water only, however they can react with alkalis as well.

[11] This definition does not include some water-insoluble acidic oxides (e.g. silicon dioxide) or amphoteric oxides (e.g. aluminium oxide) which exhibit acid properties when they react with strong alkalies to give a salt and water.

water-soluble salts of weak acids (e.g. carbonates) that hydroyse in water to give alkaline solutions are excluded by this definition.

Reasonably satisfactory definitions of a base at this level might be either:

– A base is a metal oxide or hydroxide (although this ignores ammonia and related bases), or

– A base is a substance that reacts with an acid to form a salt and water only (usually).

A salt can be considered to be a substance that contains a cation derived from a base combined with an anion derived from an acid[12].

Given these simple definitions I would expect students to know the following reactions of acids:

1) Acids react with reactive metals to give a salt plus hydrogen gas[13].

   It should be noted that this reaction is not recommended with highly reactive metals such as sodium and potassium, which react violently with acids.

2) Acids react with bases to give a salt and water only.

3) Acids react with carbonates (and hydrogencarbonates) to give a salt, water, and carbon dioxide.

4) Acids react with indicators. Indicators are derived from weak acids that have salts that are a different colour from the acid itself. In order for an acid to change the colour the indicator must be in its salt form, when an acid competition reaction occurs, thus:

   Strong acider + indicator salt → weaker acid (indicator) + salt of stronger acid.

   Note that the acid being tested must be stronger than the indicator acid for this reaction to take place (assuming that the indicator is not at a very high concentration relative to the acid – this is a reasonable assumption as generally very little indicator is used, so that its concentation is low relative to the acid).

   When an indicator reacts with an alkali (water-soluble base) the indicator must be in its acid form, in which case a simple acid-base reaction occurs (as in 2 above).

Reactions 3 and 4 are really the same, as they are both acid competition reactions. In 3, however, the weak acid, carbonic acid, is formed by the reaction of a (stronger) acid with a salt of carbonic acid.

Strong acid + carbonate → carbonic acid + salt of strong acid

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[12] You might like to consider how these simple definitions compare with other definitions of acids and bases (e.g. Brønsted-Lowry or Lewis acid-base definitions). The anion of a salt, for example, would be considered to be a Brønsted-Lowry base.

[13] There are some exceptions to this, particularly with oxidizing acids such as sulfuric acid and nitric acid, which may cause some reactive metals to become "passive" by becoming coated with an insoluble oxide layer, so they stop reacting. On the other hand some unreactive metals may react with oxidizing acids (as discussed for copper in C above) but in these cases the environment is too oxidising for hydrogen gas to form, and any gaseous products are likely to be reduction products of the acid.

In an enclosed system carbonic acid exists in equilibrium with carbon dioxide and water

$$\text{Carbonic acid} \rightleftharpoons \text{carbon dioxide + water}$$

In an open container the carbon dioxide gas escapes from the solution gradually using up all the carbonic acid, thus:

$$\text{Carbonic acid} \rightarrow \text{carbon dioxide + water.}$$

This is sometimes considered to be an example of a reaction in which a non-volatile acid releases a volatile acid from one of its salts. (Carbonic acid is considered volatile because it releases gaseous carbon dioxide so easily.) You might like to consider which other volatile acids could behave like this.

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10. This question is concerned with an industrial application of Le Chatelier's principle. Remember that, although equilibrium considerations are important in deciding the conditions under which a process is going to operate, a continuous process such as this one is operated under steady state conditions – it is not given the time to achieve equilibrium.

The reaction is:

$$4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)};\ \Delta H = -950\ \text{kJ}\bullet\text{mol}^{-1}$$

Let us consider each of the suggested changes in conditions in turn:

A. Increasing the pressure

There are 9 moles of gas on the left hand side of the equation and 10 moles on the right hand side, i.e. when the products are formed the number of moles of gas increase, so the total pressure would increase (if the system were enclosed). If the operating pressure is increased the reaction will tend to swing back to the side of the reactants, so that the yield of nitrogen oxide would be decreased. The answer cannot be A.

B. Drying the reagents used

Some students I spoke to found it difficult to accept that water (a product of the reaction as shown in the equation) could be added with the reactants. It should be remembered, however, that equilibrium reactions are reversible, and that any combination of reactants and products can be mixed together to give an equilibrium system.

Almost all chemicals involved in industrial processes are contaminated by water to some extent, and it is therefore important to consider the effect of water on reactions. As water is a product in this reaction, its presence will favour the reverse reaction, decreasing the yield of nitrogen oxide. Removing water from the reagents will therefore help the forward reaction, producing more nitrogen oxide. The answer to this question is therefore **B**.

We shall continue to discuss the other keys in order to check our answer.

C. Increasing the temperature

ΔH for this reaction is negative, which means that heat is given out in the reaction, i.e. the temperature tends to increase as the reaction proceeds. Increasing the operating temperature is equivalent to adding heat, and this heat is consumed by promoting the endothermic reaction: the reaction swings to the left, and less nitrogen oxide is formed. The answer cannot therefore be C.

D. Adding nitrogen to the reaction mixture

Nitrogen is inert in this reaction (although air rather than oxygen is used in the industrial process, you are told that only the oxygen reacts). Adding nitrogen whilst maintaining the overall pressure would reduce the partial pressure of oxygen, making the equilibrium swing to the left so less nitrogen oxide would be formed. (Adding nitrogen and allowing the overall pressure to increase would maintain the partial pressures of the components and make no difference to the yield.)

The same students I spoke to thought that adding nitrogen would create more nitrogen oxide by direct reaction with some of the oxygen, thus:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

This reaction clearly does not take place at normal temperatures (in fact its equilibrium constant is in the order of 10^{-31} at 25 °C). It is an endothermic reaction with $\Delta H \approx +180$ kJ•mol^{-1} but even at 3000 °C its equilibrium constant is only about 0.06, so it is unlikely to have a major effect at 900 °C. (Please note that you would not be expected to know this, and, as you are not given the data, then it is reasonable to ignore it.)

However, if a oxygen were to be used to make nitrogen oxide, then the fact that each mole of oxygen would produce two moles of nitrogen oxide, would mean that the main reaction would simply swing back again, and the less nitrogen oxide would be produced from the ammonia.

E. Using a nickel catalyst instead of platinum

Changing the catalyst might change the rate of reaction, but it would not change the position of equilibrium. It could, conceivably, increase the yield of product obtained in a given contact time in a continuous process (an important consideration in an industrial process), however nickel is not generally as good a catalyst as platinum, and, in view of the fact that the more expensive platinum is being used, I think it is safe to assume that it will be the better catalyst in this case, so that the yield of nitrogen oxide will not be increased by using nickel.

The best answer is therefore **B**.

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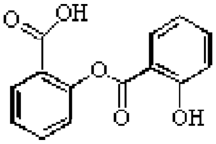
11. This question is concerned with organic functional groups. In order to simplify this exercise for provinces that do not include this topic (even though it is on the Pan-Canadian protocol) the functional groups that students are expected to know for the NHSCE are:

alkane, alkene, alkyne, phenyl, alkyl halide, amine, alcohol, ether, aldehyde, ketone, carboxylic acid, ester and amide

(formulae for these are given in the answer to Question 6 of the 2002 NHSCE).

In the present question, the salsalate molecule is given as:



This contains:

- A carboxylic acid group (on the top of the left ring)
- An ester group (joining the two rings), and
- A hydroxyl – or more specifically a phenol group – on the bottom of the right ring

The answer is therefore **D**. The phenol group was not included in the choice because it was not on the list given in last year's answers. I**n future the phenol group will be included in the functional groups that students are expected to know** (it is a hydroxyl group joined onto an aromatic ring as shown above).

Note that no carbon atoms are shown in this structural formula. They are indicated by the corners of rings or by the bends in lines. Also the hydrogen atoms that are connected to carbon atoms are not shown: it has to be assumed that hydrogen atoms will be attached to carbons in such a way as to complete the valency requirement of each carbon atom (4). Students are expected to be able to recognize organic structures from various kinds of condensed formulae as well as displayed formula.

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12. The logic of determining the polarity of the molecules given is summarized in the following table:

Molecule	**Central atom**	**# of valency electrons on central atom**	**# Bonding pairs**	**# Lone pairs**	**Shape of molecule**	**Symmetry of molecule**	**Polarity**
BF_3	B	3	3	0	Trigonal planar	Symmetrical	Non-polar
CBr_4	C	4	4	0	Tetrahedral	Symmetrical	Non-polar
CCl_3Br	C	4	4	0	Tetrahedral	Asymmetrical	Polar
$GeBr_2$	Ge	4	2	2	Bent (angular)	Asymmetrical	Polar
NF_3	N	5	3	1	Trigonal pyramidal	Asymmetrical	Polar

You could use this information to draw your own Lewis structures and 3-dimensional diagrams of the molecules. Note that CCl_3Br is asymmetrical, and therefore polar, whereas CBr_4 is not. This is because the C-Cl and C-Br bonds have different polarities due to the different electronegativities of Cl and Br [1].

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

It is interesting to observe here that carbon is 4-valent in CBr_4 whilst germanium is 2-valent in $GeBr_2$, even though both carbon and germanium are in the same group of the Periodic Table (Group 14). There is a general trend from mainly 4 valency to mainly 2 valency going down this group. This trend is often attributed to the "inert pair" effect, in which the ***s*** electrons are not used in bonding because it is more difficult for the atoms to lose ***s*** electrons than ***p*** electrons in the same shell. This is presumably due to the fact that the ***d*** electrons (and possibly ***f*** electrons) from the previous shell(s) have been added in between the ***s*** and ***p*** electrons, and because there is a particular stability associated with having the ***d*** orbital completely filled. This effect is observed even though the atoms become larger down the group (one might expect that it would be easier for ionisation to occur, as the nucleus becomes less able to attract outer shell electrons, which are increasingly distant, and also shielded from it by inner electrons). A similar inert pair effect can be seen in Group 13, in which the valencies gradually change from mainly 3 to mainly 1.

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13. This question requires students to know about the nature of Period 3 elements and their oxides. There is a trend in the elements from metallic to non-metallic going from left to right across the Period, which is associated with an increase in electronegativity value. As the elements are combined with oxygen (itself a highly electronegative element) we can observe a trend from ionic to covalent in the bonding of the oxides of the element. It must, however, be remembered that there is also a difference in the structures, with the oxides on the far left of the Period being simple molecules rather than giant networks. This is summarized in the following table for the oxides given:

Oxide	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_4O_{10}**
Bonding	Ionic	Ionic with some covalent character	Ionic with more covalent character	Covalent	Covalent
Structure	Giant network	Giant network	Giant network	Giant network	Simple molecular

As the covalent bonding **inside** simple molecules is combined with weak intermolecular forces **between** the molecules, the melting point of simple molecular compounds such as P_4O_{10} is low in comparison with giant networks (whether ionic or covalent) since, when the solid melts, the molecules themselves stay intact (with their atoms still covalently bonded together) even as they move around within the liquid. This is because the weaker bonds between the molecules are loosened first when the compound is heated. (These weak bonds become completely broken when the compound changes into the gas state.) Phosphorus pentoxide P_4O_{10} thus has the lowest melting point, so the answer to this question is **E**.

The actual melting points of the Period 3 oxides are shown in the table below, with the values for sulfur trioxide and chlorine heptoxide included for completeness (note how they continue the trend towards lower melting points).

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[1] There is no need to know the exact electronegativities of Cl and Br to establish this. They are in the same group in the Periodic Table (Group 17) and so they are not on a diagonal, which might make their electronegativities the same or very similar (e.g. Cl has a similar electronegativity to N at 3.0).

Oxide	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_4O_{10}**	**SO_3**	**Cl_2O_7**
Melting point, ^oC	1132	2824	2053	1722	562	16.8	– 91.5

This question was originally written asking which of the oxides had the **highest** melting point. As can be seen from the table, magnesium oxide has the highest melting point. The question was changed, because, without having met this before, many people would probably have guessed that the giant covalent network of silicon dioxide would have the highest melting point (because covalent bonds are generally stronger than ionic bonds). Even aluminum oxide has a higher melting point than silicon dioxide, presumably because of the fact that aluminum oxide has a high charge and a small cation. It appears, however, that the stoichiometry is a more important factor here, because a 1:1 stoichiometry allows the ions to get very close together, giving much stronger bonding than with the other stoichiometries involved. Because of its high melting point magnesium oxide is a refractory material (i.e. it can withstand high temperatures), which allows it to be used as a lining for furnaces.

A look at the enthalpy changes of formation (ΔH_f) of these oxides – or better still ΔH_f per mole of oxygen atoms – also shows how strong the magnesium oxide bonds are. (Remember that a large negative value of ΔH_f indicates thermodynamic stability with respect to the elements, which is one indication of the strength of the bonds.)

Oxide	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_4O_{10}**	**SO_3**	**Cl_2O_7**
ΔH_f, kJ·mol^{-1}	– 416	– 602	– 1670	– 911	– 2984	– 395	+250
ΔH_f, kJ per mole of oxygen atoms	– 416	– 602	– 557	– 456	– 298	– 132	+ 36

Note the distinctive trend in the ΔH_f values per mole of oxygen atoms, with magnesium oxide having the most negative value, and the values rising steadily for the oxides of the elements to the right of magnesium in the period, with highly unstable (explosive) chlorine heptoxide having a positive value.

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14. This is not a difficult question, but it needs to be tackled carefully. It is a development on the (very easy) Question 4 of last year's exam.

It is probably best to work from the hydrated chromium sulfate rather than go through the calculation key by key. This is how I would do it:

Starting with $Cr_2(SO_4)_3{\cdot}18H_2O$

The chemical amount of $Cr_2(SO_4)_3{\cdot}18H_2O$ can be calculated using

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

You are given M_r (the relative molar mass) as 716.478 for $Cr_2(SO_4)_3{\cdot}18H_2O$, thus the molar mass, M = 716.478 g·mol^{-1}. Therefore

the chemical amount = 17.912 g / 716.478 g•mol^{-1}
= 0.025000 mol .... (14.1)

Then using

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

Note that the volume of the solution is given in mL (millilitres) rather than in L (litres) so it needs to be converted into the right units, thus

The volume of the solution = 250.00 mL / 1000 mL•L^{-1}
= 0.2500 L .... (14.2)

Thus the concentration of $Cr_2(SO_4)_3$•$18H_2O$ in the solution = 0.025000 mol / 0.2500 L
= 0.1000 mol•L^{-1}

<u>So the answer cannot be E</u>. (Answer E means that the calculation was finished at equation 14.1 with units of mol instead of the required mol•L^{-1}).

Now considering the Cr^{3+} ions:

The chemical amount of Cr^{3+} = 2 x the chemical amount of $Cr_2(SO_4)_3$•$18H_2O$ (as shown by the formula)
i.e. the chemical amount of Cr^{3+} = 2 x 0.02500 mol (from equation 14.1 above)
= 0.0500 mol

Now since M_r for Cr = 51.9961

The mass of Cr^{3+} = 51.9961 g•mol^{-1} x 0.0500 mol
= 2.5998 g

<u>So the answer cannot be A</u>. (Answer A arises from forgetting to multiply by 2.)

Considering the SO_4^{2-} ions:

The chemical amount of SO_4^{2-} ions = 3 x the chemical amount of $Cr_2(SO_4)_3$•$18H_2O$ (as shown by the formula)
i.e. the chemical amount of SO_4^{2-} ions = 3 x 0.02500 mol (from equation 14.1 above)
= 0.07500 mol

<u>So the answer cannot be B</u>. (Answer B arises from using mol•L^{-1} instead of mol.)

Considering the H_2O molecules

The chemical amount of H_2O molecules = 18 x the chemical amount of $Cr_2(SO_4)_3$•$18H_2O$
= 18 x 0.02500 mol (from equation 14.1 above)
= 0.4500 mol

M_r for H_2O = 18.0153

Therefore the mass of H_2O = 18.0153 g•mol^{-1} x 0.4500 mol = 8.107 g

This looks like the answer, **BUT** water is also present as the solvent in the solution!

So the answer cannot be C.

(Note that the water of crystallisation would contribute towards the mass of water required to make the solution, so that less than 250 g of water would need to be added.)

Finally, considering anhydrous $Cr_2(SO_4)_3$

M_r for anhydrous $Cr_2(SO_4)_3$ = 392.203 (this can be calculated from the relative atomic masses given in the Periodic Table, or from {M_r of $Cr_2(SO_4)_3{\bullet}18H_2O$ – 18 M_r of H_2O}

The chemical amount of $Cr_2(SO_4)_3$ = the chemical amount of $Cr_2(SO_4)_3{\bullet}18H_2O$ = 0.02500 mol

The mass of $Cr_2(SO_4)_3$ = 392.203 g•mol^{-1} x 0.02500 mol = 9.805 g

Therefore the concentration of $Cr_2(SO_4)_3$ in **g·L^{-1}** = 9.805 g / 0.2500 L (see 14.2 above) = 39.219 g·L^{-1}

So the correct key is **D**.

---

15. This question involves interpretation of a graph that really was obtained by a high school student who planned the experiment himself. He was investigating the rate of decomposition of hydrogen peroxide.

The rate of reaction can be defined as the change of chemical amount (of a reactant or product) in a given time. It can be measured by monitoring the chemical amount itself or any property of a reactant or product that is proportional to the chemical amount (often the concentration of a solution.). In this case the student chose to monitor the volume of oxygen gas produced over time. Assuming that the temperature and pressure of the gas is constant then the volume is proportional to the chemical amount of oxygen (from Avogadro's principle).

If a graph is drawn of the property being monitored versus time, then the slope of the graph at any point gives the rate of the reaction at any particular time. A straight line graph indicates that the rate is constant, but this is rarely the case, unless readings are only taken at the very beginning of the reaction. If the line has a positive slope then it shows that a product is monitored, because the amount is increasing as the reaction proceeds. If the line has a negative slope then it is because a reactant is being monitored. It is unusual for the line to be completely straight, because the rate normally depends on the concentration of the substance being monitored, and this changes during the course of the reaction [2]. (A reactant will gradually be used up, or all the product that can possibly be produced will have been made, and the reaction slows down until it stops completely.) If the rate is directly proportional to the concentration of a particular reactant throughout the experiment then the reaction is said to be "first order" with respect to that reactant, and an exponential curve is obtained (the slope of which changes uniformly with the concentration).

Let us consider the graph given in the question:

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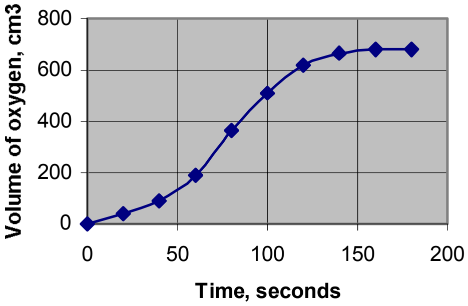
[2] Note that the rate expression, which relates rate to the concentrations of substances involved in the reaction, can only be determined experimentally, and it is often very different from the stoichiometric equation. The rate may depend on concentration of a reactant without necessarily being proportional to it – rate may, for example, be proportional to the concentration squared (or raised to some other power).



The graph starts off as a straight line (more or less) with a positive slope, because a product is being monitored. The slope of the line then gets steeper (the reaction has speeded up) and then it becomes less steep, eventually flattening out because the reaction has slowed down and then finished (and no more oxygen is being produced). The rate increases then decreases and finally becomes zero. It does not increase all the way so B cannot be the correct key, nor does it decrease all the way, so that C cannot be the correct key. It is not a straight line so the rate is not constant, thus D is not the correct key. And the curve is not consistently concave so it is not a first order reaction, and E cannot be the correct key. All that can be said about this reaction is that the rate changes during the reaction, so that the answer is **A**.

It is, in fact, very unusual to see a graph like this, because it shows a reaction that speeds up before it dies down. This is sometimes seen when a reaction is "autocatalyzed". This means that one of the products of the reaction acts as a catalyst, and speeds the reaction up until it is forced to stop because there are no reactants left. In this case, however, the reaction was observed to be highly exothermic (the flask containing the mixture became very hot). The rate of reaction probably simply increased with temperature, although the increase in temperature will also invalidate the assumption that the volume of oxygen produced was proportional to its chemical amount (Avogadro's principle no longer applies). The reaction might even be first order, but with the temperature changing we cannot infer it any more than we can rule it out.

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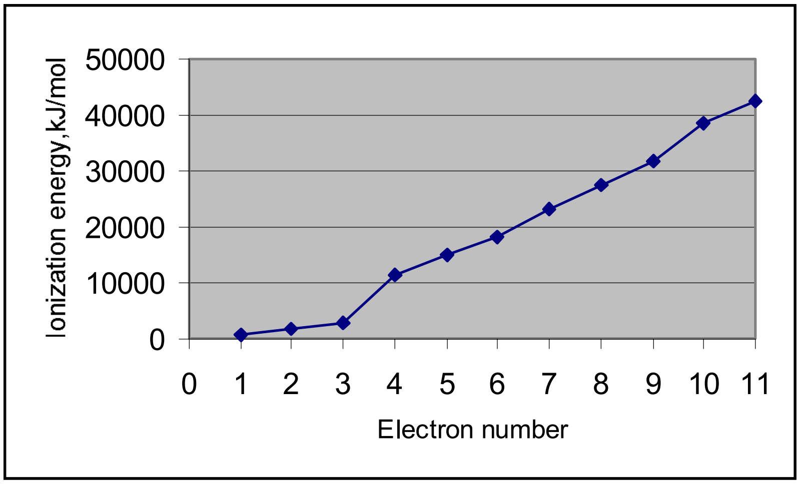
16. This is a classic type of question involving ionization energies. It involves being able to visualize trends in ionization energies from the raw data.

For example, the graph below shows the successive ionization energies of aluminium, which has an electron configuration of 2,8,3:



From this chart it can be seen that the ionization energy increases for each successive electron that is removed from the atom [1]. This is because it becomes increasingly difficult to remove electrons from ions that have an increasing positive charge.

The line is not, however, completely straight. There is, for example, a sudden increase in ionization energy between electrons 3 and 4. The first three electrons come off the atom relatively easily because they are in the valence shell. It is a lot more difficult to remove the fourth electron, which comes from the next shell in.

When we look at the numerical data given in a question like this we need to look at the sudden "jumps" in the data for a pair of ionization energies. These jumps will tell us how many electrons have been removed before a noble gas configuration has been achieved, i.e. it will tell us which group the element is in. You are helped in this particular question because the elements themselves are in a sequence, so that if you are not sure about one element you may be able to tell from the jumps observed in the ionization energies on either side of it.

The table given in the question is redrawn overleaf to show the differences between ionization energies, rather than the ionization energies themselves. Students are often told to look for changes in order of magnitude (i.e. a 10-fold increase) in these sort of exercises, but the changes are rarely that clear.

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[1] Remember that each ionization energy value refers to just one electron being lost: it is **not** the energy required to remove all the electrons up to a particular number.

Ionization energy difference, kJ/mol Element key	Between electrons 1 and 2	Between electrons 2 and 3	Between electrons 3 and 4
A.	1693	2677	2357
B.	1871	2170	3258
C.	4067	2350	2631
D.	713	6282	2808
E.	1239	928	8833

For elements “A” and “B” it is difficult to see any “big jumps”, but this could simply be because we have not been given enough values for one to become apparent. In “C”, however, the difference between ionization energies 1 and 2 is much bigger than that between 2 and 3, which is an indication that the second electron is relatively difficult to remove, and that this is where electrons have to be removed from a complete shell. Element “C” is therefore likely to be in Group 1 of the Periodic Table. A similar pattern is seen for “D” for which the ionization energy difference between electrons 2 and 3 is much greater than that between electrons 1 and 2 or 2 and 4. This indicates that “D” is in the second group of the Periodic Table, i.e. it is likely to form a divalent ion. The answer to this question is therefore **D**. The large jump between ionization energies 3 and 4 of element “E” confirms this, although the ionization energy for the 5th electron to be removed has not been given. The difference in ionization energies between electron immediately preceeding the “big jump” and the penultimate one (e.g. between electrons 2 and 3 in E) is relatively small – this is because the ion achieves noble gas stability once the last valence electron has been lost.

The keys A, B, C, D and E refer, in fact, to the elements F, Ne, Na, Mg and Al respectively. As one might expect, the “big jumps” occur between electrons 7 and 8 for fluorine, and between 8 and 9 for neon, so they do not appear on this table. It is also difficult to see all the jumps if they are plotted in a graph like the one shown above for aluminium. This is because there is such a big range of orders of magnitude in ionization energy values (from 10^2 to 10^5) and this masks the changes due to the first few electrons being removed. For this reason the logarithms of the ionization energies are often plotted rather than the actual values – the “big jumps” in value can still be observed, but smaller changes due to electrons coming from different orbitals are less easily seen.

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17. The Pan-Canadian protocol states that students should to be able to identify some important natural and synthetic polymers. This question requires them to be able to focus on the salient characteristics of some common large molecules. Looking at each of the examples given:

    A. **Rubber:** Rubbers (whether they are natural or synthetic) are characterized by C=C double bonds in the polymer chain. (This is different from many addition polymers which have C=C bonds in the monomer form, but these are “broken open” on polymerization to give chains of C-C single bonds.)

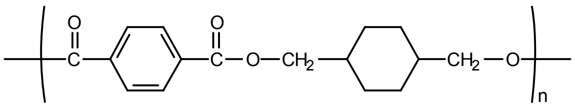
    B. **Polyester:** Polyesters are characterized by an ester linkage in the middle of the mer (repeated) unit of the polymer. The ester linkage is essentially –(C=O)-O-.

    C. **Polyamide:** Polyamides have an amide linkage in the middle of the mer unit. This is essentially –(C=O)-(N-H)- . In naturally occurring compounds, such as polypeptides and proteins this link is called a peptide link.

    D. **Polysaccharide:** Polysaccharides are carbohydrates (i.e. they have the general formula $C_x(H_2O)_y$). They consist of smaller carbohydrate molecules, such as sugars, linked together by oxygen atoms.

    E. **Natural oil or fat:** These are tri-esters derived from 1,2,3-propanetriol (glycerol) and long chain fatty acids.

The molecule given in the question is:



This contains an ester link in the middle of the mer unit (and also, in fact, between mer units). It is not a tri-ester nor does it involve a long straight carbon chain so it must be a polyester rather than a fat or oil. The correct answer is therefore **B**. This polymer is called Kodel and was originally developed by Kodak as a film base, but it is now widely used in fibre form for making fleeces and other fabrics.

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18. **Enantiomers** are pairs of **isomers**, the molecules of which are **mirror images** of each other. They used to be called **optical** isomers because they generally rotate plane polarized light in opposite directions. They are a kind of **stereoisomers**, because the atoms in the molecules are connected to each other in the same way, but they have different arrangements of their atoms in space. Enantiomers can be identified because they have an **asymmetric** carbon atom or **stereocentre**. In order to establish which of the molecules given in this question can exist as a pair of enantiomers you need to find one that has no plane of symmetry, which means that, in these fairly simple molecules, you need to find one that has a carbon with four different atoms or groups of atoms attached to it.

    Let us consider each of the suggested answers in turn:

    A. **$CH_3(CH_2)_2NH_2$** (1-aminopropane) As all the carbons in this molecule are attached to more than one hydrogen (as CH_3 or CH_2 groups) none of them can act as stereocentres, so the answer cannot be A.

    B. **$CH_3CH(OH)CH_3$** (2-propanol) The first and last carbons are in CH_3 groups and the central carbon is attached to these two methyl groups (as well as H and OH) so it does not have four different groups, and the answer cannot be B.

    C. **$(CH_3)_2CHCONH_2$** (3-methylpropanamide) Counting from the left of the molecule, the first two carbons are in CH_3 groups, and they are both attached to the next carbon so that none of these three carbons can be stereocentres. The next carbon is attached to one hydrogen, one NH_2 and one oxygen. The oxygen is attached to the carbon by a double bond, so this ties up two valencies of the carbon. There are only three atoms or groups of atoms attached to this carbon, i.e. it is planar (which means it has a plane of symmetry) so it cannot be a stereocentre, and the answer cannot be C.

    D. **$CH_3(CH_2)_2COONH_4$** This is the ammonium salt of butanoic acid ($CH_3(CH_2)_2COOH$). The first three carbons from the left are in CH_3 or CH_2 groups, the next carbon is attached to only three other atoms/groups so it is planar (not a stereocentre), and the answer cannot be D.

    E. **$CH_3CH_2CH(NH_2)COOH$** The answer now has to be **E**! Checking this is done as follows:

    The first two carbons on the left are in CH_3 or CH_2 groups and the last carbon is attached to oxygen so these carbons are not stereocentres. The third carbon is, however attached to (1) CH_3CH_2 , (2) H, (3) NH_2 and (4) COOH. Four different groups means that the carbon is asymmetric and thus the formula represents a pair of enantiomers.

Carbons that are stereocentres are often marked with an asterisk, so the formula would be shown thus:

$CH_3CH_2C^*H(NH_2)COOH$.

Note that this compound is an amino acid (because it contains both $–NH_2$ and –COOH groups). Many amino acids are biologically important, however, although this one has been isolated from proteins, it does not appear to be an essential component of the human diet. Its name is 2-aminobutanoic acid or α-aminobutyric acid.

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19. This question was nearly removed from the exam as one reviewer thought that it was only testing whether students could calculate a fifth root. However, one teacher said it was a great question. The interesting thing about it is, of course, that a compound containing lead and arsenic (both highly poisonous) should be used to spray on fruit. The low solubility presumably protects humans from any adverse effects, although it is enough to kill off insects. I am not so sure I would trust it though!

    Anyhow, this is the way the calculation can be done:

    The solubility equation is:

$$Pb_3(AsO_4)_{2(s)} \rightleftharpoons 3Pb^{2+}{}_{(aq)} + 2AsO_4{}^{3-}{}_{(aq)}\text{ , with } K_{SP} = 4.1 \text{ x } 10^{-36}$$

    Let the solubility be "s" mol•L^{-1} (This is the concentration of a saturated solution of lead arsenate)

    The solubility product expression in terms of concentrations is then:

$$\begin{aligned} K_{sp} &= [Pb^{2+}]^3\,[AsO_4{}^{3-}]^2 \\ &= (3s)^3\,(2s)^2 \\ &= 27 \times 4 \times s^5 \end{aligned}$$

    so the solubility, $s = \sqrt[5]{\frac{K_{sp}}{27 \times 4}}$

$$= 3.28 \times 10^{-8} \text{ mol•L}^{-1}$$

    and the lead ion concentration is therefore given by:

$$\begin{aligned} [Pb^{2+}] &= 3s \\ &= 9.8 \text{ x } 10^{-8} \text{ mol•L}^{-1} \end{aligned}$$

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

See over for the answer to Question 20.

20. The composition of blast furnace gas is given as containing N_2, CO and CO_2 , of which only carbon monoxide will burn.[2] As the blast furnace gas contains 40% of carbon monoxide by mass, then one tonne (1000 kg) contains 400 kg of carbon monoxide.

    The chemical amount (in mol) of carbon monoxide equivalent to this is given by:

    $$(400 \text{ kg x } 1000 \text{ g}\bullet\text{kg}^{-1}) / 28.0104 \text{ g}\bullet\text{mol}^{-1} \qquad \text{(since } M_r \text{ for CO = 28.0104)}$$
    $$= 14280 \text{ mol}$$

Now since $\Delta H^{\circ}_{\text{combustion}}(\text{CO}) = -283.0 \text{ kJ}\bullet\text{mol}^{-1}$, the heat released by burning 14280 mol of CO is

$$14280 \text{ mol x } 283.0 \text{ kJ}\bullet\text{mol}^{-1}$$
$$= 4.041 \text{ x } 10^6 \text{ kJ}$$

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

(The enthalpy change of formation of CO_2 is not required in the calculation.)

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[2] In fact blast furnace gases also contain small amounts of hydrogen and methane, which are also combustible, but these were ignored for the sake of simplicity.

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21. This question is really just a standard pH calculation, dressed up as a practical application (reducing biological activity in a sewage plant).

The mass of $Ca(OH)_2$ added per litre is 0.37 g and its molar mass is 74.1 $g \cdot mol^{-1}$ (M_r is given as 74.1), so the chemical amount added per litre is

$$0.37\ g/74.1\ g \cdot mol^{-1} = 0.00499\ mol$$

The chemical amount of hydroxide ions added is therefore 2 x 0.00499 mol = 0.00999 mol (as there are two moles of (OH) shown in the formula).

The concentration of hydroxide ions in the water is therefore 0.00999 $mol \cdot L^{-1}$ ………… (21.1)

Now the dissociation of pure water can be represented by the following equation:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant used for this dissociation is $K_w = [H^+_{(aq)}]\ [OH^-_{(aq)}]$ and $K_w = 10^{-14}$ at 25°C (given on the data sheet)

It is probably easier to use this expression in the logarithmic form, i.e.

$$\log K_w = \log[H^+_{(aq)}] + \log[OH^-_{(aq)}] = -14$$

or

$$pK_w = pH + pOH = 14$$

The concentration of hydroxide ions, $[OH^-_{(aq)}]$, = 0.00999 $mol \cdot L^{-1}$ (from 21.1 above) so

$$\log[OH^-_{(aq)}] = -2.00 \qquad \text{i.e. } pOH = 2.00$$

Therefore the pH of the solution = 14 – 2 = 12 and the answer to this question is **E**.

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22. Some teachers said that they enjoyed this question, however their students seem to have been less enthusiastic! It is intended to be an interesting practical application of stoichiometry to rhodonite, the "stone of love".

The first step is clearly to find the percentage of manganese in each of the constituent compounds of rhodonite. Using the M_r values given and looking up that of manganese (it is 54.938) gives:

The proportion by mass of manganese in MnO_2 = (54.938 / 86.937) = 0.6319 and
The proportion by mass of manganese in $MnSiO_3$ = (54.938 / 131.022) = 0.4193

Consider a 100g sample of the rhodonite, in which the mass of MnO_2 is $\boldsymbol{x}$ g , then the mass of $MnSiO_3$ is (100 – $\boldsymbol{x}$) g then the total mass of Mn is given by:

$$\boldsymbol{x} \text{ x } 0.6319 + (100 - \boldsymbol{x}) \text{ x } 0.4193 = 49.16$$

Now solving for $\boldsymbol{x}$:

$$63.19\boldsymbol{x} + 4193 - 41.93\boldsymbol{x} = 4916$$

and $\quad 21.26\,\boldsymbol{x} = 723$

giving $\quad \boldsymbol{x} = 34$

so the answer to the question is **A**.

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23. This question refers to an experiment that is often done by high school students. The question is designed to get students to think about where errors might arise during the experiment, and, in particular, to encourage them to think about the assumptions that are made when we perform this kind of simplistic experiment. The expression used for the calculation was fully displayed, so that students would not get “hung up” on the calculation itself, but could focus on how changes in the various values used would affect the final result. It is expected that students would at least recognize the various components of the expression.

Unfortunately there was an error in the units of the specific heat capacity for water that was given in the expression. (I apologize for this – mistakes seem to slip through, even though the exam papers are checked by several people.) The value given should have been 4.18 $J{\bullet}g{\bullet}K^{-1}$. We do not, however, feel that this would have prevented students from determining the correct answer to the question.

The expression used to calculate the enthalpy change is

$$\Delta H = -\frac{\{(25.00 \text{ mL x } 1.00 \text{ g}{\bullet}\text{mL}^{-1}) \text{ x } 4.18 \text{ J}{\bullet}\text{g}{\bullet}\text{K}^{-1} \text{ x } 49.8 \text{ K}\}}{(1.00 \text{ mol}{\bullet}\text{L}^{-1} \text{ x } 0.02500 \text{ L x } 1000 \text{ J}{\bullet}\text{kJ}^{-1})}$$

$$= -\ 208 \text{ kJ}{\bullet}\text{mol}^{-1}$$

The literature value is given as – 217 $kJ{\bullet}mol^{-1}$, so all the various factors must be considered in terms of how they could have contributed to the difference between the experimental value and the literature value. It simplifies the thought processes if you “forget” the negative, and just look at whether the answer becomes closer to 208 or 217 $kJ{\bullet}mol^{-1}$ or not.

Let us consider each key in turn.

A. **The density of the solution is less than that of water**

The density of water is given in the expression as 1.00 $g{\bullet}mL^{-1}$. If the density of the solution is, in fact, less than this, then the numerator in the calculation is too large and ΔH comes out closer to 217 than 208 $kJ{\bullet}mol^{-1}$ so this error would not contribute to the observed error, i.e. the key must be **A**.

Continuing to check through the different answer keys:

B. **The heat capacity of the solution is greater than that of water**

The heat capacity term is given (or should have been given) as 4.18 J•g•K^{-1}. If the heat capacity of the solution is, in fact, greater then this term is too small and ΔH comes out closer to 208 than 217 kJ•mol^{-1}, so the key cannot be B.

C. **The time taken for the temperature to rise has not been considered**

Although there is no time factor in the calculation expression, the time will affect the result, because the reaction takes some time to take place. As the reaction proceeds it gives out heat, which causes the temperature of the system to increase. If insufficient time was allowed the reaction may not be complete so the temperature rise might be too small.

Even if plenty of time is allowed for the reaction to take place, the system is already beginning to cool by the time it has finished, so that the temperature never becomes as high as it would do if the reaction was instantaneous. (In fact when you do this experiment it is best to draw a temperature vs time graph, and to extrapolate to get the maximum temperature increase.)

Either way, if 49.8 K is too small a temperature rise, it will result in ΔH coming out closer to 208 than 217 kJ•mol^{-1}, so the key cannot be C.

D. **The heat capacity of the excess zinc has not been included in the calculation**

If some of the heat is used to increase the temperature of the zinc, then the temperature rise of the rest of the system would be reduced, so the key cannot be D.

E. **The heat capacity of the thermometer has not been included in the calculation**

If some of the heat is used to increase the temperature of the thermometer then the temperature rise of the rest of the system would be reduced, so the key cannot be E.

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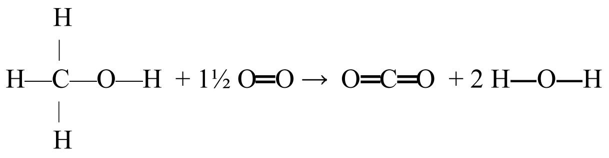
24. The first step in a bond enthalpy term calculation of this type is to write the equation for the reaction it refers to. For the combustion of methanol this is:

$$CH_3OH_{(l)} + 1\tfrac{1}{2}\,O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

Note how the equation is written in terms of one mole of methanol, even though this means that the stoichiometric coefficient for oxygen is not a whole number. This is because the enthalpy change of combustion of methanol, $\Delta H^{\circ}_{\text{combustion}}(CH_3OH)$, refers to one mole of methanol being burned.

The next step is to draw out the bonds of the molecules shown in the equation, thus:



$$H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}O{-}H + 1\tfrac{1}{2}\,O{=}O \rightarrow O{=}C{=}O + 2\,H{-}O{-}H$$

This shows that the following bonds can be considered to be broken or formed:

Bonds broken: $3 \times (C{-}H) + 1 \times (C{-}O) + 1 \times (O{-}H) + 1\tfrac{1}{2}\,(O{=}O)$

Bonds formed: 2 x (C═O) + 2 x 2 x (O—H)

The enthalpy changes associated with the bond forming and breaking can be calculated using the bond enthalpy terms given in the question. Remember that bond enthalpy terms refer to bond **breaking** which is endothermic: the enthalpy change associated with **forming** the same bonds is exothermic, so the values used for bond forming are negative rather than positive.

The overall enthalpy change of the reaction can now be seen to be:

$$\{3 \times 413 + 358 + 464 + 1.5 \times 498\} - \{2 \times 805 + 4 \times 464\} = (2808 - 3466) = -658 \text{ kJ•mol}^{-1}$$

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

Note that this value is considerably different from the literature value for the enthalpy change of combustion of methanol, which is $-$ 726 kJ•mol^{-1}. This is due to the fact that bond dissociation enthalpies are **average** values and may not be very realistic for the bonds in the particular environment they are being applied to.[1]

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25. This question is concerned with standard electrode potentials, $E^{\ominus}$, which many high school students do not meet until after the date of the NHSCE. The question is not, however, a very difficult one, particularly if you appreciate that the standard oxidation potentials are numerically the same as the standard reduction potentials, but with the opposite sign. This can easily be seen if we tabulate the values. I have included the oxidation states, because these are not immediately obvious in the oxy-vanadium ions (although they can, of course, be easily calculated using the oxidation number rules).

    Students also need to be aware that although this table only shows half-equations, it is not necessary to convert them to full, balanced equations because stoichiometry does not affect the size of electrode potentials. (Concentrations, however, do affect electrode potentials, but the values given here are are **standard** electrode potentials so all the solutions of vanadium-containing species can be assumed to be 1.0 mol·kg^{-1} ≈ 1.0 mol·dm^{-3} .)

Reduction			**Oxidation**		
Ox. # change	Equation	$E^{\ominus}_{red}$ / Volts	Ox. # change	Equation	$E^{\ominus}_{ox}$ / Volts
2 to 0	$V^{2+} + 2e^- \leftrightarrow V$	– 1.175	0 to 2	$V \leftrightarrow V^{2+} + 2e^-$	+ 1.175
3 to 2	$V^{3+} + e^- \leftrightarrow V^{2+}$	– 0.255	2 to 3	$V^{2+} \leftrightarrow V^{3+} + e^-$	+ 0.255
4 to 3	$VO^{2+} + 2H^+ + e^- \leftrightarrow V^{3+} + H_2O$	+ 0.337	3 to 4	$V^{3+} + H_2O \leftrightarrow VO^{2+} + 2H^+ + e^-$	– 0.337
5 to 4	$VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O$	+ 0.991	4 to 5	$VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + e^-$	– 0.991

It can easily be seen from the table that a standard **oxidation** potential $E^{\ominus}_{ox}$ of + 0.255 Volts is needed for V(II) to be oxidized to V(III), however, if we wish to prevent V(IV) forming then we must not allow the value to get as low as – 0.337 Volts. Converting back to the more commonly used standard **reduction** potentials then $E^{\ominus}_{red}$ needs to be between – 0.255 and + 0.337 Volts. The answer to this question is therefore **B**.The interconversion

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[1] There are two related definitions that are sometimes confused: 1) The **bond dissociation enthalpy** (or bond dissociation energy) is the enthalpy increase that accompanies the homolytic fission of one mole of bonds in a covalently bonded species to give individual atoms or radicals, with both the original species and the resulting fragments being in their standard states, under standard conditions. 2) The **bond enthalpy term** (or bond energy) is the average value of the bond dissociation enthalpy for the same type of bond in a number of different compounds.

between different oxidation states of vanadium involves a variety of beautiful colour changes, and can easily be done in a high school lab. It is a good way of demonstrating how the oxidation number changes can be limited by judicious choice of oxidizing or reducing agent.