

ANSWERS TO PART A OF THE CANADIAN CHEMISTRY CONTEST EXAMINATION 2007

These answers are designed to help students who are preparing to take the Canadian Chemistry Contest for High School and Cégep Students (CCC) – formerly known as the National High School Chemistry Examination – in 2008 or subsequent years. Note that information given here will generally not include material from answers given for previous years' exams, so that students should go through the 2001 to 2006 exams (questions and answers) before attempting the 2007 examination.

Students should try to do the questions in Part A of the 2007 Examination on their own, and then compare their answers with the solutions given below. They should not be put off by the length of the explanations, which do not reflect the length of time needed to think out answers to the questions. Rather, these notes are designed as a teaching aid. They discuss subjects arising from the questions, as well as how to work out the answers. They also contain tips about how to set about doing a multiple choice examination in general.

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

The people involved in preparing the CCC very much appreciate all the comments and feedback that we get from teachers. We have tried to incorporate some of these comments in with the solutions. We have also tried to indicate how students did in particular questions, although, unfortunately, we have much less information about this for the 2007 examination than we did for 2006. Nevertheless, it should be pointed out, that students in different parts of the country sometimes perform very differently in the examination, with regional averages ranging from 35.4% to 55.0%. We feel that these differences are partly because the provincial curricula do not necessarily follow the Pan-Canadian protocol, or, if they do, then they emphasize different aspects of the curriculum. Most of the statistical information given in these solutions comes from Manitoba, courtesy of the Regional Coordinator, François Gauvin, and the District Coordinator, Krystyna Koczanski. Some data was also available from Alberta, thanks to Christie McDermott, the Regional Coordinator there.

This year the examination questions were prepared by a panel of five writers, with the National Examiner acting as editor, rather than as the sole question writer. The aim was to prepare an examination that was more accessible to students than has been the case in previous years, but, regrettably, the average marks stayed more or less the same. Individual marks were, however, much higher than usual in some cases, with several of the students obtaining perfect scores. These students were mostly from the ranks of those who were taking Part C in conjunction with Part A of the examination, i.e. they were students hoping to be considered for the Olympiad competition. The Olympiad competitors are generally much better prepared for the examination than students who take it as part of their general chemistry coursework. The solutions given here are intended to level the playing field so that all students can prepare for the examination, irrespective of their particular provincial curriculum or whether they are enrolled in an Olympiad preparation program or not.

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

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

1. Every year since 2002, the first question of the exam has been devoted to a safety issue. In recent years this has generally involved some aspect of WHMIS, but this year's question required students to know something about the flammability of different substances. Students in different provinces succeeded to different extents with this question, with 51% choosing the correct answer in Alberta (AB), compared with just 38% in Manitoba (MB).

The students are asked to identify which one of the 5 substances listed **MUST** be kept away from flames. It is, of course, good practice to keep all substances away from flames, but people working in labs need to be aware of the relative dangers of different materials.

The substances listed in this question were all anesthetics, but information about this particular application was intended to introduce an element of reality into the problem, rather than to be required knowledge for reaching the solution.

Let us consider each of the substances listed as possible answers in turn:

A. Xenon, Xe. This is a noble gas, and so it is unlikely to be reactive enough to cause a problem with flammability. (Personally, I find it surprising that anyone should contemplate using such an unreactive, rare and expensive material for use as an anaesthetic, but it certainly has been considered as such.)

B. Nitrous oxide, N₂O. About 30% of students chose this answer, which was very disappointing as nitrous oxide is, in fact, an oxidant, which means that it cannot also be a fuel¹.

Students may have been confused here, because they likely know that "lower oxides", i.e. oxides combined with an element in a low oxidation state, may often be oxidized to "higher oxides", i.e. oxides that are combined with the element in a higher oxidation state², however they also need to be aware that combustion is a special kind of oxidation reaction in which heat does not have 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).

Lower oxides, however, can also be reduced (by the removal of oxygen) so that they can, themselves, act as oxidants. In other words, it is possible for the oxides to be reduced or oxidized depending on the conditions.³ It is important to remember that simple **inorganic** compounds containing oxygen can often be oxidants. Note, however, that inorganic compounds containing carbon, such as carbon dioxide or metal carbonates are neither oxidants nor fuels. Carbon dioxide and metal carbonates are, in fact, often used in fire extinguishers.

The final 3 of the suggested answers given in this question are:

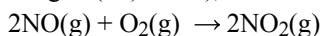
C. Chloroform (trichloromethane), CHCl₃

D. Ether (ethoxyethane), CH₃CH₂-O-CH₂CH₃

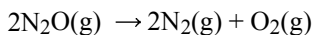
E. Isoflurane (2-chloro-2-(difluoromethoxy)-1,1,1-trifluoroethane), CF₃-CHCl-O-CHF₂

¹ See the answer to question 1 of the 2004 National High School Chemistry Exam, in which the fire triangle is discussed, along with the differences between fuels and oxidants.

² An example of the oxidation of a lower oxide to a higher one is the oxidation of nitric oxide (i.e. nitrogen (II) oxide) to nitrogen dioxide (i.e. nitrogen (IV) oxide), thus:



³ Note that nitrous oxide (i.e. nitrogen(I) oxide), does not, itself, appear to be oxidized under any conditions. It functions as an oxidizing agent because it is broken down into nitrogen and oxygen when it is heated, thus:



and it is the oxygen formed that is the true oxidant in reactions involving nitrous oxide.

These options all involve **organic** compounds, and, although a detailed knowledge of organic chemistry is not required in the Pan-Canadian protocol, students should be aware that **most organic compounds are flammable** (and, indeed, are often used as fuels). Exceptions to this rule are halogenated organic compounds, i.e. carbon-containing compounds containing one or more of the halogens (fluorine, chlorine, bromine or iodine): in fact halon fire extinguishers use compounds of this type. Knowledge of this rule would eliminate options C and E.

Another simple rule of organic chemistry is that **organic compounds containing oxygen tend to be more flammable than simple carbon-hydrogen compounds** (c.f. the rule for inorganic substances). This is because the oxygen within the organic molecule can behave as an oxidant in the combustion process, unlike the oxygen in inorganic molecules⁴. Knowledge of this rule would support the choice of option D.

Finally the choice of **D** (which is the correct answer to this question) should be supported by the knowledge of the compound by any student who might have used ethoxyethane (ether) in the laboratory. Such students should know that it is, in fact, very dangerously flammable. Although it is unusual, these days, to find it in a school chemistry lab, it is sometimes used to anaesthetize fruit flies in biological experiments.

General anaesthetics are used in surgery to render a patient unconscious whilst undergoing surgical procedures which would otherwise be very painful. Nitrous oxide is non-toxic but it only produces a light anaesthesia: it is also known as “laughing gas”, because the person who has been anaesthetized may awake to feel euphoric, but it is equally likely to make them feel like crying, or to become otherwise emotionally unstable and “dissociated”. Ether is an effective anaesthetic, but its flammability is a major disadvantage, and also doctors and nurses who administer it regularly have been known to become addicted to it. Chloroform produces deep anaesthesia, and was, in fact, used to help Queen Victoria during the birth of her son Prince Leopold, but it is toxic and can cause liver damage, and the dose has to be carefully controlled as the difference between an effective dose and a lethal dose is very small. Other halogen compounds, such as isoflurane, have been developed and these avoid the disadvantages of chloroform. Xenon is rarely used as an anaesthetic as it is expensive and requires special methods of delivery and removal of waste.

/solution to Question 2 begins on the next page

⁴ Ethanol (C₂H₅OH) is increasingly being used as a fuel in internal combustion engines. It is not nearly as flammable as its isomer ethoxyethane, which is much less stable. The presence of oxygen in the molecule means that its combustion is very clean, because all the carbon in the molecule can be oxidized rather than being liberated as soot.

2. This is a very simple question, with most students (69% in AB, 78% in MB) choosing the correct answer. The question requires the students to determine the number of lone pairs on a series of simple molecules and one ion. The methodology required to solve the problem was extensively discussed in questions 12 and 15 of the 2006 exam, but in the case of the 2007 question, most of the species given were standard examples that most students should have met.

	A. NH ₃	B. BrF ₃	C. H ₂ O	D. CH ₄	E. NH ₄ ⁺
1. Central atom	N	Br	O	C	N
2. Group in the periodic table of the central atom (IUPAC number)	15	17	16	14	15
3. Number of valence electrons on the central atom	5	7	6	4	5
4. Valence electrons from central atom used in bonding	3	3	2	4	4
5. Electrons removed to create charge	0	0	0	0	1
6. Nonbonding electrons on central atom = line 3 – line 4 – line 5	2	4	4	0	0
7. Total number of lone pairs of electrons on central atom = ½ x line 6	1	2	2	0	0

The species that has only one lone pair (non-bonding pair) of electrons on the central atom is therefore NH₃, and the answer to this question is therefore **A**.

Note that bromine does not obey the octet rule in BrF₃. It has 2 more electrons than the octet “rule” predicts⁶.

/solution to Question 3 begins on the next page

⁶ The “octet” rule is based on the fact that an atom or ion has a peculiarly stable electron configuration when all the s and p orbitals in its valence shell are occupied (this is the “noble gas” configuration). It is, however, possible for atoms with empty d-orbitals in the same shell, to use these orbitals to receive electrons from other atoms. Bromine uses its 4d orbitals in addition to its 4s and 4p orbitals to accept electrons from fluorine in BrF₃, and, in doing so it breaks the octet rule. The central atoms of the other species involved in this question (N, O and C) are all in the second period of the Periodic Table, and fill up 2s and 2p orbitals to achieve an octet – they have no d orbitals to call into action to accept any further electrons. The octet rule is discussed in further detail in the Solution to Question 8 of the 2002 exam.

3. This is another simple question, but with a very varied success rate (65% of students chose the correct answer in MB, compared with only 37% in AB). It requires students to choose the atom with the smallest atomic radius, which means that they need to know (1) that periods that are lower in the periodic table have larger atoms in them (because larger atoms have more electrons and some of these will be in shells that are further away from the nucleus), and (2) that going from left to right within a particular period of the periodic table means that atoms become smaller (because electrons are being added into the same shell, but the nuclear charge is increasing, pulling the shell closer towards the nucleus).

Of the atoms given, Se and Br can be eliminated from consideration, because they are in a lower period than P, S and Cl. Of these remaining atoms, Cl must be the smallest, because it is further to the right than P and S, whilst being in the same period. The answer to this question is therefore **B**.

4. This is a straightforward question, and it was disappointing that only 49% of the contestants (in both AB and MB) chose the correct answer. The question required students to identify the atom with the largest first ionization energy.

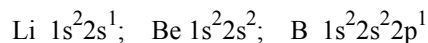
The first ionization energy⁷ may be defined as the enthalpy increase that occurs when one electron is removed from each atom in a mole of gaseous atoms of a specified element, to give one mole of ions, each with a single positive charge, at standard temperature and pressure. All ionization energies are positive, because energy is required to remove an electron from the influence of the positive charge of the nucleus.

In order to predict the relative sizes of first ionization energies, students need to appreciate that larger atoms have lower first ionization energies because the electrons being removed are further away from the nucleus, and also because electrons in the inner shells of the atom shield the outer electrons somewhat from the effect of the nucleus. The atomic size rules that were given in Question 3 above apply here, so that, for the atoms given in the question, Al and Si will have lower first ionization energies than B, C and N, which are in a higher period of the periodic table. Furthermore of the three latter elements, N will have the largest first ionization energy as it has the smallest atomic size, being the furthest to the right in its period.

It should be noted that, with respect to ionization energies, the rules are not quite as clear cut as for atomic size, because there is another effect to be considered, namely that of the electronic configurations of the atom, and of the ion that is formed when an electron is removed from that atom. For example, the numerical values of the first ionization energies of the elements in the second period are:

Li 520; Be 900; **B 801**; C 1086; N 1402; O 1314; F 1681; Ne 2081 (all values in kJ mol⁻¹)

It can be seen that, although the values generally increase going from left to right, the first ionization energy for B is lower than might be expected. The reason for this can be understood by looking in more detail at the electronic configurations involved, which are:

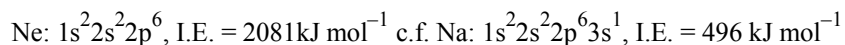


Beryllium has an s orbital with two electrons in it, i.e. it has a complete s orbital, and this confers some stability on it, which makes it difficult to take an electron away from it. Boron, on the other hand, has a p orbital with just one electron in it, which is a rather unstable arrangement: if, however, it loses that electron

⁷ Enthalpy changes that occur when subsequent electrons are removed are also called ionization energies. For example, the second ionization energy would refer to the removal of one electron from each ion, in a mole of ions each with a single positive charge, to give one mole of ions each with a double positive charge, in the gaseous state. Note that electrons are removed from the outermost (valence) shell of the atom first, because these electrons are furthest away from the influence of the nucleus so less energy is required to remove them. As increasing numbers of electrons are removed the ionization energies become larger and larger, because there are fewer electrons left and the relative attraction of the nucleus for the remaining electrons becomes greater.

it attains the stability of the complete s orbital (like Be has to start off with) and so it is relatively easy for it to become ionized.

A similar effect may be observed further along in the period, with nitrogen having the relatively stable arrangement of a half-filled p orbital ($1s^2 2s^2 2p^3$), giving it a slightly higher first ionization energy than one might expect. Oxygen (with the electron configuration of $1s^2 2s^2 2p^4$) has one electron more than the relatively stable half-filled p orbital so that it loses that electron fairly easily (although it is not sufficient to break the generally increasing trend). The greatest effect of this kind is, of course, observed with the noble gas at the far right of the period, which has a complete p orbital – a very stable electron arrangement, which is very difficult to break into. The first element on the left of the next period is very easily ionized, because it needs to lose just one electron from the new outer shell, to achieve the stable noble gas electron configuration, as can be observed with neon and sodium:



5. This question was somewhat more unusual than the rest of the introductory questions, because it required students to interpret information given in a tabular format. The examination team feels, however, that interpretation of tables is an important skill that students need to develop, and that it is therefore worth examining. The question elicited very different results in the two reporting provinces, with only about 38% of contestants in MB choosing the correct answer, compared with 69% of students getting the correct answer in AB. This discrepancy might have been due to the fact that it required knowledge of metallic bonding, which is often not covered in all provincial curricula, even though it is included in the Pan-Canadian protocol.

The question required students to identify the structures of some solid substances in the solid state. A starting point for the question is to establish whether the elements involved in each substance are metals, non-metals or a mixture of the two, and thence to determine its bonding type. Students need to be aware that bonding between metals will be metallic bonding, bonding between non-metals will be covalent, and bonding between metals and non-metals will be ionic. All that is required after the bonding has been established is to work out whether covalently bonded substances have molecular or covalent network structures. Note that this question does not demand that the students know anything about intermolecular bonding, nor do they have to identify the arrangement of the atoms or ions within the structure.

The table shown in the question is given below:

Substance \ Response	LiCl	HCl	CH ₃ OCH ₃	C(graphite)	K
A.	Ionic	Ionic	Molecular	Covalent network	Atomic
B.	Ionic	Metallic	Molecular	Covalent network	Atomic
C.	Ionic	Molecular	Molecular	Covalent network	Metallic
D.	Ionic	Molecular	Metallic	Atomic	Metallic
E.	Molecular	Ionic	Ionic	Atomic	Metallic

Let us consider each of the substances given in the table in turn:

LiCl: This is a compound between a metal (Li), identified as such because it is in IUPAC Group 1 on the left hand side of the periodic table, and a non-metal (Cl), identified as such because it is in Group 17 on the right hand side of the periodic table. As it is a compound between a metal and a non-metal it must be ionic, which eliminates response E for the question.

HCl: This is a compound between two non-metals, therefore it must be covalently bonded.⁸ It cannot therefore be ionic or metallic, so A, B and E cannot be the correct responses. Note that the only covalent option given in this column of the table is “molecular”, so that students do not have to make a decision about the type of covalent bonding here.

CH₃OCH₃: This is a compound formed from the non-metals, C, H and O, so it must be covalently bonded, which eliminates responses D and E. Again the students do not have to make a decision about the type of covalent bonding involved, because the only option is “molecular”.

C(graphite): Carbon is, of course, a non-metal. It might be tempting here to choose “atomic” as its bonding type, since it is in the elemental state, but there is really no such thing as “atomic” bonding or structure. Individual atoms might exist in the gaseous state, but in the solid state they would interact through induced dipole interactions, and would involve some sort of array of atoms (structure). Any temptation to choose “atomic” as the correct structure for C(graphite) should have been dispelled by the fact that responses D and E have already been eliminated as options. The only other option given is “covalent network”, which is the better choice here. In fact, in solid graphite, carbon atoms are covalently bonded within 2-dimensional sheets, with induced dipole interactions (i.e. London forces) between sheets.

K: Potassium is, of course, a metal, so it has a metallic bonding and structure. With options D and E out of the question, this means that only **C** is left as the correct answer. Students might be tempted again to choose “atomic” here, because, once again, they are looking at an element, but this is an inappropriate choice, for the same reasons as given for C(graphite) above. In fact there is some indication that many students did indeed choose “atomic”, because the most popular choice of answer to this question was A (which means that they also chose “ionic” as the structure of HCl).

⁸ Remember that you are told that all the substances are pure and in their solid state. Students are often so used to thinking of HCl(aq), hydrochloric acid, as being ionic that they may well have mistakenly chosen “ionic” here, but HCl(aq) is a solution of HCl in water, so it is not a pure substance – and the solution is, of course, in the liquid state (not a solid).

ANSWERS TO PART A OF THE CANADIAN CHEMISTRY CONTEST EXAMINATION 2007 continued

6. This question was generally quite well done, with about 71% of students choosing the correct response in Alberta (AB), compared with 58% in Manitoba (MB). Students were required to select the response that listed a set of three bonds in order of increasing polarity. This was a relatively simple task in that each of the bonds involved fluorine combined with one of three other elements in the same period of the periodic table as fluorine.

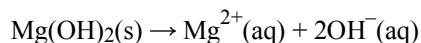
In order to answer this question, students needed to know that the polarity of a bond may be predicted by the difference in electronegativity¹ of the elements. A greater difference in electronegativity indicates that a bond is more polar than a bond between atoms of elements with smaller electronegativity differences. (A bond between atoms of the same element will be non-polar because it will involve no difference in electronegativity.)

Within a particular period of the periodic table, the electronegativities of the elements increase going from left to right within the period, with the more non-metallic elements having the greatest electronegativities. The electronegativities of the elements given in this question can thus be said to follow the trend: $\text{Be} < \text{C} < \text{O} < \text{F}$ (i.e. fluorine is the most electronegative element in the period, and in fact within the whole periodic table¹).

The polarity of the bonds thus increases in the order $\text{O-F} < \text{C-F} < \text{Be-F}$ (i.e. the Be-F bond is the most polar one), meaning the correct answer to this question was **A**. Note that the most popular *incorrect* answer was D (Be-F, C-F, O-F), which indicated that students had probably got as far as determining the increase in electronegativity of the elements involved, but that they had not then applied this to determining the polarity of the bond.

7. This question was poorly done, with only about 30% of students choosing the correct answer in the two provinces (AB and MB) for which data was available. It required students to calculate the pH of a solution of $\text{Mg}(\text{OH})_2$ with a concentration of $0.0001 \text{ mol L}^{-1}$ at 25°C . This problem can be solved by a brief calculation as shown below.

Students are told that $\text{Mg}(\text{OH})_2$ is a strong base, which is completely dissociated in water (therefore answers A and B can be immediately disregarded as these pH values refer to acidic solutions!). The solution equation can be written as follows:



So that

$0.0001 \text{ mol L}^{-1}$ of $\text{Mg}(\text{OH})_2(\text{s})$ gives $0.0001 \text{ mol L}^{-1}$ of $\text{Mg}^{2+}(\text{aq})$ and $0.0002 \text{ mol L}^{-1}$ of $\text{OH}^{-}(\text{aq})$

Therefore the hydroxide ion exponent, $\text{pOH} = -\log [\text{OH}^{-}(\text{aq})]$
 $= -\log (0.0002)$
 $= 3.70$

¹ The electronegativity of an element may be defined as the power of an atom of that element to attract electrons towards itself from another atom to which it is covalently bonded. The most commonly used measure of electronegativity is the Pauling scale, which attributes an electronegativity value of 4.0 to the most electronegative element (fluorine), with the electronegativities of other elements being established by comparison with this value. Note that all elements are assigned an electronegativity value, even if their atoms can barely be said to attract electrons at all (as is the case with the elements in the lower left part of the table.)

Students are expected to know that the ionic product of water, K_w , is 1.0×10^{-14} at 25°C (although this is actually given in the next question), and that $K_w = [\text{H}^+] \times [\text{OH}^-]$, or, more usefully here, that

$$pK_w = \text{pH} + \text{pOH} = 14 \text{ at } 25^\circ\text{C}$$

i.e. $\text{pH} = 14 - \text{pOH}$,

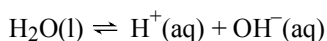
therefore for the solution given here $\text{pH} = 14 - 3.70$
 $= 10.30$

and the answer to this question is therefore **E**.

Note that key "B" ($\text{pH} = 4.0$) was just as popular as E as a choice of answer, which indicates that many students simply calculated $-\log(0.0001 \text{ mol L}^{-1})$, i.e. $-\log(\text{concentration of Mg(OH)}_2)$, without even beginning to consider even the hydroxide ion concentration, let alone the hydrogen ion concentration.

8. This question was poorly done, with about 29% of AB students choosing the correct result, compared with 37% for MB. It was a fairly simple question requiring students to have some understanding of basic phenomena: it did **not** require a complicated calculation.

The question concerned the ionic product of water, K_w , which is the special equilibrium constant that governs the dissociation of water molecules according to the following equation:



The equilibrium constant for this dissociation can be written in terms of concentrations thus:

$$K_c = \frac{[\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O(l)}]} \dots \dots \dots \text{Equation (1)}$$

The concentrations of the ions in water is very small, however, and the concentration of undissociated water molecules is so large in comparison with the ion concentrations, that the concentration of water molecules can be considered to remain constant even when the ionic concentrations change (due, for example, to a change in temperature). The concentration of water molecules can then be combined with the equilibrium constant to create a new constant, which is known as the ionic product of water, thus:

Rearranging equation (1) gives

$$K_c [\text{H}_2\text{O(l)}] = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = \text{constant}$$

i.e. the ionic product of water, $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$

At 298 K (25°C) $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})] = 10^{-7} \text{ mol L}^{-1}$ (2)

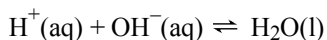
So $K_w = 10^{-7} \text{ mol L}^{-1} \times 10^{-7} \text{ mol L}^{-1}$
 $= 10^{-14} (\text{mol}^2 \text{ L}^{-2})$

The question on the exam asks you to choose the most likely value for K_w at 273 K (0°C), given that the

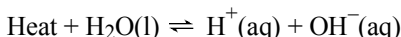
(2) Note that there are equal numbers of hydrogen ions and hydroxide ions in neutral water, but their concentrations are only $10^{-7} \text{ mol L}^{-1}$ at 298 K. This means that the pH of water (where $\text{pH} = -\log[\text{H}^+(\text{aq})]$) is only equal to 7 at 298 K.

neutralization of a strong acid with a strong base is an exothermic reaction. Note how the wording indicates that you should estimate a value rather than attempt to calculate it.

The neutralization reaction refers to the following equation:



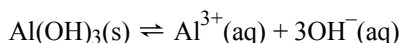
This is the **reverse** of the equation given for the dissociation of water, so that, if the neutralization reaction is exothermic (giving out heat), then the dissociation reaction must be endothermic (taking in heat).³ We can now include “heat” in the dissociation equation, thus:



Applying Le Châtelier’s principle to this equation tells you that reducing the amount of heat available (by lowering the temperature from 298K to 273K), will cause the reaction to “swing to the left”, leaving fewer ions in the equilibrium mixture. If the ion concentrations each become $<10^{-7} \text{ mol L}^{-1}$, then K_w will be $<1.0 \times 10^{-14}$. The only values given for K_w for which this is the case are given in keys A and E, but, as neither the ionic concentrations nor K_w can be negative, A can be ruled out, so the answer to this question must be **E**.

9. This was another question that was poorly done, with only 28.6% of AB students and 34.6% of MB students choosing the correct answer.

The question effectively required students to establish an expression for the solubility⁴ of aluminium hydroxide in units of kg /1000 L, given the solubility product constant. The solubility product constant is another example of a special equilibrium constant, which, in this specific case, governs the following equilibrium reaction:



The concentration equilibrium constant for this reaction is:

$$K_c = [\text{Al}^{3+}(\text{aq})] [\text{OH}^-(\text{aq})]^3 / [\text{Al}(\text{OH})_3(\text{s})]$$

The aluminium hydroxide is, however, a solid, so its concentration is equal to its density and this does not change (at constant temperature)⁵, so that we can say that:

$$K_c [\text{Al}(\text{OH})_3(\text{s})] = [\text{Al}^{3+}(\text{aq})] [\text{OH}^-(\text{aq})]^3 = \text{constant}$$

This constant is called the solubility product constant of aluminium hydroxide,

$$K_{\text{sp}} = [\text{Al}^{3+}(\text{aq})] [\text{OH}^-(\text{aq})]^3$$

³ Note that this can be surmised from the equations, because the neutralization reaction involves forming bonds (an exothermic process), and the dissociation reaction involves breaking bonds (an endothermic process).

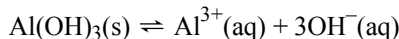
⁴ The question actually asks the students “What mass (in kg) will be required to saturate 1000 L of water at 298 K” – students are expected to know that solubility is defined as the mass (or amount in moles) of a substance that is required to give a saturated solution at a specified temperature, and that a saturated solution is one that is in equilibrium with undissolved substance at that temperature.

⁵ Note that solubility constant expressions may become unreliable when the solid is somewhat soluble, when the ionic concentrations are appreciable and ion-pairing occurs in solution: this causes the observed concentrations to be lower than expected. The solid “concentration” is reliably constant.

The value of $K_{sp}\{\text{Al}(\text{OH})_3\}$ is given as 1.0×10^{-32} at 298 K.

We can determine the relationship between the solubility, s in mol L^{-1} , and K_{sp} using the following logic:

If s moles of solid aluminium hydroxide dissolve in water to give a saturated solution, then, using the equation:



we can see that $[\text{Al}^{3+}(\text{aq})] = s$ in mol L^{-1} and $[\text{OH}^{-}(\text{aq})] = 3s$ in mol L^{-1}

so that

$$\begin{aligned} K_{sp} &= [\text{Al}^{3+}(\text{aq})] [\text{OH}^{-}(\text{aq})]^3 \\ &= s \times (3s)^3 \\ &= 27s^4 \end{aligned}$$

and the solubility

$$\begin{aligned} s &= (K_{sp}/27)^{1/4} \\ &= (1.0 \times 10^{-32}/27)^{1/4} \end{aligned}$$

Remember that this value for solubility has the units of mol L^{-1} , which now need to be converted to the required units of mass in kg per 1000 L.

You are given the relative molar mass⁶, M_r , of aluminum hydroxide in the question (it is 78.0), which means that the molar mass of aluminum hydroxide is 78.0 g mol^{-1} .

The solubility of the aluminium hydroxide in the required units can now be calculated as

$$s \text{ mol L}^{-1} \times 78.0 \text{ g mol}^{-1} / \{(1000\text{g} \times 1 \text{ kg}^{-1}) \times 1000 \text{ L}\}$$

Cancelling units and “1000s” gives the solubility as $s \times 78.0 \text{ kg per 1000 L}$, and substituting for s gives the required expression, which is

$$\{1.0 \times 10^{-32}/27\}^{1/4} \times 78.0$$

So that the answer to this question is **A**.

Note that the question states that aluminum hydroxide is used in the dyeing industry. It is not, itself, a dye. It is a **mordant**, which means that it is a substance that is impregnated onto the cloth before it is treated with dye. The small, highly charged aluminium ions attract both the cloth and the dye, so that the colour is less likely to come off the cloth when it is later washed.

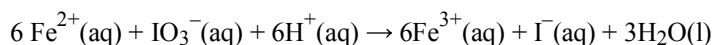
⁶ The relative molar mass is also (incorrectly) called the relative molecular mass or the molecular weight. It is a **relative** value so it does not have units. It is defined as the ratio of the mass of one mole of the specified substance to one-twelfth of the mass of one mole of carbon-12 atoms. As the mass of one mole of carbon-12 atoms is defined as exactly 12 g, then the molar mass of the specified substance (in g mol^{-1}) is simply being divided by one twelfth of 12 g mol^{-1} (i.e. by 1 g mol^{-1}), so that the relative value is numerically the same as the molar mass, but without units. Its unitless value is simply a shorthand way of writing the value you need to know.

10. 37.1% of AB students and 32.7% of MB students chose the correct answer to this question. This poor performance may be explained by the fact that it concerned a redox reaction, and many teachers had not reached this part of the syllabus by the date of the exam. We had, however, hoped that students would manage to cope with this relatively simple question, particularly as previous exams have covered the subject, and the methodology has been discussed extensively in the solutions.

For students who have learned about oxidation numbers the problem can easily be solved by this method. As a reminder, the rules for assigning oxidation numbers in the Appendix to this section of this year's answers⁷. Using these rules we can see that the oxidation numbers of Fe^{2+} to Fe^{3+} are +2 and +3, respectively (i.e. equal to their valencies). This means that every time one Fe^{2+} ion is oxidized to Fe^{3+} it changes by +1 oxidation number (which is the same thing as saying that it loses one electron).

When Fe^{2+} is oxidized to Fe^{3+} , the iodate (IO_3^-) ion is reduced to iodide (I^-). It is easy enough to see that iodine is in the -1 oxidation state in the iodide ion, but we need to calculate its oxidation state in iodate. In order to do this we need to apply Rule 3, which states that, in ions, the algebraic sum of the oxidation numbers equals the charge on the ion, and Rule 6, which states that the oxidation number of oxygen is always -2 (although there are exceptions). The overall charge on the iodate ion is -1, and there are three oxygen atoms in the ion, which are "worth" $(3 \times -2) = -6$ oxidation numbers, this means that the one iodine atom in the ion must have an oxidation number of +5 (because $-1 = +5 + -6$). The oxidation number of iodine therefore changes from +5 to -1, i.e. a difference of 6 oxidation numbers, in the reduction process, meaning that 6 moles of Fe^{2+} are oxidized to Fe^{3+} in this process, and the answer to this question is therefore **E**. An equally popular answer to this question was B (3 moles), which probably indicates that students choosing this key were confused by the fact that an iodate ion contains 3 oxygens.

If you have not covered oxidation numbers, it is still perfectly possible to solve this problem by writing a balanced reaction equation. What you have to remember, however, is that the reaction is done in acid solution, so you need to add some H^+ ions, which can take care of the oxygen atoms in the iodate ion by reacting with them to make water. The equation you should get is:



⁷ These rules were originally given with the 2001 answers.

APPENDIX

RULES FOR ASSIGNING OXIDATION NUMBERS (OXIDATION STATES)

In simple binary compounds the oxidation number is equal to the valency of an ion.⁸ Valency, however, is a value that is determined experimentally by looking at the formula of a lot of compounds containing an element or group of elements. On the other hand oxidation numbers are theoretical values that assume every element in a compound is present as an ion – even though it may, in fact, be covalently bonded! Oxidation number is an indication of the number of electrons that an atom is using for bonding.

The rules for assigning oxidation numbers (also called oxidation states) are mainly common sense, and are not difficult to learn. They are:

1. The oxidation number of atoms in uncombined elements = 0.
2. In neutral compounds the algebraic sum of the oxidation numbers = 0.
3. In ions, the algebraic sum of the oxidation numbers equals the charge on the ion.
4. In any substance, the more electronegative atom has the negative oxidation number, and the less electronegative atom(s) has the positive oxidation number.

Remember that the elements in a formula are written in order of increasing electronegativity.

5. The oxidation number of hydrogen in all its compounds, except metal hydrides, is +1. (In metal hydrides it is -1.)
6. The oxidation number of oxygen is always -2 (except in peroxides when it is -1, and in OF₂ when it is +2).

⁸ Remember that for the main groups of the periodic table: all Group I elements have a valency of +1. All group II elements have a valency of +2. All Group III (or IUPAC 13) elements have a valency of +3, but thallium also has a valency of +1. Group IV (or IUPAC 14) elements have a valency of +2 or +4, with +4 being more common at the top of the group, and +2 being more common at the bottom. The transition metals and most non-metal exhibit variable valencies, but transition metals will usually have +2 as one of their valencies. The non-metals will have negative valencies if they are written at the end of the formula. The negative valency of a non-metal will equal (simple group number - 8), thus sulfur has a valency of (6 - 8) = -2.

ANSWERS TO PART A OF THE CANADIAN CHEMISTRY CONTEST EXAMINATION 2007 continued

11. Students in Manitoba did moderately well in the question, with 52.7% of them choosing the correct answer, but students in Alberta did very poorly with a success rate of only 22.9%. This huge difference can surely be attributed mainly to curriculum differences, however, it should be noted, that this question was very similar to questions on previous exams – it was particularly like Question 17 on the 2005 exam.

The question concerns the determination of the acid dissociation constant, K_a , of a monoprotic acid (ascorbic acid, i.e. vitamin C). The formula of vitamin C is given as $C_6H_8O_6$, so you can calculate its molar mass ($6 \times 12.011 + 8 \times 1.008 + 6 \times 15.999$) = 176.124 g mol⁻¹. You are also told that the solution contains a 500-mg tablet of pure vitamin C dissolved in 100 mL of water, therefore

$$\begin{aligned} \text{the molar concentration of vitamin C} &= \{500 \text{ mg}/1000 \text{ mg g}^{-1}\} / \{100 \text{ mL}/1000 \text{ mL L}^{-1}\} \div 176.124 \text{ g mol}^{-1} \\ &= 5.00 \div 176.124 \text{ mol L}^{-1} \\ &= 0.02839 \text{ mol L}^{-1} \end{aligned}$$

Although the formula is given to you, it is probably simplest to represent the acid simply as HA when considering its dissociation equilibrium, which can be written as:



The equilibrium constant for this reaction is known as the acid dissociation constant or acid ionization constant, K_a , and can be expressed in terms of the equilibrium concentrations of the species in solution, thus:

$$K_a = [\text{H}^+(\text{aq})] [\text{A}^-(\text{aq})] / [\text{HA(aq)}]$$

The equilibrium concentration of $\text{H}^+(\text{aq})$ can be determined from the pH of the solution, since $\text{pH} = -\log [\text{H}^+(\text{aq})]$, therefore:

$$\begin{aligned} [\text{H}^+(\text{aq})] &= 10^{-\text{pH}} \\ &= 10^{-2.83} \\ &= 0.00148 \text{ (mol L}^{-1}\text{)} \end{aligned}$$

The initial state is assumed to be the non-dissociated acid and the equilibrium concentrations can be determined using the following table:

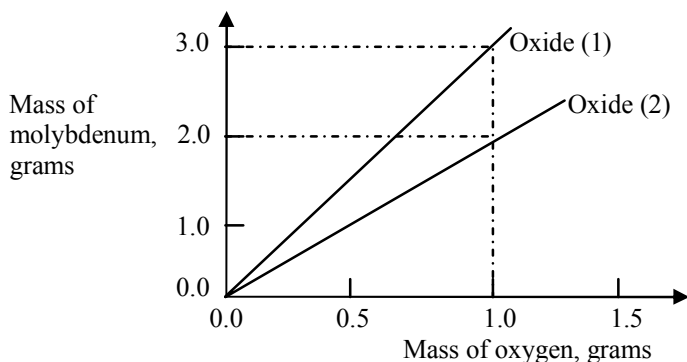
Concentration, mol L ⁻¹	[HA(aq)]	[H ⁺ (aq)]	[A ⁻ (aq)]
Initial	0.02839	0	0
Change	- 0.00148	+ 0.00148	+ 0.00148
Equilibrium	0.02691	0.00148	0.00148

These equilibrium values can now be inserted into the expression for the acid dissociation constant given in equation (1) above, thus:

$$\begin{aligned} K_a &= 0.00148 \times 0.00148 / 0.02691 \\ &= 0.000081397 \text{ (or } 8.1397 \times 10^{-5}\text{)} \end{aligned}$$

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

12. Results for this question were disappointing with 45.7% of AB students and 36.4% of MB students choosing the correct answer. The question required students to determine the empirical formulae of two oxides of molybdenum given the reacting masses in the form of the following graph which purported to be based on a series of experiments done by a group of researchers:



From this graph it can be established that, for Oxide (1), 3.0 g of molybdenum react with 1.0 g of oxygen, whilst, for Oxide (2), 2.0 g of molybdenum react with 1.0 g of oxygen. The empirical formulae can then be calculated in the usual way, as shown in the tables below:

Oxide (1)	Mo	O
Mass, g	3.0	1.0
Molar mass, g mol ⁻¹	96	16
Chemical amount, mol	0.03125	0.0625
Simplest ratio	0.03125 ÷ 0.03125 = 1	0.0625 ÷ 0.03125 = 2
Empirical (simplest) formula	MoO ₂	

Oxide (2)	Mo	O
Mass, g	2.0	1.0
Molar mass, g mol ⁻¹	96	16
Chemical amount, mol	0.02083	0.0625
Simplest ratio	0.02083 ÷ 0.02083 = 1	0.0625 ÷ 0.02083 = 3
Empirical (simplest) formula	MoO ₃	

The answer to this question was therefore **D**. The chief distractor in this question was C, which some students presumably chose because they simply looked at the mass ratios shown on the graph, rather than performing the calculation to find the ratio of chemical amounts. Note how the numbers work out so neatly here because the molar mass of molybdenum just happens to be exactly six times the molar mass of oxygen.

Note also how the graphs illustrate two fundamental chemical laws, which were well-known to earlier chemists, long before they knew about atoms and moles. These laws are:

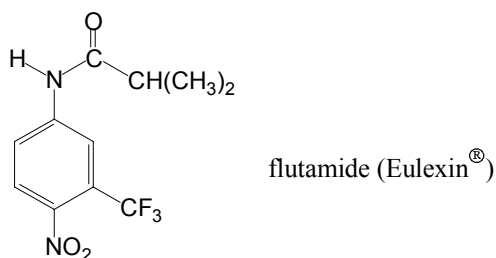
(1) The Law of Constant Composition (also called the Law of Constant Proportions or Definite Proportions), which states that a pure chemical compound always contains elements in the same proportions by mass, irrespective of the method of preparation. This means that a graph of the masses of any two of the elements in different samples of the compound will be a straight line through the origin. The graph given in this question gives a straight line through the origin for each of the oxides.

(2) The Law of Multiple Proportions, which states that where two elements can combine to form more than one compound, then the mass of one of the elements to a fixed mass of the other are in the ratio of small whole numbers. In the example given in this question, if we take a fixed mass, 1.0 g of oxygen, we can see that it combines with 3.0 g of molybdenum in oxide (1) and 2.0 g of molybdenum in oxide (2), so that the ratio of molybdenum to oxygen is 3/2:1 or 1.5 to 1.0. This is not, of course, a small whole

number, however we can double both the numbers to give a mass ratio of 3:2, which **does** involve small whole numbers, so the law is obeyed.

13. This question was similar to Question 12 in that it involved an empirical formula calculation, but it was somewhat better done, with 48.6% of AB students and 40.0% of MB students choosing the correct answer. Although it was essentially a calculation question, it was “counted” by the exam writers as one of the 5 questions on organic chemistry (along with questions 1, 16, 24 and 25). We try to balance the questions between the different sections of the Pan-Canadian protocol, but we are aware that some provinces do, in fact, do very little in the way of organic chemistry.

The connection with organic chemistry lies in the application of the empirical formula calculation to the organic compound, flutamide (Eulexin[®], structure below, which is used in the treatment of prostate cancer. Scientists have known for over sixty years that steroid hormones such as testosterone and androsterone (commonly known as “androgens”) stimulate the growth of prostate tumors. Eulexin[®] acts as an anti-androgen by inhibiting the uptake of steroid hormones in the prostate.



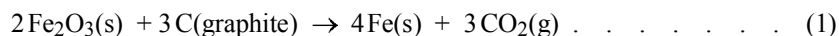
Students are told that the tablet used for an analysis weighed 203.21 mg, and that the residue (containing non-medicinal ingredients) after an extraction procedure weighed 128.23 mg, which means that the flutamide extract weighed $(203.21 - 128.23) = 74.98$ mg.

Given that the extract is found to contain 15.47 mg of fluorine, and that each molecule of flutamide contains 3 atoms of fluorine, we can use the fact that the ratio of the mass of fluorine to the mass of flutamide is equal to the ratio of three times the molar mass of fluorine to the molar mass of flutamide, in order to obtain the molar mass of flutamide. The following table summarizes the calculation:

	Fluorine	Flutamide
Mass in g (scaled up from masses in mg) ¹	15.47	74.98
Molar mass, M, in g mol ⁻¹	19.00 (for one atom of fluorine) or 3 x 19.00 (for three atoms)	$\frac{74.98}{3} \times 3 \times 19.00 = 276.3$ 15.47

The answer to this question is therefore **C**. (Note that the value of 276.2 g mol⁻¹ given in the question is obtained because a more precise value for the molar mass of fluorine has been used there.)

14. This question was moderately well done, with 65.7% of AB students and 52.7% of MB students choosing the correct answer. The solution to the question requires an equation calculation involving a limiting reagent. Various methods can be used for the calculation, one of which is shown in the tables on the next page which use the stoichiometric amounts as indicated in the balanced equation given in the question. (Note that no values need to be calculated for the CO₂(g) produced in the reaction.)



¹ This scaling up is permissible because we are looking at ratios. So that, providing the same units are used for both fluorine and flutamide, the units of mass will cancel out.

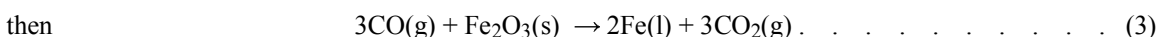
	Fe ₂ O ₃ (s)	C(graphite)
Mass, m, in g (scaled down from masses in kg) ²	1235	154.0
Molar mass, M, in mol ⁻¹	159.7	12.0
Chemical amount, n = m/M, mol	7.733	12.833
Ratio of chemical amounts used	7.733: 12.833 = 0.603	
Ratio of chemical amounts shown in equation	2:3 = 0.667	

As the value of the ratio used is less than the ratio shown in the equation (0.603 < 0.667), the limiting reagent must be Fe₂O₃ (with C in excess), so that the remainder of the calculation is performed using the chemical amount obtained for Fe₂O₃, as shown in the following table:

	Fe ₂ O ₃ (s)	Fe(s)
Ratio of chemical amounts shown in the equation	2:4	
Chemical amount, n, mol	7.733 (from table above)	7.733 x 4/2 = 15.466
Molar mass, M, g mol ⁻¹	(not required here)	55.85
Mass, m = nM, in g	(not required here)	15.466 x 55.85 = 863.8

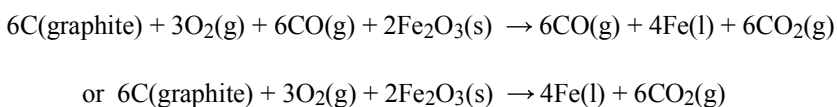
Scaling the masses back up again from g to kg shows that 1235 kg of Fe₂O₃ give 863.8 kg of Fe, so the answer to this question is **B**.

The thermite (or thermit) reaction is a type of highly exothermic redox reaction that usually occurs between a reactive metal and the oxide of a less reactive metal (the classic example is the reaction between aluminum and iron oxide, which is used in welding and in incendiary bombs). The blast furnace reaction is an unusual example of this type of reaction because it involves carbon, which is, of course, a non-metal. Carbon is also generally less reactive than iron, but relative reactivities change with temperature, so that it is possible that carbon itself might reduce iron oxide. In fact it seems that, at the high temperatures of the blast furnace, the carbon is oxidized first to carbon monoxide by hot air, and it is the carbon monoxide that actually reduces the iron oxide, thus:



Note that, at the high temperatures of the blast furnace, the iron that is formed is in the liquid state.

Multiplying equation (2) x 3 and equation (3) x 2 and adding the two together gives:



Comparing this with equation (1) on the last page shows how the same amount of iron can still be produced from the iron oxide ore, but that extra carbon needs to be supplied, along with oxygen (air), to ensure that the ore is effectively reduced.

² Again the scaling is permissible because we are looking at ratios, but, in this case, we shall have to remember to scale up to kg again at the end of the calculation.

15. This question was generally well done with 71.4% of AB students choosing the correct answer and 55.6% of MB students. The question required a two-step calculation, with step (1) being determination of the mass of oxalic acid in an impure sample using the titration data given, and step (2) being the calculation of the mass percent of the pure acid in the sample. The answers to both steps are required in the correct answer to the question. The following table outlines the calculation for step (1):

Reactant	H ₂ C ₂ O ₄ (aq)	OH ⁻ (aq)
Concentration, c, mol L ⁻¹		0.485
Volume, V, in L		34.47 mL/1000 mL L ⁻¹
Chemical amount, n = cV mol		0.01672
Ratio of chemical amounts as given in the equation	1:2	
Chemical amount, n, mol	0.01672/2 = 0.008359	0.01672 (as above)
Molar mass, M, g mol ⁻¹	90.04	
Mass, m = nM, g	0.008359 x 90.04 = 0.7526	

At this point it looks as though the answer is D. To confirm this answer we need to perform the calculation for step (2).

$$\begin{aligned} \text{The mass percent of oxalic acid in the impure sample} &= \{0.7526 \text{ g} / 1.034 \text{ g}\} \times 100 \% \\ &= 72.79 \% \end{aligned}$$

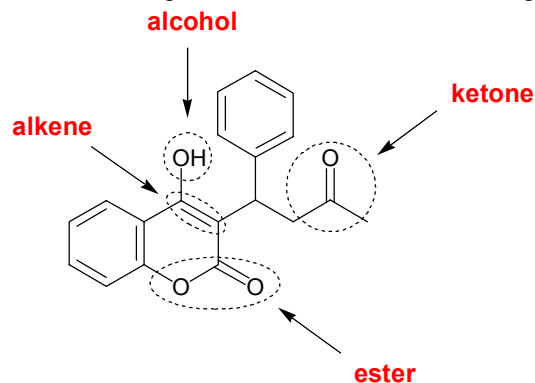
which confirms that the answer to this question is **D**.

Oxalic acid (or, more correctly, ethanedioic acid) is found in many fruits and vegetables, and is responsible for the gritty taste of food such as spinach and rhubarb. Although it is harmless enough in small amounts in foodstuffs, it can cause problems by inhibiting the absorption of calcium in the body (forming calcium oxalate), and it is poisonous if ingested in significant amounts (it is fatal at about 5 g). The commonly used antifreeze known as ethylene glycol (ethane 1,2-diol) is poisonous due to its propensity of forming calcium oxalate crystals in the kidneys, causing acute renal failure and death. Indeed, calcium oxalate is the main constituent of kidney stones, and oxalic acid forms many other insoluble salts. The latter is used as a mordant in textile dyeing, because it forms insoluble oxalate salts in the fibres of a fabric when it reacts with solutions of coloured cations such as chromium (see answer to question 9).

The use of oxalic acid in cleaning wood and metals is due to its corrosive action – it is a very strong acid, with $\text{p}K_{\text{a}1} = 1.27$. It is also a reducing agent, so that it will actively inhibit oxidative corrosion in metals (such as rusting of iron and steel), and it can be used as a reducing bleach (c.f. chlorine, which is an oxidizing bleach). Salts of oxalic acid are sold as “salts of lemon” or “salts of sorel” and can be used to remove ink stains from clothes. Oxalic acid is also used as a reducing agent in photography.

ANSWERS TO PART A OF THE CANADIAN CHEMISTRY CONTEST EXAMINATION 2007 continued

16. This question was poorly done, both by Alberta students and Manitoba students (respectively 37.1% and 38.2 % of students in these provinces chose the correct answer). The question requires students to recognize the functional groups in the organic compound Warfarin, the structural formula of which is given in the question. The structural formula is repeated below with the functional groups indicated on it.



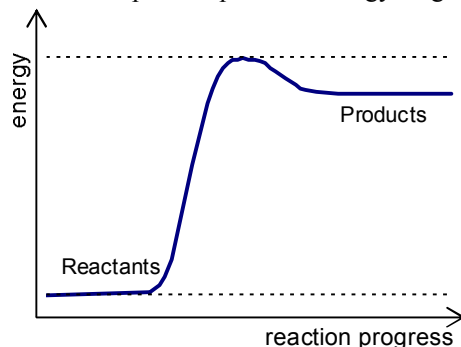
As can be seen in the diagram, this compound contains the following functional groups: alkene, alcohol, ketone and ester, which means that the answer to this question is **C**. (Two phenyl rings are also present in the structure).

Although it is recognized that some students will not yet have covered much in the way of organic chemistry, it is expected that serious contestants for the CCC will be able to recognize the following: the hydrocarbon skeletons for alkane, alkene, alkyne and phenyl (whether in the full or condensed structural versions), and the functional groups of alkyl halides, amines, alcohols (primary, secondary and tertiary) and phenols, aldehydes and ketones, ethers, carboxylic acids and carboxylates, esters, amides and nitriles. Note that in this question it was particularly important to be able to distinguish between an ether $-C-O-C-$ and a ketone $-C-(C=O)-C-$, and also between an ether or ketone and an ester $-C-(C=O)-O-C-$.

Warfarin is a synthetic derivative of coumarin, a compound found naturally in plants such as woodruff. Warfarin was first developed as a poison for rats and mice, but it is now more commonly used (in small amounts) as an anticoagulant medication and indeed was administered to U.S. President Eisenhower when he suffered a heart attack in 1956. It decreases the clotting ability of blood, by inhibition of vitamin K 2,3-epoxide and so protects patients against thrombosis.

17. This question was very well done (the best of all the questions on the exam) with 80.0 % of AB students choosing the correct answer, and 85.5 % of MB students: teachers, however, said that they thought it was too easy!

The question requires students to interpret the potential energy diagram shown below:

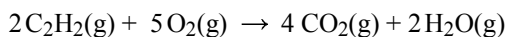


It can be seen from this diagram that the energy of the products is higher than that of the reactants, which means that energy must be taken in during the course of the reaction, i.e. that the reaction is endothermic. Only two keys, D and E, refer to an endothermic reaction, so it must be one of these, and the correct reason is given in **E**, so that this must be the answer to the question. Basically all you needed to remember is that **exothermic** means (heat) energy is given **out** (c.f. exo and exit), and that endothermic means that (heat) energy is taken in.

Note that we usually include questions in the Canadian Chemistry Contest exams that require students to interpret data, graphs and diagrams, and students probably found that this was relatively easy because they were familiar with this kind of diagram, which is often included in textbooks.

18. After the success of the last question it seems a pity that this next question was poorly done, with only 37.1% of AB students and 34.5% of MB students choosing the correct answer. The question involved a standard sort of calculation for determining the enthalpy change of combustion from enthalpy changes of formation¹.

The reaction involved was the combustion of acetylene (ethyne), the equation for which is given as:



The formula for determining the enthalpy change of reaction (in general) is

$$\Delta H_{\text{r}}^{\ominus} = \sum \Delta H_{\text{f}}^{\ominus}(\text{products}) - \sum \Delta H_{\text{f}}^{\ominus}(\text{reactants})$$

Applying this formula to the above equation gives:

$$\begin{aligned}\Delta H_{\text{r}}^{\ominus} &= 4 \times \Delta H_{\text{f}}^{\ominus}\{\text{CO}_2(\text{g})\} + 2 \times \Delta H_{\text{f}}^{\ominus}\{\text{H}_2\text{O}(\text{g})\} - \Delta H_{\text{f}}^{\ominus}\{\text{C}_2\text{H}_2(\text{g})\} \\ &= (4 \times -393.5 \text{ kJ mol}^{-1}) + (2 \times -241.8 \text{ kJ mol}^{-1}) - (2 \times +226.7 \text{ kJ mol}^{-1}) \\ &= -1574.0 + (-483.6) - (+453.4) \text{ kJ mol}^{-1} \\ &= -2511.0 \text{ kJ mol}^{-1}\end{aligned}$$

Note that this is, however, the enthalpy change for the reaction shown in the equation, which involves the combustion of 2 moles of ethyne. The question asks students to determine the enthalpy of combustion ($\Delta H_{\text{c}}^{\ominus}$) **per mole of ethyne**, which is **half** the value of $\Delta H_{\text{r}}^{\ominus}$, or $-2511/2 = 1256 \text{ kJ mol}^{-1}$. The answer to this question is therefore **A**.

Note that combustion reactions are often written in terms of multiple numbers of moles of the substance burned, in order to have stoichiometric coefficients that are whole numbers through the equation. Enthalpy changes of reaction are usually determined in terms of enthalpy change of the reaction **as given in the equation**. On the other hand, enthalpy changes of combustion that are given in tables of data are always quoted in terms of the enthalpy change per mole of the substance burned.

It is also interesting to observe that the enthalpy change of combustion for ethyne is such a large negative number. Enthalpy changes in general are often in the hundreds of kJ mol^{-1} , but enthalpy changes of combustion are usually in the thousands of kJ mol^{-1} . Ethyne gives out a lot of heat when it burns in oxygen, such that its flame is capable of melting metal, which is why it is so useful in welding.

¹ The question actually refers simply to enthalpies of formation and combustion rather than enthalpy changes. It is, in fact, more correct to refer to enthalpy changes because only changes in enthalpy can actually be measured. There is no way of determining an absolute value of enthalpy.

Furthermore, ethyne also has a low molar mass compared with many other fuels, so that its efficiency per unit mass is also very good.

19. This question was only slightly better done than the last one, with 42.9% of AB students and 37.0% of MB students choosing the correct answer.

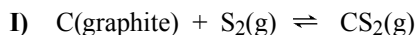
The question was concerned with the solubility of a mixture that is 50.0% by mass in each of sodium nitrate and lithium chloride. Note that the two salts have no common ion, so this is not a factor that needs to be considered. A 40.0-g sample of the mixture is dissolved in 20.0 g of water at 60°C and then cooled down to 20°C, at which point some solid has crystallized out. The question requires you to find the composition of this solid. This can be done as shown in the table below. Note that the solubilities of the two salts are given in the question for 20°C and 60°C, but, as you are told that the mixture is completely dissolved at 60°C, the data for this temperature is redundant.

	Sodium nitrate	Lithium chloride
Mass of substance dissolved in 20.0 g of water at 60°C	$40.0 \text{ g} \times (50/100) = 20.0 \text{ g}$	$40.0 \text{ g} \times (50/100) = 20.0 \text{ g}$
Solubility in 100 g of water at 20°C	87.5 g	78.0 g
Solubility in 20.0 g of water at 20°C (this mass will remain dissolved in the water)	$87.5 \text{ g} \times (20.0 \text{ g}/100 \text{ g}) = 17.5 \text{ g}$	$78.0 \text{ g} \times (20.0 \text{ g}/100 \text{ g}) = 15.6 \text{ g}$
Mass of substance in the solid that has crystallized out	$20.0 \text{ g} - 17.5 \text{ g} = 2.5 \text{ g}$	$20.0 \text{ g} - 15.6 \text{ g} = 4.4 \text{ g}$
Total mass of solid	$(2.5 \text{ g} + 4.4 \text{ g}) = \mathbf{6.9 \text{ g}}$	
Percentage of substance in the solid that has crystallized out	Not required	$(4.4 \text{ g}/6.9 \text{ g}) \times 100\% = \mathbf{63.8\%}$

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

20. This was another question for which the performance was mediocre, with only 40.0% of AB students, and 38.2% of MB students choosing the correct answer. It concerned the application of Le Châtelier's principle to some equilibrium systems involving gases. Students needed to remember two essential points: (1) increasing pressure (by reducing the volume, and with the temperature kept constant) will affect only the gases in the equilibrium system (the effect of pressure on pure solids, pure liquids or aqueous solutions can be ignored here), and (2) increasing the pressure will reduce the amounts of gas on the side of the equilibrium with the greatest number of moles (as shown in the equation), displacing the equilibrium increase the amounts of gas on the side with fewer moles. If the reaction has equal numbers of moles of gas on each side of the equation, then pressure changes will have no effect on the position of equilibrium.

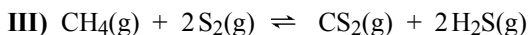
Let us consider each of the reactions given in the question in turn:



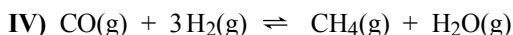
This equation has one mole of gas on the left-hand side (S_2) and one mole of gas on the right hand (CS_2) side: $\text{C}(\text{graphite})$ is a solid, so it will not be affected by pressure changes. The numbers of moles of gas do not change, therefore the pressure change will have no effect on the equilibrium position.



This equation has one mole of gas on the left hand side and two moles of gas on the right hand side. The numbers of moles of gas change, therefore the pressure change will affect the equilibrium (by increasing the amount of CO_2).



This equation has a total of 3 moles of gas on the left hand side and 3 moles of gas on the right hand side. The numbers of moles of gas do not change, therefore the pressure change will have no effect on the equilibrium position.



This equation has a total of 3 moles of gas on the left hand side and 2 moles of gas on the right hand side, so that the pressure change will affect the equilibrium position (by increasing the amount of products of the reaction).

The following table provides a summary of the above analysis:

Reaction	I	II	III	IV
Moles of gas on the reactant side of the equation	1	1	3	4
Moles of gas on the product side of the equation	1	2	3	2
Change	0	1	0	-2
Pressure effect?	No	Yes	No	Yes

Reactions I and III are NOT affected by an increase in pressure, therefore the answer to this question is **B**.

Note that, although no calculations were involved in solving this problem, the pressure effects can be explained by considering the universal gas law and the equilibrium law expression.

First let us consider the universal gas law expression², which is usually stated as:

$$PV = nRT$$

where P is the pressure of the gas, V is its volume, n its chemical amount, T its absolute temperature, and R the universal gas constant (expressed in units compatible with the units of the other values).

This law can also be written as:

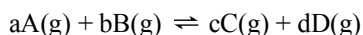
$$P = n/V \times RT$$

$$\text{or } P = c \times RT$$

where c is the concentration of the gas, which equals n/V.

We can see from this that, as V is decreased (with n and T held constant), then both c and P increase.

Now let us consider a generalized gas reaction, given by the equation:



where a moles of A and b moles of B react to form c moles of C and d moles of D.

² Note that the gas laws, and, by extension, the equilibrium constant for gases written in terms of partial pressures are not on the Pan-Canadian protocol curriculum (although they are on most provincial curricula). Questions which require the gas laws for their solution will not be included on the CCC.

The equilibrium constant in terms of concentration may be given as:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where [A], [B], [C] and [D] indicate the concentrations of gases A, B, C and D respectively.

If the pressure of the gas mixture is increased then the concentrations of **all** the gases are increased, however if $(a + b) > (c + d)$ then the effect of the increase in concentration will be multiplied for the reactants (A and B) in the denominator of the expression, and the only way that K_c can be kept constant is by decreasing the concentrations of A and B whilst increasing the concentrations of C and D (displacing the equilibrium to the right hand, product, side of the equation). Conversely if $(a + b) < (c + d)$ the concentrations must change in the opposite direction increasing the concentrations of the reactants, A and B.

ANSWERS TO PART A OF THE CANADIAN CHEMISTRY CONTEST EXAMINATION 2007 continued

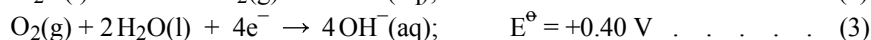
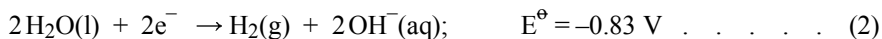
21. This question was very badly done in Alberta, with only 14.3% of contestants choosing the correct answer (below the “guess” rate of 20%); it was done somewhat better in Manitoba where 39.6% of students chose the correct answer.

The question involved the use of standard reduction potentials to determine the electromotive force of a fuel cell. We are aware that many teachers will not have covered this topic by the date of the contest, and that some teachers will not manage to cover it at all by the end of the school year, even though it is on most, if not all, of the provincial curricula. Nevertheless we intend to include one simple example of this type of question on each contest exam, hoping that better students who prepare for the exam will be rewarded.

The overall equation for the fuel cell reaction is given as:



Also given are the standard reduction potentials for the two half cell reactions:



The electromotive force or e.m.f. of a cell is simply the maximum potential difference that can be obtained with a particular cell. It can be calculated using the equation:

$$E^\ominus(\text{cell}) = E^\ominus(\text{cathode}) - E^\ominus(\text{anode})$$

The easiest way of telling which is the cathode (reduction) half cell and which is the anode (oxidation)² half cell is to look at the E^\ominus values: the more positive value will be the cathode reaction and the more negative value will indicate the anode reaction. Note that most tables of standard reduction potentials these days place the more negative E^\ominus values above the more positive ones, but that is not something that can be relied on.

Subtracting the more negative half cell reduction potential (E^\ominus value) from the more positive one gives the overall cell e.m.f., thus:

$$E^\ominus(\text{cell}) = +0.40 \text{ V} - (-0.83 \text{ V}) = +1.23 \text{ V}$$

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

Note that, if you get the anode and cathode half cells the wrong way round the e.m.f. value of the reaction will come out negative, which means that the reaction will not occur. **The reactions in cells and batteries are spontaneous reactions so they will always have positive e.m.f. values.**

² There are two simple mnemonics to help you remember the rules of redox:

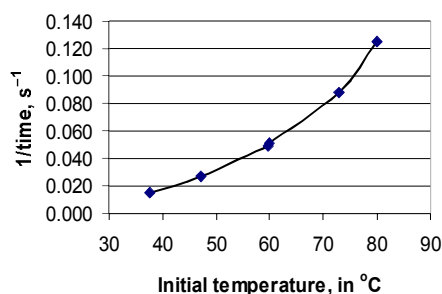
(1) **OIL RIG**, which tells you that **O**xidation **I**s **L**oss of electrons and **R**eduction **I**s **G**ain of electrons, and

(2) **O**xidation occurs at the **A**node (**O** and **A** are both vowels), **R**eduction occurs at the **C**athode (**R** and **C** are both consonants).

Note also that, **unlike other functions, E^\ominus values do not change when the equation is multiplied** by a common factor. It is not necessary, therefore, to balance the equation when the two half cell reactions are combined³.

22. This question was somewhat better done than the last one, with almost 50% of students choosing the correct answer (48.6% in AB and 49.1% in MB). It was a question that was concerned with rates, and we have some difficulty about what to do about testing students on this topic, because it is on the Pan-Canadian protocol for Grade 10 rather than Grades 11 and 12, but it is included at some point in most provincial curricula. We therefore try to keep the questions very simple, and we expected that students might have performed somewhat better than they did.

Students were required to interpret the following graph, which they were told shows the effect of initial temperature on the rate of reaction for a series of experiments performed on the same reaction, with the same initial concentrations of reactants. Students are also told that each experiment was performed as a “clock” reaction, so it is only timed up to a certain point, and that it can be assumed that the rate is proportional to $1/\text{time}$.



Let us consider each of the possible answers in turn in order to establish what might be deduced from the graph:

A. The reaction is exothermic

An exothermic reaction is one that gives out heat, so that one expects the temperature of the reaction mixture to increase as the reaction proceeds. Although temperature is increasing as shown on the abscissa (x-axis), this is the **initial** temperature, which is controlled by the experimenter – it does not indicate that the temperature of the reaction is increasing. Note that the rate of reaction would be increasing if the reaction were exothermic, but this would simply be a complicating factor, which would need to be compensated for by experimental design.

B. The reaction is endothermic

An endothermic reaction is one that takes in heat, so one might expect the temperature of the reaction mixture to decrease as the reaction proceeds. This possibility is not indicated by the graph.

C. The rate of reaction increases with initial temperature

Students are told that it can be assumed that the rate is proportional to $1/\text{time}$, which is the value given on the ordinate (y-axis). The value of $1/\text{time}$, and therefore rate, is greater at higher initial temperatures, so

³ The reason why an E^\ominus value does not change when multiplying the chemical equation by a common factor is that it represents electrical potential or voltage, which is defined as (electrical) potential energy per unit charge. If the equation is multiplied by 2, both the energy and the charge (number of electrons transferred) are multiplied by 2, and their ratio is unchanged. In practical terms this means that the size of the e.m.f. is independent of chemical amount so that larger batteries still give the same voltage as smaller ones made out of the same chemicals.

it appears that this statement is correct, but you should always check out the rest of the statements in this type of question if you have time.

D. The rate of reaction decreases with initial temperature

There is no possible way of looking at this graph that can support this statement, and, indeed it cannot be true if C is true.

E. The time taken for the reaction to be completed increases with initial temperature

This statement was the second most popular choice of students, likely because they mis-read the legend on the y-axis as time instead of 1/time. The time taken for a reaction to be completed is, however, likely to **decrease** with temperature, because the particles are moving more quickly and are therefore more likely to collide and react. In any case this graph does not give any information about the time taken to complete the reaction. In clock reactions the time is only measured at a particular point partway through the reaction, usually when about one eighth of the reactants have reacted, at which point it is still reasonably true to say that rate is proportional to 1/time. Note that reactions tend to go more and more slowly as they proceed, and sometimes it is very difficult to tell when the reaction has actually finished, so measuring the completion of the reaction is not usually attempted.

The best deduction that can be made from the graph is given in **C**, and this is therefore the answer to the question.

Examples of clock reactions that you might have met, and possibly even investigated experimentally, are the reaction of hydrochloric acid with sodium thiosulfate (which is stopped when the cloudiness of the sulfur produced reaches a certain point) or the reaction of excess hydrochloric acid with magnesium (which is stopped when all the magnesium has “disappeared”). A somewhat more complicated reaction is the one between peroxodisulfate(VI), $\text{S}_2\text{O}_8^{2-}$, and iodide ions, in the presence of starch indicator and thiosulfate ions, $\text{S}_2\text{O}_3^{2-}$, which is timed when the blue colour of the starch-iodine complex appears.

23. This question was poorly done with 42.9% of AB students and only 27.3% of MB students choosing the correct answer. In fact it was such a easy question it could be considered to be a “trick question”, because it simply asked students what would happen to the value of the equilibrium constant of a particular reaction if the concentration of one of the reactants were to be doubled (at the same temperature). The answer, of course, is that the value of the equilibrium constant will not change – the concentrations of the other components of the mixture will adjust so that the equilibrium constant remains just that – constant. Thus, if the equilibrium constant is given the value K , then it will still be K after the concentration has been changed, and the answer to this question is therefore **C**.

The most popular answer to this question was A, indicating that students had inserted the double value into the equilibrium law expression, without thinking of the basic principles of equilibrium.

24. This question was very poorly done, with only 25.7% of AB students and 14.6% of MB students choosing the correct answers, perhaps because students were panicking towards the end of the exam.

The question required students to identify the types of reaction taking place in three different reactions involving vanillin. Although the structure of vanillin might appear at first sight to be somewhat complex, students might reasonably be expected to know how to recognize some basic types of reaction. A list of the reaction types given in this question, together with an explanation of their meanings, is given below:

Addition: A reaction in which an atom or group of atoms is added to each of the atoms at the end of a multiple carbon-carbon bond, so that typically a double bond becomes a single bond, or a triple bond becomes a double bond.

Elimination: A reaction in which an atom or group of atoms is lost from each of the atoms at the end of a single carbon-carbon bond so that a double bond or triple bond is formed (along with a small molecule that is created from the atoms that have come out of the original molecule).

Oxidation: There are a number of different definitions of oxidation, but the ones that might be relevant here are:

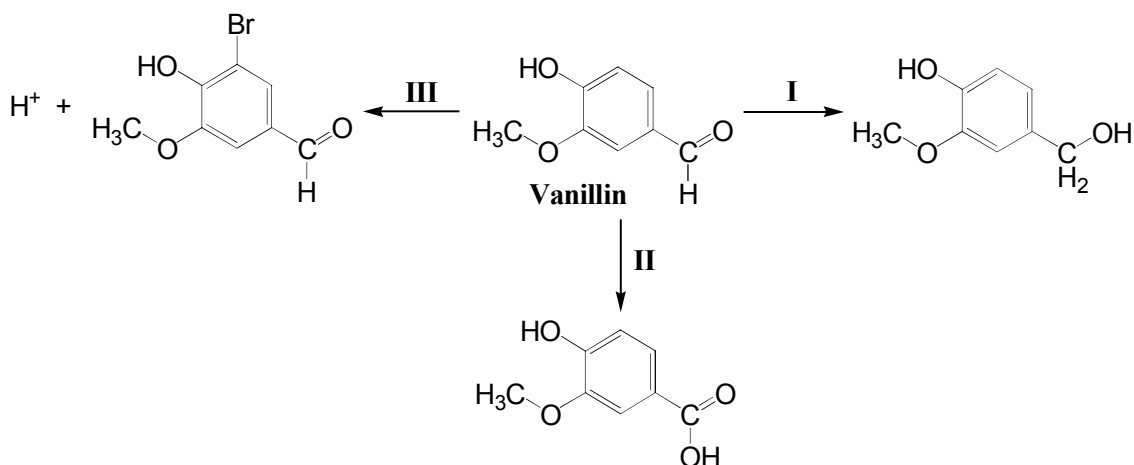
- (1) oxidation is a reaction in which oxygen is added to a molecule, or
- (2) oxidation is a reaction in which hydrogen is removed from a molecule

Reduction: There are a number of different definitions of reduction, but the ones that might be relevant here are:

- (1) reduction is a reaction in which oxygen is removed from a molecule, or
- (2) reduction is a reaction in which hydrogen is added to a molecule

Substitution: A reaction in which an atom or group in a molecule is replaced by another atom or group

The reaction schematic is given below:



Let us consider each of the steps shown, bearing in mind the choices given for the different steps in the original question which are:

	I	II	III
A.	reduction	oxidation	substitution
B.	oxidation	reduction	substitution
C.	reduction	oxidation	elimination
D.	reduction	oxidation	addition
E.	oxidation	reduction	addition

Reaction I: Here the change occurs in the group on the lower right hand side of the molecule as written. The $-(C=O)-H$ (aldehyde) group changes to a $-CH_2-OH$ (primary alcohol) group. This involves addition of hydrogen, so it is a reduction reaction. Looking at the list of possible choices for Reaction I it can be seen that the answer to this question must therefore be A, C or D.

Reaction II: Here the change is again on the lower right hand side of the molecule as written. The $-(C=O)-H$ (aldehyde) group changes to a $-(C=O)-OH$ (carboxylic acid) group. This is an oxidation reaction, so that the answer to this question must be A, C or D. We have not yet whittled down the possible answers, and we must consider Reaction III in order to establish the answer to this question.

Reaction III: Here the change occurs on the top of the molecule, where we can see that a bromine atom has appeared. This might make you think that an addition has taken place, but look again! There is no change in the bonding in the aromatic ring (shown here by alternating double and single bonds): also a

hydrogen ion H^+ has appeared on the left hand side along with the organic product. In order to work out exactly what is happening here we need to realize that the benzene ring in vanillin and its derivatives is shown as a condensed formula. In this method of drawing structures a straight line indicates a bond, but a bend, or an end point in a line, indicates a carbon atom: furthermore only the functional groups are shown in these formulae – any hydrogen atoms that are simply required to take up the 4 bonds around carbon are not shown (see also the answer to Question 25). Remember that the formula of benzene is C_6H_6 , but it is simply represented in a condensed formula as a 6-sided ring (either with alternating double and single bonds, or with a circle in the middle to indicate aromaticity). The hydrogen atoms are not shown, therefore we need to remember here that there is a hydrogen atom at the top of the vanillin ring, which is being replaced by bromine in Reaction III. (This is the hydrogen that ends up as a hydrogen ion (H^+) at the end of the reaction.) In other words, **Reaction III is a substitution reaction**, and this possibility is only given for keys A and B in the question. Combining the possibilities given for all the keys means that the answer to this question must be **A**.

The favourite answer from students was C. It is difficult to see how they could logically have arrived at this answer, which would have meant that they thought that Reaction III was an elimination reaction – perhaps they simply used the expedient “when in doubt guess C” mode here.

25. This question was the worst done in the whole exam, with only 20% of AB students and 14.5% of MB students choosing the correct answer. It was, however, the last question on the exam and traditionally that has always been a very challenging one, and it is particularly difficult for students if they are short of time.

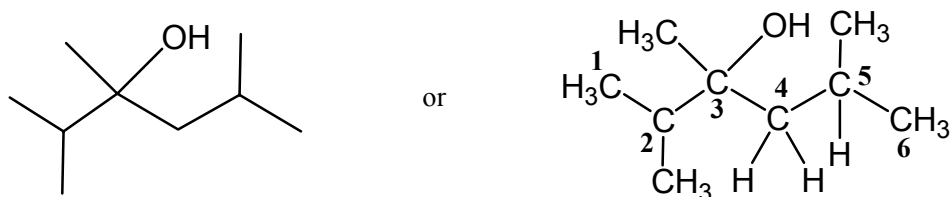
This question is concerned with geometric isomers. The Pan-Canadian protocol requires students to know about organic isomers, but it does not specify which ones. Different provinces may have interpreted this differently, but we expect students to know about (i) the different types of constitutional isomers (chain isomers, position isomers and functional group isomers); (ii) optical isomers (chirality); and (iii) geometric (*cis-trans*) isomers⁴.

Geometric isomers (often known as *cis-trans* isomers) exhibit stereoisomerism, which means that they have different spatial arrangements of atoms, without any differences in connectivity or bond multiplicity between the isomers. (Optical isomers also show stereoisomerism but of a different type.) Geometric isomers often contain carbon-carbon double bonds or rings with atoms (or groups) attached to the carbon atoms: these atoms or groups differ in their positions relative to a reference plane – in the *cis*-isomer the atoms are on the same side, in the *trans*-isomer they are on the opposite side.

The compounds that have to be examined for geometric isomerism in this question are formed when 2,3,5-trimethyl-3-hexanol is dehydrated, and, although it is not really necessary to know the structure of this compound in order to answer the question, it is a help to be given it, because it limits the number of structures that you might be tempted to consider. This is because dehydration is a specific case of an elimination reaction (see Question 24) in which the small molecule freed in the reaction is water. The water is formed, in this case, from the alcohol ($-OH$) group on the original molecule plus a hydrogen atom attached to a neighbouring carbon atom, which, when they are removed, leave a carbon-carbon double bond. Non-neighbouring carbon atoms need not be considered. It is the atoms or groups on the carbons joined by the double bond that we need to examine closely, and, in particular, we need to think about what happens if we try to twist the molecule about the axis of the double bond. (Note that it is not actually possible to twist the molecule like this, which is why geometric isomers are different compounds, with different physical and chemical properties.)

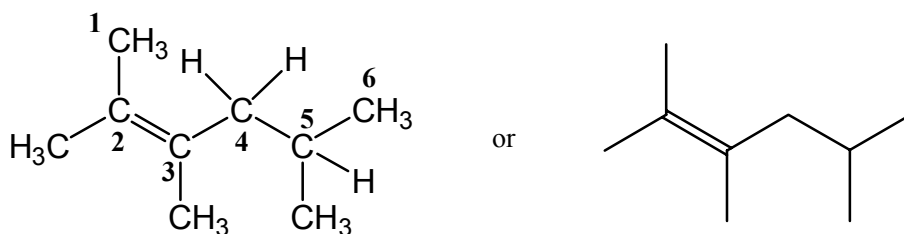
⁴ Note that the terms “geometric” and “*cis/trans*” have been used in this question and its solution, because these are terms generally used in high schools. Students should, however, appreciate that, at university level, geometric isomerism is simply treated as a type of stereoisomerism (*cis/trans* isomers are, more specifically, called “diastereomers”). The terms *cis* and *trans* are replaced by *Z* (zusammen = together) and *E* (entgegen = opposite), which take into account the priority of the groups attached to the carbons connected by the multiple bond. See also <http://www.chem.qmul.ac.uk/iupac/stereo/BC.html#26>.

The condensed formula for 2,3,5-trimethyl-3-hexanol was given in the question and is shown on the left below for reference. An expanded version of the formula, showing all the atoms with the carbon atoms correctly numbered, is given on the right.



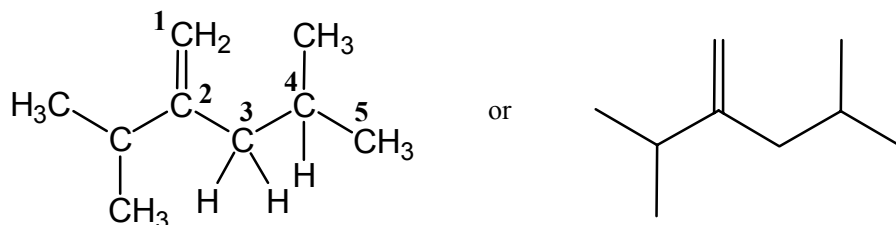
We shall consider the three alkene products in turn:

2,3,5-trimethyl-2-hexene (I):



In this molecule the left hand carbon of the double bond (the number 2 carbon in the name of the molecule) has two methyl groups on it. This means that if you could twist the molecule about the double bond you would not see any difference, so that this molecule cannot have *cis-trans* isomers. It does not matter that the other carbon in the double bond has two different groups on it.

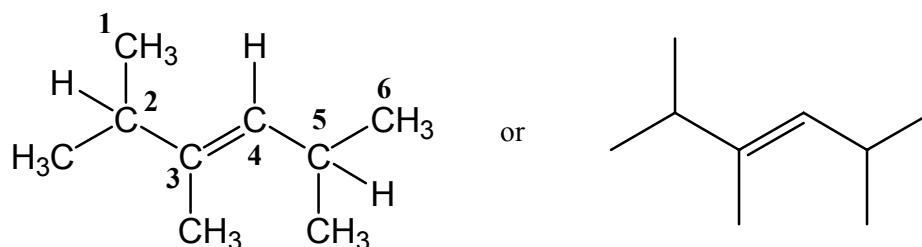
2-isopropyl-4-methyl-1-pentene (II):



In this molecule the top carbon of the double bond (the number 1 carbon in the name of the molecule) has two hydrogens on it. This means that if you could twist the molecule about the double bond you would not see any difference, so that this molecule cannot have *cis-trans* isomers. It does not matter that the other carbon (the number 2 carbon in the name of the molecule) in the double bond has two different groups on it.

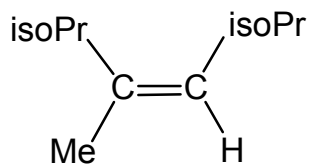
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2,3,5-trimethyl-3-hexene (**III**)

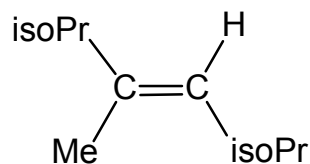


In this molecule the number 3 carbon atom has a methyl group ($-\text{CH}_3$, sometimes given the abbreviation “Me”) and an isopropyl group ($-\text{CH}(\text{CH}_3)_2$, sometimes given the abbreviation “isoPr”) attached to it. The number 4 carbon atom has a hydrogen atom and an isopropyl group attached to it. If the molecule could be twisted around the double bond a difference would be observed in the relative positions of the atoms. The molecule shown in the diagram above has the isopropyl groups in *trans* to one another (on the opposite sides of the double bond). When the isopropyl groups are on the same side of the double bond they are said to be *cis* to one another.

The simplified diagrams below show the differences between the two isomers:



Isopropyl groups *cis*



Isopropyl groups *trans*

To sum up: Geometric isomers do not exist for products I and II, but they do exist for product III, therefore the answer to this question is **E**.