ANSWERS TO PART A OF THE
NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2001

These answers are designed to help students who are preparing to take the Canadian National High School Chemistry Examination in 2002, or subsequent years. Students should attempt to do the questions in Part A of the 2001 Examination on their own, and then compare their answers with the solutions given below. Students should not be put off by the length of the explanations, which do not reflect the length of time needed to think out answers to the questions. Rather, these notes are designed as a teaching aid, and 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.

These notes have been prepared in order give students (and teachers) some indication of the sort of things that the National Examiner expects high school students to know - and what topics might appear on future exams. Note that the multiple choice part of the National High School Chemistry Examination is based on the requirements of the Pan-Canadian Protocol for Collaboration on School Curriculum - Common Framework of Science Learning Outcomes (unless otherwise stated).

It is unfortunate that problems of putting this file on a web page as a universally readable file has meant that some of the equations may appear distorted. Also diagrams have had to be avoided. It is strongly recommended, therefore, that students read these explanations in conjunction with a text book, and try to draw their own diagrams, where appropriate, in order to gain a thorough understanding of the verbal explanations.

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1. This question is testing you on the precision to which numerical answers should be given (this knowledge is needed in most areas of science). The rule is:

After **addition or subtraction** the answer should be rounded off to keep only the same number of **decimal places** as the least precise item.

After **multiplication or division** the answer should be rounded off to contain only the same number of **significant figures** as are contained in the factor with the least number of significant figures.

Make sure that you know what is meant by decimal places and significant figures . (For example the number 20.0 has one decimal place, but three significant figures.)

This question involves the use of multiplication and division rule because it requires the formulae:

$d = m/V$ Where d is the density in g mL^{-1}
m is the mass in g
V is the volume in mL

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

The density of the solution is given to 5 significant figures, but all the other numbers are given to 3 significant figures, so the final answer should be given to 3 significant figures as well. This means that only keys **C** or **D** are possible. The question is now reduced to working out what the third significant figure is. The next step depends on how much of a risk taker you are! If you believe that E is a possible distractor, i.e. that it is the value you would get if you worked out the answer to 4 significant figures, then the answer must be **D**, because the rule for rounding is:

For final digits of 1 to 4 round down: for final digits of 5 to 9 round up.

A final digit of 7 means rounding up so that 0.02017 rounds to 0.0202.

It is probably worth taking a risk at this stage of the exam, because you don t know yet how easy or difficult you will find the rest of the exam. If you have time at the end you can come back to this question and work it out properly. This is how the calculation goes:

Using $m = d \times V$

Mass of solution $= 0.96864 \text{ g mL}^{-1} \times 4.80 \text{ mL} = 4.6495 \text{ g}$

Mass of ethanol in the 20.0% solution $= 4.6495 \text{ g} \times 20.0 \div 100 = 0.92989 \text{ g}$

Now using $n = m/M$

Chemical amount of ethanol $= 0.92989 \text{ g} \div 46.1 \text{ g mol}^{-1} = 0.02017 \text{ mol}$

(Note that all the significant figures are retained through the calculations. Adjusting the significant figures is done after the very last step.)

Note the difference between **M** and $\mathbf{M_r}$ in this question. **M** is the molar mass and has units of g mL^{-1}. $\mathbf{M_r}$ is the relative molar mass and has no units. Terms such as atomic weight and molecular weight etc. are obsolete and will not be used in the CIC Exam.

Note also that an **aliquot** means a portion of known size. It is usually used to refer to a known volume of solution.

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2. This is a trick question, albeit one with a serious point to make. The major component of a solution is (usually) the solvent, which is water here. So the answer is **B**.

If water were not one of the options, then you would have to consider the reactions going on in this titration, which would have two endpoints. Bearing in mind that the wording of the question implies that Na_2CO_3 is being run out of a burette into HCl, so that the HCl is in excess at first, the reactions involved would be:

$$2HCl(aq) + Na_2CO_3(aq) \text{--->} 2NaCl(aq) + H_2CO_3(aq) \quad . . . . \quad (1)$$

or possibly (if the concentration is high enough, so that H_2CO_3 breaks down to give H_2O and CO_2)

$$2HCl(aq) + Na_2CO_3(aq) \text{--->} 2NaCl(aq) + H_2O(l) + CO_2(g)$$

then as more Na_2CO_3 is added:

$$Na_2CO_3(aq) + H_2CO_3(aq)\text{--->} 2NaHCO_3(aq) \quad . . . . \quad (2)$$

At the first endpoint the HCl and Na_2CO_3 would be exactly balanced according to equation (1), and the pH of the solution would be essentially that of the NaCl (i.e 7) or possibly slightly less (due to the presence of the very weak acid, H_2CO_3). The pH of the solution being titrated would therefore have gone from about 2 (due to 0.1 M HCl) to about 7, passing through the methyl orange endpoint (around 3.7) along the way. At this point NaCl would be the solute with the highest concentration (the equation shows the mole ratio of NaCl:H_2CO_3 is 2:1), so, if water had not been an option, the answer would have been C.

If the titration was continued to the second endpoint (shown by equation 2) the solute with the highest concentration would be $NaHCO_3$ (which gives an alkaline reaction). An indicator such as phenolphthalein ($pK_{In} = 9.3$) would be suitable for establishing the second endpoint - although the colour change would be difficult to see if the methyl orange used for the first endpoint was still in the solution. In fact, when this double indicator titration is performed it is usually done the other way round (with HCl being run into Na_2CO_3): the phenolphthalein is colorless in the acid range, so it does not interfere with the methyl orange colour change.

3. This question needs some clear thinking. The first thing to establish is why the volume of acid used is considered to be discrepant. HCl and NaOH react in a 1:1 mole ratio, as shown in the following equation:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Now using n = cV where n is the chemical amount in mol
c is the concentration in mol L^{-1}, and
V is the volume of solution in L
and remembering that there are 1000 mL in one L.

the chemical amount of HCl = 0.050 x 19.75 ÷1000 = **0.000987 mol**

Now using n = m/M where n is the chemical amount in mol
m is the mass in g
M is the molar mass in g mol^{-1}

and using M = 40.0 g mol^{-1} for NaOH

the chemical amount of NaOH dissolved in 1 L of water = 4.021g ÷ 40.0 g mol^{-1} = 0.1005 mol
i.e. the concentration of the solution is 0.1005 mol L^{-1}

and using n = cV again gives the chemical amount of NaOH in the 10.00 mL of solution used in the titration = 0.0100 L x 0.1005 mol L^{-1} = **0.0010 mol**

So less acid has been used than might have been expected, which means that some NaOH has been lost somewhere.

Now let us consider the options on offer, these are:

A. The NaOH having absorbed CO_2 from the air after its mass was measured.

This would have converted the NaOH to Na_2CO_3, according to the equation:

$$2NaOH(s) + CO_2(g) \longrightarrow Na_2CO_3(s \text{ or } aq) + H_2O(l) \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

However, the Na_2CO_3 would react with HCl to give NaCl just like NaOH would, according to the equation:

$$2HCl(aq) + Na_2CO_3(aq) \longrightarrow 2NaCl(aq) + H_2CO_3(aq) \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

Combining equations (3) and (4) shows that this would require the some amount of NaOH as HCl (overall), so the absorption of CO_2 cannot affect the titration and the key cannot be A.

B. The NaOH having absorbed H_2O from the air after its mass was measured

Once the mass of NaOH has been measured the chemical amount of NaOH has been assured, and the inclusion of extra water will not make a difference to the reaction. So the key cannot be B.

C. The pipette having been rinsed with water instead of NaOH

The pipette is used to measure out a known volume of NaOH solution. If it is rinsed with water the solution will be diluted, and less NaOH will be measured out than intended. This would result in a loss of NaOH, and the answer would be discrepant in the direction indicated in the question. The key is therefore **C**.

To continue checking the other keys (which is worth doing if you have time):

D. The flask having been rinsed with NaOH instead of water

The NaOH solution is pipetted into the flask as a means of measuring out an exact amount of NaOH. If the flask has been rinsed with NaOH then it will contain more NaOH than you think, and the result will be discrepant, but in the opposite direction to the one indicated in the question.

E The burette having been rinsed with water instead of HCl

If the burette is rinsed with water instead of HCl then the HCl will be diluted, this means that a greater volume of it will be required to neutralize the NaOH, so that the NaOH will appear more concentrated than it really is. The result will be discrepant, but in the opposite direction to the one indicated in the question.

So remember: **When doing titration it is important**

to rinse the burette with the burette solution
to rinse the pipette with pipette solution, and
to rinse the flask with distilled water.

4. For this question you need to know that one mole of carbon (whether it is in the elemental form or combined in a compound) will produce one mole of carbon dioxide, according to the following equation:

$$C + O_2 \text{ ---> } CO_2$$

where C indicates that the carbon is combined in a compound.

Now using n = m/M (see above for definition of symbols), and a value of M = 44.01 g mol^{-1} , the chemical amount of CO_2 = 27.50 g ÷ 44.01 g mol^{-1} = 0.6249 mol.

For Key A, using n = m/M again, and a value of M = 32.04 g mol^{-1} , the chemical amount of CH_3OH (methanol) = 20.0 g ÷32.04 g mol^{-1} = 0.6242 mol, and as each mole of CH_3OH contains one mole of carbon, it will give one mole of CO_2. We have shown that 0.6242 mol of methanol gives 0.6249 mole of CO_2.This is close enough for **A** to be the correct key, and there is no need to continue checking the other keys.

If you have enough time at the end of the exam you could calculate the amount of CO_2 you might expect from 20.0 g of the substances given in the other keys (remembering to allow for the number of carbon atoms in the molecules), this would give you (approximately):

For B,	CH_3CHO (ethanal)	0.91 mol
For C,	CH_3OCH_3 (methoxymethane) . . .	0.87 mol
For D,	CH_3CO_2H (ethanoic acid)	0.67 mol
For E,	CH_3COCH_3 (propanone)	1.03 mol

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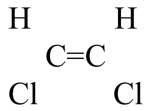
5. **Geometric (*cis-trans*) isomers** are found in organic compounds that have the same structure but different configurations of dissimilar atoms or groups attached to two atoms that are joined by a bond that does not allow rotation about it. Usually this is a double bond, but it could also be a bond in a ring system.

If you consider the compounds suggested in this question, none of them can be ring compounds, as none of them more than two carbon atoms in them. Now if you look at the number of atoms attached to each of the carbon, you will be able to identify the ones that have double bonds (these have only two other atoms attached to each carbon) and which have single bonds (these have three atoms attached to each carbon), thus the options become:

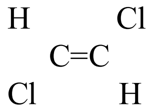
A. $Cl_2C{=}CH_2$ B. $HClC{=}CH_2$ C. $HClC{=}CHCl$ D. $HCl_2C\text{-}CH_2Cl$ E. $HCl_2C\text{-}CHCl_2$

D and E, which have single bonds between carbons are therefore eliminated immediately. In A, one carbon has two chlorines attached to it, and the other has two hydrogens, so if it were possible to twist around the C=C bond here, there would be no difference in the configuration. So the key cannot be A. Nor can the key be B, because even with two atoms the same (hydrogen) on only one of the carbons, twisting about the C=C bond would make no difference. This leaves us with C, which can exist in two different forms, thus:



$$\begin{array}{ccc} \mathrm{H} & & \mathrm{H} \\ & \mathrm{C{=}C} & \\ \mathrm{Cl} & & \mathrm{Cl} \end{array}$$

and



$$\begin{array}{ccc} \mathrm{H} & & \mathrm{Cl} \\ & \mathrm{C{=}C} & \\ \mathrm{Cl} & & \mathrm{H} \end{array}$$

cis-1,2-dichloroethene

trans-1,2-dichloroethene

Twisting one of these around the axis of the C=C bond (if that were possible) would form the other. The key is therefore **C**.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2001 cont.

6. According to the Pan-Canadian protocol students should know something about polymers and polymerization processes by the end of Grade 12. Nylon is specified as an example. **Nylon** is, in fact, the name given to an entire class of **polyamide materials**, which are made by copolymerizing dicarboxylic acids with diamines. Dicarboxylic acids have two -COOH (or -CO_2H) groups. Diamines have two -NH_2 groups. So **D** is the only possible answer. (Note that you need to be able to recognize these groups written backwards - which is often done with the first group shown, in order to indicate which atom is joined onto the first carbon in the chain).

For the record, the polymers formed from the pairs of compounds given are:

A. H_2N-CO-NH_2 and CH_2O: melamine (a resin used for unbreakable plates etc.)
B. CH_2=CH-CN and CH_2=CH-CH=CH_2: nitrile rubber
C. CH_2=CH-CN and CH_2=CH-O-CO-CH_3: Acrilan (a synthetic fibre)
D. H_2N-$(CH_2)_6$-NH_2 and HO_2C-$(CH_2)_4$-COOH: Nylon 6,6 (so-called because both the dicarboxylic acid and the diamine have 6 carbons in their molecules)
E. CH_3-O-CO-C_6H_4-CO-O-CH_3 and HO-CH_2-CH_2-OH: Dacron (a synthetic fibre)

Note that students are NOT expected to memorize these combinations. They should, however, be able to recognize a Nylon, and they should be able to recognize whether a particular pair of monomers will give an addition polymer or a condensation (a.k.a. addition-elimination) polymer. (Of the above, A, D, and E give condensation polymers, while B and C give addition polymers.)

7. The **first ionization energy** of an element (in kJ mol^{-1}) is the energy required to remove one mole of electrons from one mole of atoms of the element in the gas state to give one mole of ions in the gas state each with a single positive charge, under standard conditions.[1] This can be shown by the following equation for the hypothetical element, X:

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

The second ionization energy of an element (in kJ mol^{-1}) is the energy required to remove one mole of electrons from one mole of singly charged ions of the element in the gas state to give one mole of ions in the gas state each with two positive charges, under standard conditions, thus:

$$X^+(g) \text{ ---> } X^{2+}(g) + e^-$$

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[1] Note that most ionization reactions will not actually occur under standard conditions, which refer here to ambient temperature (298 K) and 1 atmosphere (101.3 kPa) pressure, and concentrations of 1.0 mol L^{-1} where these is relevant. Enthalpy changes generally have to be calculated back to what they would be if the reaction were done under standard conditions

The third ionization energy can be similarly defined as the formation of X^{3+} from X^{2+}; and the fourth ionization energy for X^{4+} from X^{3+}. Note how the ionization equations involve only one electron (or, more correctly, one mole of electrons) at a time.

Each ionization will require a larger amount of energy than previous ones because electrons are being removed from ions that are already positively charged, and which will therefore be increasingly attractive to electrons. However, a very much larger increase in energy will be observed when all the valency electrons have been removed from an atom, at which point the stable noble gas arrangement of electrons has to be broken into. This increase in energy is often said to be an order of magnitude different from previous increases. In the sequence of ionization energies given 578; 1817; 2745; 11,578 (kJ mol^{-1}) the major increase (from thousands to tens of thousands) is between 2745 and 11,578, i.e. between the third and fourth ionization energies. This tells us that the element has three valency electrons. Therefore, from the options given, it must be aluminium (Key **C**).

There is a secondary increase between the first and second ionization energies (between hundreds and thousands), which is when the 3p electron is removed from the atoms, leaving a relatively stable complete s orbital, but the differences between orbitals are much more difficult to see than those between shells. The easiest way of visualizing them is to plot a graph of sequential ionization energies. (This is very often done using a log scale in order to accommodate the order of magnitude increases in ionization energy with each shell.) You could practice seeing the differences that indicate that all the valency electrons have been removed by looking at the ionization energies given for the elements in a data book. (You do NOT need to memorize them!)

Another way of using ionization energies to show the electron arrangements in atoms is to plot the first ionization energies of consecutive elements. You might like to try this to see what this looks like.

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8. Partially filled d orbitals (in an atom or ion) are associated with transition properties. Some of the atoms and ions of elements in the so-called d-block or transition metal block may have no d-electrons or, alternatively, they may have a completely filled set of d orbitals: these species do not exhibit transition properties.

An element is said to exhibit **transition properties** if it is has some or all of the following characteristics:

it is a metal with several oxidation states
the element and/or its compounds have catalytic properties
it has coloured compounds
it forms complex ions

it is paramagnetic

As the species listed in this question are all ions, the mostly easily spotted of these characteristics is colour. I would expect most students to recognize that Cu^{2+} ion are coloured (blue in aqueous solution), therefore the correct answer is **B**.

I do not expect students to have memorized electronic configurations, although this is very easy to do up to element 20 (calcium).[2] However, I do expect them to know that, when building up the electron configuration of an atom, the 3d electrons come after the 4s. And that when a positive ion is formed from these elements the 4s electrons come off before the 3d. Most of the d-block elements therefore form 2+ ions, so one of their oxidation states is +2.

For the specific ions given in this question:

A. Ag^+ Ag has an exceptional configuration (as does Cu). An Ag atom borrows an s electron in order to make its d orbital complete, and this s electron is the one that is lost when Ag^+ is formed, so it is non-transition (and the ion is colourless). Borrowing the s electron is energetically favourable because it ensures that the spatial arrangement of the outer electrons is totally symmetrical.

B. Cu^{2+} The Cu atom has lost one of its d electrons as well as its s electron, so it is transition and coloured. (The colour is due to absorption of energy in the visible region. This is relatively low energy, but it is sufficient to enable electrons to move to marginally higher energy levels within 3d electron system.) Note how it is possible for the ions to be a transition whilst its atoms are not, and vice versa, in fact.

C. Pb^{2+} Pb is a p-block element. It loses two p electrons to become Pb^{2+}, which has a complete d-orbital. This is sometimes called a pseudo noble gas configuration and is very stable. Pb^{2+} is non-transition and colourless.

D. Sc^{3+} The element scandium is a transition metal, because its configuration is $[Ar]4s^2 3d^1$. However it does not form 2+ ions, presumable because having just one d electron is just too unstable once the 4s electrons have been lost. And once it has lost its d electron it has an empty d-orbital and is non-transition. This is an example of an the element that is a transition element whilst its ions are not.

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[2] I do, however, usually discuss the configurations of elements up to element 30 (zinc) including the exceptional configurations of chromium and copper, because they illustrate the importance of the spatial arrangement of electrons, and the effect this has on their relative energy levels. I find that students tend to confuse the spatial (s,p,d,f orbital) model of the atom with the energy level model, and this is one way to compare and contrast the two models.

E. Zn^{2+} The electron configuration of Zn is $3d^{10}$ $4s^2$, so it is non-transition. When it forms the Zn^{2+} ion it loses the $4s^2$ electrons so it is still non-transition. (Note how Zn^{2+} has a pseudo noble gas configuration cf. Pb^{2+}.)

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9. I originally wrote this question to test the students ability to distinguish between the three main types of bonding, but it ended up by being somewhat more complicated than that!

A chemical bond can be defined as the force of attraction that holds particles together. This attraction may arise from electrostatic forces or magnetic forces or a combination of the two.

The theory of chemical bonding involves the following principles:

1. Electrons, especially the outermost (valence) electronic shell, play a fundamental role in chemical bonding.
2. When atoms are involved in bonding they tend to acquire a particularly stable electronic configuration. Usually this configuration is that of a noble gas, i.e. with eight outer-shell electrons - an arrangement called an octet.

The three main types of bonding are **ionic, covalent and metallic bonding**.[3] Ionic bonding results from the transfer of one or more electrons from one atom to another. This leads to the formation of positive and negative ions which are held together by electrical attraction. Covalent bonding involves sharing of electrons between atoms. The shared electrons are attracted to the nuclei of both the atoms involved in the bond, holding the atoms togther. (This attraction applies even in double bonds and other multiple bonds in which some of the bonding electrons are not on the axis between two nuclei.)

Metallic bonding involves the attraction between the positive charges on a group of metal ions and their electrons. In metallic bonding the electrons are shared between all the ions in the group and their electrons, which are said to be delocalised (i.e. it is no longer clear which particular atom an electron has come from). Metallic bonding is often overlooked in beginner chemistry courses, but it is just as important as the other two. Metallic bonding is the bonding found in metals and alloys, whereas covalent bonding is found in non-metal elements and in compounds between different non-metals, and ionic bonding is found only in compounds of

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[3] Int**er**molecular bonding (hydrogen bonding, dipole-dipole interactions, dispersive forces etc.), which is found **between** molecules that have covalent int**ra**molecular bonding, is not under consideration here, as it is generally much weaker than the main forms of bonding.

metals with non-metals.[4] Thus for the options given the main types of bonding are:

A. C, O B. F, F and E. O, O - covalent
C. Na, Cl - ionic
and D. Na, K - metallic

The electrical force in a bond will be derived from attraction between the positively charge protons in the nucleus and negatively charged electrons. The closer the centres of positive and negative charges are to each other, the stronger the bond will be (other things being equal). The strongest of the three main types of bonding might therefore be expected to be covalent bonding, which involves the positive charge at the centre of an atom and the bonding pair of electrons on the periphery, one atomic radius away. Ionic bonding will be between the centre of one ion and the centre of a neighboring oppositely charged ion (about two ionic radii away). Pure metallic bonding is inherently weaker, because it involves attraction between the positive charge on a metal ion and its delocalised, shared, electron(s), which could be anywhere between the ion and any number of its neighbors.

Unfortunately, this is rather a simplistic interpretation of the situation. A solid is not just simply held together by bonding between two particles, but each particle can be considered to be interacting with all the others in the sample. The structure of the solid (i.e. the arrangement of the particles in the lattice) must also be considered, as this will determine how closely particles can get to each other. This is clearly indicated in metals where a structure may be close-packed or not, but it can also be observed ionic compounds, which have the additional factor of the stoichiometry affecting the packing of the ions. Thus MgO, which has an alternating arrangement of Mg^{2+} and O^{2-} ions, can form a much stronger lattice than $MgCl_2$, because in the latter case two negative Cl^- ions have to be packed in for each Mg^{2+}. (One could also consider the degree of intermediate bonding here, as there can be considerable covalent character in ionic bonding, or, indeed, in metallic bonding. Students who are interested in investigating this concept further should refer to a textbook that discusses the bonding continuum or the bonding triangle.)

The bonding in Group I metals such as Na and K, and presumably any alloy formed between them, is very weak. They have body centred cubic structure, which is not close-packed. The weak bonding is indicated by their low melting points and the ease with which they can be cut.

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[4] If you are unsure about which elements are metals and which are non-metals, then you should look at a copy of the Periodic Table. Metals are all on the lower left-hand side of the table, whilst non-metals are all on the upper right-hand side. There is a gradation of properties between metals and non-metals going (more or less) from bottom left to top right of the table in a diagonal sweep. A zig-zag line diagonal is sometimes drawn on the table, going on the left hand sides of the squares for boron, silicon, arsenic, tellurium and astatine, indicating the formal demarcation between metals and non-metals.

So Key D can be discounted. Sodium chloride, NaCl, on the other hand has a regular structure, and a tightly bonded lattice. It has a moderately high melting point. So C cannot be easily discounted as a possible correct answer.

On the other hand, the non-metal/non-metal combinations offered in this question might look as though they have weak bonding, because they can all form molecules that are gases at room temperature. Thus C and O form carbon monoxide, F and F form fluorine molecules and O and O form oxygen molecules. In these cases, however, the solid state is held together by weak intermolecular bonding. The bonding in the molecules themselves is covalent and strong. In fact the covalent bonding inside fluorine and oxygen molecules is not as strong as might be expected due to the repulsions between non-bonding electrons on these small atoms, which are forced close together in the molecule. It looks as if A might be the correct answer here. What clinches it is a consideration of the number of covalent bonds in the molecule. Carbon monoxide has a triple bond, whereas oxygen has a double bond, and fluorine a single bond. The triple bond with its three bonding pairs of electrons between the two nuclei is extremely strong, and is much stronger than the Na^+Cl^- bond could possibly be, even in a lattice. So the correct key is **A**.

A final note: this question does not suggest any combination of non-metals that might give giant covalent networks. Examples of such networks are C, C (e.g. in diamond), Si,Si and Si,O. These networks are extremely strong and have very high melting points. These networks generally involve non-metal atoms (often of group IV elements), each atom of which can form several covalent bonds. The C,O combination does not, however, form a network. This is thought to be because the process involved in forming the network would require using d electron orbitals, which carbon does not have in its valency shell.

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10. The point to focus on in this question is the term pure substances . **Pure substances** can be elements on their own or compounds in which elements are chemically combined. Pure substances need to be clearly distinguished from **mixtures**, which contain more than one element and/or compound. In particular, in this question, it is important to realise that solutions are mixtures, because they contain a solute mixed with a solvent.

Let us consider some of the possible examples of the different types of bonding suggested in the question.

A. Covalent bonds	Pure covalent bonds, in which two atoms share a pair of electrons equally, are found in H_2 molecules. Polar covalent bonds, in which the pair of electrons tend to be attracted more to one atom than the other (due to an electronegativity difference between the atoms) are found in molecules such as HCl. Both these types of covalent bonds can both be found as pure substances, so the key cannot be A. (Note that hydrogen cannot found in giant covalent networks because it cannot form more than one covalent bond per atom.)

B. Coordinate bonds

These are also known as **dative covalent bonds** or simply dative bonds. They are a type of covalent bond in which both of the electrons in the bonding pair come nominally from the same atom. This type of bond is often represented by an arrow, thus A B where A is the atom donating the electrons (cf. A - B for a regular covalent bond). Because the donation of a pair of electrons modifies the balance of charge, the bond is sometimes written as A - B . Note that these charges do not necessarily correspond to the electronegativity difference, and therefore this latter representation of coordinate bonds is not recommended.

Coordinate bonds involving hydrogen can be found for example in NH_4^+ ions and can therefore be found in pure compounds such as NH_4Cl, so the key cannot be B.

C. Hydrogen bonds

These are also known as **hydrogen bridges**. They are bonds formed when a hydrogen atom in one molecule or functional group is simultaneously attracted to a highly electronegative atom of a neighbouring molecule or group. In practice hydrogen bonding almost always occurs when a hydrogen atom can come between nitrogen, oxygen or fluorine (other atoms are either not electronegative enough or not small enough): the two atoms do not have to be the same. Hydrogen bonding is usually int**er**molecular, e.g. between water molecules, but it some cases it can be int**ra**molecular, e.g. between oxygens in the two different carboxylic acid groups of *cis*-butenedioic acid. Hydrogen bonding may occur between molecules of the same kind, such as water, i.e. in pure substances, and, although it can also occur between different molecules, such as water and sulfur dioxide, i.e. in mixtures, so the key cannot be C.

Note that hydrogen bonds are formed in molecules that have strongly polar bonds between an electronegative element and hydrogen, and may therefore be considered to be a special case of dipole-dipole interactions.

D. Ionic bonds involving H^+ ions

This is the correct key! This question is making an important point, namely that H^+ ions do not occur in pure compounds. We are so used to thinking of hydrogen ions being present in acid solutions, we tend to forget that (1) the hydrogen ions do not exist as simple protons, but they are attached to water molecules, giving **hydroxonium ions** (also known as **hydronium** or **oxonium** ions), and (2) pure acids, i.e. ones that are not dissolved in water, are covalent compounds - they are non-metal/non-metal compounds. They are ionized by reacting with water (or another compound acting as a Brønsted-Lowry base). Furthermore, only when they are ionized do acids start to exhibit their characteristic behaviour (turning litmus red, etc.).

E. Ionic bonds involving H^- ions Yes, unlikely as it may seem on first sight, pure compounds containing H^- do exist, so the key cannot be E. These compounds are called salt-like hydrides, because at room temperature they are white crystalline solids that look like salt. They are formed when hydrogen reacts with metals that are considerably more electropositive than it is (e.g. Na or Ca), forcing it to accept an electron and take on a helium (noble gas) electron configuration.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2001 continued

11. This question is another one that is essentially about bonding, because **a low boiling point means that interactions are weak** (compare it with Question 11 in Part A of the 2000 Exam, which asks about the highest boiling point).

There are three major types of intermolecular forces: **dipole-dipole interactions**, **hydrogen bonding** and **London forces**. As all the substances listed in the 2001 question contain only carbon and hydrogen then we are looking at molecules that have strong (covalent) int**ra**molecular bonding. The question therefore focuses on the relative strengths of the int**er**molecular bonding.

In addition, all the molecules contain only carbon and hydrogen (which have a negligible electronegativity difference) so their dipole moments are zero. We are looking at molecules that have neither polar bonds nor heteroatoms (oxygen, nitrogen sulfur, halogens), which eliminates the possibility of dipole-dipole interactions and hydrogen bonding. This means that the only type of bonding that we need to consider is **temporary dipole-dipole interactions**, also known as **induced dipole-dipole interactions, London forces, dispersion forces**, or (in the UK) **Van der Waals forces.**[1] In effect, what we need to consider is the molar mass of the molecules and their shape. (If we were looking at melting point rather than boiling point then the packing of the molecules in the solid would also be a consideration, as tightly packed solids will have stronger bonding, and higher melting points, cf Question 9.)

The molar mass of the molecules is important because molecules with a high molar mass generally have more electrons in them. Temporary dipole-dipole interactions occur when there can be a temporary imbalance in the electron cloud around a molecule, allowing it to become a temporary dipole and thus setting up induced dipoles in neighboring molecules. The more electrons in the cloud the more likely it becomes that this initial imbalance can occur.

The shape is important because it affects the size of the dipole moment associated with the molecule (even if this is only a temporary dipole moment). If the centres of positive and negative charge associated with a dipole are at points X and Y, distance d apart, and the size of the charge is q, thus:

<--- d --->
X --------- Y
(+q) ------- (-q)

---

[1] In U.S. textbooks the term Van der Waals forces may be used to refer to all types of intermolecular forces (including hydrogen bonds) or to both permanent and temporary dipole-dipole interactions. In view of the discrepancy between US and UK usage this ambiguous term is best avoided.

then the size of the **dipole moment = d x q** (irrespective of whether the charge is considered to be positive or negative). A long thin molecule will therefore have a greater dipole moment than a short fat one, even if they have the same molar mass/number of electrons.

Now let us consider the possible answers in the light of this information. Note that all the formulae given are condensed structural formulae. If you have trouble visualizing the structures you should try building models of the molecules.

A. C_6H_6 This is benzene, $M_r = 78.1$. It consists of a ring of 6 carbon atoms, with a hydrogen atom attached to each carbon. Nominally the bonding between the carbons alternates between single and double bonds, but in fact the bonds are all equivalent (1½ bonds) with p electrons overlapping to give a delocalized (pi) electron system above and below the planar ring. These delocalized electrons make it relatively easy for temporary dipole-dipole interactions to be set up between the top of one ring and the bottom of a neighboring ring, so that, in fact, the boiling point is higher than hexane, for example, even though hexane has a higher molar mass ($M_r = 86.2$).

B. $(CH_2)_6$ This looks a bit odd, but it is, in fact cyclohexane, $M_r = 84.2$. (I couldn t use a ring formula, and didn t want to write it as C_6H_{12}, which could also be the formula of one of the hexene isomers - this would have complicated the question, as hexenes may have permanent dipole moments, due to the double bond in them.) This has the highest molar mass of all the compounds to be considered, but its boiling point is almost exactly the same as that of benzene, because it does not have the delocalized electrons to help with the formation of induced dipoles.

The next three suggested answers are all pentane isomers (in spite of their systematic names, which relate to the longest chain of carbons in the molecules). All the pentanes have the same molecular formula (C_5H_{12}) and the same molar mass ($M_r = 72.2$), which is lower than that for either benzene or cyclohexane. The answer is therefore likely to be one of these three. The question is now one of resolving which molecule has the most compact shape.

C. $C(CH_3)_4$ This is 2,2-dimethylpropane, formerly known as neopentane. This beautiful molecule is like a little ball, with a carbon in the middle and four methyl groups around the central carbon. It is the most compact molecule of the three isomeric pentanes, and therefore has the least possibility of forming a temporary dipole, so it has the weakest bonding between molecules and the lowest boiling point. The correct key is therefore **C**.

D. $CH_3(CH_2)_3CH_3$ This is pentane, formerly known as normal pentane (or *n*-pentane). It is a so-called straight chain molecule (although in reality the carbon chain is zig-zagged, because the angle between carbons is the tetrahedral angle of 109.5°, not the 180° that would be needed for a straight chain). It is the longest molecule of the three isomers, and so it has the highest boiling point.

E. $CH_3CH_2CH(CH_3)_2$ This is 2-methylbutane, formerly known as isopentane. It is a branched chain molecule, but with just one methyl group coming off the straight chain, so it has a boiling point intermediate between those of the other two pentane isomers.

Actual boiling points: **A.** (81°C), **B.** (80.7°C), **C.** (10°C), **D.** (36°C), and **E.** (28°C)

---

12. It is not possible to determine a numerical value of the dipole moment from the information given here, but it is possible to gain some insight into its size by considering both the **polarity of the individual bonds** in the molecule and the **symmetry of the molecule.**

Some idea of the magnitude of the of the polarity of a bond is indicated by calculating the difference between the electronegativities of the atoms on either side of it. (The direction of the polarity is, of course, with the more electronegative element being at the more negative end of the bond.[2]) A symmetrical molecule will not itself be polar, however, even if its bonds are polar, because the symmetry will cause the various bond polarities to cancel each other out.

There is a third factor that is not generally considered, and that is the effect of **lone pairs of electrons**. Just as lone pairs cannot be ignored when working out the shape of molecules, they also need to be recalled when considering its polarity, because they behave as a strongly negative charge centre on their side of the molecule. **Double bonds**, with their extra electrons, have a similar effect, but they are not relevant to the molecules to be considered in this question.

We are now going to consider these effects for the options given in this question. If you do not understand why the shape of the molecules is as stated, then you should draw out their Lewis diagrams and work out where the bonding pairs and lone pairs go around the central atom.

A. BF_3 Boron is the central atom here. It has only three valency electrons, so that

---

[2] The electronegativity values most often used are Pauling electronegativity values, which do not really have a very precise definition. They have been determined by comparing the polarities of bonds between different elements. The best description of electronegativity is the power of an atom to attract electrons towards it from a covalent bond between it and another atom .

when these are paired with a single electron from each of the fluorine atoms, there are only 6 electrons in its outer shell. BF_3 is thus an example of a species that disobeys the octet rule. The three pairs of bonding electrons are equally distributed around the boron, so the shape of the molecule is thus trigonal planar. This is symmetrical so the polarity of the bonds is irrelevant here - the dipole moment of the molecule is zero.

B. NH_3 Nitrogen is the central atom. It has five valency electrons, but only three bonds. It therefore has one lone pair of electrons, which must be counted in along with the three bonding pairs when establishing its shape: it is therefore trigonal pyramidal. The electronegativity difference for each N-H bond is (3.0 - 2.1) = 0.9 with the nitrogen being at the more negative end. The lone pair is also on this nitrogen so this reinforces the negative effect on this side of the molecule.

C. PH_3 Phosphorus is the central atom, and, as it is in the same group of the periodic table as nitrogen, it also has five valency electrons. Like NH_3, PH_3 is trigonal pyramidal, but the electronegativity difference for the P - H bond is zero, so that the polarity of this molecule is due only to the lone pair on the phosphorus. Key C can be eliminated because the dipole moment of PH_3 must be less than that of NH_3.

D. PCl_3 Phosphorus is again the central atom, and, like NH_3 and PH_3, the molecule is trigonal bipyramidal. The bonds are polar because there is an electronegativity difference for each P - Cl bond of (3.0 - 2.1) = 0.9, but in this case the more negative end is the chlorine end, so that the lone pair of electrons and the electronegativity are working in opposite directions, and any dipole moment that the molecule might have will be small. So Key D can be eliminated.

E. SO_3 Sulfur is the central atom, and it has six valency electrons. The oxidation number[3] of sulfur here is +6, which means that all of its six valency electrons are involved in bonding. The three S - O bonds are generally considered to be two dative covalent bonds and one double bond, but some books describe them as three double bonds, in which case the molecule breaks the octet rule by having too many electrons in its valency shell. The best description is a resonance hybrid of all possible structures. In any case

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[3] The rules for allocating oxidation numbers are given in the Appendix. In this example, the rule that is being applied is that the oxidation number of oxygen is -2. The sum of the oxidation numbers due to the three oxygen atoms in SO_3 is 3 x (-2) = -6. This has to be balanced by sulfur, so S must be +6.

the three sets of bonding electrons are evenly distributed around the sulfur, and the molecule is symmetrical. Thus the molecule is non-polar even though the sulfur-oxygen bonds are polar, and Key E can be discounted.

Amongst these options, the molecule with the greatest polarity/dipole moment must be NH_3. So the key is **B.**

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13. This is another question in which it would be helpful to be able to draw the shape of the molecules. Let us take each option in turn:

A. H_2O This is water, of course, and can be written as H-O-H. So it certainly contains a hydroxyl group, and the key cannot be A.

B. CH_4O This is methanol, and can be written as CH_3OH. So it certainly contains a hydroxyl group, and the key cannot be B.

C. CH_2O This is methanal (formerly called formaldehyde). As carbon has four valency electrons its structural formula must involve a double bond to the oxygen, thus HCHO. There is no possibility of a hydroxyl group here. So the key must be C.

Checking ourselves by continuing with the other options:

D. H_2SO_4 This is sulfuric acid, of course. It might be a tempting choice for students who tend to think of acids as providers of hydrogen ions, and bases as providers of hydroxyl ions, but in fact the way we write the formulae of acids is rather misleading. Virtually all acids that contain both oxygen and hydrogen are in fact hydroxy acids, with a central non-metal atom (here sulfur) surrounded by oxygens, and with the acid hydrogens on the outer part of the molecule attached to oxygens.[4] Thus sulfuric acid might be written $SO_2(OH)_2$, and the key cannot be D.

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[4] The difference between an acidic hydroxy group and a basic hydroxy group lies in the electronegativity of the atom to which the hydroxy group is attached. If this atom is electronegative (i.e. a non-metal) it will help the oxygen to drag electrons away from the O - H bond, releasing the hydrogen as an ion. If the atom is electropositive (i.e. a strong metal) then it will push electrons away from it towards the hydroxy group, releasing it as a negative ion. The atoms of weaker metals (amphoterics) are insufficiently electropositive, so that their hydroxy compounds can be persuaded to break apart differently according to the species with which they are reacted. Amphoteric hydroxides (and oxides) can behave both as weak acids and weak bases.

E. C_6H_6O This is phenol (also known as hydroxybenzene, and by its IUPAC name, benzenol) C_6H_5OH. It contains a hydroxyl group, so the key cannot be E. Note that this is another example of a hydroxy group with some acidic properties, i.e. it loses H^+ rather than OH^-.

---

14. A **low pH means that the solution is acidic**, so that Key A (NH_3) can be discounted right away, because ammonia is a Brønsted-Lowry base, and dissolves in water to give an alkaline solution.

Apart from that, the rule that you need to apply here is:

When an element makes more than one compound with oxygen, then the compound with the highest proportion of oxygen in it will be the most acidic.

This is because, when an oxide dissolves in water it becomes a hydroxy compound. (Oxide ions do not exist in solution). Oxygen is very electronegative, so that the more oxygens there are in the compound the greater the pull of electrons towards them will be, and more easily the hydrogen(s) attached to them will be released. The more hydrogen ions that are released the more acidic the solution is.

The question now resolves itself into working out the proportion of nitrogen:oxygen in each of the nitrogen oxides. These are indicated by the formulae of the oxides, and are respectively:

B. N_2O 2:1, C. NO 1:1, D. NO_2 1:2, E. N_2O_3 1: 1.5

NO_2 thus has the highest proportion of oxygen, and the correct key is **D**.

---

15. This question looks a little odd because we are so used to working at 25°C. At higher temperatures more water molecules ionize (bond breaking is endothermic), so the ion product of water, K_w, increases. (Note also that, in neutral water, the pH will be < 7, but that pH = pOH still applies.)

This question is designed to test whether students understand the calculation that they can probably do very easily for problems at 25°C. There are various ways of setting about it, but this is what I would do:

$K_w = 5.5 \times 10^{-14}$ at 50°C
Therefore $pK_w = 13.26$ at this temperature, since pK = - logK (just like pH = - log $[H^+]$)
Now $pK_w = pH + pOH$
Therefore $pOH = (13.26 - 6.0) = 7.26$,

then making this negative, and using the 10^x calculator button,

$$[OH^-] = 5.49 \times 10^{-8} \text{ (mol L}^{-1}\text{)}$$

So the Key is **D**. (Other keys would be obtained from some of the calculation errors that students commonly make.) If logs are only taken to one decimal place (and there is a case for this since pH and K_w are given to only one decimal place) then the $[OH^-]$ comes out as 5.0 mol L^{-1}, and D is still the closest answer. (I generally prefer to work through the calculation at a slightly greater degree of precision than is needed, then round for the final answer.)

Note that logs, and by extension, pK, pH and pOH values, have no units. $[H^+]$ and $[OH^-]$ have units of mol L^{-1}. Strictly speaking K_w should be given units of mol^2 L^{-2}, but it is unusual to give units for equilibrium constants in North America (even when they are obtained from concentration values). Different concentration units would change the values of the logs, but it is rare for units other than mol L^{-1} (or mol dm^{-3}, which are numerically the same) to be used in equilibrium calculations.

ANSWERS TO PART A OF THE NATIONAL HIGH SCHOOL CHEMISTRY EXAMINATION 2001 continued

16. **The Brønsted-Lowry definition of an acid is a substance that can donate a proton: a base is a proton acceptor.** If an acid-base reaction is considered to be an equilibrium, system then a generalized equation can be written, thus:

$$\begin{array}{cc} HA \;+\; B^- & HB \;+\; A^- \\ \text{Acid 1 + Base 2} & \text{Acid 2 + Base 1} \end{array}$$

Base 1 is called the conjugate base of Acid 1, because it can be converted back to Acid 1 by the addition of hydrogen (a proton). Acid 2 is called the conjugate acid of Base 2, because it can be converted back to Base 2 by the removal of hydrogen.

This question is very similar to Question 22 in Part A of the 2000 Exam. The 2001 question is, however, made complicated by the fact that glycine (aminoethanoic acid) has an acid group at one end of the molecule, and a base group at the other end. The formula for glycine is given in Key B, it is $H_2N\text{-}CH_2\text{-}COOH$ (which means, of course, that the answer is not B). The conjugate acid must be formed by the addition of a proton to glycine, so that, when that proton is removed we get back to glycine, with the base end in the same form as in the neutral molecule. The correct Key is therefore **C** ($H_3N\ \text{-}CH_2\text{-}COOH$). The reaction involved is:

$$H_2N\text{-}CH_2\text{-}COOH + H_2O \quad H_3N\ \text{-}CH_2\text{-}COOH + OH^- \quad \text{. . . . .} \quad (1)$$

As for the other suggested keys: D. ($H_2N\text{-}CH_2\text{-}CO_2$) would be the conjugate base, because it would form the original molecule on the addition of a proton. A. (H_3O) is a hydrated proton or hydroxonium ion, and is the conjugate acid of water. The species given in A and D would be formed in the following reaction between glycine and water:

$$H_2N\text{-}CH_2\text{-}COOH + H_2O \qquad H_2N\text{-}CH_2\text{-}CO_2 \quad + H_3O \quad \text{. . . . .} \quad (2)$$

Reactions (1) and (2) both start with the same reactants, but in (1) the water is behaving as a Brønsted-Lowry acid (donating a proton), whereas in (2) it is behaving as a base. Water is an **amphiprotic** substance meaning it can react as either an acid or a base. (Glycine is also amphiprotic, of course, as are all amino acids.) Which reaction predominates, (1) or (2), depends on the pH of the reacting medium. Reaction (1) would be the main reaction to occur in strongly acidic solutions, whilst reaction (2) would predominate in strong basic solutions. (This can be seen if you apply Le Châtelier principle to the equilibrium systems involved.)

The species suggested as an answer in E ($H_3N\ \text{-}CH_2\text{-}CO_2$) is called a **zwitterion** or **dipolar ion**.

Zwitterions are present in the dry solid form of amino acids, and also in solution when they exist in equilibrium with the conjugate acid and base forms. At a certain specific pH the zwitterion reaches a maximum concentration, and the concentration of the other two ions are equal. This pH is called the **ioselectric point**, and is given the symbol **pI** (pI = 6.0 for glycine).

One of the people reviewing the exam objected to the positioning of the charges on the various ions. Strictly speaking the positive charge should be shown on top of the nitrogen. I am sorry to say that I have not found out a way of doing this, but students should be reassured to think that there are people who check the exam to see that it doesn t run away with me too much!

A final note about this question: Brønsted-Lowry theory is in the Pan-Canadian protocol for chemistry, but the theory of zwitterions is not. It is, however, an interesting application of Brønsted-Lowry, and of particular importance to biology students.

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17. This is a routine type of calculation involving a solubility product constant, albeit one that requires a good deal of care to avoid calculation errors.

The equilibrium equation involved is:

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

Thus if x mol L^{-1} is the concentration of dissolved $Ca_3(PO_4)_2$, then there will be 3x mol L^{-1} of Ca^{2+} and 2x mol L^{-1} of PO_4^{3-} in the solution at equilibrium.

The solubility product constant, $K_{SP} = [Ca^{2+}]^3[PO_4^{3-}]^2$ where the square brackets [] around a symbol or formula indicate the equilibrium concentrations of these species.

Therefore $K_{SP} = (3x)^3 (2x)^2 \qquad = 108\ x^5$

and $x \ = \ {}^{5}\ 1 \times 10^{-26} \div 108 \ = 2.473 \times 10^{-6}$

Remembering that the concentration of PO_4^{3-} = 2x mol L^{-1}

$[PO_4^{3-}]$ = 4.95 mol L^{-1}

This is approximately 5.0 mol L^{-1} , so the correct key is **D**. Other keys would be obtained from some of the calculation errors that students commonly make.

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18. This question is very similar to Question 18 in Part A of the 2000 exam. The reaction given in the 2001 question is used in the industrial production of methanol. Although the industrial process is a continuous one, so the reaction is never allowed to go to completion , it is run in a steady state, the conditions for which are derived from consideration of the equilibrium system. A qualitative idea of the way in which the conditions need to be manipulated in order to maximize the production of methanol in a reasonable time can be achieved by application of Le Châtelier s principle.

The reaction equation is:

$$\mathrm{CO(g)} + 2\mathrm{H_2(g)} \quad \mathrm{CH_3OH(l)}; \quad H = -\ 615.5\ \mathrm{kJ\ mol^{-1}}$$

Let us consider each of the suggested changes in turn:

A. Increasing the proportion of carbon monoxide. This would stress the left hand side of the equation, swinging the reaction to the right, and increasing the amount of methanol formed.

B. Increasing the proportion of hydrogen. Again this would stress the left hand side of the equation, swinging the reaction to the right, and increasing the amount of methanol formed.

C. Increasing the pressure. There are more moles of gas on the left hand side of the equation, so that if the pressure were increased by adding more moles of either gas the left hand side of the equation would again be stressed, swinging the reaction to the right, and increasing the amount of methanol formed. Alternatively, if the pressure were increased by adding an inert gas this would have no effect on the amount of methanol formed.

D. Increasing the temperature. The reaction has a negative enthalpy change, so that heat can be treated as a product of the reaction, thus:

$$\mathrm{CO(g)} + 2\mathrm{H_2(g)} \quad \mathrm{CH_3OH(l)} + \text{heat}$$

Increasing the temperature would therefore stress the right hand side of the equation, swinging the reaction to the left and decreasing the amount of methanol formed. **D** is therefore the correct key.

E. Removing the methanol as it is produced. This would stress the right hand side of the equation, requiring methanol to be replaced by reaction of the species on the left hand side. This would increase the amount of methanol formed..

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19. In order to determine which of the mixtures would give a neutral solution we have to consider exactly how each pair of substances might react. We need to think about the solubilities of the various species and the possibility of hydrolysis of soluble species. We must also bear in mind that limiting reagent considerations may apply.

The reactions for each pair of substances given in the question are:

A. $2HCl(aq) + Pb(NO_3)_2\ (aq) \text{ ----> } PbCl_2(s) + 2HNO_3(aq)$

This reaction would give an acidic solution, because the aqueous product of the reaction is nitric acid (lead(II) chloride is water-insoluble at ambient temperature). There is a limiting reagent here (hydrochloric acid), but the excess lead(II) nitrate would, if anything, be acidic due to hydrolysis, and the final solution is unquestionably acidic.

B. $H_2SO_4(aq) + 2NaOH(aq) \text{ ----> } Na_2SO_4(aq) + 2H_2O(l)$

This reaction would give an acidic solution, because, although the sodium sulphate formed is more or less neutral, there is a limiting reagent here (sodium hydroxide) so there would be an excess of sulfuric acid.

C. $H_2SO_4(aq) + K_2O(s) \text{ ----> } K_2SO_4(aq) + H_2O(l)$

This reaction would give a neutral solution and there is no limiting reagent, so the correct key is **C**.

D. $CH_3COOH(aq) + NaOH(aq) \text{ ----> } CH_3COONa(aq) + H_2O(l)$

This reaction would give an alkaline solution, because the sodium ethanoate would dissociate into sodium ions and ethanoate ions, and the ethanoate ions would then be hydrolysed. There is no limiting reagent.

E. $CH_3COOH(l) + CH_3OH(l) \text{ <===> } CH_3COOCH_3(l) + H_2O(l)$

This reaction would give an acidic solution, even though the products of the reaction are neutral, and there is no limiting reagent. This is because it is an equilibrium reaction, so some of the ethanoic acid will always be present in the mixture.

I feel that this is a rather weak question. I originally had the following pair of compounds for C: $CH_3COOH + NH_4OH$. These would react according to the following equation:

$$CH_3COOH(aq) + NH_4OH(aq) \text{ ----> } CH_3COONH_4(aq) + H_2O(l)$$

This would give a neutral solution because ethanoic acid has $pK_a = 4.8$, and ammonia solution has $pK_b = 4.8$, so that the CH_3COO^- and NH_4^+ are equally hydrolyzed. Although these are examples of a weak acid and a weak base that most students will have come across, some of the people reviewing the exam felt that it was unfair to expect them to know this curious little fact, so we changed the pair of compounds in C. It turned out to be more difficult that one might expect to find a pair of compounds that actually give a neutral solution when they react!

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20. The enthalpy change of a reaction (H_r) can be calculated from the enthalpy changes of formation of the reactants and products using the equation:

$$\mathbf{H_r = \quad H_f\,(products) - \quad H_f\,(reactants)}$$

Thus for the lime kiln reaction, $CaCO_3(s) \quad CaO(s) + CO_2(g)$

$$H_r = \quad H_f\,(CaO(s)) + \quad H_f\,(CO_2(g)) - \quad H_f\,(CaCO_3(s))$$

$$= (-635.1) + (-393.5) - (-1207)\ \text{kJ mol}^{-1}$$

$$= +\ 178.4\ \text{kJ mol}^{-1}$$

Note that the + sign indicates that the reaction is **endothermic**, i.e. that heat is required for the reaction, therefore keys D and E cannot be correct.

The H_r calculated indicates the energy required by one mole of equation, i.e. the energy required to produce one mole (56.1 g.) of CaO.

Therefore the energy required to produce one tonne (1000 kg) of CaO

$$= 178.4\ \text{kJ mol}^{-1} \times 1000\ \text{kg} \times 1000\ \text{g kg}^{-1} \div 56.1\ \text{g mol}^{-1}$$

$$= 3.18 \times 10^6\ \text{kJ}$$

Thus the correct answer is **C**.

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21. This question requires the calculation of entropy, which is not on the Pan-Canadian protocol, although students considering taking Part C (Olympiad section) of the National High School Chemistry Exam should be able to do this. Other students should be able to recognize that the evaporation of water involves an increase in entropy (disorder) i.e. the entropy change is positive. Keys A, B and C cannot therefore be correct.

The equation required for the calculation is:

G = H - T S Where G is the Gibbs free energy change for the reaction in kJ mol^{-1}
H is the enthalpy change for the reaction in kJ mol
T is the temperature at which the reaction is taking place, in K
and S is the entropy change for the reaction in J mol^{-1} K^{-1}

The chemical equation for the evaporation of water is:

$$H_2O(l) \text{ ----> } H_2O(g)$$

Now, as in question 20, **H_r = H_f (products) - H_f (reactants)**

And similarly, **G_r = G_f (products) - G_f (reactants)**

This means that, for the evaporation of water:

$$\begin{aligned} H &= H_{f,298}(H_2O(g)) - H_{f,298}(H_2O(l)) \\ &= (-241.8) - (-285.8) \text{ kJ mol}^{-1} \\ &= +44.0 \text{ kJ mol}^{-1} \end{aligned}$$

(Note that the positive sign indicates that the process is endothermic, this agrees with evaporation being a bond-breaking process.)

Likewise:

$$\begin{aligned} G &= G_{f,298}(H_2O(g)) - G_{f,298}(H_2O(l)) \\ &= (-228.6) - (-237.2) \text{ kJ mol}^{-1} \\ &= +8.6 \text{ kJ mol}^{-1} \end{aligned}$$

Rearranging the equation: G = H - T S, gives the entropy change, thus:

$$\begin{aligned} S &= (H - G) \div T \\ &= (44.0 - 8.6) \text{ kJ mol}^{-1} \div 298 \text{ K} \\ &= 0.1188 \text{ kJ mol}^{-1} \text{ K}^{-1} \\ &= 118.8 \simeq 120 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

So the correct answer is **E**. (Note how very important the units are in this question.)

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22. This question tests a similar concept to Question 16 in Part A of the 2000 exam, namely that **absorption of energy is required to break bonds**.

The 2001 question goes a little further. The absorption of energy initiates a chain reaction by causing the homolytic fission of a covalent bond to form two free radicals. So the correct answer is **D**. (The sequence in which other reactions in the chain occur are not as easily predicted.)

If you are not familiar with the terminology, then here are some definitions:

A **chain reaction** is a reaction in which intermediates (chain carriers) can initiate further reactions. In chemical chain reactions these intermediates are often free radicals or atoms, whereas in nuclear reactions they are neutrons.

A **free radical** is an atom or group of atoms with unpaired electrons. Some of these may be quite stable, e.g. NO molecules, but most radicals are very short lived. The unpaired electron on a radical is often marked with a dot, thus chlorine atoms are represented as Cl when they are behaving as free radicals in the chain reaction shown in this question. Note, however, that the oxygen atoms are only shown as O in this question although they can behave as free radicals: they actually have two unpaired electrons. (An oxygen atom has six valency electrons, four of which are paired to form two electron pairs, and two are unpaired.)

Homolytic fission occurs when a covalent bond is broken in such a way that one electron from the bonding pair goes to each of the fragments formed at either end of the broken bond. This results in the fragments becoming free radicals. Compare this with **heterolytic fission** which occurs when a covalent bond is broken in such a way that both the electrons in the bond go to one of the fragments, which then becomes a negative ion: the remaining fragment is electron deficient, so it becomes a positive ion. The greater the polarity of a covalent bond the more likely it is to undergo heterolytic fission rather than homolytic fission, but external factors such as solvents can also affect the nature of the fission.

Chemical chain reactions are initiated by the formation of radicals by the action of heat or light on a normal molecule, so in the example given in the question the **chain initiation step** is:

D. $CF_2Cl_2 \qquad CF_2Cl + Cl$

Once the free radicals have been formed, the chain is propagated by a reaction involving a molecule producing a product molecule and another radical, which can continue the chain. Examples of **chain propagation steps** are:

B. $ClO + O \quad Cl + O_2$
and C. $Cl + O_3 \quad ClO + O_2$

Inhibition occurs when a free radical attacks the (desired) product of the reaction There is no example of an **inhibition step** given in this series of reactions.

The chain terminates when two free radicals combine. An example of a **termination reaction** is:

E. $CF_2Cl + CF_2Cl \quad C_2F_4Cl_2$

The termination reaction is often the reverse of the initiation reaction, which in this case would be the reverse of D, thus:

$CF_2Cl + Cl \quad CF_2Cl_2$ (this is not shown as an option in the question)

The reaction given in key A is an interesting one:

$O + O_3 \quad 2O_2$

This shows how the oxygen atoms generated in reaction B can react with ozone to make oxygen. It is an example of how ozone can be destroyed by the reactions originating with a chlorofluorocarbon. It is true that the reverse reaction can also occur, generating oxygen atoms, but these oxygen atoms can then be used in reaction B, creating chlorine radicals which can then attack ozone in reaction C. Either way, the ozone layer will be reduced.

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23. There are a number of ways in which redox reactions can be recognized. For simple inorganic reactions such as these the best method is probably to look at oxidation numbers.

Redox reactions are characterized by a change of oxidation numbers. (The rules for assigning oxidation numbers are given in the Appendix.) If the redox is considered in two parts, reduction and oxidation, then the oxidation number goes down in the reduction part and up in the oxidation part.

One important point to realise is that **any reaction that involves an element** (as either reactant and product) must involve a change in oxidation number (to or from zero) and is therefore redox. This eliminates keys A, B and D.

If you think of the oxidation number rule about oxygen and peroxides, you can immediately see that key C refers to a redox reaction. This leaves **E** as the correct answer.

Some of the reactions suggested as options in this question are of interest for a number of reasons, which are considered below.

A. $\mathbf{Br_2 + H_2O \quad HBr + HBrO}$

This reaction is interesting because it is an example of a **disproportionation reaction**. In this kind of reaction the **same element is both oxidized and reduced**. Here elemental bromine (oxidation state zero) is reduced to oxidation state -1 (in hydrogen bromide) and oxidized to oxidation state +1 (bromic(I) acid - also known as hypobromous acid).

B. $\mathbf{I_2 + 2Na_2S_2O_3 \quad 2NaI + Na_2S_4O_6}$

In this reaction iodine is reduced from oxidation state zero (in the elemental state) to -1 (in sodium iodide), whilst sulfur is oxidized from oxidation state +2 (in sodium thiosulfate) to +2.5 (in sodium tetrathionate). The tetrathionate ion is a good example of a species containing a **partial oxidation number** (see also question 4 from Part A of the 2000 exam). A partial oxidation number is, in fact, an indication that the element is present in two different oxidation states in the same compound, or that some of the atoms of the element are linked to atoms of the same element. In fact sulfur is linked to other atoms of sulfur in both the thiosulfate ion and in the tetrathionate ion (as well as being linked to oxygen atoms). This can be seen if you draw out the structural formulae of the ions. Note that this does not preclude the use of the oxidation number method for balancing the equation (check here that the total oxidation number change up equals the total oxidation number change down).

In reactions containing more complex systems than those represented in this question, the oxidation number method of identifying redox reactions, and of balancing them, becomes difficult, and other methods are more practicable. In organic chemistry, for example, it is often easier to see whether oxygen is being added to a compound (oxidation), or whether hydrogen is being added (reduction).

C. $\mathbf{Na_3AsO_3 + H_2O_2 \quad H_2O + Na_3AsO_4}$

In this reaction arsenic is being oxidized from oxidation state +3 to oxidation state +5, whilst oxygen is being reduced from -1 in hydrogen peroxide to -2. Note that one of the product oxygens is in water whilst the other is in sodium arsenate(V). Also see how that there is a greater proportion of oxygen in Na_3AsO_4 than in Na_3AsO_3, indicating that the arsenic is in a higher oxidation state. A comparison of the proportions of oxygen in the corresponding acids also signals that H_3AsO_4 is more strongly acidic than H_3AsO_3 (cf Question 14).

D. $\mathbf{3I_2 + 6NaOH \quad NaIO_3 + 5NaI + 3H_2O}$

This is another disproportionation reaction in which elemental iodine (oxidation state zero) is oxidized to iodate(V) (with iodine in oxidation state +5) and reduced to iodide (oxidation state -1). Note how the stoichiometry works in order to balance the oxidation number changes.

E. $\mathbf{2K_2CrO_4 + H_2SO_4 \quad K_2Cr_2O_7 + K_2SO_4 + H_2O}$

This is NOT a redox reaction, even though potassium dichromate is often used as an oxidizing agent. Some teachers recommend that students learn the names and formulae of common oxidizing and reducing agents, just so that they can recognize redox reactions - but you can get caught out by this approach!

This reaction is, in fact, a condensation (addition-elimination) reaction. Potassium ions and sulphate ions are spectators , and the essential reaction is that two chromate ions add together and water is eliminated, as shown in the following ionic equation:

$$2CrO_4^{2-} + 2H^+ \quad Cr_2O_7^{2-} + H_2O$$

The chromium ions remain in the +6 oxidation state. Note that this is a good example of an equilibrium system that can be manipulated by changing the pH. Addition of acid swings the equilibrium to the dichromate side of the reaction, and, in fact, dichromate ions are only found to any appreciable extent in acid media. On the other hand, chromate ions require to be in an alkaline environment.

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24. Note that reaction kinetics are not on the Pan-Canadian protocol, however a question on rates will be included in Part A of the National High School Chemistry Exam, because of the importance of this topic, particularly to chemical engineers. Questions will be restricted to testing knowledge of the meaning of rate of reaction, methods of measuring rates of reaction, and the factors affecting rates. Students will be expected to know the meaning of activation energy, but the rate expression and the Arrhenius equation will no longer be included on Part A of the exam (but they may appear on Part C).

Question 24 tests the student s understanding of the way in which the stoichiometry of the reaction can influence the measured rate, and of the different ways in which rates can be measured experimentally. Generally the rate of reaction is defined as the change of concentration of a particular reactant in unit time, which would give units of mol L^{-1} min^{-1} (mol L^{-1} s^{-1}, mol L^{-1} h^{-1} etc. would also be possible). The rate may, however, be monitored in a variety of ways apart from measuring concentration changes. Any quantity that changes in proportion to concentration may form an acceptable basis for rate measurement, for example the volume of gas at constant temperature and pressure could be used.

Note that, in this question, the rate is taken as positive, irrespective of whether it applies to the decrease in concentration of a reactant, or to the increase of concentration of a product. Some authors consider the rate to be negative if it refers to a decrease in concentration with time. This question refers to the reaction between mercury(II) chloride and ethanedioate (oxalate) ions, which is represented by the following equation:

$$2HgCl_2(aq) + C_2O_4^{2-}(aq) \quad 2Cl^-(aq) + 2CO_2(g) + Hg_2Cl_2(s)$$

It is (presumably) possible to measure the rate of reaction at a particular stage of the reaction in terms of the mercury(II) chloride concentration (or, more likely, the Hg^{2+} ion concentration). Let us consider what happens to the other components of the mixture at this point.

The rate of reaction in terms of the ethanedioate (oxalate) ion, $C_2O_4^{2-}$ will be half that of the rate in terms of $HgCl_2$, because according to the equation, 2 moles of $HgCl_2$ are required to react with each mole of $C_2O_4^{2-}$, so the $HgCl_2$ will be used up twice as fast. Thus, if the rate of reaction is terms of $HgCl_2$ is 5.00×10^{-5} mol L^{-1} min^{-1}, then the rate of reaction in terms of $C_2O_4^{2-}$ will be 2.50×10^{-5} mol L^{-1} min^{-1}, so key A cannot be correct.

The equation shows, however, that 2 moles of $HgCl_2$ produce 2 moles of aqueous chloride ions, Cl^-, so that the rate in terms of Cl^- will be the same as that for $HgCl_2$, and key **B** is correct.

If you have time you could continue to consider the other keys, all of which require assumptions that are not really valid.

The rate of reaction in terms of carbon dioxide gas could be measured by measuring the loss of mass to the system if the reaction were performed in an open container. The rate in terms of mol L^{-1} min^{-1} would be the same for CO_2, as for $HgCl_2$, because the equation shows that 2 moles of $HgCl_2$ produce 2 moles of CO_2. Supposing that we have one litre of reaction mixture, and that 5.00×10^{-5} mol of CO_2 are produced from this in a minute, then the mass produced in the same time would be 2.20×10^{-3} g (= 5.00×10^{-5} mol x 44.0 g mol^{-1}) not 1.14×10^{-6} g ($\underline{=}$ $5.00 \times 10^{-5} \div 44.0$), so that key C cannot be correct.

Another method of measuring the carbon dioxide gas, would be to trap it and measure its volume. Again supposing that we have one litre of reaction mixture, and that 5.00×10^{-5} mol of CO_2 are produced from this in a minute, and supposing that the volume of gas is measured at standard ambient temperature and pressure, then the volume of gas produced in a minute would be 1.21×10^{-3} L (= 5.00×10^{-5} mol x 24.2 L mol^{-1}), so key D cannot be correct.

The rate of reaction could also be measured by filtering off the solid mercury(I) chloride, drying it, then measuring its mass. The equation tells us that one mole of Hg_2Cl_2 is formed from 2 moles of $HgCl_2$, so that the if we start with 5.00×10^{-5} mol of $HgCl_2$ we would expect to obtain 2.50×10^{-5} mol of Hg_2Cl_2. (Again we would have to suppose that we start with one litre of reaction mixture.) 2.50×10^{-5} mol of Hg_2Cl_2 corresponds to a mass of 1.18×10^{-2} g (= 2.50×10^{-5} mol x 472.1 g mol^{-1}) not 1.05×10^{-7}g ($\underline{=}$ $5.00 \div 472.1$), so key E cannot be correct.

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25. This equation could be solved using the Nernst equation. This is not, however, on the Pan-Canadian protocol, although it is something that students taking Part C (Olympiad section) of the exam should know. The Nernst equation would give an exact numerical value for the overall cell potential under non-standard conditions, but this is not in fact required. The question as it stands can be solved by applying Le Châtelier s principle to the redox equilibria.

Let us first consider the reduction potentials that are given, namely:

$Zn^{2+}(aq) + 2e^{-} \quad Zn(s);\ E \ = -\ 0.76V$

$Ni^{2+}(aq) + 2e^{-} \quad Ni(s);\ E \ = -\ 0.25V$

These are both standard reduction potentials, meaning that they refer to standard ambient temperature (298 K), 1 atmosphere (101.3 kPa) pressure, and solution concentrations of 1.0 mol L^{-1} . They are also determined with reference to the standard hydrogen electrode, which may be written as:

$2H^{+}(aq) + 2e^{-} \quad H_2\,(g);\ E \ = 0.00V$

The reduction potentials of zinc and nickel half-cells are negative because in both cases the metals are more likely to dissolve when placed in a solution of their own ions than hydrogen gas is when it is placed in a solution of hydrogen ions. When these metals dissolve they tend to be oxidized rather than reduced, so the equilibrium reactions are reversed and electrons are produced, thus

$Zn(s) \quad Zn^{2+}(aq) + 2e^{-}$

$Ni(s) \quad Ni^{2+}(aq) + 2e^{-}$

If the concentration of a metal ion solution is lowered, then it can be predicted that the equilibrium will shift so that more metal will dissolve in order to replace the ions, making the electrode more negative. Conversely, if the concentrations of the metal ions are increased the electrode becomes more positive.

Now let us return to the equations originally given for the two half-cells under consideration:

$Zn^{2+}(aq) + 2e^{-} \quad Zn(s);\ E \ = -\ 0.76V$

$Ni^{2+}(aq) + 2e^{-} \quad Ni(s);\ E \ = -\ 0.25V$

As the zinc half-cell is more negative than the nickel half-cell, oxidation is more likely to occur at the zinc electrode, whilst reduction will occur at the nickel electrode. The sign of the standard electrode potential for zinc must therefore be reversed when calculating the overall cell potential under standard conditions, thus:

$$E_{cell} = E_{redn}\ (Ni^{2+}/Ni) - E_{redn}\ (Zn^{2+}/Zn)$$

$$E_{cell} = -0.25\ V - (-0.76\ V) = +0.51\ V$$

Now, we saw above that if the concentration of the nickel ion solution is increased the standard reduction potential becomes more positive, i.e. less negative. The overall cell potential will therefore become more positive than + 0.51 V, and the correct key is **A**.

APPENDIX

RULES FOR ASSIGNING OXIDATION NUMBERS (OXIDATION STATES)

In simple binary compounds the oxidation number is equal to the valency of an ion.[1] 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 OF_2 when it is +2).

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* 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.